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Molecular and Crystal Structure of Two Organic Acid–Base Salts from 2-amino-6-methylpyridine and *meta* and *para* Methylbenzoic Acids

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*Two crystalline organic acid-base salts 2-amino-6-methylpyridinium 3-methylbenzoate [(2A6MP)$^+$.(3MBA)$^-$] (**1**) and 2-amino-6-methylpyridinium 4-methylbenzoate [(2A6MP)$^+$.(4MBA)$^-$] (**2**) were obtained from self-assembly of the corresponding acidic components with the 2-amino-6-methylpyridine, and their structures were fully characterized by FTIR, ^{1}H NMR, ^{13}C NMR spectroscopic techniques, and single crystal X-ray diffraction. Both compounds are ionic, with proton transfer occurring to the pyridine nitrogen (NH) of 2-amino-6-methylpyridinium moiety. These structures adopted supramolecular heterosynthons [$R_2^2(8)$]. The compound (**1**) crystallizes in the monoclinic crystal system with the space group $P2_1/c$ with* a = *7.3175(3) Å,* b = *23.6223(12) Å,* c = *7.5523(4) Å, β = 106.323(3) °,* v = *1252.84 (11) Å^3,* Z = *4. The compound (**2**) crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions* a = *7.1580(7) Å,* b = *13.4242(13) Å,* c = *14.3238(14) Å, α = β = γ = 90°,* v = *1375.4(2) Å^3,* Z = *4. Supramolecular architectures of the compounds 1 and 2 involve N—H… O hydrogen bonds as well as other nonvocalent associations. The role of these noncovalent interactions in the crystal packing is analyzed. For the presence of these weak noncovalent interactions, both compounds displayed two and three dimensional framework structure.*

Keywords Aminopyridine-acidic components; crystal structure; hydrogen bond; organic salt; structure characterization; supramolecular heterosynthon; X-ray diffraction

1. Introduction

Supramolecular interactions have attracted considerable attention during the past few years because the utilization of intermolecular noncovalent interactions is relied upon for the design and development of functional materials [1, 2]. Noncovalent interactions form the backbone of supramolecular chemistry and include classical/nonclassical hydrogen bond,

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stacking, electrostatic, and charge-transfer interactions [3–5]. Intermolecular interactions can be used as key molecular recognition elements in the design of crystalline multiple component systems. Multicomponent crystalline systems can be divided into cocrystals, solvates, and salts. Active pharmaceutical ingredients have been reported to exist in various forms including salts, solvates, hydrates, and recently cocrystals [6, 7].

In pharmaceuticals, salt formation is often used in order to modify the properties of the compounds [8, 9], such as increasing or decreasing solubility, improving stability, and reducing hygroscopicity of a drug product. There are many interesting hydrogen bonded topological structures ranging from infinite 1-D chain to 3-D supramolecular framework [10, 11]. The carboxylic acid bears the important hydrogen bonding functional group for crystal engineering [12]. Carboxylic acids aggregate in the solid state as dimer, catemer, and bridged motifs [13, 14]. It is interesting to exploit the robust and directional recognition of carboxylic acids with N-containing basic building blocks [15–19]. In this regard, the most frequently used moieties with hydrogen bonding capability are aminopyridine derivatives.

2-Aminopyridine and its derivatives are used as dyes [20] and pyridinium cation derivatives often possess antibacterial and antifungal activities [21]. Some aminopyridines are found to demonstrate pharmacological activity as K^+-channel inhibitors. By investigating three-dimensional iso-Laplacian diagrams Nino & Munoz-Caro (2001) [22], found a common reactivity pattern in the charged forms. The aminopyridine–carboxylate/carboxylic acid systems may adopt two different proton-limiting structures, namely, O—H . . . N (1) $\rightarrow$ O^-—H . . . N^+(2), which yield hydrogen-bonding and ionic interactions, respectively. These two types of configurations can be represented by the graph-set designator $R^2_2(8)$ [23] [supramolecular heterosynthon (Scheme 1)]. The $R^2_2(8)$ motif [robust motif] has been observed in DHFR-TMP [2, 4-diamino-5-(3′,4′,5′-trimethoxybenzylpyrimidine] complexes [24] and it is one of the 24-most frequently observed cyclic-hydrogen bonded motifs in organic crystal structures [25]. The various hydrogen-bonding patterns involving aminopyrimidine–carboxylate interactions have been recently reported in the literatures [26–28]. Many of the hydrogen-bonded, frequently occurring motifs leading to supramolecular architectures play a significant role in crystal engineering [29, 30].

