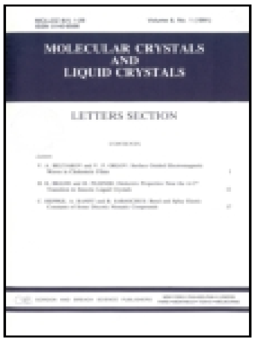

Molecular Crystals and Liquid Crystals

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Synthesis and Structural Characterization of Two New Charge-Assisted Hydrogen-Bonded Supramolecular Networks in 2-Amino-4-methylpyridinium Isophthalate Dihydrate and 2-Amino-5-methylpyridinium Hydrogen Isophthalate

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Synthesis and Structural Characterization of Two New Charge-Assisted Hydrogen-Bonded Supramolecular Networks in 2-Amino-4-methylpyridinium Isophthalate Dihydrate and 2-Amino-5-methylpyridinium Hydrogen Isophthalate

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*Two new supramolecular compounds, $2C_6H_9N_2^+$. $C_8H_4O_4^-$.$2H_2O$ /(4AMPIP) (**1**) and $C_6H_9N_2^+$.$C_8H_5O_4^-$/(5AMPHIP) (**2**), were synthesized and characterized by IR spectra, ^{1}HNMR, ^{13}CNMR, and single-crystal X-ray diffraction. Compound 1 crystallizes in the monoclinic system, space group Cc, with $a = 7.8914(3)$, $b = 38.4226(16)$, $c = 7.3354(3)$ Å, $\beta = 107.9460(10)$å, $V = 2115.94(15)$ Å^3, $D_c = 1.314$ g/cm^3, $F(000) = 888$, $\mu = 0.10$ mm^{-1}, $Z = 4$, the final $R = 0.0298$, and $wR = 0.0835$ for 3135 observed reflections with $I > 2\sigma(I)$; and compound **2** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 9.0126(2)$, $b = 12.2055(3)$, $c = 12.3170(2)$ Å, $\beta = 104.2160(10)°$, $V = 1313.42(5)$ Å^3, $D_c = 1.387$ g/cm^3, $F(000) = 576$, $\mu = 0.103$ mm^{-1}, $Z = 4$, the final $R = 0.0454$, and $wR = 0.1130$ for 2799 observed reflections with $I > 2\sigma(I)$. The 2-amino-4-methylpyridinium (4AMP) and 2-amino-5-methylpyridinium (5AMP) cations are protonated at one of the pyridinium N atoms. In both compounds, the isophthalate anion interacts with protonated cations through a pair of N—H···O hydrogen bonds to form a cyclic hydrogen-bonded motif with graph-set notation ($R_2^2(8)$). In the crystal structure of 1, the ion pairs (whether cation/anion) are linked by water molecules through O—H···O, N—H···O, and weak C—H···O hydrogen bonds, forming a three-dimensional network. In the crystal structure of 2, there are chains and layer made up of the O—H···O, N—H···O, and C—H···O hydrogen bonds, forming a two-dimensional network.*

Keywords Aminopyridine; crystal structure; FTIR and NMR spectra; hydrogen- bond network; isophthalic acid; proton-transfer; supramolecular heterosynthon

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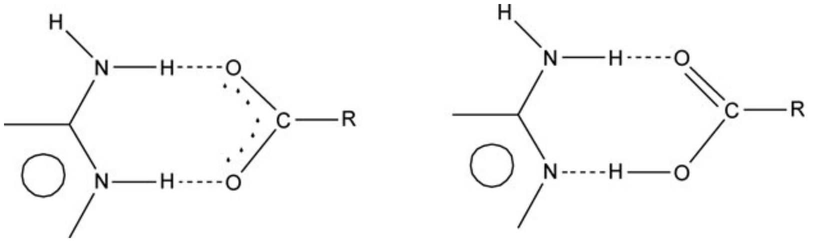


Scheme 1. Supramolecular Heterosynthons that can be formed between carboxylic acids and 2-aminopyridines: 2-aminopyridinium-carboxylate supramolecular heterosynthon I and 2-aminopyridine-carboxylic acid supramolecular heterosynthon II.

1. Introduction

Hydrogen bonding has been widely used to drive supramolecular aggregation because of their strength and directionality tend to favor the formation of crystals in which neighboring molecules are positioned predictably [1, 2]. The field of crystal engineering, which is a subdiscipline of supramolecular chemistry, deals with the construction of crystalline materials from molecules or ions using non-covalent (hydrogen bonding, π-π stacking, C—H$\cdots\pi$, and vander Walls) interactions. These interactions are very useful in devising gas-storage devices, sensors, optical switches, and solar cells [3]. The design of supramolecular nano architectures, layers, ribbons, rosettes, rods, tapes, and sheets can be achieved through N—H$\cdots$O, O—H$\cdots$N, N—H$\cdots$N, O—H$\cdots$O, and C—H$\cdots$O hydrogen bonds [4].

2-Aminopyridine and its derivatives are used as dyes [5] and pyridinium cation derivatives often possess antibacterial and antifungal activities [6]. Some aminopyridines are found to demonstrate pharmacological activity as K+ channel inhibitors. By investigating three-dimensional (3D) iso-Laplacian diagrams Nino & Munoz-Caro (2001) [7], found a common reactivity pattern in the charged forms. The aminopyridine–carboxylate/carboxylic acid systems may adopt two different proton-limiting structures, namely, O—$\cdots$H—N+ and O—H$\cdots$N, which yield hydrogen-bonding and ionic interactions, respectively. These two types of configurations can be represented by the graph-set designator $R^2_2(8)$ [8] [supramolecular heterosynthon (Scheme I)]. The $R^2_2(8)$ motif [robust motif] has been observed in DHFR-TMP [2,4-diamino-5-(3′,4′,5′-trimethoxybenzylpyrimidine] complexes [9] and it is one of the 24-most frequently observed cyclic-hydrogen bonded motifs in organic crystal structures [10]. The various hydrogen-bonding patterns involving aminopyrimidine–carboxylate interactions have been recently reported in the literatures [11]. Many of the hydrogen-bonded, frequently occurring motifs leading to supramolecular architectures play a significant role in crystal engineering [12, 13].

