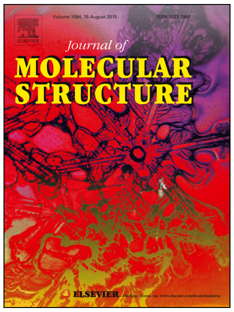

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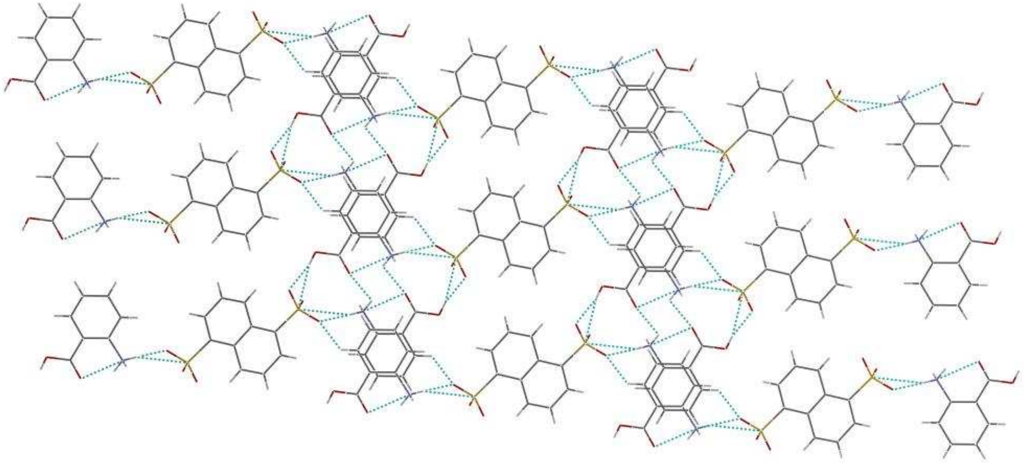

Single-crystal and Molecular Structures of Six Hydrogen-Bonding 3D Supramolecular Salts from 2-aminobenzoic Acid, 3-aminobenzoic Acid, 4-aminobenzoic Acid, and Acidic Components

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Abstract:

Cocrystallization experiments of the commonly available 2-aminobenzoic acid/3-aminobenzoic acid/4-aminobenzoic acid, with a series of organic acids gave a total of six anhydrous molecular salts. The structures of these salts were subsequently characterized by IR, EA, and XRD analysis technique, and the melting points of all salts were also reported. In the six salts, the NH_2 of the aminobenzoic acids are protonated when the organic acids are deprotonated, and the crystal packing is interpreted in terms of strong N-H···O H-bonds from the NH_3^+ and deprotonated acidic groups. Except the N-H···O H-bond, the O-H···O H-bonds were also found at**1**-**6**. The salts of the aryl sulfonates exhibited the N-H···S H-bonds, and salt **4** has the additional O-H···S H-bond. In these structures homo or hetero supramolecular synthons or both were produced, making $R_1^2(3)$, $R_1^2(5)$, $R_1^2(7)$, $R_2^1(6)$, $R_2^2(4)$, $R_2^2(5)$, $R_2^2(8)$, $R_2^2(12)$, $R_2^2(16)$, $R_2^3(6)$, $R_3^2(7)$, $R_3^2(9)$, $R_3^3(8)$, $R_3^3(9)$, $R_3^3(10)$, $R_4^2(8)$, $R_4^2(18)$, $R_4^2(14)$, $R_4^4(12)$, $R_4^4(22)$, $R_6^5(18)$, and $R_6^6(26)$ rings which could have important function in the formation and stabilization of the crystals. But not all of them were appeared repeatedly, as most of them occurred only in some structures. Nevertheless $R_4^2(8)$, $R_4^3(10)$ and $R_4^4(12)$ usually observed in organic solids of organic acids with amine, were again shown to be involved in most of these H-bonding networks. Further inspection into the crystal packing of the salts indicated that a large variety of different secondary interactions were also existed in **1**-**6**, which contribute to the

stabilization and expansion of the total 3D framework structures.

Keywords: Supramolecular salts; Crystal structures; Hydrogen bonding; Aminobenzoic acids.

Introduction

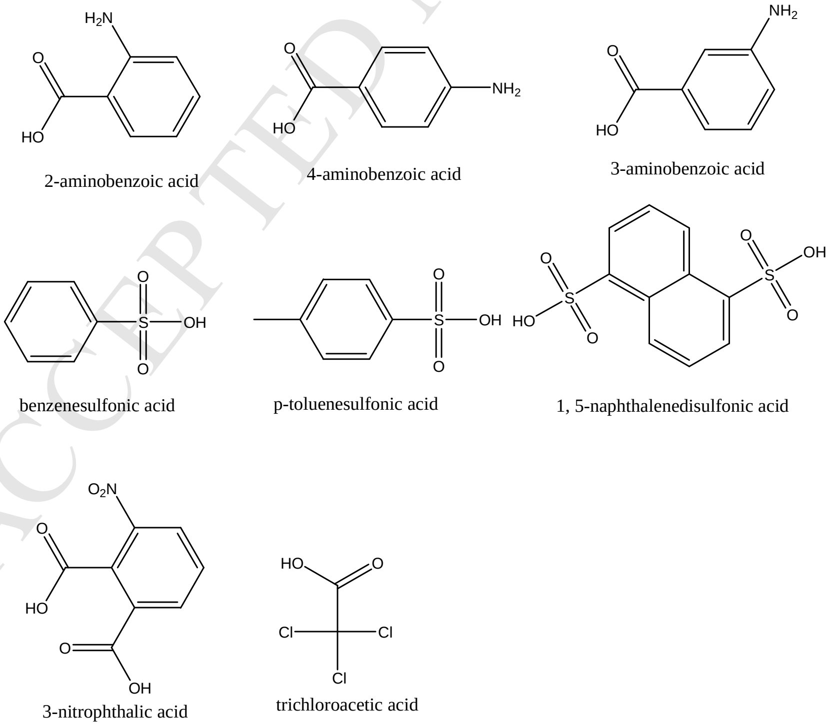
H-bond is one of the most important non-covalent interactions, and it has very important roles in the area of molecular recognition, crystal engineering, supramolecular chemistry, materials science, and biological systems [1]. There were many different types of H-bonds including conventional and unconventional H-bond in the literatures [2], in which short strong H-bonds were also frequently found [3-5].

Hydrogen bonding is also an important driving force in the organic salts formation in terms of its short lengths, high selectivity and direction, and salt formation is often used to tailor the biopharmaceutical properties including the solubility, stability and hygroscopicity [6]. Up to date there are documented many fascinating hydrogen bonded topological structures from one dimensional chain to three dimensional frameworks [7]. The organic acid bears the nice donor-acceptor units for the crystal engineering [8], and they self-assemble in the solid by homosynthons exhibiting many different motifs [9].

