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# Investigation on nucleation, growth and physical properties of low soluble 4-N, N-dimethylamino-4-N'-methylstilbazolium 4-aminotoluene-3-sulfonate crystal – A potential NLO material



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#### ABSTRACT

Terahertz generation requires materials with excellent nonlinear optical (NLO) properties and environment stability. 4-N, N-dimethylamino-4-N'-methylstilbazolium 4-aminotoluene-3-sulfonate (DAAS) an organic ionic compound is found to match these conditions but it is one of the sparingly soluble compounds among the stilbazolium derivatives causing difficulty in crystal growth. Therefore, in this article, the nucleation and growth kinetics of DAAS in different solvents are examined in order to understand and improve its crystal growth. The structural properties like symmetry, hydrogen bonding that contribute to crystal growth and morphology are studied and discussed. As nonlinear optical properties in organic compound is affected by vibration of the molecules, the existence of functional groups and various modes of vibration present in the molecule are identified and categorized by Fourier transform infrared (FT-IR) and FT-Raman analyses. Linear optical properties of the DAAS at molecular level, liquid and solid phases are investigated using density functional theory and UV-Visible spectroscopic technique. The NLO properties of DAAS molecule like the first order hyperpolarizability and mean polarizability is predicted using density function theory and the second harmonic generation efficiency is determined using Kurtz powder test. The thermal stability of DAAS is compared with other highly nonlinear optical stilbazolium derivatives.

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### 1. Introduction

THz region of the electromagnetic spectrum offers diverse applications such as wireless communications, inspection of drugs, detection of explosives and metals, analysis of DNA, gas sensing, spectroscopy and imaging [1,2]. Ionic organic crystals are emerging as THz emitters than the commonly used semiconductors or inorganic electro-optic emitter due to their attractive characteristics such as high second nonlinear optical properties and broadband THz emission [3-5]. 4 -N, N-dimethylamino-4-N'-methyl stilbazolium tosylate (DAST) is one such material that is widely discussed and also commercialized. DAST crystal is composed of stilbazolium cation and tosylate anion [6]. The advantages and limitations of DAST have been discussed in detail elsewhere [3,7,8].

Based on these considerations, researchers are aiming at the development of new stilbazolium derivatives by effectively varying the counter anion of DAST. Tan et al reported that so far 72 stilbazolium derivatives with different counter anions has been synthesized and only 29% were grown in non-centrosymmetic structure with only 15 % showing second harmonic generation (SHG) efficiency comparable with DAST. Among them only DSTMS, DASC and DSMOS which is 4% of the crystals were grown as high-quality single crystals and these materials are demonstrated to have either comparable or even better optical and physicochemical properties than DAST crystal [3,9-12]. The major difficulty in the remaining 7 % of crystals is the low solubility of these salts in most solvents.

Here we report yet another organic stilbazolium single crystal 4 -N, N-dimethylamino-4-N'-methyl stilbazolium 4-aminotoluene 3-sulfonate (DAAS), which is environmentally and thermally stable and possess acentric crystal structure for NLO applications but shows poor crystal growth properties [13]. One of the salient features is that, DAAS is not forming hydrated centrosymmetric struc-

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ture even when it is crystallized in water or water containing solvent. Therefore, DAAS offers the freedom from air-humidity damage and thus avoids strict protecting conditions if employed as crystal-based devices. The research group of Sun et al in their maiden attempt successfully synthesized DAAS and have grown crystals of few micrometers by temperature lowering method. It is interesting to find that DAAS could not be grown into large crystal and hence attracts that attention to investigate further the possible reasons.

Therefore, an effort has been made to grow large single crystals of this low soluble DAAS in a mixed solvent system by exploiting the Oswald ripening process using the slow evaporation technique [3,14-16]. It is believed that the use of mixed solvent of water and methanol along with prolonged period for Oswald ripening have promoted the growth of crystal with improved size. This method can be adopted for other low soluble materials to grow larger crystals of reasonable size suitable for various applications. Along with growth, linear, nonlinear optical and detailed spectral properties of DAAS are investigated. In this article, we have carried out the growth experiment with the vision to further improve the size of the crystal and did a systematic study on various physical chemical properties. To the best of authors knowledge Hirshfeld surface analysis, molecular orbital analysis, vibrational spectroscopy and photoluminescence of DAAS are reported for the first time.