Picoline derivatives have pharmaceutical and biological applications, they have intense hypolipidemic effects, antineoplastic, and anti-inflammatory activity [14]. They have good activity against leukemia and human glioma cell growth [15]. In particular 2-amino-4-picoline and 2-amino-5-picoline are a sumpathomimetic agent which has been reported to have a marked presser effect in the experimental animals [16]. In addition, isophthalic acid is a good hydrogen-bonding donor and its two carboxylic acid moieties make an angle of 210° [17]. In this paper, we report the preparation and structural characterization of these two compounds, in which a complex hydrogen-bonding network involving charged organic molecules occur.

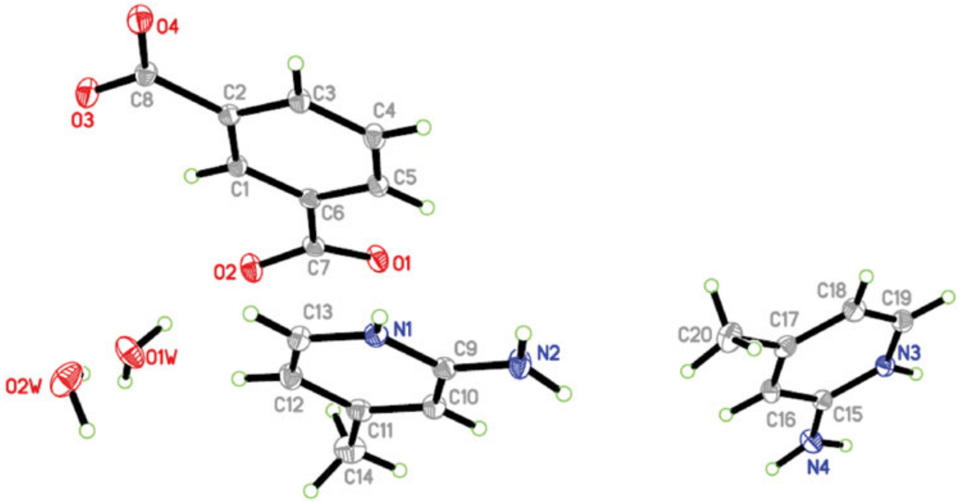


Figure 1. The molecular structure of compound 1, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

2. Experimental

2.1 Materials

All reagents and solvents employed were commercially available and used as received without further purification.

2.2 Physical Measurements

FTIR spectra were recorded on a PerkinElmer FTIR ATR Frontier Spectrophotometer in the form of KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 500 MHz, in DMSO-d$_6$, on Bruker 500MHz Avance III spectrometer. The chemical shifts are reported in parts per million (ppm) downfield from internal tetramethylsilane (TMS) (chemical shift in δ values). Single-crystal X-ray diffraction measurement of the title compounds were carried out with a Bruker Apex II CCD diffractometer at 100(1) K.

2.3 Preparation of 4AMPIP (1)

A hot methanol/water solution (10/10 mL) of 2-amino-4-methylpyridine (4AMP) (54 mg, Aldrich) and isophthalic acid (IP) (41 mg, Aldrich) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound (1) appeared after a few days. IR. Data(cm^{-1}, KBR pellet): 3268, 3033.7, 2814.4, 2575.2, 1989.13, 1713.77, 1644.49, 1605.93, 1542.64, 1490.78, 1422.33, 1372.15, 1291.34, 1224.73, 1157.09, 1069.86, 983.52, 873.54, and 761.98. ^{1}H NMR (500 MHz, DMSO), δ(ppm): 2.16 (s, 3H), 6.34–6.41 (m, 3H), 7.59–7.63 (m, 1H), 7.77 (t, $J = 5.1$ Hz 1H), 8.14–8.15 (m, 2H), and 8.50–8.51 (m, 1H). ^{13}C NMR (500 MHz, DMSO), δ (ppm): 167.2, 158.8, 148.7, 145.0, 133.0, 131.8, 129.9, 128.8, 113.4, and 108.7.

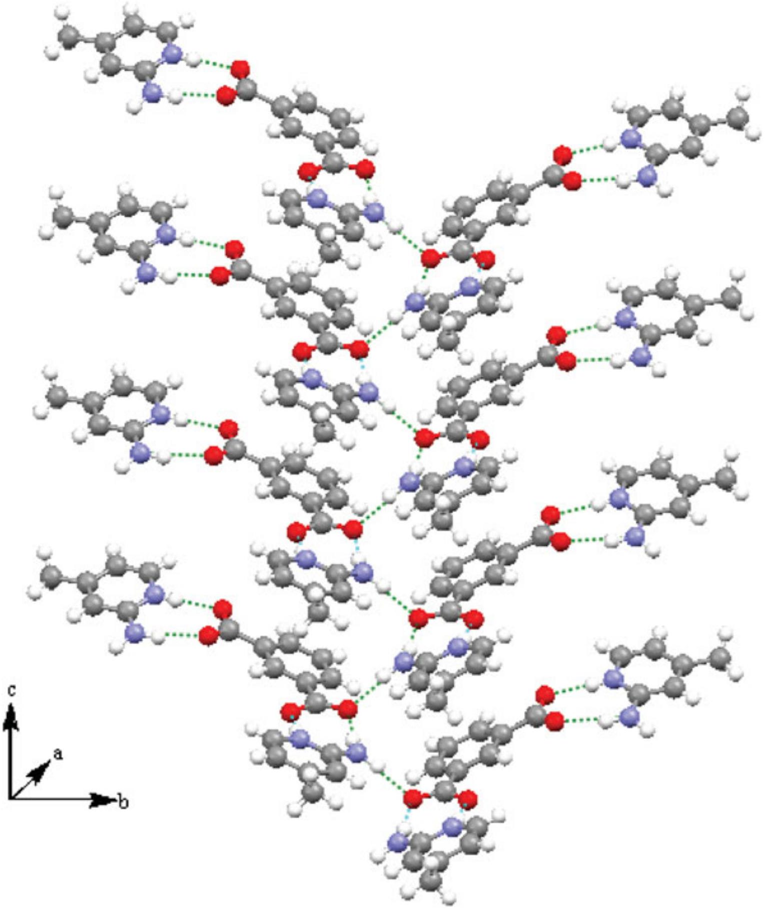


Figure 2. Supramolecular zigzag chain along the crystallographic c axis in 1.