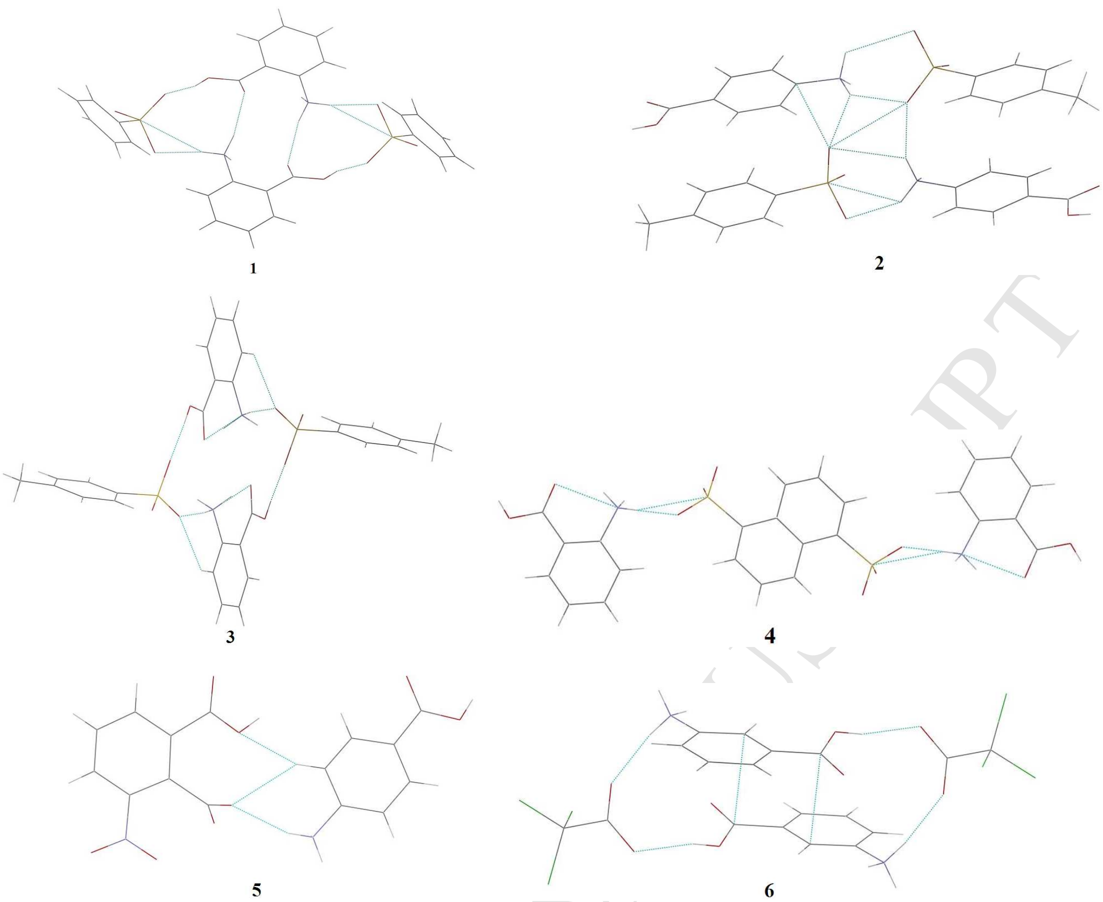
There have been of great interest to study the robust and directional recognition mode from the organic acids and the basic components of aromatic amine, aliphatic amine and pyridyl derivatives [10]. In addition to the acidic groups, the NO_2, CH_3, Cl, and aromatic moieties are all excellent groups in building the organic crystalline solids *via* various non-covalent bonds [11], thus we chose some organic acids bearing the above mentioned groups.

The amino benzoic acid contains equal number of the electron withdrawing $-CO_2H$ and the electron giving $-NH_2$ connected by the conjugated aryl ring, which can exhibit more complex nonbonding associations as it interacted with the organic acids. To the best of our knowledge, there are a few papers involving the organic acid-base adducts in which the amino benzoic acid functioned as the H-acceptor in proton transfer compounds [12, 13].

Recently, we have focused our continuing efforts on studying the hydrogen bonding, π-stacking, and halogen bonding interactions concerning the N-containing bronsted bases [14], herein we will hope to report the synthesis and structures of six organic salts based on 2-aminobenzoic acid (L1), 4-aminobenzoic acid (L2), 3-aminobenzoic acid (L3) and the corresponding organic acids (Scheme 1). The six organic salts are (2-aminobenzoic acid) : (benzenesulfonic acid) **(1)** $[(HL1)^+ \cdot (bzs^-)$, bzs^- = benzenesulfonate], (2-aminobenzoic acid) : (p-toluenesulfonic acid) **(2)** $[(HL1)^+ \cdot (pts^-)]$, (4-aminobenzoic acid) : (p-toluenesulfonic acid) **(3)** $[(HL2)^+ \cdot (pts^-)$, pts^- = p-toluenesulfonate], (2-aminobenzoic acid)$_2$: (1, 5-naphthalenedisulfonic acid) **(4)** $[(HL1)_2^{2+} \cdot (nds^{2-})$, nds^{2-} = 1, 5-naphthalenedisulfonate], (4-aminobenzoic acid) : (3-nitrophthalic acid) **(5)** $[(HL2)^+ \cdot (Hnpa^-)$, $Hnpa^-$ = 3-nitrohydrogenphthalate], and (3-aminobenzoic acid) : (trichloroacetic acid) **(6)** $[(HL3)^+ \cdot (tca^-)$, tca^- = trichloroacetate], respectively (Scheme 2). The supramolecular synthons of **1**-**6** were listed at Scheme 3.



Scheme 1 Molecular structures of the components in **1**-**6**.



1

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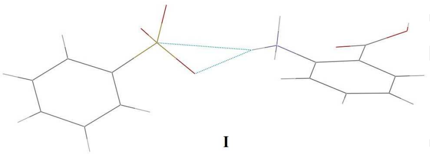
5

6

Scheme 2 The organic salts **1-6** in this work.



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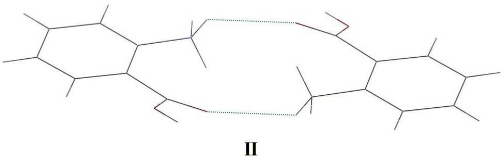

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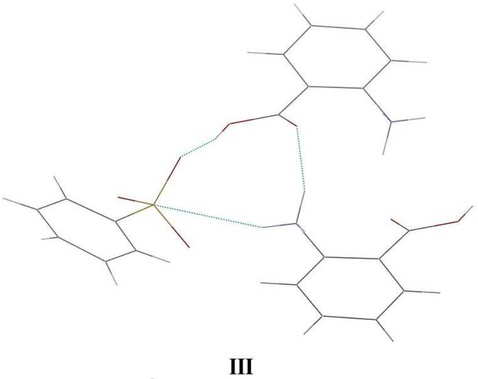

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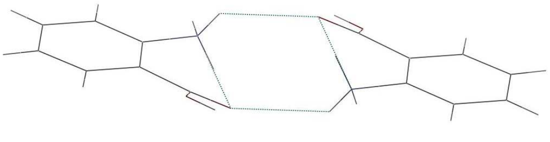

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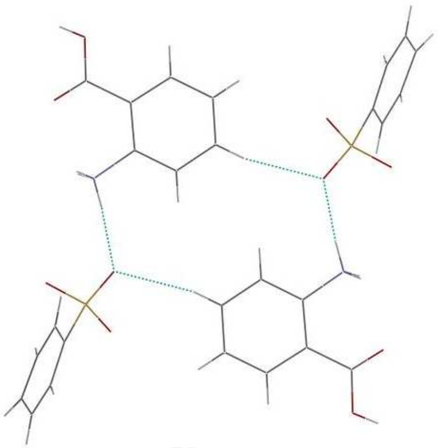

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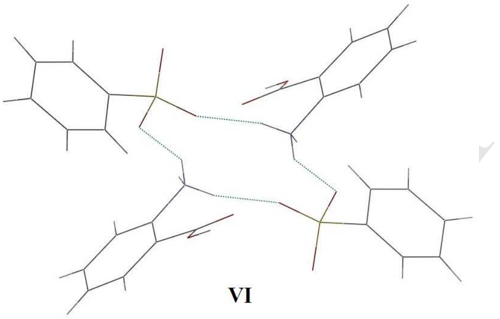

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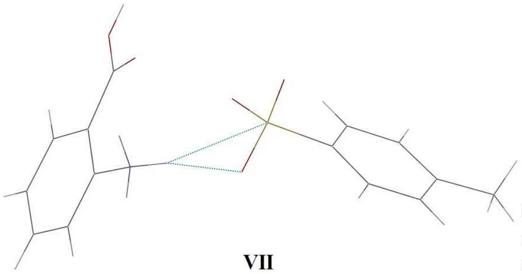

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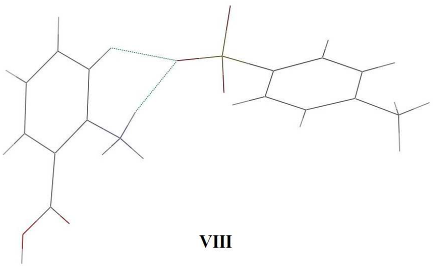

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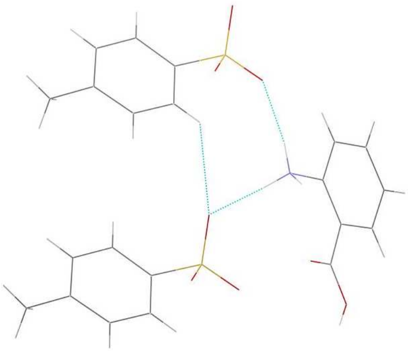

