Influence of classical N–H...O and C–H...O hydrogen bonding interactions on 2-amino-5-methylpyridinium hydrogen succinate crystal: experimental and theoretical perspectives

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Abstract

An organic nonlinearly active crystal 2-amino-5-methylpyridinium hydrogen succinate (2A5MPHS) was successfully synthesized and 2A5MPHS single crystals have been grown by a slow evaporation method. The crystal structure was determined by single crystal x-ray diffraction method and the result reveals that it belongs to the orthorhombic structure with noncentrosymmetric space group P2₁2₁2₁. The 1H and 13C nuclear magnetic spectra (NMR) are recorded in order to establish the molecular structure of the title compound. The identification of functional groups and their vibrational modes in the synthesized compound was analysed by Fourier Transform infrared (FT-IR) spectral studies. The optical transparency of 2A5MPHS has been studied by UV-Visible spectroscopic studies. Photoluminescence (PL) spectrum was recorded to investigate the emission properties of the crystal. Thermal behavior of the title compound was determined by using thermogravimetric/differential thermal analysis (TG/DTA). The nonlinear optical (NLO) property of the crystal was confirmed by Kurtz and Perry method and was found to be 2 times greater than that of pure KDP. Density functional theory (DFT) was used to execute the quantum chemical calculations to explore various intermolecular interactions using B3LYP functional with 6–31 G (d,p) basic set.

1. Introduction

In recent years, organic crystals are suitable to be prospective alternatives for inorganic crystals in the nonlinear optical applications. This is due to the possession of high damaged thresholds, a domain of large transparency, large birefringence values and the nonlinear coefficients [1]. By involving carboxylic acids in crystal engineering, a new method in synthesizing organic nonlinear optical crystal has emerged and this is due to the potential to generate foreseeable supramolecular modes with the interactions of the hydrogen–bonding amongst them. Pyridine derivatives with large π-electron delocalization have received much attention from the material scientists due to their large second and third order nonlinearities. Hydrogen bonding between the carboxylic acid and pyridinium derivatives has been proved to be a powerful devising force in supramolecular architecture [2, 3]. Conjugated π electron system incorporated in organic crystals has both electron donor and acceptor groups which exhibit a good non-linear optical activity [4, 5]. In nonlinear optical molecules, π-bond plays a major role in order to acquire information regarding their NLO properties through the structural analysis and by their physiochemical properties. The delocalization of electronic charge distribution is owing to the overlay of π orbitals in organic molecules which determines very high molecular polarizability. Phase matching of nonlinear crystals which depend on optical transparency makes it suitable for photonic applications. Nonlinear photonic crystals added to the quadratic periodic nonlinear susceptibility can be employed effectively for the
conversion of second-harmonic generation (SHG) and parametric frequency \[6\]. Optical properties can be fine-tuned through the changes in the chemical structure of the materials owing to molecular flexibility \[7\].

Pyridine is a heterocyclic organic compound which possesses hydrogen bond interactions. They are widely used in optoelectronics, especially in organic OLEDs in order to improve its performance \[8\]. It also finds its application in the field of medicine, pharmacology and also used as corrosion inhibitors \[9, 10\]. 2-amino-5-methyl pyridine (2A5MP) is a pyridine-based molecule in which nitrogen atom acts as proton acceptor plus electron donor. 2A5MP is similar to the structure of 2-amino-5-chloro pyridine with alternating hydrogen-bonded along with the van der-Waals bonded zones \[11\]. Recently, 2-amino-5-methylpyridine based crystals, such as 2-amino-5-methylpyridinium 4-nitrobenzoate \[12\], 2-amino-5-methylpyridinium Salicylate \[13\], 2-Amino-5-methylpyridinium Hydrogen Isophthalate \[14\], 2-Amino-5-methylpyridinium-2-hydroxy-5-chlorobenzoate \[15\] has been reported and their physiochemical properties had been discussed. In this point of view, a methodical approach has been done to synthesize pyridine family based organic NLO materials that have been resulted in the design of 2-amino-5-methyl pyridinium hydrogen succinate.

In the current investigation, the synthesis, crystal growth, structural as well as thermal properties of the title compound, 2-amino-5-methylpyridinium hydrogen succinate are reported. The characterization of the grown crystals is done using the single crystal x-ray diffraction, NMR \(^{13}\)C and \(^1\)H\), FT-IR, UV-Vis spectroscopy, photoluminescence, thermal analysis, and SHG analysis. In addition to these studies, quantum chemical calculations for the titled compound were studied such as optimized geometry, HOMO-LUMO calculation, static dipole moment, first hyperpolarizability and polarizability have been calculated. The determined value of the hyperpolarizability specifies that this compound is an efficient applicant for nonlinear optical applications. Hirshfeld surface analysis, Mulliken charges, the density of states, molecular electrostatic potential and natural bond orbital (NBO) analysis are explored and discussed in detail.