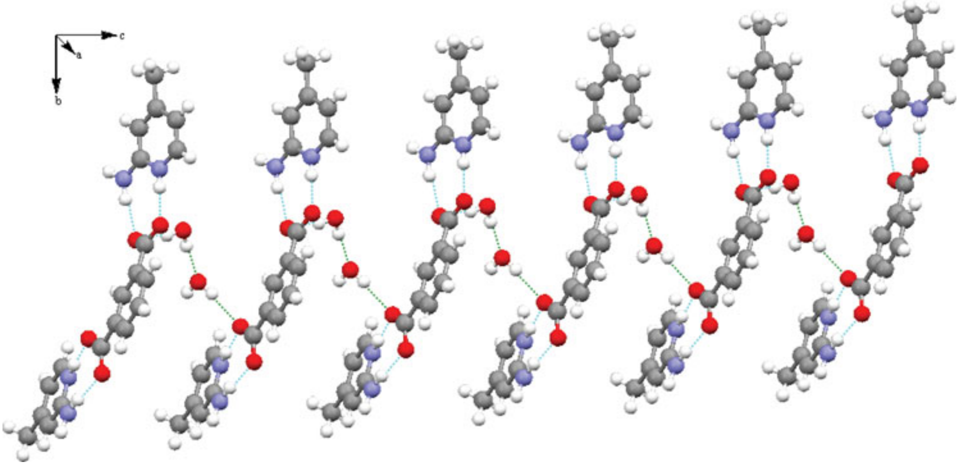


Figure 3. Hydrogen-bonded supramolecular chain made up of carboxylate groups and water molecules along the *c* axis.

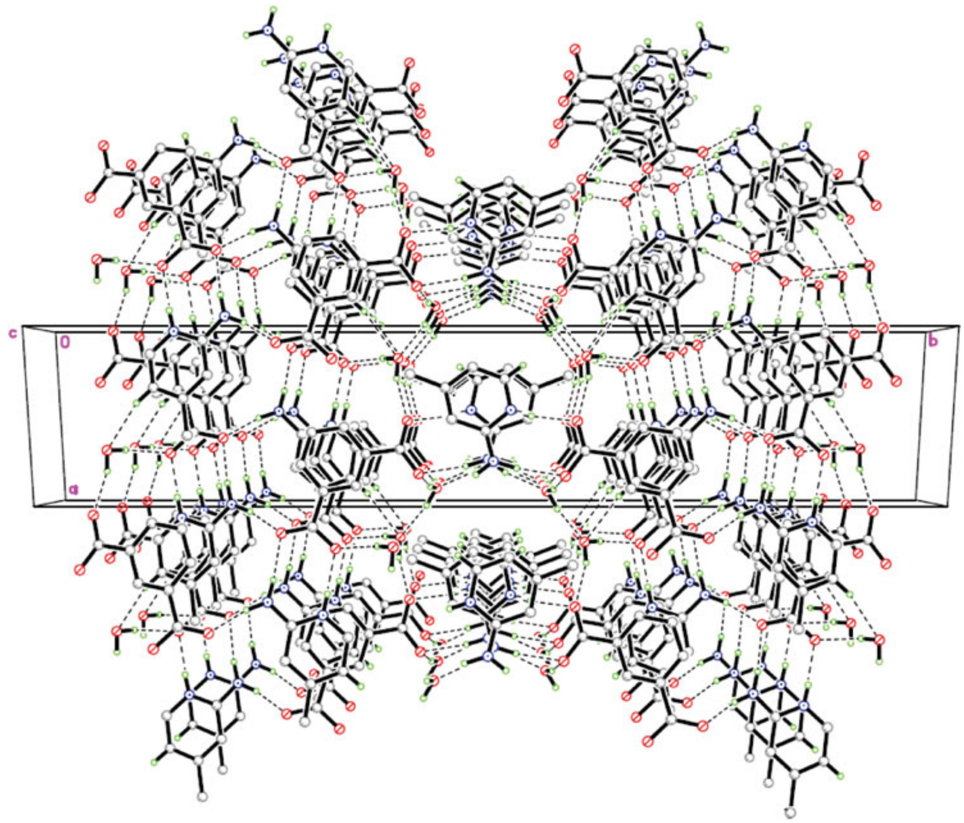


Figure 4. The crystal packing of compound 1. The H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

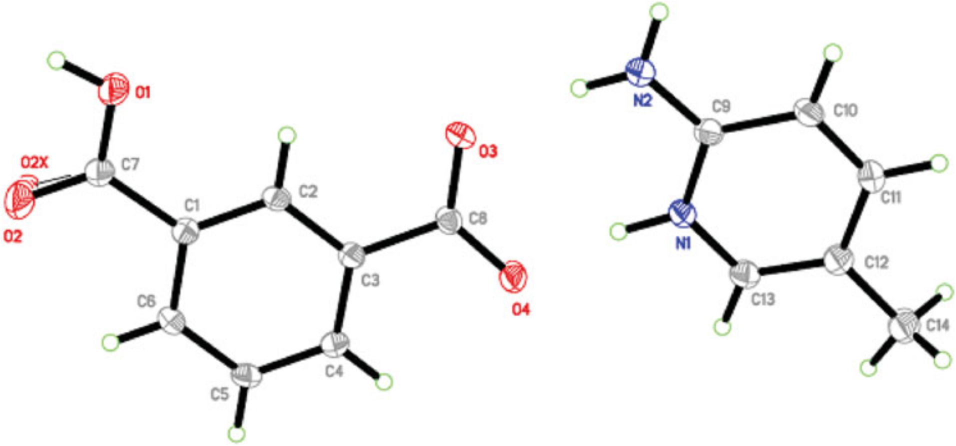


Figure 5. The molecular structure of compound 2, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

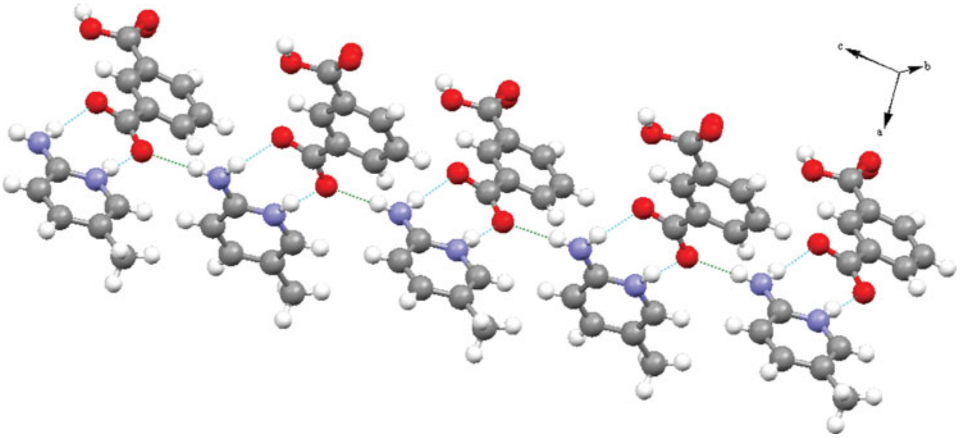


Figure 6. In compound 2 supramolecular adducts are sustained via charge-assisted heterosynthons I that form 1D chains.

