



## Spectral, thermal and optical properties of adenosinium picrate: A nonlinear optical single crystal

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### ARTICLE INFO

#### Article history:

Received 7 October 2011

Received in revised form 3 December 2011

Accepted 15 December 2011

#### Keywords:

Crystal growth  
X-ray diffraction  
Optical material  
Thermal studies

### ABSTRACT

A new organic nonlinear optical material adenosinium picrate ( $C_{10}H_{14}N_5O_4^+$ ,  $C_6H_2N_3O_7^-$ ) was synthesized. The single crystal X-ray diffraction revealed the non-centrosymmetric crystal structure, which is an essential criterion for second harmonic generation. The crystalline nature of the grown crystals was confirmed using powder XRD techniques. Molecular structure was confirmed by NMR spectral analysis and functional groups were identified by FT-IR spectral analysis. The optical transmittance window and the lower cutoff wavelength of the AP have been identified by UV–vis–NIR studies. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study its thermal properties. Powder test with Nd:YAG laser radiation shows second harmonic generation.

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## 1. Introduction

Recent advances in organic nonlinear optical (NLO) materials have invoked a large revival of interest in this area of research on account of their widespread industrial potential applications [1–3]. Organic molecules have much greater design flexibility than inorganic compounds, which allows for the fine-tuning of NLO responses, and they can be much cheaper and easier to fabricate. The NLO effects in organic molecules are usually electronic in nature, which leads to fast nonlinear response. The architectural flexibility allows for precise molecular design and the determination of structure–property relationships. Low-lying electronic transitions in the UV–visible region improve the NLO efficiencies of organic systems [4]. Many of these molecular organic crystals owe their nonlinear optical properties to the presence of delocalized  $\pi$ -electron systems linking donor and acceptor groups which enhance the necessary asymmetric polarizability [5].

Adenosine (6-amino- $\beta$ -D-ribofuranosyl-9H-purine) is an essential biological nucleoside. Adenosine derivatives have been the subject of investigations owing to biological significance [6,7]. Adenosine interacts with carboxylic acids, resulting in protonation of the purine ring, giving salts with enhanced crystallinity due to hydrogenbonding interactions [8,9]. Picric acid is an interesting

organic acid because of the presence of three electron withdrawing nitro groups which makes it as a good  $\pi$ -acceptor for neutral carrier donor molecule. The picrate has increased molecular hyperpolarizability because of the proton transfer and remarkable second-order NLO activity ( $\chi^2$ ) [10]. Picric acid is having a tendency to form the stable picrate compounds with various organic molecules such as l-tryptophan [11], l-proline [12], and glycine [13], due to the presence of active  $\pi$ - and ionic bonds [14]. The title compound adenosinium picrate (AP) crystallizes in non-centrosymmetric space group  $P2_12_12_1$  and the structure exhibit interesting patterns of N–H...O hydrogen bonding. Adenosine acts as the donor and picric acid as electron acceptor which provides the ground state charge asymmetry of the molecule required for second-order nonlinearity (Fig. 1). The crystal structure of the title compound has already been reported [15]. The present study includes the growth of AP by slow evaporation method. The grown crystal has been subjected to X-ray diffraction study, FT-IR, UV–vis spectral analysis and thermal analysis. The NLO properties of the title compound were confirmed by the Kurtz–Perry technique.

## 2. Material synthesis and crystal growth

Commercially available adenosine and picric acid were taken in stoichiometric ratio were dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which yielded yellow crystalline

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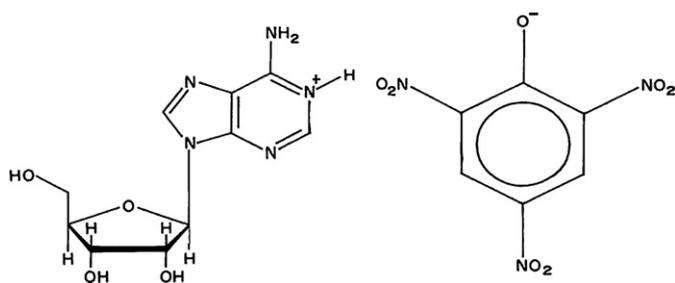


Fig. 1. Chemical structure of AP.

salt of AP. The process of recrystallization was carried out to purify the synthesized salt. As the water solvent yielded very small crystals attempts were made to grow AP crystals from mixed solvents. From several trials it was observed that the mixture of equal volume of acetone and water yielded relatively transparent crystals of AP (Fig. 2).