2. Materials and methods

2.1. Synthesis and growth of 2A5MPHS

The title compound is synthesized by taking 2-amino-5-methyl pyridine (Sigma-Aldrich 99 %) and succinic acid (Merck 99 %) in an equimolar ratio. The intended volume of 2-amino-5-methyl pyridine and succinic acid are dissolved in methanol and then the solutions are mixed slowly in a magnetic stirrer at room temperature for an hour. A white color precipitate was observed in the first 30 min The obtained precipitate was washed several times with methanol to remove unreactants. After washing, the precipitate was carefully filtered and dissolved in double distilled water. Due to strong basic nature, the nitrogen atom of 2-amino-5-methylpyridine accepts a proton from succinic acid forming 2-amino-5-methylpyridinium cation. The reaction scheme is depicted in figure 1.

The saturated solution of 2A5MPHS was prepared with doubly distilled water at room temperature and stirred for 5 h. The saturated solution was filtered by using Whatman filter paper into a beaker of 300 ml and then it is covered firmly using the perforated sheets. In order to obtain good quality crystal, the solvent is allowed to evaporate. After the time duration of 35 days, 2A5MPHS crystals of size \(17 \times 8 \times 5 \text{ mm}^3\) are harvested and are shown in figure 2.

2.2. Characterization techniques

The single crystal x-ray diffraction data of the title compound were recorded with good transparent single crystal to confirm the crystal structure. Exact unit cell parameters are determined on three various crystallographic zones from the reflections of thirty-six frames which are measured using the difference vectors technique. Collecting the data, reducing the data and absorption correction are done by SADABS, SAINT-plus, and APEX2 programs. The thermal ellipsoids plot was drawn using the program ORTEP III \[16\]. The structure is solved with the help of direct methods procedure using the SHELXS-97 program and refined by Full-matrix least squares
procedure on F2 using SHELXL-97 program [17]. The structures were checked for missing symmetry elements with PLATON [18]. In order to understand the functional groups in the structure FT-IR spectrum was recorded in the range of 4000 to 400 cm$^{-1}$ by using the KBr pellet technique. The $^1$H and $^{13}$C NMR spectrum of 2A5MPHS was recorded using D$_2$O as a solvent at 23 °C (300 MHz for $^1$H NMR and 75 MHz for $^{13}$C NMR). Optical absorption was taken using a Perkin Elmer Lambda35 UV-Visible spectrometer between the range of 200–800 nm. The thermal analysis was carried out using a Perkin Elmer Diamond TG/DTA instrument in the range between 35°C and 600°C at a heating rate of 10 °C min$^{-1}$ in a nitrogen atmosphere. Kurtz-Perry powder SHG method [19] was employed to measure the SHG efficiency of 2A5MPHS with a Q-switched Nd: YAG laser operating at 1064 nm wavelength.

2.3. DFT calculations

The molecular geometry of the 2A5MPHS was optimized by using the Density Functional Theory (DFT) method with a hybrid functional B3LYP using Gaussian 09 with 6–31 G (d,p) basis set [20]. The molecular structure of 2A5MPHS was optimized from the crystallographic information file (CIF) as the source, and all calculations were computed. The Gaussian 5.0 visualization program was used to shape the HOMO and LUMO orbitals. Hirshfeld surface analysis was carried out to explore noncovalent interactions in 2A5MPHS using Crystal Explorer version 17.5 [21]. The first order hyperpolarizability, the Mulliken analysis and natural bond orbital (NBO) were also studied.

3. Results and discussion

3.1. Single crystal x-ray diffraction analysis

The title compound 2A5MPHS was crystallized from a slow evaporation technique. The data collection of crystallography with the help of x-ray with a wavelength of 0.71073 Å, is collected at the room temperature with MoK$_\alpha$ radiation with the help of BrukerAXS KAPPA APEX-2 diffractometer which is fully equipped with graphite monochromator [22]. All the H atoms except the H atoms that are attached to the nitrogen’s are placed geometrically calculated bond distances, viz., –CH = 0.93 Å (for aromatic) or 0.96 Å (for methyl) and–OH = 0.82 Å constrained to ride on the concerned parent atom with U$_{iso}$(H) = 1.2 or 1.5 U$_{eq}$(parent atom). The hydrogen atoms attached to the two nitrogen atoms in 2-aminopyridine cations are located from different Fourier map and refined isotropically. The convergence of the structure refinement is confirmed from the R-factor (3.35%) and largest difference peak and hole values. The crystallographic data, details of data collection and the structure refinement are presented in table 1. The ORTEP view of the compound plotted at 50% probability thermal displacement ellipsoids with the atom-numbering scheme is shown in figure 3(a). The protonation on the nitrogen site of the cation (2-amino 5-methyl pyridinium) is confirmed by the C-N bond distances [1.349(3) and 1.360(3) Å] and C-N-C bond angle [122.9(2)$^\circ$]. The hydrogen from the one of the −COOH groups of the succinic acid is transferred to the N-site, the title compound is formed as ionic pair. The resultant anion (hydrogen succinate) is evident from the asymmetric C-O bond distances in one of the -COOH groups and symmetric bond distances in the −COO$^-$ group. This ionic crystal is crystallized in the non-centrosymmetric orthorhombic crystal structure in P2$_1$2$_1$2$_1$ space group. The hydrogen bonding interactions are listed in table 2 and the packing arrangement of molecules are depicted in figure 4 along a-axis of the unit cell. The formation of crystalline solids is due to the intermolecular interactions of classical as well as non-classical hydrogen bonds which are used in analysing the molecular conformations, its stability, and crystalline lattices