2.4 *Preparation of 5AMPHIP (2)*

A hot methanol solution (10 mL) of 2-amino-5-methylpyridine (5AMP) (54 mg, Aldrich) and IP (41 mg, Aldrich) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound (2) appeared after a few days. IR. Data(cm^{-1}, KBR pellet): 3298.3, 2627.61, 2022.08, 1919.5, 1722.63, 1673.97, 1605, 1556.75, 1490.21, 1433.86, 1387.41, 1313.94, 1285.11, 1216.74, 1153.92, 1074.41, 983.55, 858.21, 758.38, and 685.03. ^{1}H NMR (500 MHz, DMSO), δ(ppm): 2.1 (s, 3H), 6.48 (d, 2H), 7.63 (t, 1H), 7.30 (dd,1H), 7.73 (s, 1H), 8.14–8.16 (d, 2H), and 8.50 (s, 1H). ^{13}C NMR (500 MHz, DMSO) δ (ppm):167.6, 157.5, 145.0, 139.7, 133.5, 132.3, 130.45, 129.3, 120.5, and 109.1.

2.5 *X-ray Crystallography Determination*

Single-crystal X-ray diffraction measurement of the title compounds was carried out with a Bruker Apex II CCD diffractometer at 100(1) K. Intensity of reflections was measured using a graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) with an ω scan mode in the ranges of $2.76 < \theta < 30.51°$ for **1** and $3.03 < \theta < 30.10°$ for **2**. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXTL [18]. Molecular graphics: SHELXTL [18], software used to prepare materials

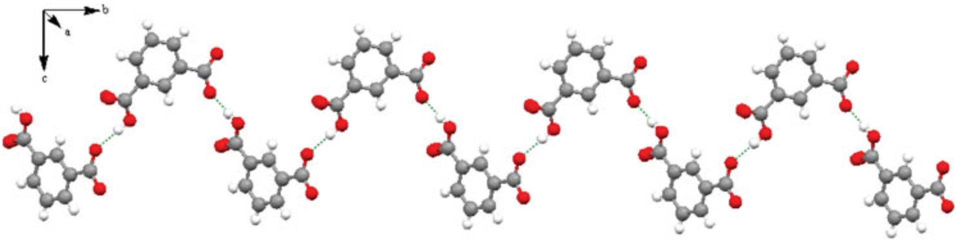


Figure 7. Supramolecular zigzag chain along the crystallographic b axis in 2.

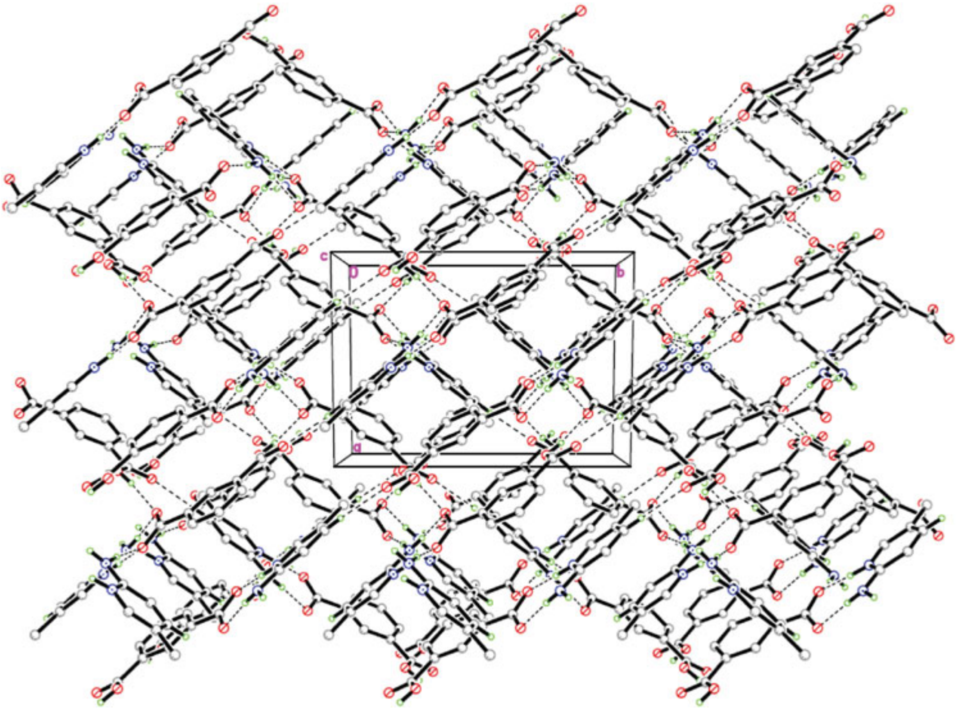


Figure 8. The crystal packing of compound 1. The H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

for publication: SHELXTL and PLATON [19]. For **2**, O2 of the carboxylic group was found to be disordered over two positions with an occupancy ratio of 0.55(8)/0.45(8) for O2/O2X. Anisotropic thermal factors were assigned to all non-hydrogen atoms. H atoms bonded to O or N were located in a difference Fourier map and were refined freely. The rest of the hydrogen atoms were positioned geometrically and were refined using a riding model, with Uiso(H) = 1.2 Ueq(C) or 1.5Ueq(methyl C). A rotating-group model was used for the methyl group. For **1**, in the final refinement, 3114 Freidel pairs were merged to determine the absolute structure. Crystallographic data and experimental details for the structural analyses are summarized in Table 1. The selected bond lengths and bond angles are given in Tables 2 and 4.