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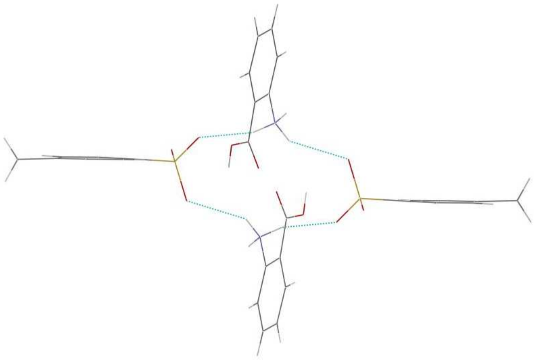

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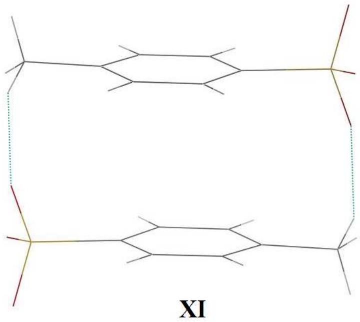

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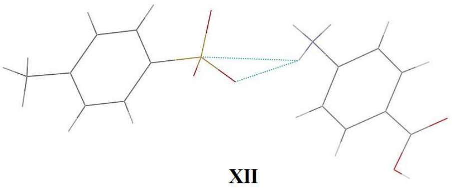

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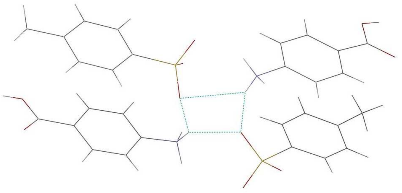

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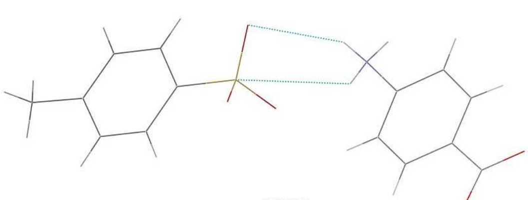

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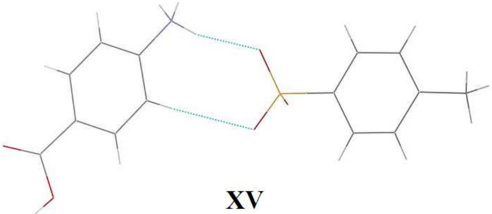

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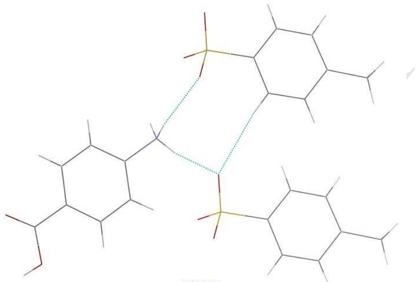

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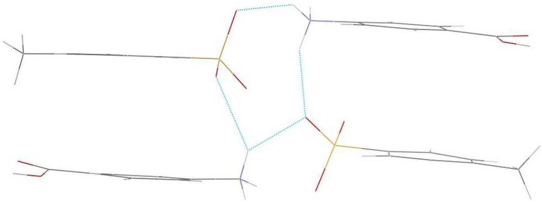

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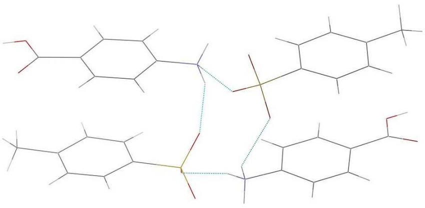

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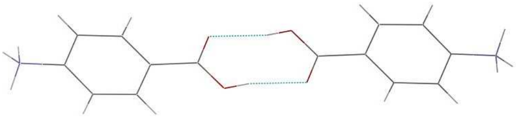

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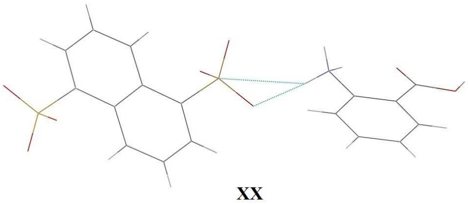

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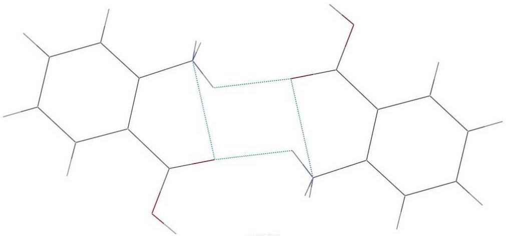

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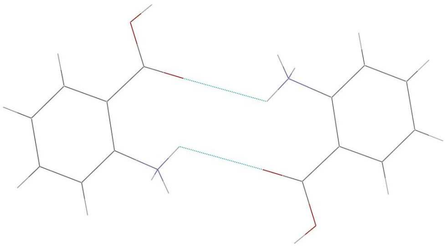

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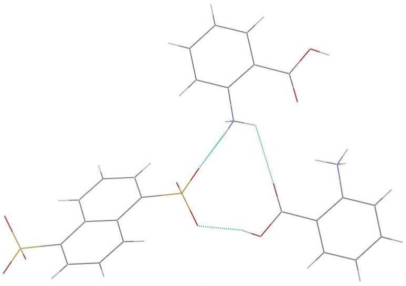

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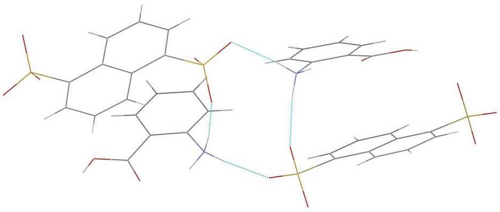

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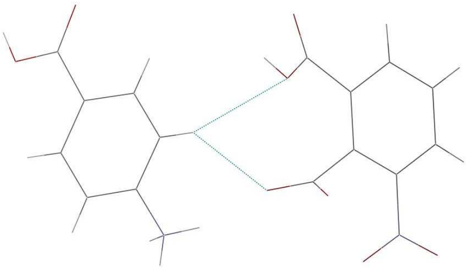

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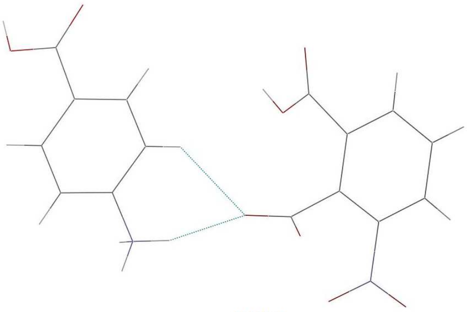

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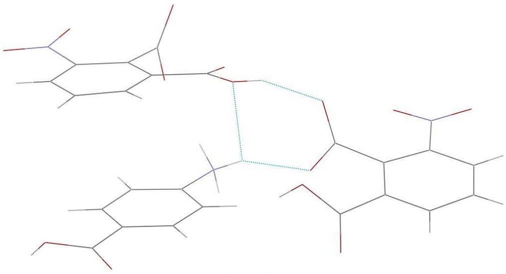

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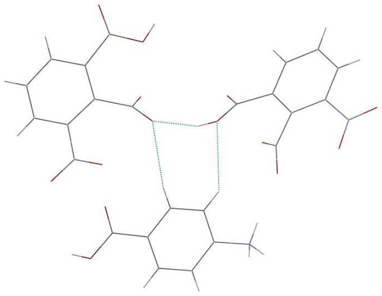

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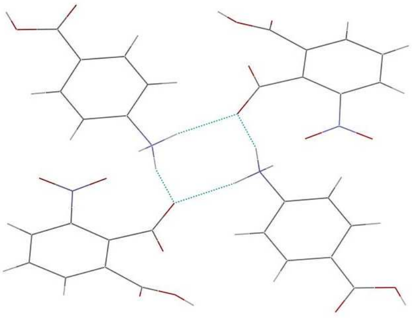

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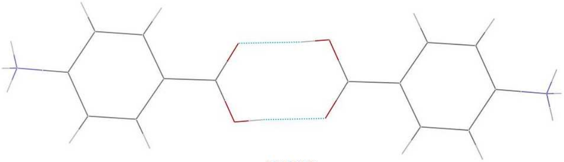