Figure 2. Grown crystal of 2A5MPHS.
**Table 1.** Crystal data and structure refinement details of 2-Amino-5-methylpyridinium hydrogen succinate.

| Property                        | Value                        |
|--------------------------------|------------------------------|
| Empirical formula              | C_{10}H_{14}N_{2}O_{4}       |
| Formula weight                 | 226.23                       |
| Temperature                    | 296(2) K                     |
| Wavelength                     | 0.71073 Å                    |
| Crystal system                 | Orthorhombic                 |
| Space group                    | P2_12_12_1                    |
| Unit cell dimensions           | a = 5.36910(10) Å           |
|                               | b = 13.2807(3) Å            |
|                               | c = 15.4031(3) Å            |
| Volume                         | 1098.32(4) Å^3              |
| Z                              | 4                            |
| Density (calculated)           | 1.368 Mg m^{-3}              |
| Absorption coefficient         | 0.107 mm^{-1}                |
| F(000)                         | 480                          |
| Crystal size                   | 0.150 × 0.100 × 0.100 mm^3   |
| Theta range for data collection| 3.341 to 24.996°             |
| Index ranges                   | -6< h< 6, -15< k< 15, -18< l< 18 |
| Reflections collected          | 24555                        |
| Independent reflections        | 1926 [R(int) = 0.0260]        |
| Completeness to theta          | 99.5 %                        |
| Absorption correction          | Semi-empirical from equivalents |
| Max. and min. transmission     | 0.7456 and 0.7042            |
| Refinement method              | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 1926/4/158                   |
| Goodness-of-fit on F^2         | 1.05                         |
| Final R indices [1 > 2sigma(I)]| R1 = 0.0335, wR2 = 0.0869    |
| R indices (all data)           | R1 = 0.0358, wR2 = 0.0891    |
| Absolute structure parameter   | 0.2(2)                       |
| Extinction coefficient         | n/a                          |
| Largest diff. peak and hole    | 0.164 and -0.160 e.A^{-3}    |

**Table 2.** Various hydrogen bonding interactions present in 2A5MPHS.

| D–H...A | d(D–H) | d(H...A) | d(D...A) | <(DHA) |
|---------|--------|----------|----------|--------|
| C(9)–H(9)...O(1)#1   | 0.93   | 2.57     | 3.394(3) | 147.8  |
| O(2)–H(2)...O(4)#2   | 0.82   | 1.84     | 2.605(2) | 154.1  |
| N(2)–H(2B)...O(3)#3  | 0.804(19) | 2.06(2)  | 2.824(3) | 157(3) |
| N(1)–H(1 A)...O(4)   | 0.85(2) | 1.89(2)  | 2.73(2)  | 171(3) |
| N(2)–H(2 A)...O(3)   | 0.847(19) | 1.958(19)| 2.800(3) | 173(3) |

Symmetry transformations used to generate equivalent atoms: #1 = x+1, y+1/2, z; #2 = 2-x,y-1/2, z; #3 = 3x+1/2, y+1/2, z+1.
between the similar molecules [23]. The crystal packing is stabilized through classical N–H…O and O–H…O hydrogen bonds and non-classical C–H…O hydrogen bonds. The bond lengths and bond angles are present in table 3.

The classical N–H…O hydrogen bonds formed between the cation and anion are making a ring R3(8) motif between the ions. This is the key pattern which is responsible to connect the molecules along a-axis of the unit cell in a zig-zag fashion (figure 5). These ring motifs are connected through C–H…O interaction leading ring R3(6) motif. These ring motifs are adjacently packed in the crystalline lattice leading to chain C(10) motif. Further, the same ring R3(8) pattern is connected through another classical N–H…O hydrogen bond along the a-axis of the unit cell. This lead to another zig-zag chain C2(4) motif along the same axis. This molecular aggregation is stacked alternately along the axis with the stacking angle of 77.4° as shown in figure 6. This intricate three dimension hydrogen bonding interactions are playing a crucial role in the compound to be suitable for nonlinear optical applications.

3.2. FT-IR spectral analysis

Fourier transform infrared spectroscopy has been attested to be an effective tool for the confirmation of the title compound by analysing the functional groups present in it. A JASCO FT-IR 410 spectrophotometer was used to record the spectrum and is shown in figure 7. The N–H stretching of primary amine is positioned at 3354 cm\(^{-1}\). The C–H asymmetric vibration of the pyridinium ring and the C–H stretching vibrations of the methyl group appears around 3024 cm\(^{-1}\) and 2758 cm\(^{-1}\) respectively. The band at 1020 cm\(^{-1}\) is owing to the C-N stretching of primary amine. The N–H bending vibration and carbonyl group are obtained at 1641 cm\(^{-1}\) and 1687 cm\(^{-1}\), respectively. The asymmetric and symmetric COO\(^-\) stretching vibrations of succinic acid are observed at 1552 cm\(^{-1}\) and 1490 cm\(^{-1}\) respectively. The band observed at 1294 cm\(^{-1}\) is due to C–O stretching. The band at 952 cm\(^{-1}\) and 833 cm\(^{-1}\) are attributed to in-plane and out-of-plane bending vibrations of C–H. The rocking and wagging vibrations of COO\(^-\) are observed at 451 cm\(^{-1}\) and 642 cm\(^{-1}\) respectively. Hence the identification of functional groups in the 2A5MPHS confirms the formation of compound.