### 3. Discussion

#### 3.1. X-ray diffraction studies

The single crystal X-ray diffraction analysis of AP was carried out using ENRAF NONIUS CAD4 single crystal X-ray diffractometer equipped with MoK $\alpha$  ( $\lambda=0.71071\text{ \AA}$ ) radiation. The compound crystallizes in orthorhombic form with lattice parameters  $a=8.776\text{ \AA}$ ,  $b=33.013\text{ \AA}$ ,  $c=6.728\text{ \AA}$  and  $V=1949\text{ \AA}^3$ . These values agreed well with the reported values [15]. The recorded powder X-ray diffraction pattern of AP sample is shown in Fig. 3. The sharp and well-defined Bragg peaks at specific  $2\theta$  angles testimonies the crystallinity of the material.

#### 3.2. Vibrational studies

The vibrational analysis of adenosinium picrate was performed on the basis of the characteristic vibrations of amino group, carbonyl group, nitro group vibrations and phenyl ring modes. The observed FT-IR spectra are presented in Fig. 4.

The hydroxyl stretching and bending can be identified by their broadness and strength of the band which is dependent on the extended of hydrogen bonding. The non-hydrogen bonded or free hydroxyl group absorbs strongly in the  $3600\text{--}3500\text{ cm}^{-1}$  region while the existence of intermolecular hydrogen bond formation can lower the O–H stretching wavenumber to the  $3500\text{--}3200\text{ cm}^{-1}$  region with the increase in IR intensity and broadness [16]. In saturated amines, the asymmetric NH $_2$  stretch and their symmetric counterpart are usually expected in the region  $3380\text{--}3350\text{ cm}^{-1}$

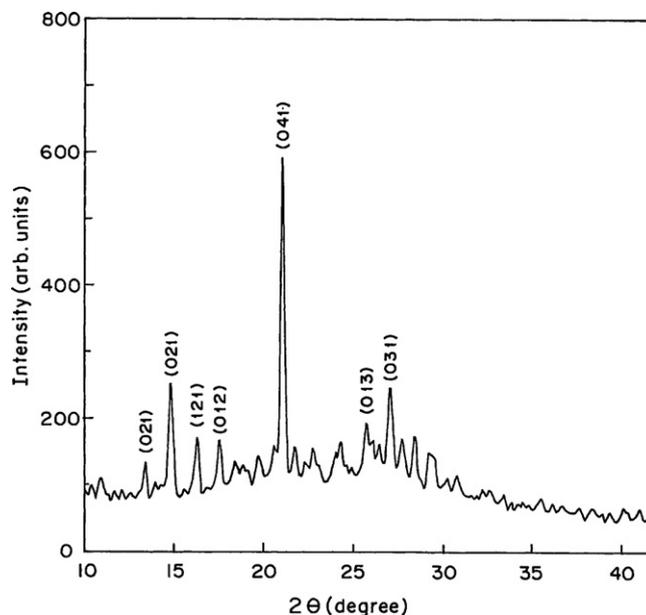


Fig. 3. Powder X-ray diffraction AP.

and  $3310\text{--}3280\text{ cm}^{-1}$ , respectively [17,18]. In adenosinium picrate the O–H stretch and asymmetric NH $_2$  stretching vibration fall in the same region. The broad band in IR spectrum at  $3430\text{ cm}^{-1}$  corresponds to the asymmetric NH $_2$  stretch. The internal deformation vibrations known as NH $_2$  scissoring wavenumber is found in the region  $1615\text{--}1650\text{ cm}^{-1}$  [17–19]. The intense IR bands at  $1631\text{ cm}^{-1}$  can be attributed to scissoring mode of the NH $_2$  group. The in-plane bending O–H deformation vibration usually appears as a strong band in the region  $1400\text{--}1260\text{ cm}^{-1}$  in the IR spectrum, which gets shifted to higher wavenumbers in the presence of hydrogen bonding. The O–H in-plane bending vibration is observed in IR at  $1367\text{ cm}^{-1}$ . The C–N stretching vibrations are observed in the region  $1250\text{--}1340\text{ cm}^{-1}$  in all the primary aromatic amines. The observed strong band at  $1273\text{ cm}^{-1}$  in IR is ascribed to C–N stretching. The rocking mode of the NH $_2$  group appears in the range  $1000\text{--}1100\text{ cm}^{-1}$  with variable IR intensity [20]. The observed weak band at  $1048\text{ cm}^{-1}$  in IR spectrum is attributed to the appreciable contribution from the CNH angle bending suggesting its origin due to the rocking mode. It is a strongly mixed mode containing contribution from the ring stretching and the rocking modes. The wagging mode of the NH $_2$  group appears in the range  $500\text{--}700\text{ cm}^{-1}$ . The