# 2. Experimental procedure

# 2.1. Material preparation

The title compound (DAAS) was prepared via metathesization reaction between 4-N, N-dimethylamino-4-N'-methyl stilbazolium

iodide (DMSI) and sodium salt of 4-aminotoluene-3-sulfonate. The DMSI cation was synthesized by the condensation reaction method employing the same procedure reported by our research group [16]. The metathesization reaction was carried out as follows: Initially, DMSI (0.7324, 2 mmol) was dissolved in 100 ml of Millipore water with continuous heating. Aqueous solution of 4aminotoluene-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 Millipore water and the content was mildly heated. This solution was thoroughly mixed with the already prepared DMSI solution and further heated for an hour at 70°C with continuous stirring. The resulting solution was cooled down to room temperature and then kept undisturbed for a day. A red colour precipitate was obtained due to the cation and anion exchange reaction. The left out aqueous solution of sodium iodide was later separated by vacuum filtration. The scheme for synthesizing DAAS is illustrated in Fig. 1.

DAAS. Yield: 76%. <sup>1</sup>H-NMR (500 MHz, CD3OD):  $\delta$ (ppm) = 8.51 (d, 2H, J =6.5 Hz, C<sub>5</sub>H<sub>4</sub>N), 7.98 (d, 2H, J =7 Hz, C<sub>6</sub>H<sub>4</sub>N), 7.862 (d, 1H, J = 16 Hz, C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 7.639 (d,2H, J = 9 Hz,C<sub>6</sub>H<sub>4</sub>-N), 7.495 (d,1H,J= 2Hz, C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 7.119 (d, 1H, J = 16 Hz, C<sub>6</sub>H<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 7.002 (d, 1H, J = 10 Hz, CH), 6.82 (d, 1H, J = 9Hz, CH), 6.696 (d, 2H, J = 8Hz, C<sub>6</sub>H<sub>4</sub>-N), 4.64(s, 2H, NH<sub>2</sub>), 4.232 (s, 3H, NCH<sub>3</sub>), 3.088 (s, 6H, NC2H6), 2.223 (s, 3H, CH<sub>3</sub>). Anal. Calcd. For C<sub>23</sub> H<sub>27</sub> N<sub>3</sub> O<sub>3</sub> S: C, 64.92; H, 6.39; N, 9.87. Found: C, 64.69; H, 6.31; N, 9.83.

## 2.2. Solubility

In the present work, several solvents in pure or mixture forms were used to determine the solubility of DAAS. It is noted that solvents like methanol, water and mixed solvent like water-methanol showed reasonable solubility compared to other solvents. In water-



4-aminotoluene-3-sulfonate (DAAS)

Fig. 1. Preparation method of DAAS.



Fig. 2. Solubility curve for DAAS in methanol and water-methanol mixed solvent.



Fig. 3. Nucleation mechanism of DAAS in methanol.

methanol mixed solvent system, the material showed positive solubility coefficient. In a 250 ml beaker, 100 ml of water-methanol (1:1) was taken and kept in a water bath. The beaker was closed with appropriate sheet and the initial temperature was set as 35 °C. By adding the powdered sample, the solution was stirred continuously. The amount of sample in the solution was analysed with saturation level by gravimetric analysis. In a warmed pipette, 10 ml of saturation solution was taken and poured in to a cleaned and dried Petri dish. By gentle heating, the solution was allowed to evaporate completely. The mass of DAAS in 10 ml of solution was determined by weighing the Petri dish with salt. With this method, the solubility of DAAS was measured for various temperatures (35, 40, 45, 50 and 55  $^\circ\text{C})$  for the mixed solvent system of water: methanol (1:1) and Fig. 2 depicts the solubility curve of DAAS. The same procedure was used to determine the solubility of DAAS in methanol solvent.