3. Results and Discussion

3.1 Infrared Spectrum

IR spectroscopy is an efficient method to determine the geometric structure of the molecules, and has been used widely in studying the structural consequences, such as in plane or out-of-plane vibrations. Herein, we have discussed the vibrational studies of substituted 2-aminopyridine derivatives (4AMP and 5AMP) with IP. The adduct formation is due to very high intermolecular hydrogen bonding forces that exist between the 4AMP and 5AMP cations and the carboxylate anions. Hence, they were pulled towards each other to form a very strong adduct. Compounds (**1**) and (**2**) have the stretches near 1850 and

Table 1. Crystal structure parameters of compound 1 and 2

Compound	**1**	**2**
Empirical formula	$C_8H_4O_4{\cdot}2(C_6H_9N_2){\cdot}2(H_2O)$	$C_8H_5O_4{\cdot}C_6H_9N_2$
Formula mass	418.45	274.27
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$
a (Å)	7.8914 (3)	9.0126 (2)
b (Å)	38.4226 (16)	12.2055 (3)
c (Å)	7.3354 (3)	12.3170 (2)
α (°)	90	90
β (°)	107.946 (1)	104.216 (1)
γ (°)	90	90
V (Å^3)	2115.94 (15)	1313.42 (5)
Z	4	4
Dc (g cm^{-3})	1.314	1.387
F(000)	888	576
θ range(°)	2.8–30.4	3.3–29.8
Measured reflns	23023	11393
Unique reflns	3246	3843
Observed reflns ($I > 2\sigma(I)$)	3135	2799
No. of parameters	313	208
$R^{(a)}$	0.030	0.045
$wR^{(b)}$	0.084	0.113
$GOF^{(c)}$	1.06	1.05
Residual peaks (e·Å^{-3})	0.28, −0.23	0.30, −0.29
$(\Delta/\sigma)_{\max}$	0.000	0.000

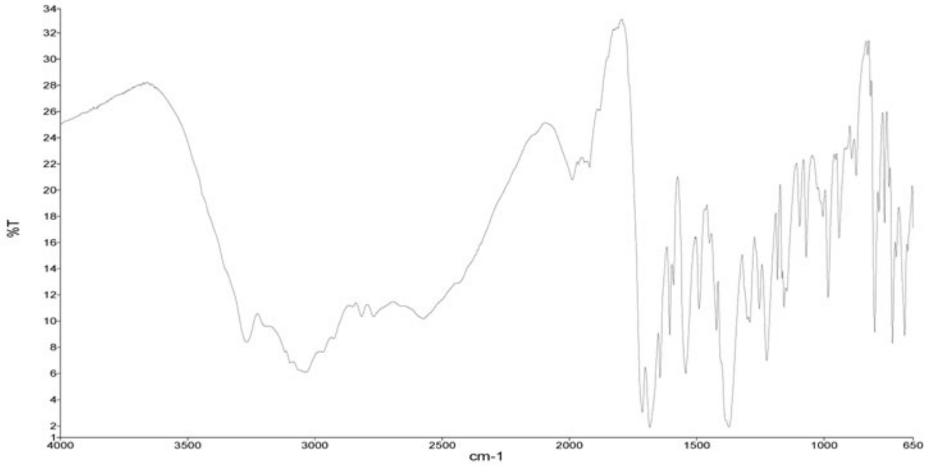
For 1, $w = 1/[\sigma^2(Fo^2) + (0.0623P)^2 + 0.2409P]$, where $P = (Fo^2 + 2Fc^2)/3$; and for 2, $w = 1/[\sigma^2(Fo^2) + (0.0487P)^2 + 0.2278P]$, where $P = (Fo^2 + 2Fc^2)/3$.

(a) $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, (b) $R_w = \{w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}\}^{1/2}$, (c) $GOF = \{\Sigma w(|F_o| - |F_c|)^2/(n\text{–}p)\}^{1/2}$, where n is the number of reflections and p the total number of parameters refined.

Table 2. Selected bond lengths (Å) and bond angles (°) for compound 1

Bond	Dist.	Bond	Dist.
O1-C7	1.2547(16)	N4-C15	1.3369(17)
O2-C7	1.2666(16)	N1-C9	1.3508(16)
O3-C8	1.2572(16)	N3-C15	1.3526(17)
O4-C8	1.2688(15)	N1-C13	1.3569(17)
N2-C9	1.3369(17)	N3-C19	1.3614(17)
C11-C14	1.5009(19)	C17-C20	1.5025(18)
Angle	(°)	Angle	(°)
C9-N1-C13	121.97(12)	C15-N3-C19	122.19(12)
O1-C7-O2	124.49(12)	O3-C8-O4	124.39(12)

(1) 4AMPIP



(2) 5AMPHIP

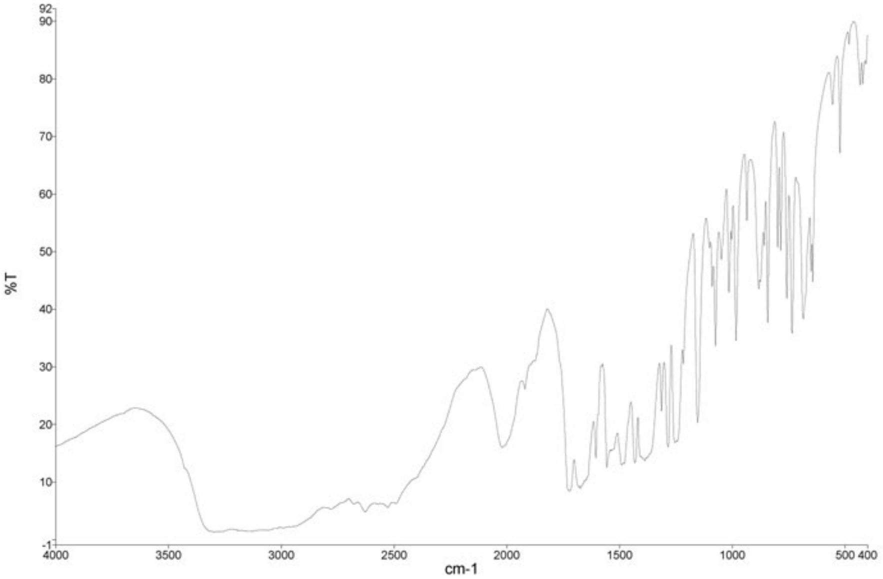
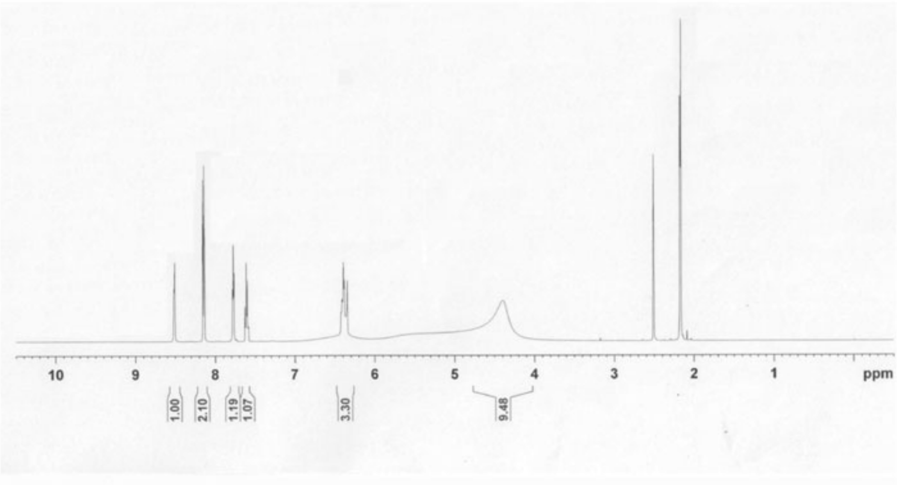