3.3. \(^1\)H and \(^{13}\)C NMR spectral analysis

Nuclear magnetic resonance (NMR) is a powerful analytical technique employed for the prediction of molecular structure. The \(^1\)H and \(^{13}\)C NMR spectroscopy were carried out using Bruker (Ultrashield TM) 300 MHz spectrometers and are shown in figures 8(a) and (b) respectively. From the \(^1\)H NMR, the peak around at \(\delta\) 2.077–2.512 ppm in 2A5MPHS is due to the methylene proton in the compound. The amino group hydrogen appears around \(\delta\) 5.70 and 6.40 ppm was observed. A signal observed in the high shielding values at \(\delta\) 7.71 due to the aromatic hydrogen also confirms the protonation of nitrogen in the pyridine ring. In \(^{13}\)C NMR spectra, the peak at \(\delta\) 20.9 ppm indicates the carbon atoms in methyl group of 2-amino-5-methyl pyridine. The peak at \(\delta\) 174.27 and \(\delta\) 158 ppm belong to the carbonyl carbon of C7 and C10 carbons in succinate moiety, respectively [24]. C6 and C1 peaks are observed at \(\delta\) 138.76 and \(\delta\) 146.78 ppm confirm the presence of pyridine moiety in the compound. Similarly, peaks observed around \(\delta\) 39–138.76 ppm are due to the carbons in the aromatic ring and methyl carbons in the compound. These chemical shifts confirm the structure of 2A5MPHS.

3.4. UV–Vis absorption studies

The UV-visible spectral study elucidates the transition of electrons from the ground state (\(\sigma\) orbital and \(\pi\) orbital) due to the absorption of UV and visible light to higher energy states [25]. The UV-visible absorption

![Figure 4.](Image)

Packing of the molecules 2A5MPHS is viewed down along a-axis. H-bonds are shown as dashed lines.
Table 3. Bond lengths and Bond angles of 2-Amino-5-methylpyridinium hydrogen succinate.

| Bond length | Experimental data | Computational data |
|-------------|-------------------|-------------------|
| C1–C2       | 1.503             | 1.506             |
| C1–O9       | 1.197             | 1.234             |
| C1–O10      | 1.308             | 1.383             |
| C2–H3       | 0.9700            | 1.100             |
| C2–H4       | 0.9700            | 1.092             |
| C2–C5       | 1.516             | 1.529             |
| C5–H6       | 0.9700            | 1.097             |
| C5–H7       | 0.9700            | 1.096             |
| C5–C8       | 1.509             | 1.523             |
| C8–O12      | 1.242             | 1.279             |
| C8–O13      | 1.265             | 1.299             |
| O10–H11     | 0.8200            | 0.982             |
| O12–H30     | —                 | 1.659             |
| O13–H29     | —                 | 1.390             |
| C14–C15     | 1.408             | 1.425             |
| C14–N26     | 1.349             | 1.366             |
| C14–N27     | 1.321             | 1.345             |
| C15–H16     | 0.9300            | 1.084             |
| C15–C17     | 1.356             | 1.380             |
| C17–H18     | 0.9300            | 1.086             |
| C17–C19     | 1.416             | 1.422             |
| C19–C20     | 1.353             | 1.382             |
| C19–C22     | 1.500             | 1.509             |
| C20–C21     | 0.9300            | 1.084             |
| C20–N26     | 1.360             | 1.361             |
| C22–H23     | 0.9600            | 1.097             |
| C22–H24     | 0.9600            | 1.094             |
| C22–H25     | 0.9600            | 1.097             |
| N27–H28     | 0.804             | 1.007             |
| O9–H11      | —                 | 2.362             |
| N26–H29     | 0.85              | 1.142             |
| N27–H30     | 0.847             | 1.051             |
| C2–C1–O9    | 124.7             | 126.7             |
| C2–C1–O10   | 112               | 111.7             |
| C1–C2–H3    | 108.6             | 107.4             |
| C1–C2–H4    | 108.6             | 108.1             |
| C1–C2–C5    | 114.5             | 112.3             |
| O9–C1–O10   | 123.3             | 121.6             |
| C1–C9–H11   | —                 | 55.4 INTRAMOLECULAR BONDING |
| C1–O10–H11  | 109.5             | 109.6             |
| H3–C2–H4    | 107.6             | 107.3             |
| H3–C2–C5    | 108.6             | 110.4             |
| H4–C2–C5    | 108.6             | 111.1             |
| C2–C5–H6    | 108.6             | 110.6             |
| C2–C5–H7    | 108.6             | 110.6             |
| C2–C5–C8    | 114.7             | 113.0             |
| H6–C5–H7    | 107.6             | 106.8             |
| H6–C5–C8    | 108.6             | 108.0             |
| H7–C5–C8    | 108.6             | 107.6             |
| C5–C8–O12   | 119.14            | 119.2             |
| C5–C8–O13   | 117.49            | 116.1             |
| O12–C8–O13  | 123.4             | 124.6             |
| C8–O12–H30  | —                 | 117.7             |
| C8–O13–H29  | —                 | 73.4 INTRAMOLECULAR BONDING |
| O10–H11–O9  | —                 | 174.4             |
| O12–H30–N27 | —                 | 175.6             |
| O13–H29–N26 | —                 | 117.5             |
| C15–C14–N26 | 117.5             | 117.6             |
| C15–C14–N27 | 123.7             | 124.0             |
| C14–C15–H16 | 120.2             | 119.0             |
| C14–C15–C17 | 119.6             | 119.9             |
| N26–C14–N27 | 118.8             | 118.4             |
| C14–N26–C20 | 122.9             | 122.3             |
Table 3. (Continued.)