# 2.3. Nucleation and growth mechanism

In the present work, the growth habit was investigated by nucleation mechanism. In order to further understand why DAAS grows rarely in methanol but reasonably good in water-methanol, the nucleation mechanism in these solvents were investigated. A drop from the saturated solution of DAAS in methanol at 30°C was cast on a glass slide and the nucleation mechanism were recorded using a polarizing microscope. It is observed from Figs. 3 and 4 that multinucleation results in precipitation of DAAS into several microcrystals rather than single crystals. It is the spontaneous multinucleation that leads to the precipitation of DAAS in methanol. Rapid evaporation of methanol is also another factor: faster nucleation resulting in few tiny crystals within 5 seconds and several crystals with complete evaporation of solvent within 17 seconds. The same experiment when performed in water-methanol solvent yielded spherulites of a different kind. It can also be observed that the growth terminates once the solution is deficient of solute. At first, nucleation takes place in the form of a cluster and then growth of this cluster into a spherulite. It took 20 seconds for first crystals to appear after nucleation and the growth progress slowly when compared to methanol system. Another, feature in this system is the growth of crystal occurring at the edge of the droplet and progressing inwards in contrast to the methanol system. Rapid multinucleation is the reason for not obtaining single crystals of sufficient size in the methanol solvent. In the water-methanol solvent system, the growth of spherulite signifies that this solvent system would yield single crystals. From the nucleation experiments, it is observed that the ability of solute to



Fig. 4. Nucleation mechanism of DAAS in water-methanol.



Fig. 5. Growth mechanism of DAAS spherulites in water-methanol.

grow into a spherulite is an indication of the tendency to grow bulk single crystals at optimized conditions [17]. The evolution of morphology of DAAS spherulite in water-methanol begins with a point nucleus, later growing of needles from this point. These needles grow in two opposite directions first and then other needles fill the space thus leading to a flat sphere. Fig. 5 is a rough indication of how a single needle branches and then the separate branches grow in 3 dimensions to form a spherulite. But for most purposes, we can treat a spherulite as composed of needles radiating from the centre. The slow growth axes all club into their neighbors, while the fast axis becomes the radial growth direction. Due to poor solubility of DAAS in water, its nucleation study was not performed.

# 2.4. Crystal growth

Crystal growth of DAAS was achieved by adopting slow evaporation along with Oswald ripening technique. For crystal growth experiment, equal amount of water: methanol (1:1) was taken, in a 100 ml of mixed solvent; 0.4 g of DAAS was dissolved by stirring vigorously. The content was heated up to 50 °C and stirred continuously until the material is completely dissolved in the sol-



Fig. 6. a) Photograph of DAAS crystals grown mixed solvent of Water-Methanol and b) its microscopic view.

vent. The filtered saturated solution was shifted to a Teflon beaker. The beaker was closed with a suitable cap and maintained at constant temperature without any disturbance. The growth solution was prepared at 50°C and the temperature was reduced 1 °C per day. When the temperature of the solution reaches 35 °C, the solution was allowed to Oswald ripening process and the concentration would be sufficient to drive the nucleation and growth. During this isothermal period, only those crystals that are larger in size will grow at the expense of smaller ones and the number of crystals available to grow further therefore reduces with the solute remaining in the solution. Within a few days, the growth of tiny needle like crystals could be observed at different parts of the beaker. The solution was then slowly allowed to evaporate, after 25-35 days, crystals with size up to 3-5  $\times$  1-2  $\times$  1-3  $mm^3$  were harvested. The size of the crystal is found to be 6 times larger than the previously reported size [13]. The crystals appeared reddish in colour (Fig. 6a) with moderately smooth surface. The quality of the surface of the crystals can be further improved by adopting slow cooing and slope nucleation techniques.