Figure 9. FTIR Spectra of 4AMPIP and 5AMPHIP.

1650 cm^{-1} which are characteristics of intermolecular N—H···O hydrogen bonds that can only come about if the two reagents form supramolecular heterosynthons (**I**). The vibrational spectra also suggest that the resulting products, in each case, can be classified as organic salts. Figure 9 shows the FTIR spectrum recorded in the range 650–4000 cm^{-1} at room temperature.

(1) 4AMPIP



(2) 5AMPHIP

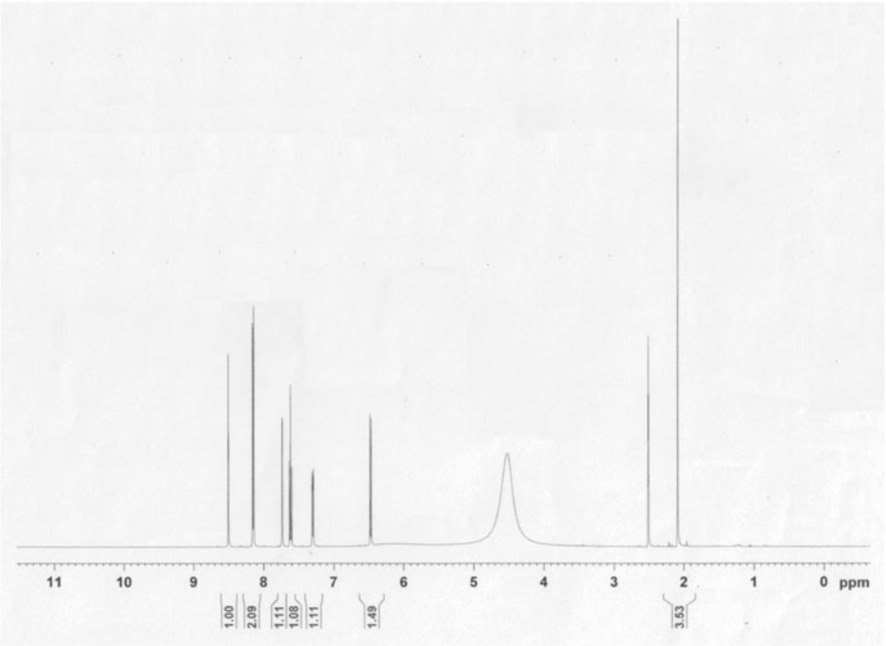


Figure 10. ^{1}HNMR spectra of 4AMPIP and 5AMPHIP.

The very strong and broad features at approximately 3700—3100 cm^{-1} in the IR spectra of the two compounds arise from N—H and O—H stretching frequencies. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [20]. The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1556–1605 cm^{-1} and 1372–1433 cm^{-1} in the two salts. The scaled -NH$_2$ symmetric and asymmetric stretches in the range of 3555–3446 cm^{-1} [21] are in agreement with the experimental values of

Table 3. Hydrogen bonding geometry (Å, °) for compound 1

D–H···A	D–H	H···A	D···A	D-H . . . A
O1W–H1W1 . . . O2	0.81	1.97(3)	2.7770(16)	172(3)
C12-H12A . . . O1W	0.95	2.55	3.463(2)	161
O2W-H1W2 . . . O1W	0.88(3)	1.92(3)	2.7987(18)	171(3)
O1W-H2W1 . . . O4^{i}	0.88(3)	1.89(3)	2.7419(17)	163(2)
O2W-H2W2 . . . O3^{ii}	0.92(3)	1.92(3)	2.8260(17)	167(3)
N1-H1N1 . . . O2^{iii}	0.85(3)	1.84(3)	2.6844(16)	175(3)
N2-H1N2 . . . O1^{iv}	0.95(2)	1.91(2)	2.8465(17)	169.0(19)
N2-H2N2 . . . O1^{iii}	0.91(3)	1.96(3)	2.8643(18)	173(2)
N3-H1N3 . . . O4^{v}	0.85(3)	1.85(3)	2.6933(16)	169(3)
N4-H1N4 . . . O3^{v}	0.95(2)	1.95(2)	2.8872(16)	170(2)
N4-H2N4 . . . O2W^{vi}	0.93(2)	1.94(2)	2.8540(17)	166(2)
C19-H19A . . . O1W^{vii}	0.95	2.60	3.3890(19)	141