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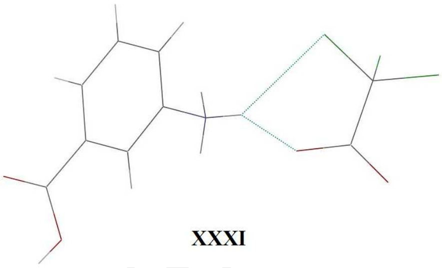

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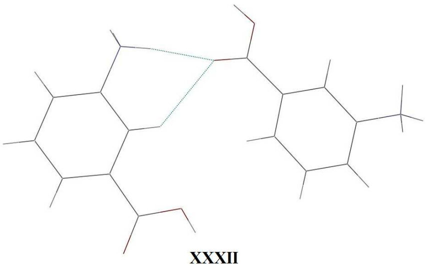

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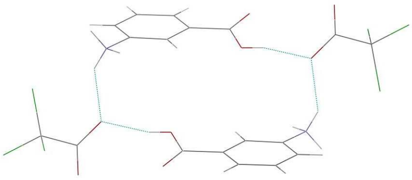

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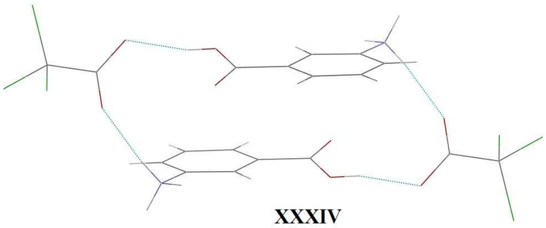

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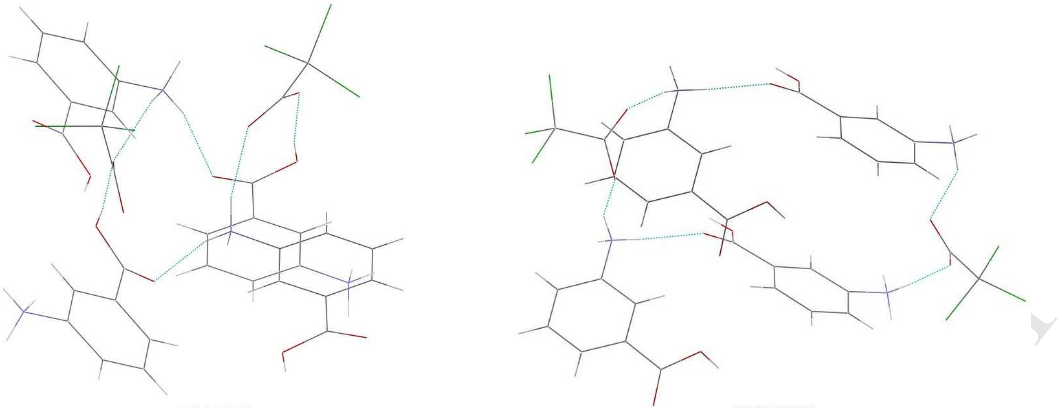

XXXV XXXVI

Scheme 3 Supramolecular synthons in **1-6**.

Experimental section

Materials and Physical Measurements

The chemicals and solvents in this work were analytical grade commercial products and were used without further purification. FT-IR spectra in 4000-400 cm^{-1} were taken on a Mattson Alpha-Centauri spectrometer from KBr pellets, and the IR bands were marked as strong (s), medium (m), and weak (w) at the preparation part. The C, H, N, and S concentrations were recorded microanalytically on a Perkin-Elmer elemental analyzer with Model 2400II, and the melting points of the salts were performed on an XT-4 thermal instrument without correction.

Synthesis of salts 1-6

a. (2-aminobenzoic acid) : (benzenesulfonic acid) $[(HL1)^+ \cdot (bzs^-)]$ (1)

To a methanol solution (12 mL) of 2-aminobenzoic acid (38 mg, 0.2 mmol) was added 80% benzenesulfonic acid (39.5 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained two weeks later. The crystals were filtered out and dried to give $[(HL1)^+ \cdot (bzs^-)]$ **(1)**, the yield was 46 mg (77.89%). m. p. 94-96 °C. Anal. Calcd for $C_{13}H_{13}NO_5S$ (295.30): C, 52.83; H, 4.40; N, 4.74; S, 10.84. Found: C, 52.70; H, 4.28; N, 4.66; S, 10.76. FT-IR (KBr disc, cm^{-1}): 3514m(br, OH), 3420m(ν_{as}(NH)), 3335w(ν_s(NH)), 3260m, 3156m, 3044m, 2950m, 2866m, 1666s(ν(C=O)), 1612m, 1568m, 1525m, 1480m, 1438m, 1396m, 1355m, 1313m 1275s(ν(C-O)), 1234m, 1196m, 1154m, 1116m, 1072m, 1030m, 988m, 948m, 905m, 863m, 820m, 777m, 738m, 696m, 654m, 612m, 605m.

b. (4-aminobenzoic acid) : (p-toluenesulfonic acid) $[(HL2)^{+} \cdot (pts^{-})]$ (2)

To a methanol solution (18 mL) of 4-aminobenzoic acid (38 mg, 0.2 mmol) was added p-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained 15 days later. The crystals were filtered out and dried to give $[(HL2)^{+} \cdot (pts^{-})]$ **(2)**, the yield was 52 mg (84.05%). m. p. 118-120°C. Anal. Calcd for $C_{14}H_{15}NO_5S$ (309.33): C, 54.31; H, 4.85; N, 4.52; S, 10.34. Found: C, 54.22; H, 4.78; N, 4.41; S, 10.26. FT-IR (KBr disc, cm^{-1}): 3566(br, OH), 3472s(ν_{as}(NH)), 3345s(ν_{s}(NH)), 3256m, 3158m, 3062m, 2966m, 2868m, 1676s(ν(C=O)), 1566m, 1524m, 1482m, 1430m, 1381m, 1340m, 1298s(ν(C-O)), 1256m, 1218m, 1185m, 1140m, 1073m, 1007m, 965m, 923m, 880m, 838m, 796m, 754m, 710m, 666m, 620m, 602m.

c. (2-aminobenzoic acid) : (p-toluenesulfonic acid) $[(HL1)^{+} \cdot (pts^{-})]$ (3)

To a methanol solution (14 mL) of 2-aminobenzoic acid (38 mg, 0.2 mmol) was added p-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained 10 days later. The crystals were filtered out and dried to give $[(HL1)^{+} \cdot (pts^{-})]$ **(3)**, the yield was 50 mg (80.82%). m. p. 98-100 °C. Anal. Calcd for $C_{14}H_{15}NO_5S$ (309.33): C, 54.31; H, 4.85; N, 4.52; S, 10.34. Found: C, 54.26; H, 4.77; N, 4.46; S, 10.29. FT-IR (KBr disc, cm^{-1}): 3549(br, OH), 3437m(ν_{as}(NH)), 3340w(ν_{s}(NH)), 3256m, 3032m, 2960m, 2874w, 1658s(ν(C=O)), 1606m, 1564m, 1524m, 1484m, 1442m, 1400m, 1358m, 1316m 1280s(ν(C-O)), 1236m, 1190m, 1148m, 1106m, 1066m, 1028m, 984m, 943m, 902m, 858m, 816m, 775m, 732m, 686m, 643m, 618m, 600m.

d. (2-aminobenzoic acid)$_2$: (1, 5-naphthalenedisulfonic acid) $[(HL1)_2^{2+} \cdot (nds^{2-})]$ (4)

To a methanol solution (30 mL) of 2-aminobenzoic acid (38 mg, 0.2 mmol) was added 1, 5-naphthalenedisulfonic acid tetrahydrate (72 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained 22 days later. The crystals were filtered out and dried to give $[(HL1)_2^{2+} \cdot (nds^{2-})]$ **(4)**, the yield was 46 mg, (81.77% based on L1). m. p. 184-186 °C. Anal. Calcd for $C_{24}H_{22}N_2O_{10}S_2$ (562.56): C, 51.19; H, 3.91; N, 4.98; S, 11.38. Found: C, 51.12; H, 3.84; N, 4.90; S, 11.32. FT-IR (KBr disc, cm^{-1}): 3589s(ν(OH)), 3451m(ν_{as}(NH)), 3371w(ν_s(NH)), 3268m, 3174m, 3012m, 2998w, 2950w, 2860m, 1672s(ν(C=O)), 1600m, 1556m, 1514m, 1472m, 1430m, 1386m, 1345m, 1302s(ν(C-O)), 1258m, 1215m, 1169m, 1127m, 1084m, 1041m, 998m, 956m, 915m, 874m, 832m, 788m, 743m, 696m, 653m, 624m, 605m.