# 3. Characterization

The grown single crystal of DAAS was subjected to the following studies. The cell parameters and the crystal structure were confirmed by single crystal XRD data which was collected from a Bruker X8 KAPPA APEX II X-ray diffractometer with MoK<sub> $\alpha$ </sub> ( $\lambda = 0.71073$  Å) radiation. Powder XRD was performed with BRUKER X-Ray diffractometer with the  $CuK_{\alpha}$  radiation  $(\lambda = 1.540598 \text{ Å})$ . The vibrational assignments were determined by the FT-IR spectrum and it was recorded in the region 400-4000 cm<sup>-1</sup> with a Perkin-Elmer FT-IR spectrometer, employing the KBr pellet technique. FT Raman spectrum was recorded with a Bruker RFS 27: standalone FT-Raman spectrometer using the Nd: YAG laser at 1064 nm with 470 mW output as the excitation source. The proton NMR spectrum was recorded using a Bruker ADVANCE III 500 MHz FT-NMR spectrometer by dissolving the sample in deuterated methanol. The optical absorption spectrum of the sample was recorded using the Cary 5000UV-Vis Spectrometer. The thermal behavior was investigated by thermogravimetric (TG-DTA) technique using the Perkin-Elmer STA 6000. The dielectric constant and dielectric loss were measured at different temperatures. The photo conducting property of the crystal was investigated with a Keithley 485 picoammeter at room temperature. The second harmonic generation test was conducted by Kurtz and Perry technique using a Q-switched mode locked Nd: YAG laser (1064 nm) with a beam of energy 10 ns pulse width and 0.68 J power. The molecular structure of DAAS was subjected to ground state optimization without any constraints on the molecular system using Density Functional Theory (DFT) at B3LYP (Becke three parameter Lee Yang Parr) /6-311+G(d,p) level [18,19]. Subsequently, frequency calculations were also performed to confirm that each stationary point was at energy minima. From the ground state optimized geometries, Time Dependant-Density Functional Theory (TD-DFT) was employed to compute the absorption properties for the 20 lowest singlet vertical excitations. In order to examine the solvent effect, self-consistent reaction field-polarisable continuum model (SCRF-PCM) was utilized in methanol medium. NLO properties and the entire computational calculations were performed using Gaussian 09 suite of program [20].

# 4. Results and Discussion

# 4.1. Structural analysis

XRD data of DAAS crystal were collected and presented in Table (T1-supplementary material). It confirms the triclinic structure of DAAS crystal with acentric space group of P1. The single crystal XRD data for DAAS crystal collected in this work is in close agreement with the earlier work [13]. It is found that the volume of crystal structure in the present study is smaller  $(534.22(3) \text{ Å}^3)$ when compared to the crystals of Sun et. Al.,  $(543.92(54) \text{ Å}^3)$  hence the density has increased slightly to 1.323 g/cm<sup>3</sup> when compared to 1.299 g/cm<sup>3</sup>. This has resulted in a stronger 1.928 Å, N-H•••O type hydrogen bonds between anions and 2.433 Å, C-H•••O type bonds between cations (Fig. 7). Hydrogen bonds play a major role in stabilizing the structure and Hirshfeld surface analysis reveals that nearly 22 % of the interactions in the crystal are hydrogen bonds (Fig. S1 and S2-supplementary material). Fig. 8 shows the Hirshfeld surfaces of anion and cation molecules of DAAS. The optimized crystal structure of DAAS was computed at B3LYP / 6-311+G (d, p) level of quantum theory and the optimized structure with its Lateral view are shown in Fig. 9. The bond length between the molecules are measured and the bond length between the N1-C20 in pyridinium ring is found to be 1.457 Å, which is slightly higher than that dimethyl amino ring, where the distance between C11-N2 is determined as 1.362 Å. Since, DAAS is a  $\pi$ -conjugated crystal; the bond length of the  $\pi$ -bridge was also measured. The bond length of C7-C8 and C13-C15 are measured as 1.431 and 1.424 Å, respectively. The planarity of the crystal plays an important role in microscopic and macroscopic NLO properties like hyperpolarizability, mean polarizability and higher order NLO properties [21]. The bond angles of  $C_{22}$  –  $S_1$ - $O_1$ ,  $C_{22}$  –  $S_1$ - $O_2$  and  $C_{22}$  –  $S_1$ - $O_3$  are



Fig. 7. (a) ORTEP diagram of DAAS molecule and (b) Strong hydrogen bonds present in DAAS molecule.



Fig. 8. Hirshfeld surface of anion and cation molecules of DAAS.

104.96, 105.74 and 106.44  $^{\rm O}$  respectively; the compression of the angles is attributed to the Thorpe-Ingold effect [22].