Picoline derivatives have may pharmaceutical and biological applications, they have intense hypolipidemic effects, antineoplastic, and anti-inflammatory activity [31, 32]. They have good activity against leukemia and human glioma cell growth [33]. In particular, 2-amino-6-methylpyridine is a sympathomimetic agent which has been reported to have a marked presser effect in the experimental animals. The crystal structures of 2-amino-6-methylpyridine [34], 2-amino-6-methylpyridinium 3-chlorobenzoate [35], 2-amino-6-methylpyridinium 4-hydroxybenzoate [36] have been reported. In addition, 4-methylbenzoic acid is used as an intermediate for polymer stabilizers, pesticides, light sensitive compounds. The crystal structures of 3-methylbenzoic acid (3MBA) [37] and 4-methylbenzoic acid (4MBA) [38] have been reported. 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.

2. Experimental Section

2.1 Materials and Physical Measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. FTIR spectra were recorded on a

PerkinElmer 2000 Spectrum 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 500 MHz 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 was carried out with a Bruker Apex II CCD diffractometer at 100(1) K.

2.2. Preparation of the Organic Acid–Base Adducts 1–2

2.2.1 *2-Amino-6-methylpyridinium 3-methylbenzoate [(2A6MP)$^+$.(3MBA)$^-$] (**1**).* A hot methanol solution (20 ml) of 2-amino-6-methylpyridine (2A6MP) (54 mg, Aldrich) and 3-methylbenzoic acid (3MBA) (34 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 (I) appeared after a few days. IR. Data(cm^{-1}, KBR pellet): 3396 s [m, ν_{as}(NH)], 3235 [νs(NH)], 3125 m, 3074 m, 3045 m, 2836 m, 2177 m, 1756 s [ν(C=O)], 1636 m, 1584 [s, ν_{as}(COO$^-$)], 1559 m, 1336 [s, ν_s(COO$^-$)], 1244 m, 1186 m, 1112 m, 905 m, 838 m, 723 m, 688 m, 659 m. ^{1}H NMR (500 MHz, DMSO; δ ppm): 2.2 (s, 6H), 6.25 (s, 1H), 6.35 (d, 2H), 7.41 (dd,1H), 7.74 (s, 1H), 7.78 (t, 3H). ^{13}C NMR (500 MHz, DMSO; δ ppm): 168.2 (C=O), 159.5 and 155.7 (=C–N–), 138.3, 138.1, 133.7, 130.2, 111.2, and 105.6 (Ar), 23.9 and 21.3 (CH_3)

2.2.2 *2-Amino-6-methylpyridinium 4-methylbenzoate [(2A6MP)$^+$.(4MBA)$^-$] (**2**).* A hot methanol solution (20 ml) of 2-amino-6-methylpyridine (2A6MP) (54 mg, Aldrich) and 4-methylbenzoic acid (3MBA) (34 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 (II) appeared after a few days. IR. Data (cm^{-1}, KBR pellet): 3480 s [m, ν_{as}(NH)], 3319 [s, νs(NH)], 3249 m, 3169 m, 2953 m, 2796 m, 2507 m, 2166 m, 1732 s [ν(C=O)], 1644 m, 1611 m, 1567[s, ν_{as}(COO$^-$)], 1534 m, 1432 m, 1340 [s, ν_s(COO$^-$)], 1245 m, 1167 m, 1047 m, 1020 m, 986 m, 940 m, 871 m, 842 m, 822 m, 775 m, 733, 694 m, 638 m, 612 m. ^{1}H NMR (500 MHz, DMSO; δ ppm): 2.22 (s, 6H), 6.33 (s, 1H), 6.34 (d, 2H), 7.27 (t, 1H), 7.30 (dd,1H), 7.85 (t, 3H). ^{13}C NMR (500 MHz, DMSO; δ ppm): 167.5 (C=O), 159.0 and 155.3 (=C−N−), 142.8, 13.5, 129.3, 129.1, 129.0, 110.7, and 105.1 (Ar), 23.5 and 21.1 (CH_3).

2.3. X-Ray Crystallography Determination

The X-ray single crystal diffraction data were collected at 100(1) K with MoKα radiation (λ = 0.71073 Å) using a Bruker Apex II CCD diffractometer equipped with a graphite monochromatic.

The data for these compounds were processed with SAINT and corrected for absorption using SADABS [39]. The structures were solved by direct methods using the program SHELXTL [40] and refined by full-matrix least squares technique on F^2 using anisotropic displacement parameters using SHELXTL [40] program. All geometrical calculations were carried out using the program PLATON [41]. The molecular graphics were drawn using SHELXTL [40] program.