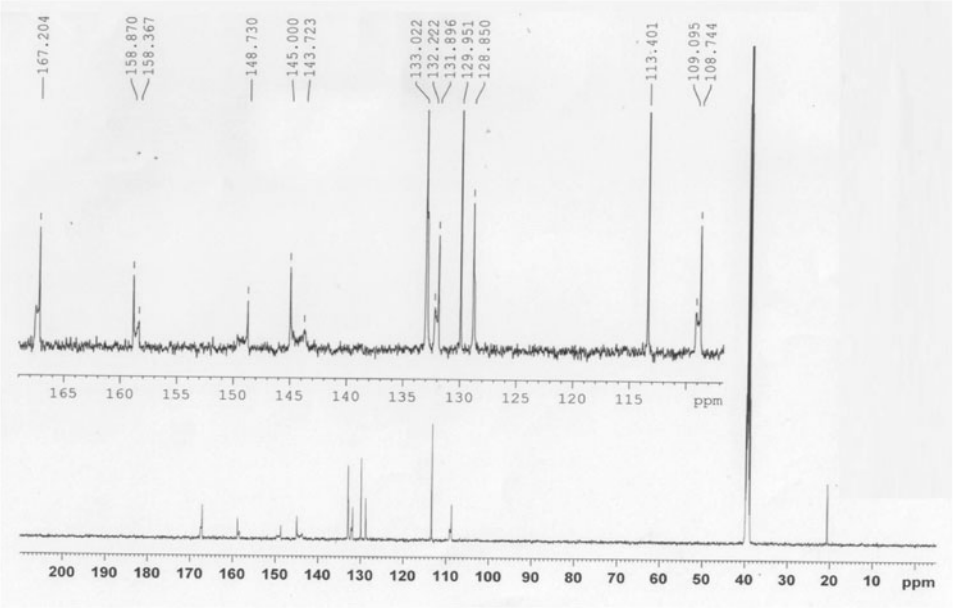
Symmetry codes: (i) $x+1$, y, $z+1$; (ii) x, y, $z+1$; (iii) $x-1$, y, z; (iv) $x-1/2$, $-y+1/2$, $z+1/2$; (v) $x+1/2$, $y+1/2$, $z+1$; (vi) $x+1/2$, $-y+1/2$, $z+1/2$; and (vii) $x-1/2$, $y+1/2$, z.

3268–3298 cm^{-1}. The -NH$_2$ scissoring vibration is at 1600 cm^{-1} [21] is also in very good agreement with the recorded FTIR value of 1644–1605 cm^{-1}. FTIR stretching mode with 1311–1331 cm^{-1} corresponding to C-NH$_2$ moiety was calculated to be 1313 cm^{-1}. The aromatic structures show the presence of C—H stretching vibrations at 3033 cm^{-1} for 1 and 3062 cm^{-1} for 2, which are the characteristic region for the ready identification of C—H stretching vibrations. The C=N stretching bands were observed at 1644 cm^{-1} for 1 and 1605 cm^{-1} for 2, respectively. The bands at 1466 and 1372 cm^{-1} are assigned to the CH$_3$ bending vibrations δ_{as}CH$_3$ and δ_sCH$_3$. In general, the phenyl ring (C=C) stretching vibration occurs in the region from 1625–1570 cm^{-1} and 1470–1430 cm^{-1}, respectively, in disubstituted benzene and pyridine derivatives [22]. For the phenyl ring C-C stretching frequency appears from 1604 cm^{-1} to 1446 cm^{-1} in 1 and from 1591 cm^{-1} to 1405 cm^{-1} in 2.

Table 4. Selected bond lengths (Å) and bond angles (°) for compound 2

Bond	Dist.	Bond	Dist.
O1-C7	1.3263(15)	N2-C9	1.3420(17)
O2-C7	1.222(14)	N1-C9	1.3506(15)
O3-C8	1.2607(14)	N1-C13	1.3632(16)
O4-C8	1.2635(15)	C12-C14	1.5095(19)
Angle	(°)	Angle	(°)
C9-N1-C13	122.44(12)	O1-C7-O2	122.6(6)
O3-C8-O4	124.24(12)		

(1) 4AMPIP



(2) 5AMPHIP

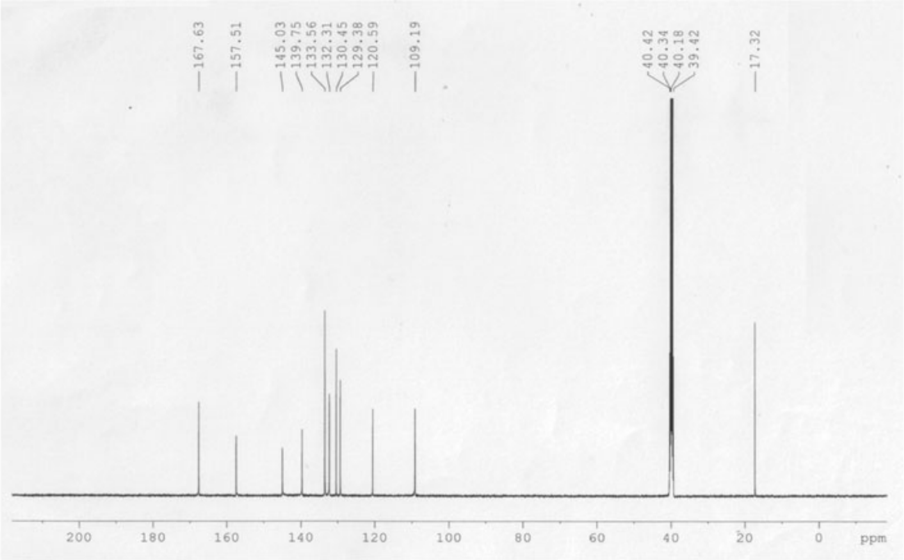


Figure 11. ^{13}CNMR spectra of 4AMPIP and 5AMPHIP.

3.2 ^{1}H and ^{13}C NMR Spectra

The ^{1}H and ^{13}C NMR spectra of two compounds (**1** and **2**) were carried out in DMSO-d_6 at room temperature using TMS as internal standard as shown in Figs. 10 and 11. The ^{1}H

Table 5. Hydrogen bonding geometry (Å, °) for compound 2

D–H···A	D–H	H···A	D···A	D-H . . . A
N1–H1N1 . . . O4	0.953(19)	1.711(19)	2.6562(15)	171.1(17)
N2-H1N2 . . . O3	0.899(18)	2.005(18)	2.8950(15)	170.2(16)
N2-H2N2 . . . O4^{i}	0.876(19))	2.02(2)	2.8949(15)	173.9(18)
O1-H1O1 . . . O3^{ii}	0.87(2)	1.81(2)	2.6755(14)	173(3)
C11-H11A . . . O2^{iii}	0.95	2.27	3.12(3)	149

Symmetry codes: (i) x, $-y+1/2$, $z-1/2$; (ii) $-x$, $y+1/2$, $-z+3/2$; and (iii) $x+1$, $y-1$, z.