# 4.2. Morphology analysis

In order to find the morphology, crystalline nature and purity, crystalline powder XRD of DAAS was performed [23]. At room temperature the diffracted pattern was recorded and plotted between10 to  $45^{\circ}$  range. Various planes at specific  $2\theta$  angles were observed from the reflections of DAAS sample and the peaks were indexed. The simulated pattern was produced from the single crystal XRD data and compared with the experimentally observed powder XRD pattern (Fig. 10 a). It is confirmed that both the experimental and simulated XRD patterns match well for DAAS crystal. The good crystalline nature of the DAAS crystal is confirmed with the sharp well-defined Bragg's peaks at the respective  $2\theta$  angles [12]. The simulated crystal morphology predicted from powder (h k l) data of DAAS is depicted in



**Fig. 9.** (a) Optimized structure of DAAS at B3LYP / 6-311+G(d,p) level of quantum theory, (b) Optimized structure showing significant dihedral angles (in ), (c) Lateral view of the optimized structure.

Fig. 10 b. It is clearly evident that  $(0\ 0\ 1)$  plane is the most dominant face of the crystal. The strong 1.928 Å hydrogen bond between the anions along the a-axis causes the (001) face grow much faster than the other faces. Also, along the b-axis, between the chromophores, the acceptor of the molecule,  $(N_1CH_3)$  and the donor of the adjacent molecule,  $N(CH_3)_2$  are bound by Van der Waals forces with distances of 2.413, 2.576, and 2.795 Å between the CH— and —HC atoms [Fig. S3-supplementary material] [24].

# 4.3. Molecular Vibrational Analysis

The vibrational spectral analysis (both FT-IR and FT-Raman) of the sample was done based on the attributing vibrations of the vinyl group, phenyl ring, methyl group, amino group, sulfonate and skeletal modes. Fig. 11 and 12 represented the FT-IR and FT-Raman spectra of the DAAS sample. The observed IR and Raman band positions with their corresponding assignments are presented in Table T2 (see supplementary material).

Vinyl group vibrations

In the conjugated systems, the alkene bond stretching vibrations without a center of symmetry is probably to have two C=C stretching bands at around 1650 and 1600 cm<sup>-1</sup> [25]. The bands observed at 1644.68 cm<sup>-1</sup> in the IR spectrum and another band at 1617.68 cm<sup>-1</sup> in Raman spectrum can be ascribed to the C=C stretching vibrations. The aliphatic C-H stretching for stilbazolium derivatives is expected in the region between 3050 and 3000 cm<sup>-1</sup> [26]. The band positioned at 3039.68 cm<sup>-1</sup> in the IR spectrum is attributed to the aliphatic C-H stretching.

Phenyl and pyridinium ring vibrations

The stilbazolium cation is made up of p-disubstituted benzene and pyridine ring, connected by ethylenic bridge; by these constituents of stilbazolium cation the ring mode vibrations in DAAS can be analyzed. C–H in-plane and out-of-plane bending vibrations generally occur in the region 1300-1000 cm<sup>-1</sup> and 1000-675 cm<sup>-1</sup> [25]. The bands at 1208.38, 1179.95, 1160.16 and 1070.81 cm<sup>-1</sup> in IR and 1210.57, 1179.22 and 1159.05 cm<sup>-1</sup> in Raman spectrum are assigned to C–H in-plane bending vibrations. In the IR spectrum the C–H out of plane bending vibrations is observed at 984.90 and 880.29 cm<sup>-1</sup>. The phenyl ring mode C–C–C deformation vibrations are noticed at 699.90, 625.06 and 530.42 cm<sup>-1</sup> in the IR spectra [27].

### Methyl group vibrations

Two kinds of methyl groups are present in the DAAS molecule, one type

 $(C-CH_3)$  is directly connected with the benzene ring, while the other type  $(N-CH_3)$  is attached with pyridine ring [26]. The asymmetric and symmetric bending vibrations for methyl groups are seen near 1450 and 1375 cm<sup>-1</sup> respectively. The medium band observed at 1500.55 cm<sup>-1</sup> (IR) is assigned to the asymmetrical bending vibration. The bands positioned at 1339.69 and 1375.69 cm<sup>-1</sup> (IR), and at 1377.47 and 1341.95 cm<sup>-1</sup> (Raman) are attributed to the symmetrical bending vibrations. For CH<sub>3</sub> group, the rocking mode usually appears in between 1070 and 1020 cm<sup>-1</sup> [28]. This mode appears at 1045.32 cm<sup>-1</sup> in IR and at 1046.97 cm<sup>-1</sup> in the



Fig. 10. (a) and (b) Powder X-ray patterns of DAAS crystal and Simulated morphology for DAAS crystal.