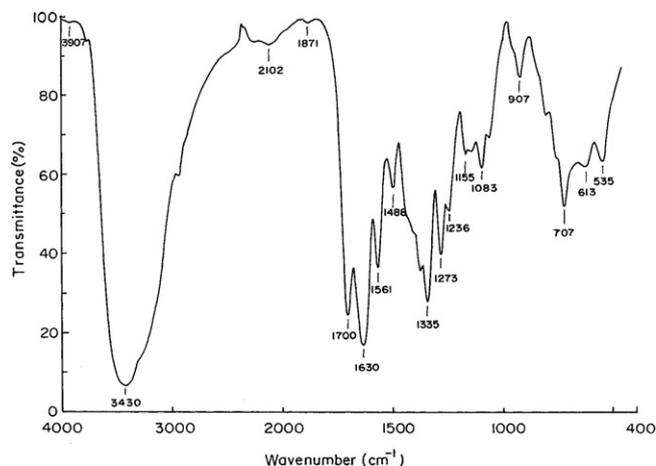


Fig. 4. FT-IR spectrum of AP.

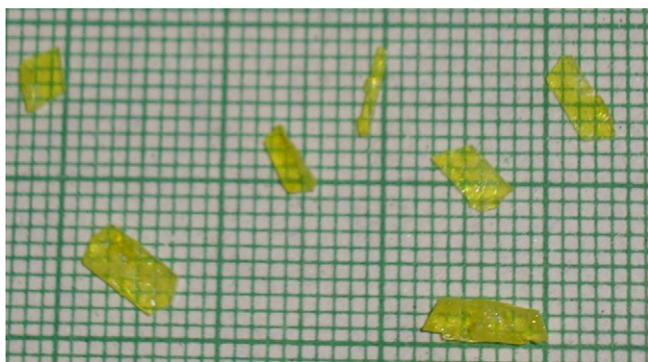


Fig. 2. Photograph of the as-grown single crystal of AP.

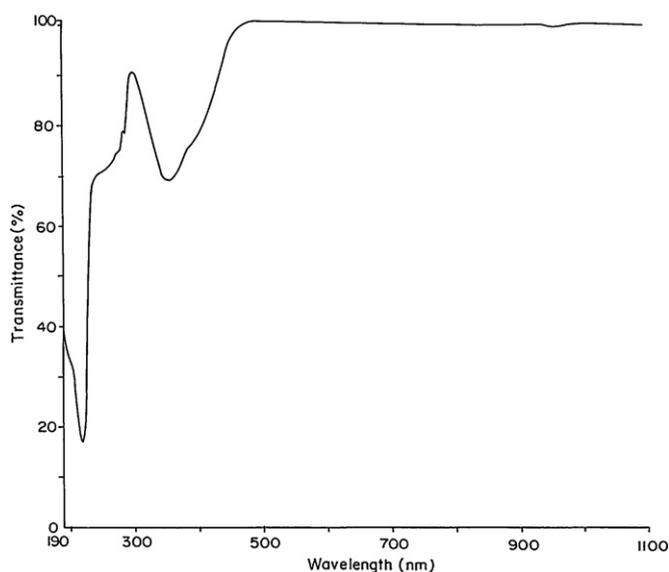


Fig. 5. UV-vis-NIR spectrum of AP.

observed weak band at  $613\text{ cm}^{-1}$  in IR spectrum corresponds to the  $\text{NH}_2$  wagging mode. The O–H out of plane bending vibration gives rise to a broad band in the region  $700\text{--}600\text{ cm}^{-1}$ . The position of this band is dependant on the strength of the hydrogen bond. The broad band at  $707\text{ cm}^{-1}$  in the infrared spectrum is attributed to the O–H out of plane bending mode.