| Bond length                  | Experimental data | Computational data |
|------------------------------|-------------------|--------------------|
| C14–N26–H29                 | 116.5             | 120.3              |
| C14–N27–H28                 | 121               | 119.5              |
| C14–N27–H30                 | 120.1             | 121.4              |
| H16–C15–C17                 | 120.2             | 121.2              |
| C15–C17–H18                 | 119               | 119.3              |
| C15–C17–C19                 | 122               | 121.5              |
| H18–C17–C19                 | 119               | 119.2              |
| C17–C19–C20                 | 116.5             | 116.2              |
| C17–C19–C22                 | 121.7             | 121.8              |
| C20–C19–C22                 | 121.8             | 122.0              |
| C19–C20–H21                 | 119.2             | 122.6              |
| C19–C20–N26                 | 121.6             | 122.5              |
| C19–C22–H23                 | 109.5             | 111.5              |
| C19–C22–H24                 | 109.5             | 111.2              |
| C19–C22–H25                 | 109.5             | 111.5              |
| H21–C20–N26                 | 119.2             | 114.9              |
| C20–N26–H29                 | 120.5             | 117.5              |
| H23–C22–H24                 | 109.5             | 107.6              |
| H23–C22–H25                 | 109.5             | 107.2              |
| H24–C22–H25                 | 109.5             | 107.6              |
| H28–N27–H30                 | 119               | 119.1              |

Figure 5. Two adjacent ring motifs, viz., R2(8) and R2(6), lead to Chain C(8) motif extending along the b-axis of the unit cell.

Figure 6. Ring R2,2(8) motif are connected in zig-zag fashion through an N–H...O hydrogen bond leading to chain C2(4) motif along the a-axis of the unit cell.
spectrum of 2A5MPHS is shown in figure 9(a). A strong absorption band is observed at 274 nm, which is attributed to $n \rightarrow \pi^*$ transition in 2A5MPHS [26]. This transition is due to transfer of an electron from the highest occupied molecular orbital (HOMO) of the donor succinic acid to the vacant lowest unoccupied molecular orbital (LUMO) of the acceptor, 2-amino-5-methyl pyridine. The absence of absorption above 468 nm enables 2A5MPHS to be a suitable applicant for the second harmonic generation. The optical band gap energy of the title compound is calculated using the formula:

$$E_g = \frac{1.24}{\lambda} \text{eV},$$

where $\lambda$ is the fundamental absorption wavelength (274 nm) and is found to be 4.52 eV. Further by using TD-DFT method, theoretical UV-Visible spectrum for 2A5MPHS was calculated and it was correlated with experimental results. Theoretically, the strong absorption band was observed at 294 nm (band gap 4.21 eV, figure 9(b)), which is slightly higher wavelength than the experimental results. The decrease in the band gap value is due to the electronic transition between the frontier orbitals and theoretical calculations were studied at gaseous state.

The density of states (DOS) plots of 2-Amino-5-methyl pyridine and 2A5MPHS were calculated using Gaussian 3.0 program [28] and are shown in figures 9(c) and (d). It is clearly seen from the DOS plots of 2-Amino-5-methyl pyridine and 2A5MPHS, the small shift was observed in the title compound. The interactions between the succinic acid and the pyridine molecule have influenced the frontier occupied and virtual molecular orbitals in the compound. These changes indicate that the pyridine compound acts as strong $\pi$-acceptor and supports the interfacial electron transfer in the molecule.

### 3.5. Photoluminescence study

Photoluminescence spectroscopy is the potential tool which deals with the electronic energy band of the material. The localized $\pi$-electron system in 2A5MPHS is responsible for the luminescence of the molecule. The photoluminescence emission spectrum of 2A5MPHS (figure 10) is recorded with an excitation wavelength of 350 nm. The emission peak at 383 nm shows that the title compound has violet fluorescence. The photoluminescence emission occurs due to proton transfer between ring nitrogen and the hydroxyl group of succinic acid in the grown crystal. The violet emission of the title compound finds it to be suitable for OLED applications [29].