Raman spectra respectively. The  $CH_3$  torsion vibrations are identified as very weak band at 76.91 cm<sup>-1</sup> in the Raman spectrum [25]. Primary amine group vibrations

For aromatic primary amines (RNH<sub>2</sub>), the asymmetrical N–H stretch and the symmetrical N–H stretch will be observed in the regions of 3380-3415 cm<sup>-1</sup> and 3460-3510 cm<sup>-1</sup>, respectively [29]. For DAAS crystal, the N–H asymmetric and symmetric stretching vibrations are found at 3334.43 and

3452.55  $\rm cm^{-1}$  in the IR spectrum, respectively. A shoulder band seen at

3223.39 cm<sup>-1</sup> is due to the overtone of the N–H bending vibration for primary amine group. The NH<sub>2</sub> bending mode for aromatic primary amine is seen to overlap with the C=C stretching band at 1644.68 cm<sup>-1</sup> in the IR and at 1617.68 cm<sup>-1</sup> in the Raman spectra, respectively. The C–N stretching mode for aromatic primary amine is expected in the region between 1340 and 1250 cm<sup>-1</sup> [29]. Thus, the bands observed at 1318.12 cm<sup>-1</sup> (IR) and at 1318.29 cm<sup>-1</sup> (Raman) correspond to the C–N stretching mode. The  $NH_2$  wagging mode for aromatic primary amine is observed at 777.06 and 723.19cm<sup>-1</sup> in the Raman spectra.

Sulfonate and skeletal mode vibrations

The SO<sub>2</sub> group gives rise to asymmetric and symmetric stretching vibrations in the infrared spectrum for the range 1420-1000  $cm^{-1}$  with high intensity peak.

In DAAS crystal, the strong bands present at 1179.95 and 1160.16  $\rm cm^{-1}$  in IR, and at 1179.22 and 1159.05  $\rm cm^{-1}$  in Raman spectra could be attributed to the

 $SO_2$  asymmetric stretching modes. The bands positioned at 1045.32 (IR) and

1046.97 cm<sup>-1</sup> (Raman) correspond to the SO<sub>2</sub> symmetric stretching. The band at 500.18 cm<sup>-1</sup> in the IR spectrum and the one observed at 500.26 cm<sup>-1</sup> in the Raman spectrum may be attributed to the SO<sub>3</sub> deformation. The observed result matches well with an earlier report [30]. The skeletal mode vibrations arising



Fig. 11. FT-IR spectrum of DAAS.



Fig. 12. FT-Raman spectrum of DAAS.

from C–N and C–C are usually measured in the region 1150-850  $\rm cm^{-1}$ . The band observed at 880.29  $\rm cm^{-1}$  in the IR spectrum corresponds to the C–N stretching.

# 4.4. Linear Optical Properties

The optical transmission window and cut-off wavelength of the crystal can be obtained by optical transmittance study. Also, it is very useful to understand about its electronic transition states. The optical absorption spectrum (Fig. 13) of DAAS crystal was carried out in solid phase. The cut-off wavelength of the sample is found to be 610 nm and below which the material shows complete absorption due to the bonding and anti-bonding transitions. The material is transparent with very low absorption beyond 610 to 1700 nm. The absence of absorption in this region paves way for NLO



Fig. 13. UV-Vis absorption spectrum of DAAS crystal.

#### Table 1

Computationally calculated absorption maxima ( $\lambda_{max}$ ) and their corresponding oscillator strengths ( $f_0$ ), major contribution, Light Harvesting Efficiency (LHE), nature of transition and Transition assignment for DAAS molecule.

Molecule	DAAS
Type of Transition	S <sub>0</sub> S <sub>1</sub>
λ <sub>max</sub> (nm)	470.5
Oscillator Strength f	1.257
LHE	0.94
Major Contribution	HOMO - LUMO (100%)
Nature of Transition	$\pi$ - $\pi^*$
Dipole Moment (Debye)	14.76
Energy gap (eV)	2.07

applications [31]. The energy band gap was calculated using the relation:

$$E_g = \frac{hc}{\lambda}$$

Where, h - Planck's constant, c - Velocity of light and  $\lambda$  - cut off wavelength. The optical energy band gap of DAAS crystal is found to be 2.03 eV.