The mode C=C is assigned as a medium band at  $1489\text{ cm}^{-1}$  in IR spectrum [21]. The asymmetric and symmetric stretching vibrations of  $\text{NO}_2$  generally give rise to bands in the regions  $1500\text{--}1570\text{ cm}^{-1}$  and  $1300\text{--}1370\text{ cm}^{-1}$  in nitrobenzene and substituted nitrobenzene [16–20] respectively. In adenosinium picrate medium IR bands at  $1561$  and  $1335\text{ cm}^{-1}$  attributed to  $\text{NO}_2$  asymmetric and  $\text{NO}_2$  symmetric stretching vibrations, respectively. The lowering in both these stretching modes, is attributed to the intermolecular hydrogen bonding and conjugation of  $\text{NO}_2$  with the aromatic ring. The nitro group deformation vibrations, which include  $\text{NO}_2$  scissoring,  $\text{NO}_2$  wagging and  $\text{NO}_2$  rocking, usually occur at wavenumbers lower than  $950\text{ cm}^{-1}$ . For the majority of compounds, the scissoring mode possesses the higher vibrational wavenumbers of the three deformations, and it is by far the most characteristic deformation mode. The  $\text{NO}_2$  rocking mode, on the other hand, has the lowest wavenumber for these three deformations [21]. The  $\text{NO}_2$  scissoring vibrations in aromatic nitro compounds are expected around  $825\text{ cm}^{-1}$ . The broad band at  $907\text{ cm}^{-1}$  in IR spectrum corresponds to the  $\text{NO}_2$  scissoring mode. The enhancement of  $\text{NO}_2$  scissoring modes is attributed to the conjugation of  $\text{NO}_2$  with the aromatic ring [16–20]. The wagging vibrations of  $\text{NO}_2$  group normally appear around  $760\text{ cm}^{-1}$ , while the rocking mode located at  $500\text{ cm}^{-1}$ . The bands corresponding to wagging and rocking vibrations of  $\text{NO}_2$  appears at  $786\text{ cm}^{-1}$  and  $535\text{ cm}^{-1}$  in IR respectively, which is supported by results reported in literatures [17–21].

### 3.3. Optical transmittance studies

Optical transmittance is an important parameter for an NLO crystal. The optical transmittance of AP dissolved in distilled water recorded using Shimadzu model 1601 in the range  $190\text{--}1100\text{ nm}$  is shown in Fig. 5. The spectrum reveals strong absorption bands attributed to the charge-transfer transition in addition to the usual  $\pi \rightarrow \pi^*$  bands of picrate ion in the complex and appears at  $356\text{ nm}$  and has low absorption in the entire visible region. The absence

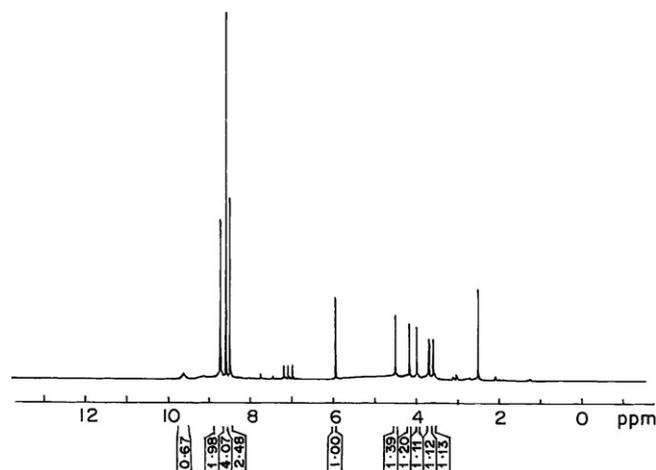


Fig. 6.  $^1\text{H}$  NMR spectrum of AP.

of substantial absorption in the entire visible region might enable achievement of microscopic NLO response with non-zero values.