### 3.6. Thermal analysis

Thermal stability of the 2A5MPHS has been assessed by TG and DTA analysis. Figure 11 shows the recorded thermograms in the temperature range of 30–700 °C. TGA analysis reveals that no weight loss is observed up to 151 °C, in turn, evident of the absence of solvent during crystallization of the compound. The TGA trace reveals that only one stage of weight loss occurs between the 151 to 248 °C. The major weight loss is about 98% was observed at 248 °C which represent the complete decomposition of the material. However, beyond this temperature leads to zero residues of 2A5MPHS. An endothermic dip is observed at 173 °C in the DTA curve due to the decomposition point of the material. From the thermal analysis study, it can be inferred that 2A5MPHS crystal has good thermal stability up to 151 °C and there is no phase transition before decomposition of the materials which helps to design the nonlinear optical crystal for optical device applications.
3.7. Second harmonic generation

Single crystals of 2A5MPHS enclosed in a microcapillary tube in powdered form were subjected to laser radiation with the beam energy of 5.65 mJ/pulse. A photomultiplier tube is used to detect the second harmonic generation output of 532 nm which is displayed on the oscilloscope. The generation of the second harmonics was confirmed by the green light emission. The measured output power is 19.8 mV and for KDP it is observed to be 9.8 mV with green light emission. Second harmonic generation (SHG) efficiency was found to be 2 times greater than of pure KDP.

3.8. Optimized geometry of 2A5MPHS

Optimized geometry of 2A5MPHS at B3LYP/6–31 G (d, p) level of theory is shown in figure 3(b). From DFT calculations, the C–C bond distances in 2-amino–5-methylpyridine cation are found to be C14–C15 (1.425 Å), C15–C17 (1.380 Å), C17–C19 (1.422 Å) and C19–C20 (1.382 Å). The variation in bond distances may be due to electron delocalization. In succinate anion, it is observed that C1–C2 (1.506 Å), C2–C5 (1.529 Å) and C5–C8...
(1.523 Å) bond distances are the same. The NH bonds present in 2-amino-5-methylpyridine cation are N26–H29 (1.142 Å), N27–H28 (1.007 Å) and N27–H30 (1.051 Å). The lengthening of N26–H29 bond is due to the existence of intermolecular interactions. The N–H….O interactions are evident from the elongation of O13–H29 and O12–H30 bond having a bond length of 1.390 Å and 1.659 Å. The bond angles having N–H….O interactions are O13–H29–N26 (175.6°), O12–H30–N27 (174.4°), C14–N26–H29 (120.3°) and C14–N27–H30 (121.4°). It is observed that the bond angles H24–C22–H25 (107.6°), H23–C22–H25 (107.2°), H23–C22–H24 (107.6°) corresponding to the methyl group in 2-amino-5-methyl pyridine are same. In addition to N–H….O

**Figure 9.** UV–Visible absorption spectra (a) Experimental; (b) Theoretical; DOS plot of (c) 2-Amino-5-methyl pyridine; (d) 2A5MPHS.

**Figure 10.** Photoluminescence spectrum of 2A5MPHS.
interactions, intramolecular bonding is also present which is evident from O9-H11 of succinate anion of bond length 2.362 Å having bond angle O10-H11-O9 of 73.4º.

3.9. HOMO–LUMO
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is the frontier molecular orbitals, which determine the molecular interactions with other species. The electron donors are HOMO orbitals and the electron acceptors are LUMO orbitals [30]. The HOMO is localized on the hydrogen, oxygen atoms in succinate ion and on entire pyridine ring as shown in figure 12. The LUMO is distributed uniformly except the methyl group in the parent molecule. The HOMO–LUMO energy gap value of 2A5MPHS compound was found to be 4.73 eV which clearly reveals that the intramolecular charge transfer (ICT) has taken place in the title compound indicating lower band gap value and it opts for optoelectronic devices [31].

3.10. Hyperpolarizability of 2A5MPHS
Quantum chemical calculation sets out to explore NLO properties of a molecule such as a dipole moment, polarizability and hyperpolarizability. The intermolecular and intramolecular interactions could be attributed...
to optical susceptibilities signifying long-range crystalline forces [32]. The dipole moment deals with the intermolecular interactions in a molecule which is due to hydrogen bonding in 2A5MPHS. This results in the enhancement of second harmonic generation. The molecule having large hyperpolarizability is opted for intermolecular interactions in a molecule which is due to hydrogen bonding in 2A5MPHS. This results in the optical susceptibilities signifying long-range crystalline forces.

The calculated values of dipole moment, polarizability and anisotropy of polarization are $6.8190 \text{ Debye}$, $36.418 \text{ esu}$ and $36.418 \text{ esu}$ respectively. The calculated first-order hyperpolarizability value is $6.26 \times 10^{-31} \text{ esu}$ for the title compound. The non-zero dipole moment and polarizability values of 2A5MPHS ($6.8190 \text{ Debye}$ and $36.418 \text{ esu}$) confirm the NLO behavior of the compound.