Anisotropic thermal factors were assigned to all non-hydrogen atoms. The N-bound hydrogen atoms was located in a difference Fourier map and refined freely [0.87(3)–0.97(3) Å]. The remaining hydrogen atoms were fixed at calculated positions with a common

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Table 1. Crystal structure parameters of compound 1 and 2

Compound	1	2
Emperical formula	$(C_6H_9N_2)^+.(C_8H_7O_2)^-$	$(C_6H_9N_2)^+.(C_8H_7O_2)^-$
Formula mass	244.29	244.29
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	7.3175 (3)	7.1580 (7)
b (Å)	23.6223 (12)	13.4242 (13)
c (Å)	7.5523 (4)	14.3138 (14)
$\alpha(^\circ)$	90	90
$\beta(^\circ)$	106.323 (3)	90
$\gamma(^\circ)$	90	90
V (Å^3)	1252.84 (11)	1375.4 (2)
Z	4	4
*D*c (g cm^{-3})	1.295	1.180
F(000)	520	520
θ range(°)	2.9–26.0	2.9–23.7
Measured reflns	13,058	7788
Unique reflns	2419	1834
Observed reflns ($I > 2\sigma(I)$)	1698	1340
No. of parameters	177	178
$R^{(a)}$	0.0803	0.0384
$wR^{(b)}$	0.1721	0.110
$GOF^{(c)}$	1.08	1.04
Residual peaks (e·Å^{-3})	0.26, −0.30	0.12, –0.12
$(\Delta/\sigma)_{max}$	0.000	0.000

Note. For 1, $w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 1.4449P]$, where $P = (F_o^2 + 2F_c^2)/3$; and for 2, $w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.0071P]$, where $P = (F_o^2 + 2F_c^2)/3$. [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] $GOF = \{\Sigma w(|F_o| - |F_c|)^2/(n–p)\}^{1/2}$, where *n* is the number of reflections and *p* the total number of parameters refined.

isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic U values of the parent carbon atoms. A rotating group model was applied to the methyl groups. The crystallographic parameters of the salts are tabulated in Table 1. Hydrogen bonding interactions are shown in Tables 2 and 3.

2.4. Infrared Spectrum and ^{1}H and ^{13}C NMR Spectra

The very strong and broad features at approximately 3700–3100 cm^{-1} in the IR spectra of the two compounds arise from O–H or N–H stretching frequencies. Pyridine ring stretching and bending are attributed to the medium intensity bands in the regions of 1500–1630 and 600–750 cm^{-1}, respectively. The intense peak at 1636 cm^{-1} (In **1**) and 1644 cm^{-1} (In **2**) are derived from the existence of the C=O stretches, and the band at 1244 cm^{-1} (In **1**) and 1245 cm^{-1} (In **2**) exhibits the presence of the C—O stretches of the *meta* and *para* methylbenzoate in both compounds. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [42, 43]. The most distinct feature in the

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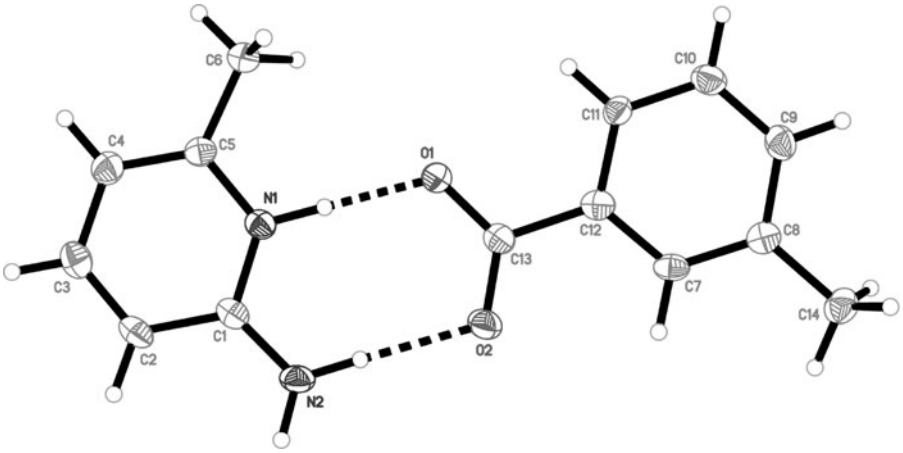

Figure 1. The molecular structure of compound 1, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1534–1644 cm^{-1} and 1245–1432 cm^{-1} in the two salts.

The ^1H 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. The ^1H NMR spectrum revealed a singlet signal at δ 2.22–2.51 ppm characteristic of methyl protons [44]. The signals at 6.24–7.85 ppm range are typical for hydrogen atoms are attached to aromatic (benzene) ring [44]. ^1H NMR spectrum is characterized by the presence of broad band in the range of δ = 7.24–7.74 are assigned to the NH_2 group [45]. In the ^{13}C spectrum [46, 47], the signals of the aromatic carbons at approx 105.6–142.7 and 155.7–159.4 ppm are assignee for (=C−N−) carbons, respectively. The (=C−H) groups appear at δ = 111.2 ppm and 138.2 ppm, respectively. Besides this, the (C=O) groups resonance is at δ = 167.5–168.2 ppm.