e. (4-aminobenzoic acid) : (3-nitrophthalic acid) $[(HL2)^+ \cdot (Hnpa^-)]$ (5)

To a methanol solution (20 mL) of 4-aminobenzoic acid (38 mg, 0.2 mmol) was added 3-nitrophthalic acid (42.2 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained 16 days later. The crystals were filtered out and dried to give $[(HL2)^+ \cdot (Hnpa^-)]$ **(5)**, the yield was 58 mg (83.27%). m. p. 201-202°C. Anal. Calcd for $C_{15}H_{12}N_2O_8$ (348.27): C, 51.68; H, 3.44; N, 8.04. Found: C, 51.58; H, 3.37; N, 7.95. FT-IR (KBr disc, cm^{-1}): 3606s(ν(OH)), 3465s(ν_{as}(NH)), 3345s(ν_s(NH)), 3252m, 3186m, 3144m, 3094m, 2984m, 2864m, 1702s(ν(C=O)), 1608s(ν_{as}(COO^-)), 1566m, 1524s(ν_{as}(NO_2)), 1482m, 1440m, 1398s(ν_s(COO^-)), 1356m, 1315s(ν_s(NO_2)), 1282s(ν(C-O)), 1238m, 1196m, 1152m, 1110m, 1066m, 1024m, 980m, 936m, 894m, 850m, 808m, 766m, 725m, 682m, 638m, 604m.

f. (3-aminobenzoic acid) : (trichloroacetic acid) $[(HL3)^+ \cdot (tca^-)]$ (6)

To a methanol solution (12 mL) of 3-aminobenzoic acid (38 mg, 0.2 mmol) was added trichloroacetic acid (32.6 mg, 0.2 mmol) with constant stirring for 15 minutes. The solution was then filtered into a test tube and allowed for slow evaporation at room temperature; colorless crystals were obtained two weeks later. The crystals were filtered out and dried to give [$(HL3)^+ \cdot (tca^-)$] **(6)**, the yield was 44 mg, (73.21%). m. p. 128-130 °C. Anal. Calcd for $C_9H_8Cl_3NO_4$ (300.51): C, 35.94; H, 2.66; N, 4.66. Found: C, 35.82; H, 2.55; N, 4.58. FT-IR (KBr disc, cm^{-1}): 3520s(ν(OH)), 3438m(ν_{as}(NH)), 3350w(ν_s(NH)), 3264m, 3170m, 2934m, 2855w, 2798w, 1664s(ν(C=O)), 1612s($\nu_{as}(COO^-)$), 1568m, 1525m, 1484m, 1440m, 1397s($\nu_s(COO^-)$), 1360m, 1322m, 1280s(ν(C-O)), 1237m, 1195m, 1152m, 1108m, 1066m, 1023m, 980m, 935m, 890m, 849m, 805m, 763m, 722m, 680m, 640m, 612m.

X-ray Crystallography

SCXRD data of **1-6** were collected on a Bruker SMART 1000 CCD diffractometer equipped with the graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA. Data collections and reductions were carried out by the SMART and SAINT softwares [15]. The structures were solved directly, and the non-Hs were refined anisotropically *via* full-matrix least squares on F^2 with SHELXL program of the SHELXTL package [16]. All Hs were placed in geometrically calculated positions and included in the refinement in a riding-model approximation. All of the associated crystallographic data are shown in Table 1, selected bond lengths and angles in Table 2, and the relevant H-bond geometrical parameters in Table 3.

Table 1. should be inserted here.

Table 2. should be inserted here.

Results and Discussion

Preparation and General Characterization

Salts **1-6** were prepared by the same method of mixing the organic acids with the aminobenzoic acid at 1:1 in CH_3OH, and the crystals were obtained at ambient conditions *via* the evaporating technique. All salts are not humidity sensitive. The elemental analysis results of the six salts support their compositions. The infrared spectra of the six compounds fit with their chemical formulas determined by elemental analysis and XRD analysis. The strong and broad bands at 3606-3335 cm^{-1}

in the IR spectra of the six compounds are attributed to the N-H/O-H stretching participated in H-bonds. The moderate intensity bands in 1500-1630 cm^{-1} and 600-750 cm^{-1} are from the aryl ring stretching and bending, respectively. The CO_2H in the aminobenzoic acid shows both ν(C=O) and ν(C-O) in 1658-1702, and 1275-1302 cm^{-1}. IR is also very useful for the diagnosis of the H-transfer compounds on the carboxylic acids [17]. The existence of the CO_2^- in **5** and **6** is elucidated by the strong asymmetrical (1608-1612 cm^{-1}) and symmetrical (1397-1398 cm^{-1}) stretching frequencies [18].

Table 3. should be inserted here.

Structural descriptions

Molecular and supramolecular structure of (2-aminobenzoic acid) : (benzenesulfonic acid) [$(HL1)^+ \cdot (bzs^-)$] (1)

Fig. 1 should be inserted here.

The compound **1** with the composition [$(HL1)^+ \cdot (bzs^-)$] obtained by reacting equal mol 2-aminobenzoic acid and benzenesulfonic acid, crystallizes as triclinic colorless crystals in the space group P-1 with Z = 2, and the asymmetric unit consists of one HL1, and one bzs^- (Fig. 1s). There is one ion pair with no solvent molecules accompanied in **1**. The C9-C13 and the respective H attached to these C were all disordered over two sites with equal occupancies.

The compound **1** is classified as a salt in which SO_3H of the benzenesulfonic acid is absolutely ionized by H transfer to the NH_2 of the L1, which is also supported by the S-O bonds (1.454(2)-1.463(2) Å) at S1-O5-O4-O3. In addition, the S-O bond lengths are comparable to those (1.4474 (13)-1.4685(13) Å) in other benzenesulfonate salt [19]. The C-N bond (N(1)-C(3), 1.465(4) Å) is significantly larger than the corresponding C-N bond (1.3732 (16) Å) at the 2-aminobenzoic acid with the NH_2 unprotonated [20]. The lengthening of the C-N bond further verified our right assignment of the cation. Protonation of the N1 was reflected in the C(4)-C(3)-N(1) and C(2)-C(3)-N(1) angles (118.6(3)° - 119.8(2)°), this also occurs in other salt of amino-benzene derivative [21]. The torsion angle O(2)-C(1)-C(2)-C(3) (23.9(5)°) clearly shows the coplanarity of the CO_2H and the benzene ring. The C-O bonds at the

O1-C1-O2 were 1.207(4) Å (O(1)-C(1)) and 1.327(4) Å (O(2)-C(1)), respectively, supporting the presence of the CO_2H.

A bzs^- was bonded to a HL1 *via* the N-H···O H-bond between one H of the NH_3^+ and one O at the SO_3^- with N-O distance of 2.816(3) Å, and N-H···S hydrogen bond from the same H of the NH_3^+ and the S at the SO_3^- with N-S distance of 3.713(3) Å to show a heteroadduct. At the HL1 there established the intramolecular N-H···O H-bond from the NH_3^+ and the C=O of the CO_2H with N-O distance of 2.725(3) Å exhibiting the S(6) type ring defined by Bernstein [22], which was also occurred in 2-carboxyanilinium nitrate [12b].