#### 4.4.1. Frontier molecular orbital analysis

To evaluate the molecular level energetic behaviour of the  $\pi$ conjugated DAAS crystal, the HOMO-LUMO analysis was carried out in a methanol medium and calculations were done using DFT method at the B3LYP /6-311+G (d, p) basis set level using Gaussian program (Table 1). This frontier molecular orbital gap is connected with the parameters like high chemical reactivity, large polarizable, low kinetic stability, and soft nature of the molecule. HOMO depicts the donor of electron and LUMO is the acceptor of the electron. In the present case, dimethylamino moiety acts as an electron donor and pyridinium moiety plays as an electron acceptor. The transmission of the electronic absorption by one electron excitation from ground state (highest occupied molecular orbital (HOMO)) to the first excited state (lowest unoccupied molecular



Fig. 14. Frontier Molecular Orbitals (HOMO and LUMO) of DAAS from ground state optimized geometries.

orbital (LUMO)) was calculated. DAAS molecule is found to have a HOMO value of -4.905 eV, while the LUMO value is -2.826 eV (Fig. 14) and the energy separation gap between the HOMO and LUMO is found to be 2.07 eV. The value of dipole moment is 14.76 Debye. This value is much better than that of well-known reference compound urea (1.3732 D). There is no complete transmission of electronic absorption from HOMO to LUMO but intramolecular charge transfer has occurred in the molecule, making it responsible for the large NLO property [32].

#### 4.5. Nonlinear Optical Properties

# 4.5.1. Molecular Hyperpolarizability

At molecular level, the first order hyperpolarizability tensors of the DAAS was computed and calculated, by density functional theory (DFT) using the hybrid functional B3LYP /6-311+G (d, p) [33-35]. The donor-acceptor system, nature of substituents,  $\pi$ conjugated system and planarity are the parameters that can make an impact on hyperpolarizability. NLO properties such as first order hyperpolarizability ( $\beta$ ), mean polarizability ( $\alpha$ ) and static dipole moment have been calculated computationally using the formula:

$$\beta_{tot} = \left({\beta_x}^2 + {\beta_y}^2 + {\beta_z}^2\right)^{1/2}$$

Where 02

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$$\beta_x^2 = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2,$$
  

$$\beta_y^2 = (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2$$
  
and  

$$\beta_z^2 = (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2$$

. 0

#### Table 2

First order hyperpolarizability ( $\beta$ ) and mean polarizability ( $\alpha$ ) of DAAS computed at B3LYP /6-311+G(d,p) level of theory.

First Order Hyperpolarizability (esu)		Mean Polarizability (esu)	
Tensors	Value	Tensors	Value
$\beta_{\rm xxx}$	-6086.49186	$\alpha_{\rm xx}$	551.210787
$\beta_{\rm xxy}$	7377.32022	$\alpha_{\rm xv}$	-158.213120
$\beta_{\rm xvv}$	-7205.17206	$\alpha_{vv}$	517.608083
$\beta_{\rm vvv}$	6811.48768	$\alpha_{xz}$	6.80565563
$\beta_{\rm xxz}$	13.0421883	$\alpha_{\rm vz}$	13.0177819
$\beta_{\rm xyz}$	70.8535186	αzz	232.199970
$\beta_{\rm vvz}$	-169.065192	-	-
$\beta_{xzz}$	-39.7391084	-	-
$\beta_{\rm vzz}$	-37.6497728	-	-
$\beta_{zzz}$	129.263797	-	-
$\beta_{\text{Total}}$	$167.963 \times 10^{-30}$ e.s.u.	$\alpha_{\mathrm{Total}}$	$6.42703 \times 10^{-23}$ e.s.u.

$$\Delta \alpha = 2^{-1/2} \Big[ (\alpha_{xx} - -\alpha_{yy})^2 + (\alpha_{yy} - -\alpha_{zz})^2 + (\alpha_{zz} - -\alpha_{xx})^2 \Big]^{1/2}$$

The first order hyperpolarizability ( $\beta$ ) and mean polarizability ( $\alpha_{total}$ ) values for DAAS are listed in Table 2. DAAS crystal is found to have the first order hyperpolarizability and mean polarizability values of  $167.96 \times 10^{-30}$  esu and  $6.42703 \times 10^{-23}$  esu respectively. The calculated  $\beta$  of DAAS is comparable with the other well-known organic stilbazolium family crystals like DAST  $(159.05 \times 10^{-30} \text{ esu})$  and DASC  $(165.05 \times 10^{-30} \text{ esu})$ .