Results and Discussion

Compound **1** crystallizes as monoclinic block crystals in the space group $P2_1/c$. The asymmetric unit of 1 consists of one cation of 2-amino-6-methylpyridinium, and one anion of 3-methylbenzate, as shown in Fig. 1. This is salt where the COOH groups of the 3-methylbenzoic acids are ionized by proton transfer to the nitrogen atoms of 2-amino-6-methylpyridinium moieties, which is also confirmed by the bond distance of O1–C13 = 1.265 (4) Å and O2–C13 = 1.256(3) Å for the carboxylates (Table 4. The difference

Table 2. Hydrogen bonding geometry (Å, °) for compound 1

D−H ... A	D−H	H ... A	D ... A	D−H ... A
N2−H2N2···O2^{i}	0.90(3)	2.00(3)	2.886(4)	167 (3)
N2−H1N2···O2	0.95(5)	1.88(5)	2.825(4)	173 (4)
N1−H1N1···O1	0.97(5)	1.68(5)	2.640(4)	176 (5)

Note. Symmetry codes: (i) $x, -y + 1/2, z - 1/2$.

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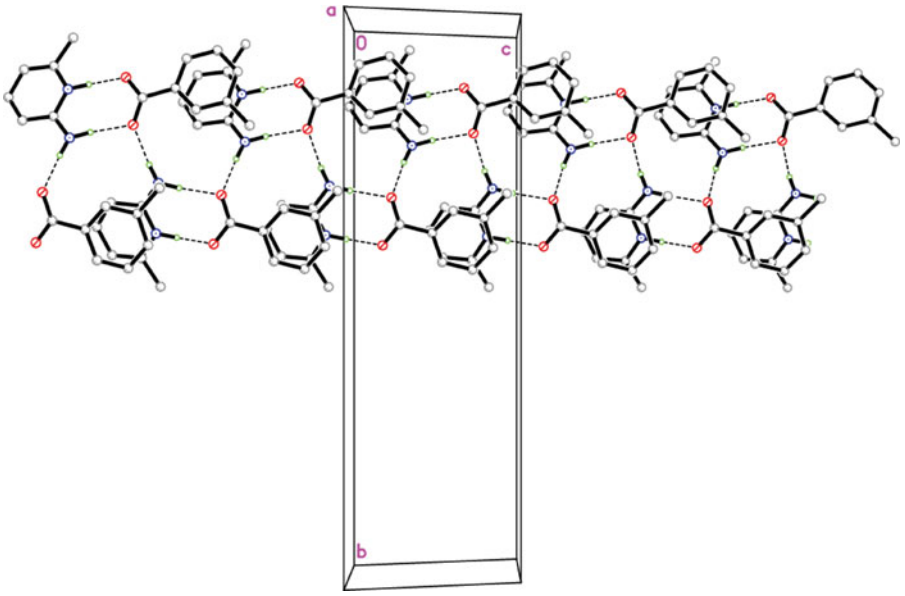

Figure 2. In compound 1 supramolecular adducts are sustained via charge-assisted heterosynthons I that form a zigzag chains.

(Δ is 0.009 Å) in bond distance between O1–C13 = 1.265 (4) Å and O2–C13 = 1.256 (3) Å in the carboxylate group in compound **1** is caused by the fact that O2 is involved in forming more hydrogen bonds than that of O1 (Table 2). In the 2-amino-6-methylpyridinium cation, a wider than normal angle [C1—N1—C5 = 123.3 (3)°] (Table 4) is subtended at