Two heteroadducts were held together by the O-H···O H-bond from the CO_2H and the second O of the SO_3^- with O-O distance of 2.693(3) Å, and N-H···O H-bond between the second H of the NH_3^+ and the C=O at the CO_2H with N-O distance of 2.909(3) Å to give a tetracomponent aggregate. At the *a*-axis the tetracomponent aggregates were linked together *via* the N-H···O H-bond between the second H of the NH_3^+ and the third O at the SO_3^- with N-O distance of 2.912(4) Å, N-H···O H-bond from the third H of the NH_3^+ and the second O at the SO_3^- with N-O distance of 2.828(3) Å, O-π contact from the third O at the SO_3^- and the aryl ring of the cation with O-Cg separation of 3.148 Å, and C-π contact from the carboxyl C and the aryl nucleus of the cation with C-Cg separation of 3.356 Å to give 1D chain. In this case the O-Cg separation is close to the archived data (3.12 Å) [23]. In the *ab* plane the 1D chains were bundled into 2D sheet (Fig. 1) by the CH-O association from the para-H of the HL1 and the first O of the SO_3^- with C-O distance of 3.383 Å. The sheet had the I $R_1^2(3)$, II $R_2^2(12)$, III $R_3^3(9)$, IV $R_4^2(8)$, V $R_4^2(14)$, and VI $R_4^4(12)$ rings. In the *c*-axis the 2D sheets were further packed into 3D network.

Molecular and supramolecular structure of (2-aminobenzoic acid) : (p-toluenesulfonic acid) $[(HL1)^+ \cdot (pts^-)]$ (2)

Fig. 2 should be inserted here.

Compound **2** was also prepared in the same manner as **1**, which belongs to triclinic colorless block crystals in the space group P-1 with Z = 2. The asymmetric unit of **2** contains one HL1, and one pts$^-$ (Fig. 2s). Similar to **1**, compound **2** is also a salt with the p-toluenesulfonic acid donated the H of the SO_3H to the NH_2 at L1.

The S-O bonds in the pts$^-$ are from 1.4394(18) Å (O(4)-S(1)) to 1.4652(19) Å (O(5)-S(1)) with the minor $\Delta = 0.0258$ Å, indicating the completely deprotonation of the p-toluenesulfonic acid. This further confirmed our right assignment of **2** as a salt. The C-O bonds at O1-C1-O2 were 1.210(3) and 1.315(3) Å, respectively. The C-N bond (1.463(3) Å) at the HL1 was longer than the corresponding C-N bond (1.3732(16) Å) at the L1 [20], and it also resembled that at **1**. Protonation of the N1 was also reflected in the C(4)-C(3)-N(1) and C(2)-C(3)-N(1) angles which were 117.7(2) - 120.6(2)º, being close to that at **1**. The torsion angle O(2)-C(1)-C(2)-C(3) (173.5(2)º) clearly shows the completely coplanarity of the CO_2H and the aryl ring.

One pts$^-$ associated with one HL1 by the N-H···O H-bond fromone H of the NH_3^+ and one O of the SO_3^- with N-O distance of 2.778(3) Å, and CH-O association from the 3-CH of the HL1 and the same O of the SO_3^- with C-O distance of 3.426 Å to form a heteroadduct. Two heteroadducts were united together by the O-H···O H-bond between the COOH and the second O of the SO_3^- with O-O distance of 2.641(3) Å to give a tetracomponent assembly. In the *a*-axis the tetracomponent assemblies were brought into 1D chain by the N-H···O H-bond from the NH_3^+ and the SO_3^- with N-O distance of 2.859(3) Å, N-H···S hydrogen bond between the NH_3^+ and the S of the SO_3^- with N-S distance of 3.821(2) Å, CH-O association between the 2-CH of the pts$^-$ and the SO_3^- with C-O distance of 3.349 Å, and O-C_π contact from the SO_3^- and the π-C of the COOH with O-C separation of 3.017 Å. The O-C separation resembled the filed value of 3.019(4) Å [24].

The chain displayed the VII $R_1^2(3)$, VIII $R_2^1(6)$, IX $R_3^2(9)$, and X $R_4^4(12)$ rings. The 1D chains were further connected together by the C_π-π association from the π-C of the COOH and the phenyl nucleus of the HL1 with C-Cg separation of 3.280 Å, and π-π stacking between the phenyl rings of the HL1 with Cg-Cg separation of 3.381 Å to show 2D sheet running parallel to the *ab* plane (Fig. 2). In the *c*-axis the 2D sheets were further propagated by the CH_3-O association from the CH_3 of the pts$^-$ and the SO_3^- of two adjacent layers with C-O separation of 3.624 Å to make 3D layer network with the neighbor sheets glided some distance from each other along the extending directions. The intersheet CH_3-O associations enclosed the XI $R_2^2(16)$ ring.

Molecular and supramolecular structure of (4-aminobenzoic acid) : (p-toluenesulfonic acid) $[(HL2)^+ \cdot (pts^-)]$ (3)

Fig. 3 should be inserted here.

The compound **3** with the composition $[(HL2)^+ \cdot (pts^-)]$ was obtained by reacting equal mol L2 and p-toluenesulfonic acid, which crystallizes as monoclinic colorless crystals in the space group P2(1)/c with Z = 8. The asymmetric unit of **3** had two HL2, and two pts^- (Fig. 3s), the molecular composition of **3** was similar to **2** and 4-chloro-anilinium 4-methylbenzenesulfonate [25].

The compound **3** is categorized as a salt where the SO_3H of the p-toluenesulfonic acid is absolutely ionized by H transfer to the NH_2 of the L2. The bond lengths and angles at SO_3^- are not perfectly equivalent, but vary with the environment around the O, their values listed in Table 2, show relatively little distortion from a regular pyramid. The S-O bonds in the SO_3^- cover the range of 1.436(6) Å - 1.480(6) Å with the average value being 1.453(6) Å, which resembled the average S-O bond length in the known case [26]. The average value of the O-S-O angles (110.9(5)-114.6(5)º) is 112.1(4)º, which fits well with the angle at the reported data [25]. The C-N bonds (N(1)-C(5), 1.449(10) Å, and N(2)-C(12), 1.452(9) Å) are significantly larger than the corresponding C-N bond (1.408(3) Å) at the β-polymorph of the 4-aminobenzoic acid [27], but the C-N bonds were comparable to the corresponding value (1.4620(19) Å) at the salt generated by 3-carboxy-4-hydroxybenzenesulfonic acid and 4-aminobenzoic acid [12c]. The lengthening of the C-N bond further verified our right assignment of the cation.

The C-O bonds at the COOH of HL2 were 1.257(15) Å (O(2)-C(1)), 1.272(15) Å (O(1)-C(1)), 1.206(10) Å (O(4)-C(8)) and 1.354(11) Å (O(3)-C(8)), respectively. The difference between the pair of C-O bonds in O(4)-C(8)-O(3) was larger than that in O(2)-C(1)-O(2), suggesting more strong conjugate effect in O(2)-C(1)-O(2) than

O(4)-C(8)-O(3). This fact was also reflected in the $C_{aromatic}$-$C_{carboxyl}$ bond where the C(1)-C(2) (1.508(14) Å) was longer than C(8)-C(9) (1.486(11) Å). The C(8)-C(9) is slightly shorter than that observed in the deprotonated 4-aminobenzoic acid [28], strengthening that the deprotonation of the carboxyl group did not occur.

A pts^- was bonded to a HL2 *via* the N-H···O H-bond from one H of the NH_3^+ and one O at the SO_3^- with N-O distance of 2.913(9) Å to form a heteroadduct A. The other pts^- was bonded to the other HL2 *via* the N-H···O H-bond from one H of the NH_3^+ and one O at the SO_3^- with N-O distance of 2.854(9) Å, and N-H···S H-bond between the same H and the S of the SO_3^- with N-S distance of 3.403(7) Å to form a heteroadduct B. The heteroadducts A and B were tied together by the N-H···O H-bond with N-O separation of 2.811(10) Å, O-O contact between the SO_3^- with O-O separation of 2.980 Å, and O-π association between one O of the SO_3^- and the aryl ring of the cation with O-Cg separation of 3.130 Å to form a tetracomponent aggregate. The O-Cg separation was close to that in **1**. In the *b*-axis the tetracomponent aggregates were connected together by the N-H···O H-bonds with N-O separations of 2.778(9)-2.830(9) Å, CH-O association from the 2-CH of the anion and the SO_3^- with C-O distance of 3.484 Å, and CH-O associations between the 2/3-CH of the cation and the SO_3^- with C-O distances of 3.182-3.507 Å to give 1D chain. The chain displayed XII $R_1^2(3)$, XIII $R_2^2(4)$, XIV $R_2^2(5)$, XV $R_2^2(8)$, XVI $R_3^2(9)$, XVII $R_3^3(8)$ and XVIII $R_4^4(12)$ rings. At the *bc* plane the 1D chains were linked together by the N-H···O H-bond from the third H of the NH_3^+ and the SO_3^- with N-O distance of 2.734(9) Å to form 2D sheet (Fig. 3). Two sheets were glued together by the dimeric O-H···O H-bond of the COOH···HOOC type with O-O separation of 2.636(10) Å to give a double sheet. The COOH···HOOC association generated the XIX $R_2^2(8)$ ring. In the *a*-axis the double sheets were further packed by the catemeric O-H···O H-bond between the COOH···HOOC with O-O separation of 2.660(8) Å to give 3D network. It was worth to point that the dimeric O-H···O hydrogen bonds were from C1-O1-O2, the C8-O3-O4 participated in the catemeric O-H···O H-bond, and the former was slightly stronger than the latter.