### 4.5.2. SHG efficiency test

The second harmonic generation test was done on the DAAS sample by Kurtz and Perry technique [34] using a O-switched mode locked Nd: YAG laser (1064 nm, Quanta ray series, Spectra Physics) with a beam of 10 ns pulse width and 0.68 J power. The sample was made into a very fine powder (particle of size in the range 100-120  $\mu$ m) and then closely packed in a microcapillary tube. The powder sample was then mounted in the path of a Q-switched Nd:YAG laser. The generated SHG signal at 532 nm is split from the fundamental frequency using an IR separator. A detector connected to power meter is used to detect second harmonic intensity and also to read the input and output. The SHG efficiency of the material was compared with microcrystalline powder sample of urea. The SHG signal recorded for the DAAS sample and it was found to be 145 mV. It is possible to achieve much higher SHG efficiency for DAAS with suitable laser arrangement since it is reported to have SHG efficiency of 0.83 times that of DAST crystal [13].

# 4.6. Thermal analysis

The thermal behavior of DAAS was investigated by thermogravimetric

(TG-DTA) and differential scanning calorimetric (DSC) techniques using the Perkin-Elmer DSC-7 and TGA-7, respectively. From the TG curve (Fig. 16), it is inferred that DAAS starts decomposing at 274 °C, after which it undergoes continuous weight loss up to 800 °C with three stages of decomposition. In the first stage, a major weight loss of 54.84% takes place between 274 and 370 °C and this may be due to the complete decomposition of stilbazolium cation. In the second stage, a loss of 13.28% is observed due to the removal of SO<sub>2</sub> molecule and in the third stage around 28.08% of the material decomposes, which may be due to the removal of aminotoluene compound. The DTA traces show a sharp endothermic peak at 287 °C, the sharpness in the peak confirms the good degree of crystallinity and purity of the sample. Interestingly, the observed melting point of the sample is not only higher than DAST crystal (256 °C) [14] but also better than a few other highly NLO active stilbazolium derivatives such as DSSS (277 °C) [3], DSTMS



Fig. 16. TG-DTA traces of DAAS crystal.

(258 °C) [10], DASC (282 °C) [15], DSMOS (264 °C) [11] and also some other extended molecules like DACSC [271 °C] [33], DCSSS [237.8 °C] [35] and DACSI (262.81 °C) [36].

#### 5. Conclusion

The single crystal of DAAS was grown by slow evaporation technique coupled with Oswald Ripening process. This process reduced the forming of several number of tiny crystals and yielded single crystals with improved size. By adopting this method, the crystals with low solubility can be grown into larger size. The X-ray diffraction study ascertained the triclinic structure of DAAS with space group P1. The characteristic vibrations of the vinyl group, phenyl ring, methyl and amino groups and the sulfonate and skeletal modes were confirmed by FT-IR and FT-Raman spectral studies. DAAS molecule is found to have a HOMO value of -4.905 eV, while the LUMO value is -2.826 eV and the energy gap 2.07 eV is calculated, experimentally the optical energy band gap of DAAS crystal is found to be 2.03 eV in solid phase and the low absorption in the region 1000 to 1600 nm suggests the suitability of the material for photonics and electro-optic applications in the infrared region. DAAS is found to have the first order hyperpolarizability and mean polarizability values of  $167.96 \times 10^{-30}$  esu and  $6.42703 \times 10^{-23}$  esu, respectively which is comparable with DAST and its derivatives. DAAS showed increased thermal stability when compared to DAST as well as a few other highly nonlinear optical stilbazolium derivatives. This projects the crystal to be used as a promising THz generation material at high temperatures. Hence the compound may be considered as potential material for photonic device fabrications.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# **CRediT** authorship contribution statement

**S. John Sundaram:** Conceptualization, Writing - original draft, Investigation. **A. Antony Raj:** Writing - original draft, Methodology. **R. Jerald Vijay:** Validation, Writing - review & editing. **M. Jaccob:** Software, Validation. **P. Sagayaraj:** Supervision, Funding acquisition.

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