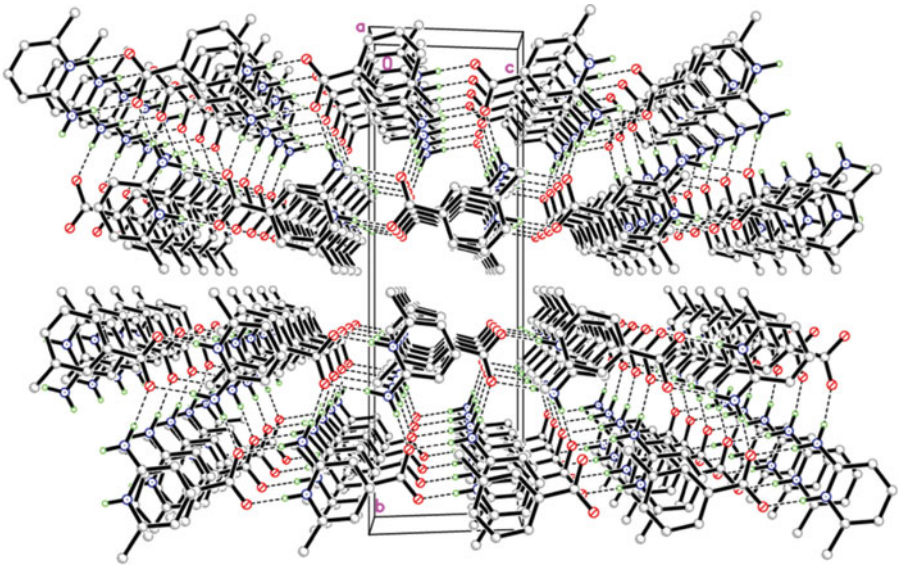

Figure 3. The crystal packing of compound 1. The H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

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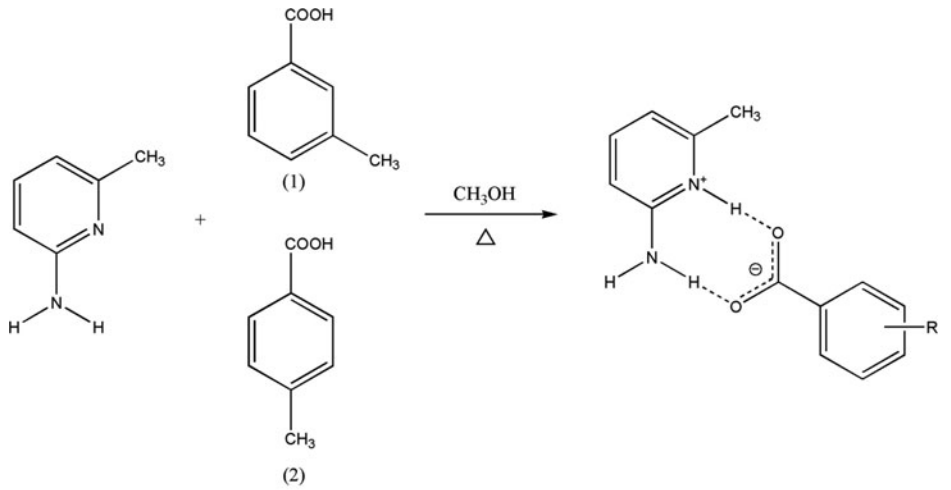

I R = 3-methyl (In **1**) and 4-methyl (In **2**)

Scheme 1. Supramolecular heterosynthons that can be formed between carboxylic acids and 2-aminopyridines: carboxylate supramolecular heterosynthon I.

the protonated N1 atom. 2-amino-6-methylpyridinium cation is planar, with a maximum deviation of 0.006(3) Å for atom C4. The dihedral angle between the pyridine (N1/C1–C5) and benzene (C7–C12) rings is 3.17(15)°. The carboxylate group of the 3-methylbenzoate anion is slightly twisted from the attached ring with the dihedral angle between C7—C12 ring and O1/O2/C13 plane being 1.9 (4)°. The bond lengths and angles are normal [48].

In compound **1**, 2-amino-6-methylpyridinium ions interact with both carboxylate group of the 3-methylbenzoate anions via N—H . . . O hydrogen bonds forming a cyclic hydrogen bonded ring motif (heterosynthon 1) represented by graphset notation $R_2^2(8)$ [49, 23, 30]. This ring motif is robust and is one of the 24 most frequently observed bimolecular cyclic