### 3.11. Hirshfeld surface analysis

Hirshfeld surface analysis discloses the intermolecular interactions encountered in the crystal which includes the hydrogen bonding interactions, van der Waals contacts, and $\pi-\pi$ stacking can be identified by 2D fingerprint plot. Hirshfeld surface is mapped by using de, di, dnorm, surface index, and curvedness with color coding in the crystal which represents the intermolecular interactions [33]. Hirshfeld surface analysis from the 2D fingerprint plots reveals that about 96% of the Hirshfeld surface is due to the hydrogen bond contacts ($\text{H...H/O...H/N...H}$) as shown in figure 13(a). The intermolecular interactions dominated in 2A5MPHS are $\text{H...H}$, $\text{O...H}$ and $\text{C...H}$ contacts. Out of total Hirshfeld surface of 2A5MPHS, the $\text{H...H}$ contacts are predominately which is found to be 46% as shown in fingerprint plot. The fingerprint plot includes other interactions such as $\text{O...H}$ (32.1%), $\text{C...H}$ (12.9%), $\text{N...H}$ (4.3%) and $\text{O...O}$ (1.8%) in 2A5MPHS crystal. From the figure 13(b), it is evident that the bright red region in the $dnorm$ surface is due to $\text{N...H}$ contacts and also shown as spikes in the 2D fingerprint plots. From the $dnorm$ surface, the $\pi-\pi$ interactions and $\text{H...H}$ contacts are observed as light red spots and other visible spots. The $\pi...\pi$ stacking interactions are confirmed in the shape index surface from the adjacent red and blue triangles on the surface and also from the flat portions in the curvedness surface.

### 3.12. Mulliken population analysis

Mulliken charge analysis explores the charge distribution in 2A5MPHS as depicted in figure 14(a) in which the atomic charges vary from $-0.793351$ to $+0.599236$. In the compound, all hydrogen atoms are positively charged and all oxygen atoms are negatively charged which could be due to the hydrogen bonding between cation and anion [34]. The positively charged carbon atom C14 (0.5992 e) has high value owing to the electrophilic nature of the cationic carbon atom. Hydrogen bonding interactions are evident from the hydrogen atoms H29 (0.4382 e) and H30 (0.4063 e) having a high value of the positive charge.

### Table 4. Theoretical polarizability and hyperpolarizability values of 2-Amino-5 methylpyridinium hydrogen succinate.

| Dipole moment | Quadrupole moment: polarizability | Octupole moment: hyperpolarizability |
|---------------|----------------------------------|-----------------------------------|
| $\mu$         | $\alpha$ Gas                      | $\beta$ Gas                       |
| $\mu_x$       | $-6.4702$                         | $\beta_{xx}$ $-51.1336$           |
| $\mu_y$       | $2.0683$                          | $\alpha_{xx}$ $-69.3212$          |
| $\mu_z$       | $-0.5980$                         | $\beta_{xx}$ $1.9525$             |
| $\sigma_{xy}$ | $-2.3882$                         | $\beta_{yz}$ $7.8685$             |
| $\sigma_{yy}$ | $-81.9417$                        | $\beta_{xy}$ $39.7209$            |
| $\sigma_{xz}$ | $-3.3163$                         | $\beta_{zz}$ $1.9797$             |
| $\sigma_{yz}$ | $2.7583$                          | $\beta_{xy}$ $3.5898$             |
| $\alpha_{zz}$ | $-99.3223$                        | $\beta_{zz}$ $-7.4104$            |
| TOTAL         | $6.8190$                          | $\beta_{xx}$ $16.2555$            |

Theoretical polarizability and hyperpolarizability values of 2-Amino-5 methylpyridinium hydrogen succinate.
3.13. Molecular electrostatic potential

Molecular electrostatic potential (MEP) deals with the molecular interactions and the reactive sites with its physiochemical property relationships [35, 36]. The electrophilic reactivity is observed by the negative potential regions (represented as red color) and the nucleophilic reactivity (represented as blue color) is observed by the positive potential regions. Molecular electrostatic potential of 2A5MPHS is illustrated in figure 14(b). It is

Figure 13. (a) Fingerprint plots of 2A5MPHS. 13(b) Hirshfeld surfaces mapped on (i) ‘a’ axis (ii) di (iii) de (iv) dnorm (v) shape index and (vi) curvedness.

3.13. Molecular electrostatic potential

Molecular electrostatic potential (MEP) deals with the molecular interactions and the reactive sites with its physiochemical property relationships [35, 36]. The electrophilic reactivity is observed by the negative potential regions (represented as red color) and the nucleophilic reactivity (represented as blue color) is observed by the positive potential regions. Molecular electrostatic potential of 2A5MPHS is illustrated in figure 14(b). It is
observed that the methyl group of pyridine ring has the maximum electropositive region. The hydrogen of succinic acid has the maximum electronegative region in 2A5MPHS. The result reveals the existence of charge polarization which enhances hyperpolarizability.