Molecular and supramolecular structure of (2-aminobenzoic acid)$_2$: (1, 5-naphthalenedisulfonic acid) [(HL1)$_2^{2+}$ · (nds^{2-})] (4)

Fig. 4 should be inserted here.

Cocrystallization of L1 and naphthalene-1,5-disulfonic acid in 1:1 gave single crystals suitable for XRD, crystal structure determination (Table 1) revealed that 2-aminobenzoic acid and naphthalene-1,5-disulfonic acid are in 2:1. The crystal structure of **4** consists of one HL1 and half an nds^{2-} in the asymmetric unit (Fig. 4s), **4** crystallizes in the monoclinic space group C2/c. The L1 is protonated at the NH_2 also. The C-N bond length concerning the NH_3^+ in HL2 was 1.457(3) Å for N(1)-C(3), which is like the corresponding bond lengths at both **1** and **2**. The S-O bond lengths in the SO_3^- ranging from 1.448(2) Å to 1.452(2) Å (Δ = 0.004 Å) are close to the corresponding reported S-O bonds [29], the C-O bonds at the COOH were 1.219(3) (O(2)-C(1)), and 1.302(3) Å (O(1)-C(1)) Å, respectively.

Two HL1, and one nds^{2-} made a tri-component adduct with the $R_1^2(3)$ rings, and there found an inversion centre at the middle of the C9-C9A. The HL1 associated with the nds^{2-} by an N-H···O H-bond from one H of the NH_3^+ and one O at the SO_3^- with N-O distance of 2.727(3) Å, and one N-H···S H-bond from the same H and the SO_3^- with N-S distance of 3.600(2) Å. The geometries of the N-H···S H-bond resembled those at bis(1H-imidazol-3-ium) naphthalene-1,5-disulfonate [30], and 2,2′-disulfanylidene-5,5′-biimidazolidinylidene-4,4′-dione-dimethylformamide-water (3/2/4) [31].

The tri-component adducts were mediated into 1D chain by the CH···O association from the 6-CH of the HL1 and the SO_3^- with C-O distance of 3.195 Å. The 1D chains were combined together and continued into 2D sheet (Fig. 4) extending at the direction that made an angle of *ca*. 60° with the *bc* plane by the N-H···O H-bond from the NH_3^+ and the C=O at COOH with N-O distance of 2.968(3) Å. At the sheet the O-H···O H-bond from the COOH and SO_3^- with O-O distance of 2.639(3) Å, and O-H···S hydrogen bond between the COOH and the SO_3^- with O-S distance of 3.641(2) Å were also observed.

In the third direction the neighbor sheets were bridged by the N-H···O H-bond from the third H of the NH_3^+ and the third O at the SO_3^- with N-O distance of 2.729(3) Å, and CH-π association from the 5-CH of the HL1 and the naphthalene ring with C-Cg separation of 3.631 Å into 3D layer network with the neighbor sheets glided some distance from each other. The C-Cg separation for the CH-π association resembled that (3.586 Å) in 4-phenethoxyaniline hemihydrate [32]. The 3D layer network had the XX $R_1^2(3)$, XXI $R_2^2(4)$, XXII $R_2^2(12)$, XXIII $R_3^3(10)$, and XXIV $R_4^4(12)$ rings.

Molecular and supramolecular structure of (4-aminobenzoic acid) : (3-nitrophthalic acid) [$(HL2)^+ \cdot (Hnpa^-)$] (5)

Fig. 5 should be inserted here.

Compared to the diacid in **4**, the dicarboxylic acid in **5** is partially deprotonated and transferred to the N of the 4-aminobenzoic acid, causing a hydrogenphthalate salt with the composition of [$(HL2)^+ \cdot (Hnpa^-)$]. Salt **5** crystallizes as monoclinic block crystals in the space group P2(1)/c, and there existed one HL2, and one $Hnpa^-$ in an asymmetric unit (Fig. 5s).

The Δ (0.117 Å) between the C-O bonds within the C8-O3-O4 is much greater than the Δ (0.011 Å) in C9-O5-O6. Also the average distance for C-O (1.256(5) Å) in C9-O5-O6 is less than the C(8)-O(4) (1.310(6) Å) single bond and greater than the C(8)-O(3) (1.193(6) Å) double bond in the COOH of the $Hnpa^-$. This supports our right assignment of the $Hnpa^-$ monoanion. The C-N bond (N(1)-C(5), 1.456(5) Å) involving the NH_3^+ was similar with the ones at **3** and 4-carboxyanilinium 3-carboxy-4-hydroxybenzenesulfonate [12c], yet it is significantly larger than the corresponding C-N bond (1.408(3) Å) in the *β*-polymorph of the 4-aminobenzoic acid [27]. The lengthening of the C-N bond further supported our right assignment of the cation. The $C_{aromatic}$-$C_{carboxyl}$ (C(1)-C(2) = 1.477(6) Å) of HL2 is also slightly shorter than that observed in the deprotonated 4-aminobenzoic acid [28]. The C-C bonds of the cationic ring were 1.360(8)-1.407(6) Å, the C(8)-C(10) and C(9)-C(11) bond lengths increased to 1.507(6) Å and 1.519(6) Å respectively, for the attachment of carboxyl groups. The C(10)-C(11)-C(9) (120.5(4)º) and C(13)-C(12)-C(11) (122.6(5)º) were smaller than the corresponding reported values [33], due to the adjacent electro negative carboxylic group, the angle C(11)-C(12)-N(2) was increased to 119.6(4)º which was also comparable with the known data [33].

The rms deviation of the phenyl plane C10-C15 at $Hnpa^-$ is 0.0168 Å, the carboxylates O3-C8-O4/O5-C9-O6 underwent twist by 30.6/80.7° out of this phenyl plane. Herein the COO^- deviated more significantly from the phenyl plane of the $Hnpa^-$ than COOH, which is different from the reported adduct from phthalate [34]. The planes defined by the two carboxyl moieties subtended at 70.1° with each other. The N2-O7-O8 rotated by 6.3(2)° from the phenyl plane of the $Hnpa^-$, and made angles of 36.8(3)°/84.3(2)° with the two carboxylates, respectively. The aryl rings of the cation and anion intersected at 4.9° with each other.

One HL2 was attached to one $Hnpa^-$ *via* the N-H···O H-bond from one H of the NH_3^+ and one O from the COO^- with N-O distance of 2.878(5) Å, and CH-O associations from the 3-CH of the HL2, the O of the COO^- that has a N-H···O H-bond, and the O at the OH of the COOH with C-O separations of 3.253-3.430 Å to give a bicomponent adduct. At the $Hnpa^-$ there were O-O contacts from the COO^-, NO_2, and the OH of the COOH with O-O separations of 2.933-3.027 Å, and the O-O distances were comparable to that at aquadipicrato(tetraethylene glycol)-gadolinium(III) picrate methanol hemisolvate [35].