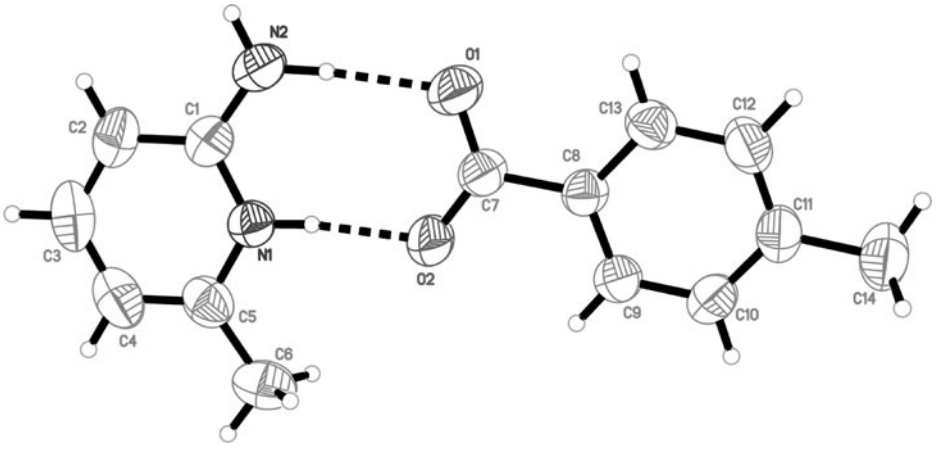

Figure 4. The molecular structure of compound 2, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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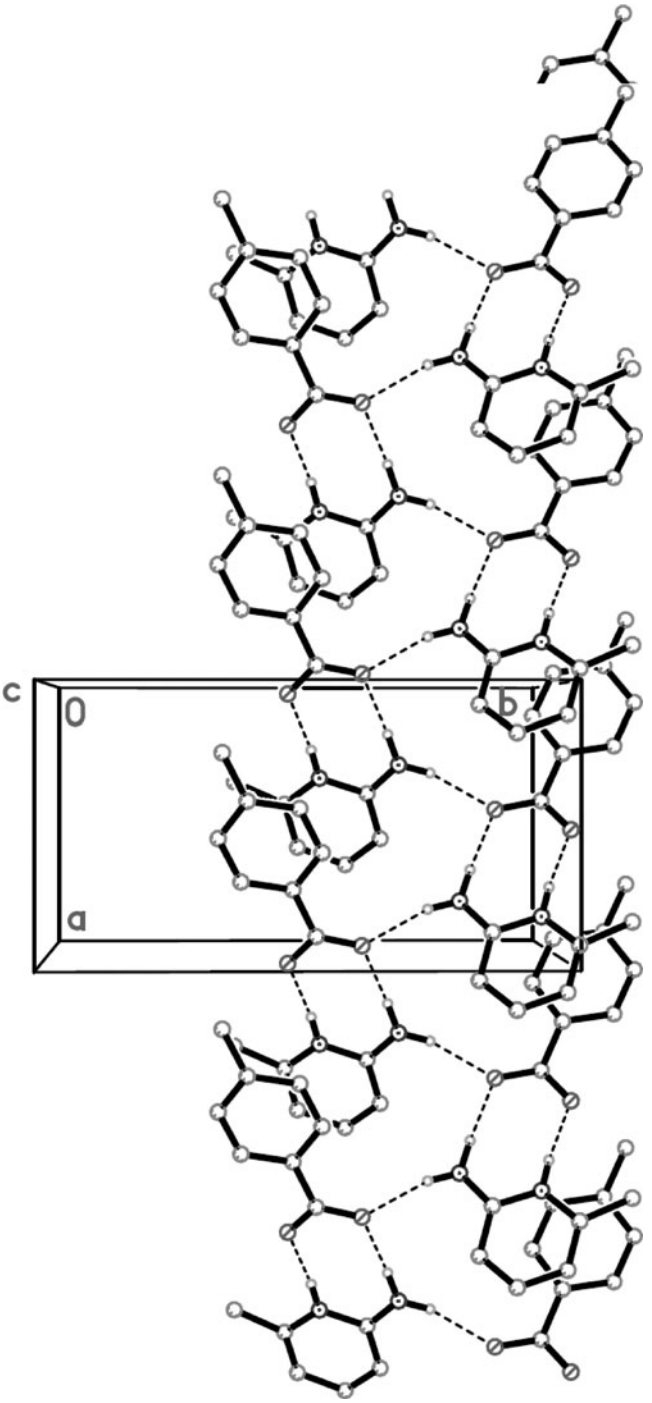

Figure 5. Helical chain formed in crystal structure 2 through interlinking of N—H . . . O bonds.

Table 3. Hydrogen bonding geometry (Å, °) for compound 2

D—H . . . A	D—H	H . . . A	D . . . A	D—H . . . A
N2—H1N2···O1^{i}	0.87(3)	1.99(3)	2.838(3)	164 (3)
N1—H1N1···O2	0.89(2)	1.76(2)	2.637(3)	173 (2)
N2—H2N2···O1	0.97(3)	1.88(3)	2.845(3)	175.0(19)
C14—H14*B*···*Cg1*^{ii}	0.96	2.81	3.617(3)	142

Note. Symmetry codes: (i) x + 1/2, −y + 3/2, − z + 1; (ii) −x + 1/2, −y + 2, z − 1/2.

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hydrogen bonded motifs in organic crystal structures [25]. The adducts are further interconnected by supramolecular heterosynthons N(am) . . . O^- hydrogen bonds (Table 2) formed between the anti oriented N—H of amine groups and carboxylate oxygen (O2), forming a zigzag chain running along the *c* axis (Fig. 2). Furthermore, the crystal structure is stabilized by the weak π—π interactions between pyridine ring of 2-amino-6-methylpyridinium cation forms stacking with the aryl rings of 3-methylbenzoate anion with the interplanar and the centroid–centroid distance of 3.4207 (12) and 3.5618 (18) Å, respectively, with a slip angle (the angle between the centroid vector and the normal to the plane) of 16.18å (Fig. 2), which lead to the formation a three-dimensional supramolecular structure that links that chains into layers along the ac plane (Fig. 3).