![Figure 14](image-url)  
(a) Mulliken atomic charges plot of 2A5MPHS, (b) Molecular electrostatic potential diagram of 2A5MPHS.

| Donor Acceptor | E(2) Kcal/mol | E(i)−E(1) a.u | F(i,j) a.u |
|----------------|---------------|---------------|------------|
| π C1−O9       | π* C1−O9      | 1.01          | 0.36       | 0.018     |
| σ C8−O13      | π* C8−O13     | 2.64          | 0.86       | 0.045     |
| π C8−O13      | π* C8−O13     | 3.57          | 0.86       | 0.053     |
| LP (2) O9     | σ* C1−C2      | 16.55         | 0.65       | 0.095     |
| LP (2) O9     | σ* C1−O10     | 34.84         | 0.54       | 0.124     |
| LP (2) O10    | π* C1−O9      | 45.75         | 0.31       | 0.108     |
| LP (2) O12    | σ* C5−C8      | 13.47         | 0.69       | 0.094     |
| LP (3) O12    | σ* C8−O13     | 26.35         | 0.45       | 0.101     |
| LP (3) O12    | π* C8−O13     | 24.68         | 0.45       | 0.099     |
| LP (1) N26    | π* C14−N27    | 96.86         | 0.2        | 0.125     |
| LP (1) N26    | π* C19−C20    | 46.04         | 0.26       | 0.106     |
| LP (1) O12    | σ* N27−H30    | 9.01          | 1.07       | 0.089     |
| LP (2) O12    | σ* N27−H28    | 0.06          | 0.74       | 0.086     |
| LP (3) O12    | σ* N27−H30    | 31.06         | 0.75       | 0.139     |
| LP (5) O12    | π* C14−N27    | 0.09          | 0.16       | 0.004     |
| LP (1) O13    | σ* N26−H29    | 10.14         | 0.89       | 0.088     |
| LP (2) O13    | σ* C14−N26    | 0.12          | 0.83       | 0.009     |
| LP (2) O13    | σ* N26−H29    | 90.04         | 0.76       | 0.235     |
| σ N26−H29    | σ* C8−O13     | 0.26          | 0.83       | 0.014     |
| σ N26−H29    | π* C8−O13     | 0.46          | 0.84       | 0.019     |
| σ N27−H30    | σ* C8−O12     | 0.21          | 1.15       | 0.014     |
| σ C14−N26    | σ* N26−H29    | 0.91          | 1.23       | 0.031     |
| σ C14−N26    | σ* N27−H28    | 1.83          | 1.31       | 0.044     |
| π C14−N27    | LP (1) N26    | 11.46         | 0.09       | 0.053     |
| π C14−N27    | π* C14−N27    | 3.84          | 0.29       | 0.035     |
| π C14−N27    | π* C15−C17    | 4.79          | 0.35       | 0.039     |
| π C15−C17    | π* C14−N27    | 34.14         | 0.23       | 0.087     |
| π C15−C17    | π* C19−C20    | 13.99         | 0.29       | 0.057     |
| π C19−C20    | LP (1) N26    | 149.3         | 0.02       | 0.083     |
| π C19−C20    | π* C15−C17    | 22.12         | 0.28       | 0.071     |
| π C19−C20    | π* C19−C20    | 1.71          | 0.29       | 0.02      |
3.14. NBO analysis

NBO analysis is useful in understanding hydrogen bonding formation and intramolecular interactions. NBO analysis reveals that the intermolecular N–H...O hydrogen bonding is formed due to the orbital overlap between the lone pairs (LP) of an oxygen atom and antibonding σ* orbitals of (N–H). The intermolecular hydrogen bonding interactions are formed by the hyper conjugative interactions of LP1(O13) → σ*(N26-H29) and LP1(O12) → σ*(N27-H30) associated with stabilization energies of 10.14 and 9.01. The hyper conjugative interactions of π (C19-C20) → LP1(N26), LP1(N26) → π*(C14-N27) and LP2(O3) → σ*(N26-H29) has maximum stabilization energy of 149.3 kJ mol⁻¹, 96.86 kJ mol⁻¹, 90.04 kJ mol⁻¹ respectively. From the NBO study (shown in table 5), it is evident that the hyper conjugative interactions in the pyridine ring are σ(C–C) → σ*(C–C) and π(C–C) → π*(C–C). In 2A5MPHS, among these two interactions π(C–C) → π*(C–C) conjugation is a dominant interaction which leads to resonance within the pyridine ring [37].

4. Conclusion

Nonlinear optical crystal of 2A5MPHS was synthesized and grown by slow evaporation solution growth technique. Single crystal XRD reveals that 2A5MPHS crystal belongs to the orthorhombic structure with noncentrosymmetric space group P2₁2₁2₁. Various characterization techniques were employed to confirm the crystal structure like FT-IR, NMR (¹H and ¹³C), UV-Visible, PL and TG/DTA. The presence of various functional groups in the crystal was investigated by the FT-IR spectrum. The proton and carbon arrangements in the molecular structure were analysed through NMR analyses which confirms the compound formation. The optical behaviour of 2A5MPHS crystals was assessed using UV-Vis from which the band gap energy of the crystal was estimated to be 4.52 eV and photoluminescence spectrum shows an emission peak at 383 nm which finds suitability in OLEDs. The TG-DTA study shows that the crystal was thermally stable up to 151 °C. In order to understand the NLO property, the SHG efficiency was performed which was found to be 2 times greater than that of KDP and theoretically, the first-order hyperpolarizability was calculated as 6.26 × 10⁻³ esu. The HOMO-LUMO energy gap of 2A5MPHS crystal was found to be 4.73 eV. Optimized geometry and NBO analysis clearly prove the presence of N–H...O hydrogen bonding interactions in the title compound. The intermolecular interactions are evident from Hirshfeld surface analysis. Mulliken charges and MEP analysis offered important information about its charge distribution, electrophilic and nucleophilic associated sites.

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