### 3.4. NMR spectral studies

The proton  $^1\text{H}$  NMR spectrum of AP was recorded using JEOL GSX 400 model at  $27^\circ\text{C}$ . The chemical shift values of the protons are plotted on the X-axis and the intensity is plotted on the Y-axis (Fig. 6). The appearance of ten proton signals in the spectrum confirms explicitly its molecular structure. The signals appearing in the aliphatic region of the spectrum are due to different methine protons of furanose ring of the sugar moiety. The methylene proton of  $\text{CH}_2\text{--OH}$  group is downfield shifted to  $\delta 8.5\text{ ppm}$  due to electronegative oxygen of the OH group. The singlet observed at  $\delta 8.754\text{ ppm}$  has been assigned to C3 and C5 aromatic protons of the kind in the picrate moiety. The same was observed at  $\delta 11.94\text{ ppm}$  in free picric acid. This upfield shift of frequency is attributed to an increase in electron density as a result of charge transfer in the complex. The absence of singlet peak around  $\delta 11.94\text{ ppm}$  which was assigned to the O–H proton of the free picric acid suggests that the picric acid is ionized and is present as a picrate ion [22,23].

### 3.5. Thermogravimetric analysis

Analysis of AP was carried out using a NETZSCH thermal analysis system between  $30$  and  $900^\circ\text{C}$ . The TGA and the corresponding DTA traces are shown in Fig. 7. The TGA trace illustrates absence

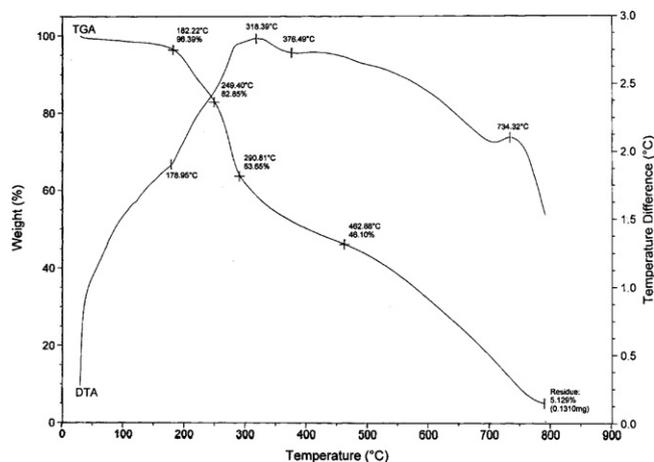


Fig. 7. TGA/DTA spectrum of AP.

of any weight loss up to 182 °C but a major weight loss occurring in three stages between 249, 290 and 462 °C. The total weight loss corresponds to 46.1% above 462 °C, and the resulting residue undergoes degradation up to 800 °C. No phase transition is observed in this region which enhances the temperature range of the crystal for NLO applications. The thermal resistance offered by the title crystal has been observed up to 182 °C. Hence the present material may be a promising candidate for all types of nonlinear optical applications.

### 3.6. SHG efficiency studies

The space group  $P2_12_12_1$  group allows contribution of a molecular nonlinearity. The study of nonlinear optical conversion efficiency has been carried out using the modified experimental setup of Kurtz and Perry [18]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, pulse width of 8 ns and with a repetition rate of 10 Hz was used. The grown single crystal of AP was powdered with a uniform particle size and then packed in a microcapillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532 nm component. The generation of the second harmonics was confirmed by the emission of green light. The SHG conversion efficiency of AP is found to be about 0.25 times that of KDP

### 4. Conclusion

Single crystals of adenosinium picrate were grown from solution method. The unitcell parameters were confirmed by single crystal X-ray diffraction analysis. The sharp well-defined peaks confirm the crystalline nature of the materials. It is found that the crystal belongs to the orthorhombic crystal system and space group  $P2_12_12_1$ . Molecular structure was confirmed by NMR spectral analysis and functional groups were identified by FT-IR spectral analysis. Thermal analyses indicated that the crystal has good thermal stability. The optical property has been assessed by UV–vis measurement showed the absence of absorption in the entire visible region. Powder test with Nd:YAG laser radiation shows second harmonic generation. Hence it could be suggested that this material is better befitted for optical applications.

### Acknowledgments

The authors are grateful to Dr. A. Chandramohan, Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore for fruitful discussions. The authors thank Laser Research Lab, B.S. Abdur Rahman University, Chennai for extending the facilities to measure SHG efficiency.

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