The compound **2** of the composition [$(2A6MP)^+$·$(4MBA)^-$] was prepared by reacting equal mol of 2-amino-6-methylpyridinium and 4-methylbenzoate in 1:1 ratio, which crystallizes as orthorhombic colorless crystals in the non-centrosymmetric space group $P2_12_12_1$. The structure of **2** with the atom numbering scheme is shown in Fig. 4. This is salt where the COOH groups of the 4-methylbenzoic acids are ionized by proton transfer to the nitrogen atoms of 2-amino-6-methylpyridinium moieties, which is also confirmed by the bond distance of O1–C7 = 1.252(2) Å and O2–C7 = 1.255(3) Å for the carboxylates (Table 5). In the 2-amino-6-methylpyridinium cation, a wider than normal angle [C1—N1—C5 = 123.6 (2)°] (Table 5) is subtended at the protonated N1 atom. The 2-amino-6-methylpyridinium cation is planar with a maximum deviation of 0.006 (2) Å for atom C1. The dihedral angle between the pyridine (N1/C1–C5) and benzene (C8–C13) rings is 9.02 (11)°. The carboxylate group of the 4-methylbenzoate anion is slightly twisted from the attached ring with the

Table 4. Selected bond lengths (Å) and bond angles (°) for compound 1

Bond	Dist	Bond	Dist
O1—C13	1.265 (4)	N1—C1	1.349 (4)
O2—C13	1.256 (3)	N1—C5	1.365 (4)
C8—C14	1.509 (4)	C1—N2	1.329 (4)
C5—C6	1.500 (4)	C12—C13	1.506 (4)
Angle	(°)	Angle	(°)
C1—N1—C5	123.3 (3)	N2—C1—N1	118.1 (3)
O1—C13—O2	124.7 (3)	N2—C1—C2	123.9 (3)
O2—C13—C12	118.4 (3)	O1—C13—C12	116.9 (3)

Table 5. Selected bond lengths (Å) and bond angles (å) for compound 2

Bond	Dist	Bond	Dist
O1−C7	1.252 (2)	N1−C1	1.350 (3)
O2−C7	1.255 (3)	N1−C5	1.358 (3)
C11−C14	1.505 (4)	C1−N2	1.324 (3)
C5−C6	1.486 (4)	C7−C8	1.498 (3)
Angle	(°)	Angle	(°)
C1−N1−C5	123.6 (2)	N2−C1−N1	118.0 (2)
O1−C7−O2	124.1 (2)	N2−C1−C2	124.0 (2)
O2−C7−C8	117.07 (18)	O1−C7−C8	118.8 (2)

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dihedral angle between C8–C13 ring and O1/O2/C7 plane being 9.6 (3)°. The bond lengths and angles are normal [48].

In compound **2**, 2-amino-6-methylpyridinium ions interact with both carboxylate group of the 4-methylbenzoate anions via charge-assisted supramolecular heterosynthons **I**, thereby affording 1:1 supramolecular adducts [$R_2^2(8)$ [23, 30, 49]. The ion pairs are linked through charge-assisted N−H···O$^-$ formed from the free amino proton and carboxylate moiety to form a helical chain running along the *a* axis (Fig. 5). Adjacently arranged heterosynthons **I** units in two different planes are attacked through π—π interactions between an anion and a pyridinium base with Cg−Cg distance 3.7986 (13) Å, interplanar distance 3.5400 (9) Å and slip angle of 21.27°. The crystal structures are further stabilized by weak C−H . . . π interactions (Table 3, Fig. 6) involving the N1/C1–C5 (centroid Cg2) ring. The $R_2^2(8)$ morif and the supramolecular chain are further interlinked by weak C−H . . . π and π−π interactions, resulting in three-dimensional network (Fig. 7).