NMR spectrum revealed a singlet signal at δ 2.16–2.50 ppm characteristic of methyl protons [23]. The signals at 6.34–8.47 ppm range are typical for hydrogen atoms are attached to aromatic (benzene) ring [23]. ^{1}H NMR spectrum are characterized by the presence of broad band in the range of $\delta = 7.59$–7.63 are assigned to the NH_2 group [24]. In the ^{13}C spectrum [25,26], the signals of the aromatic carbons at approx 108.7–148.7 and 157.5–158.8 ppm are assigned for (=C-N-) carbons, respectively. The (=C-H) groups appear at $\delta = 113.4$ and 120.5 ppm, respectively. Besides, the (C=O) groups resonance is at $\delta = 167.2$–167.6 ppm.

3.3 Crystal Structure of 1

Compound **1** is shown to be a proton-transfer organic salt, in which the asymmetric unit composed of two 2-amino-4-methylpyridinium cations, one isophthalate anion and two water molecules (Fig. 1). Each 2-amino-4-methylpyridinium cation is planar, with a maximum deviation of 0.005(1) Å for atom C10 and 0.006(1) Å for atom C17. The carboxylate C—O bond distances are 1.2548(16), 1.2667(17) and 1.2572(17), 1.2688(18) Å (Table 2) within the carboxylate groups and the C—N—C angles in the 2-amino-4-methylpyridinium cations are 121.97° and 122.18° (Table 2). The carboxylate groups are twisted from the plane of the aromatic moiety at 15.86(16)° and 5.14(16)°, respectively. The intermolecular hydrogen bonds of the heterosynthons **I** are within anticipated ranges: 2.623(2) and 2.619(2) Å for N+(py)· · ·O— and 2.788(2) and 2.799(2) Å for N(am)· · ·O—.

In compound **1**, 2-amino-4-methylpyridinium ions interact with both carboxylate groups of the isophthalate anions via charge-assisted supramolecular heterosynthons **I**, thereby affording 2:1 supramolecular adducts $R_2^2(8)$ [8]. The adducts are further interconnected into a zigzag chain of supramolecular heterosynthons via N(am)· · ·O^{-} hydrogen bonds formed between the anti oriented N—H of amine groups and adjacent carboxylates (Fig. 2). The water molecule plays a pivotal role in building the supramolecular architecture by bridging two isophthalate anions, through O—H· · ·O hydrogen bonds (Fig. 3). Each H atom of the water molecules acts as a single donor and the O atoms act as a single acceptor. In this structure, five types of classical hydrogen bonds are observed, viz. cation-anion [N—H· · ·O], cation-water [N—H· · ·O2W and C—H· · ·O1W], anion-water [O1W—H· · ·O and O2W—H· · ·O], and water-water [O2W—H· · ·O1W] (Fig. 4, Table 3). All these interactions bond link the molecules within the layers and also link the layers together, forming a 3D network. Furthermore, the crystal structure is stabilized by the π–π interactions between pyridine ring of 2-amino-4-methylpyridinium cation forms stacking with the aryl rings of isophthalate anion with the interplanar and the centroid-centroid distance of 3.3561(5) and 3.5068(8) Å, respectively, with a slip angle (the angle between the centroid vector and the normal to the plane) of 28.68°. A similar type of stacking is also observed between two 4AMP cations related by an inversion centre. The centroid-to-centroid distance and interplanar distance are 3.7942(8) and 3.3286(6) Å, respectively, the slip angle being 28.68°.

3.4 Crystal Structure of 2

Crystallization of isophthalic acid with pyridine also yields a proton-transfer organic salt, compound **2**. The asymmetric unit composed of a 2-amino5-methylpyridinium cation and a hydrogen isophthalate anion (Fig. 5). 2-amino-5-methylpyridinium cation is planar, with a maximum deviation of 0.003(1) Å for atoms C9 and C12. Isophthalic acid possesses two carboxylic groups that are amenable to the formation of **I** or **II**, but a 1: 1 complex is formed in **2** since the acid molecule only undergoes single deprotonation. The carboxylate and aminopyridinium moieties form the expected $R_2^2(8)$ supramolecular heterosynthon **I**. The C—O bond distances in the carboxylate moiety are 1.2607(15) and 1.2635(16) Å (Table 4) and the C—N—C angle of 2-amino-5-methylpyridinium is 122.44(12)° (Table 4). The C—O bond lengths in the acid moiety are 1.22(3) and 1.3264(15) Å. The hydrogen-bond distances of supramolecular heterosynthon **I** are 2.6562(15) and 2.8950(15) Å for N^+(py)···O^- and N(am)···O^-, respectively.

The antioriented N—H of the amine group interacts with another carboxylate (N···O^- : 2.8949(15) Å), thereby bridging the adjacent supramolecular heterosynthons (Fig. 6). The carboxylic acid group is involved in a charge-assisted O—H···O^- (O···O^- : 2.6755(14) Å) interaction with a neighboring carboxylate group, to form a supramolecular zigzag chain along the *b* axis, with the graph-set notation *C(8)*; this is shown in Fig. 7. The crystal structure is further stabilized by weak C—H···O hydrogen-bond (Table 5) resulting a 3D network (Fig. 8). π–π stacking interaction is observed between two hydrogen isophthalate anions related by an inversion center (*x, y, z* and *–x, 1-y, 2-z*), The interplanar distance and centroid-to-centroid distance are 3.5822(5) Å and 3.7649(8) Å, respectively, the slip angle being 17.92°.

Conclusions

Two novel title compounds [(4AMPIP) (**1**) and (5AMPHIP) (**2**)] were synthesized and they were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and single crystal XRD studies. Further the crystal structures were identified by some noncovalent interactions. In both compounds, the carboxylate anion (O atoms) are hydrogen-bonded to the protonated pyridine rings to form a hydrogen-bonded supramolecular heterosynthons (I)[(R_2^2(8)]. Furthermore, these heterosynthons (**I**) are connected via intermolecular O—H···O, N—H···O, and weak C—H···O hydrogen bonds. In conclusion, the reaction of isophthalic acid with 4AMP and 5AMP in water-methanol system constructs a two-dimensional and a 3D supramolecular networks, respectively. The experimental results show that the hydrogen bond plays an important role in the assembly of high-dimensional architectures.

Supplementary Materials

These data (CCDC 938787 (**1**) and 938788 (**2**) can be obtained free of charge at www.ccdc.cam.ac.uk.conts/retrieving.html/ or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44(0) 1223–336033; e-mail: deposit@ccdc.cam.ac.uk.

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