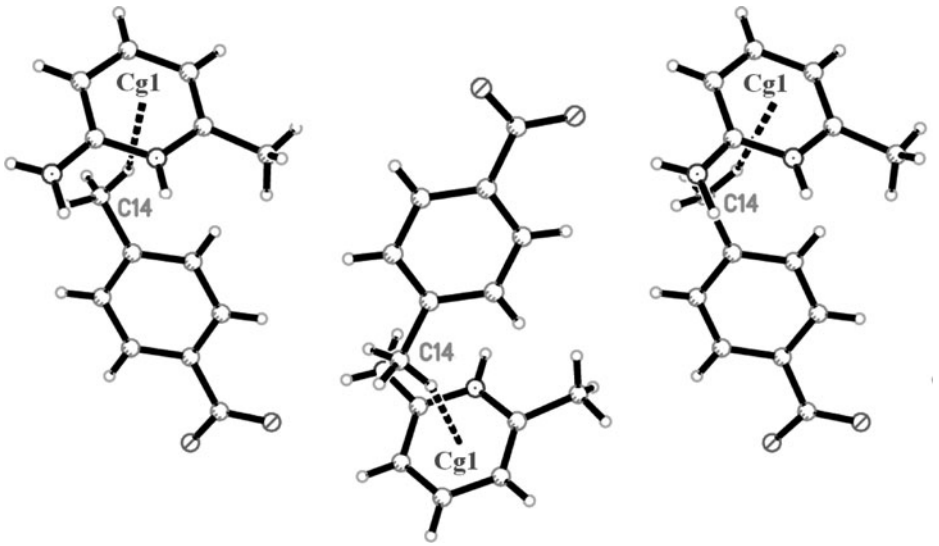

Figure 6. C−H . . . π stacking interactions observed between an anion and a pyridinium base rings in 2 is shown.

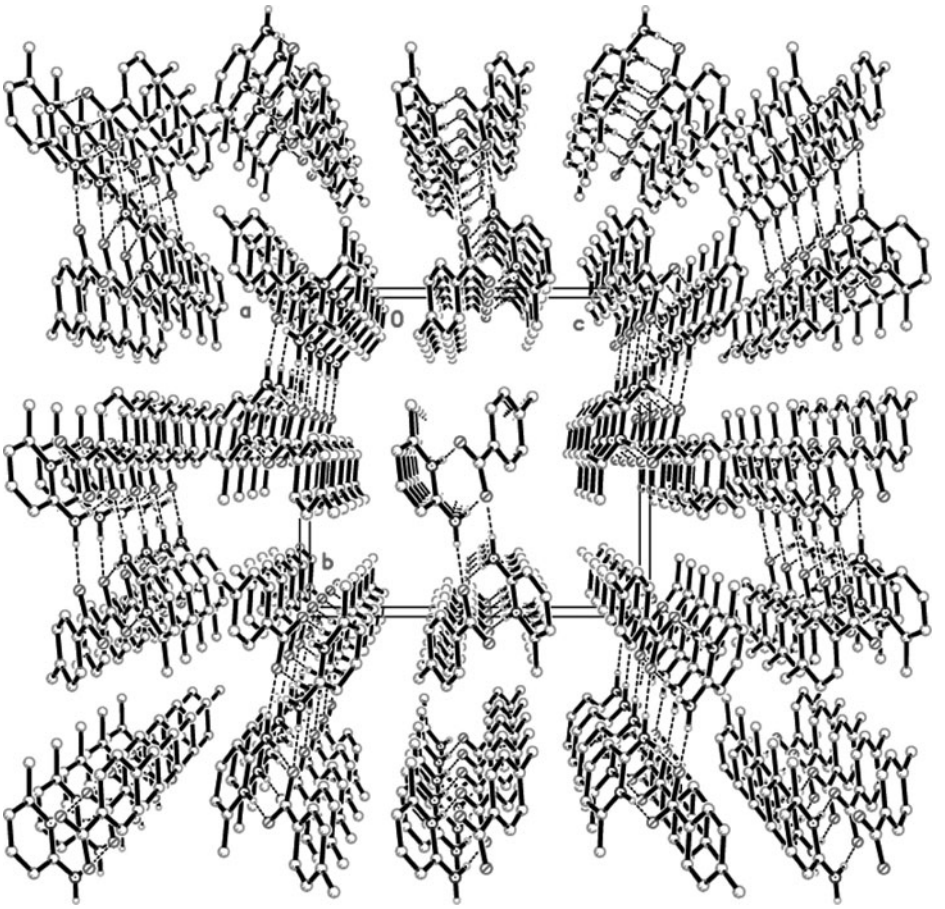

Figure 7. The crystal packing of compound 2. The H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

Conclusions

Two novel organic acid base adduct compounds [$(2A6MP)^+.(3MBA)^-$ (**1**) and $(2A6MP)^+.(4MBA)^-$ (**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 N—H... O hydrogen bonds to form supramolecular zigzag chain. Furthermore, the crystal structure also features weak π—π (In **1** and **2**) and C—H... π (In **2**) interactions. In conclusion, the reaction of 2-amino-6-methylpyridine with *meta* and *para* methylbenzoic acid in methanol system constructs a 2-D and a 3-D supramolecular networks, respectively. The experimental results show that the hydrogen bond plays an important role in the assembly of high-dimensional architectures.

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Supplementary Materials

These data (CCDC 990892 (**1**) and 990893 (**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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