In the *b*-axis the bicomponent adducts were glued into 1D chain by the CH-O association from the aryl CH of the $Hnpa^-$ and the NO_2 with C-O separation of 3.167 Å. Two chains were adhered together by the O-H···O H-bond from the COOH and COO^- with O-O distance of 2.590(4) Å, N-H···O H-bond between one H of the NH_3^+ and the OH from the COOH with N-O distance of 2.935(5) Å, and N-H···O H-bond from one H of the NH_3^+ and one O from COO^- with N-O distance of 2.885(5) Å to made a double chain. In the *bc* plane the double chains were bridged together by the N-H···O H-bond from the third H of the NH_3^+ and one O from the COO^- with N-O distance of 2.712(5) Å to show 2D sheet (Fig. 5). The sheet exhibited the XXV $R_1^2(7)$, XXVI $R_2^1(6)$, XXVII $R_2^3(6)$, XXVIII $R_3^2(7)$, and XXIX $R_4^2(8)$ rings. At the *a*-axis the sheets were further packed by the dimeric O-H···O H-bond from the COOH of the

HL2 with O-O separation of 2.599(5) Å to give 3D network. Similar to **3** the pair of O-H···O H-bonds also produced the XXX $R_2^2(8)$ ring, but there was no catemeric O-H···O H-bonds as in**3**.

Molecular and supramolecular structure of (3-aminobenzoic acid) : (trichloroacetic acid) [$(HL3)^+ \cdot (tca^-)$] (6)

Fig. 6 should be inserted here.

Compound **6** was also prepared in the same manner as **1-5**, which belongs to monoclinic colorless block crystals in the space group P2(1)/c with Z = 4. Compound **6** is also a salt with the trichloroacetic acid donated the acidic H to the NH_2 of the 3-aminobenzoic acid, there contains one HL3, and one tca^- in the asymmetric unit (Fig. 6s). Each Cl of the tca^- was disordered over two sites with equal occupancy. The C-N bond (C(6)-N(1), 1.460(5) Å) is comparable with the corresponding bond at bis(3-carboxyanilinium) hexafluorostannate(IV) [36].

The C-O bonds at COO^- were from 1.226(6) Å (C(1)-O(2)) to 1.259(6) (C(1)-O(1)) with the Δ = 0.033 Å (Table 2), in which the relative large Δ between the pair of C-O bonds can be explained by the different H-bonds the two O had (Table 3). The C-O bonds at O(3)-C(3)-O(4) were 1.319(5) Å (O(3)-C(3)) and 1.223(5) Å (O(4)-C(3)).

The HL3 are similar in conformation to that in the m-carboxyphenylammonium hydrogen pyrazine-2,3-dicarboxylate [37], with the carboxylic group out of the plane of the benzene ring with similar torsion angles O(4)-C(3)-C(4)-C(5) (167.1(4)º) for **6**, and C(2B)-C(1B)-C(11B)-O(10B) (165.9(2)°) in the m-carboxyphenylammonium hydrogen pyrazine-2,3-dicarboxylate, but different from the equivalent angle in the planar parent acid (cf. -177.8° in the parent acid) [38].

One tca^- was attached to one HL3 by the N-H···O H-bond fromone H of the NH_3^+ and one O of the COO^- with N-O distance of 2.746(5) Å to make a heteroadduct. Two heteroadducts were joined together by O-H···O H-bond between the COOH of HL3 and the other O of the COO^- with O-O separation of 2.613(4) Å, and C-π association from the carboxyl C of the HL3 and the aryl nucleus of the HL3 with C-Cg separation of 3.317 Å to give a tetracomponent aggregate with the respective units inversionally related. Along the *c*-axis the tetracomponent aggregates were bridged into 1D chain by the N-H···O H-bond from the second H of the NH_3^+ and the O of the COO^- with the O-H···O H-bond with N-O distance of 2.799(5) Å, together with N-H···Cl H-bond from the same H as just mentioned with N-Cl separation of 3.431 Å. Along the *ac* plane the 1D chains were further bridged into 2D sheet (Fig. 6) by the Cl-Cl association with Cl-Cl distance of 3.396(4) Å, the Cl-Cl separation being *ca*. 0.104 Å shorter than the van der Waals radius of Cl (1.75 Å) was in the range of a filed Cl-Cl bond [39]. In the *b*-axis the sheets were further packed by the N-H···OH-bonds from the third H of the NH_3^+ and the C=O of the COOH with N-O distance of 2.790(5) Å, and CH-O association from the 3-CH of the HL3 and the C=O with C-O separation of 3.243 Å to give 3D network. The network had the XXXI $R_1^2(5)$, XXXII $R_2^1(6)$, XXXIII $R_4^2(18)$, XXXIV $R_4^4(22)$, XXXV $R_6^5(18)$, and XXXVI $R_6^6(26)$ rings.

Influence of the anions on the architectures of 1-6

In this study, benzenesulfonic acid, p-toluenesulfonic acid, 1,5-naphthalenedisulfonic acid, 3-nitrophthalic acid and trichloroacetic acid, which has additional functional groups, were used to prepare the six salts. Our study tells that anions have a significant effect on the architectures of **1-6**. In **1-6**, the above acids are essential in making the supramolecular salts. The different acids not only have an effect on the protonation of the aminobenzoic acid, but also play an important role in establishing the final architectures *via* H-bonds and various non-covalent bonds. The major classical H-bonds had similar role in expanding **1-6**.

The salts all have the N-H···O H-bonds from the NH_3^+ and the deprotonated acids. And there were O-H···O H-bonds of the type COOH···deprotonated acidic units in **1-2**, and **4-6**, salts **3** and **5** exhibited the homo O-H···O H-bond from COOH. In **1** the SO_3^- at bzs^- plays a key role in forming the 2D net *via* CH-O contacts. For **2** the final 3D net is dependent solely on the CH_3-O association from the pts^-. For **3** the pts^- participated in chain extension by the CH-O associations. In **4** the 1D chain was completed only by the CH-O association from the SO_3^-. The CH-O association from the aryl CH of the $Hnpa^-$ and the NO_2 is the only force in **5** which bundled the bicomponent adducts into 1D chain. The Cl at **6** was responsible for linking 1D chain into 2D sheet *via* the Cl-Cl bonds. The results indicate that the different species of functional groups, as well as the number and position of the functional group at the anions, have crucial influences on both the sub and final structures in **1-6**.

Conclusions

Six examples of 2-, 3-, 4-aminobenzoic acid-organic acid salts were prepared and structurally characterized. The underlying supramolecular chemistry in the organic salts has been unfolded in this article which contributed to the further study of the aminobenzoic acid-organic acid supramolecular motifs. In the six salts, the NH_2 at the aminobenzoic acids were protonated. Although the organic acids used were different, there all found the strong intermolecular N-H···O and O-H···O H-bonds, in**1-4** there are N-H···S H-bonds. There established the additional O-H···S H-bond in**4**.

Besides the robust classical H-bonds, other different types of supramolecular interactions of CH-O/CH_3-O, Cl-Cl, CH-π, O-O, O-C, C-π, O-π, and π-π were also observed in the crystal structures. The extensive non-covalent bonds accompanied with the varying geometries and number of the acidic groups at the organic acids, has led to the creation of 3D network, and 3D layer network, however they all possessed the 1D sub-chain and 2D sub-sheet. From the analysis of the metrics exhibited by each kind of associations, it suggests that the intra- and interchain non-covalent interactions have equal importance in the structure propagation of the synthesized salts. For the conjunction of the various weak nonbonding interactions these structures had homo or hetero supramolecular synthons or both.

In summary, we have shown that the aminobenzoic acids are good building blocks in creating 3D supramolecular salts crystals *via* combination of the classical and non-classical H-bonds, and we will further scrutinize more multicomponent supramolecules from aminobenzoic acid and the other acids to further grasp the supramolecular chemistry of aminobenzoic acid-acid.

Supplementary Information: Crystallographic data for the structural analysis have been registered at the Cambridge Crystallographic data center, CCDC Nos. 1542247 for **1**, 1446816 for **2**, 1445449 for **3**, 1450203 for **4**, 1445263 for **5**, and 1813654 for **6**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK) with fax +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk.

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Figure captions

Fig. 1. 2D sheet structure of **1** extending along the *ab* plane.

Fig. 2. 2D sheet structure of **2** extending parallel to the *bc* plane.

Fig. 3. 2D sheet structure of **3** running parallel to the *ab* plane.

Fig. 4. 2D sheet structure of **4** extending at the direction that made an angle of *ca*. 60° with the *bc* plane.

Fig. 5. 2D sheet structure of **5** extending parallel to the *bc* plane.

Fig. 6. 2D sheet extending parallel to the *ac* plane

Covering information sheet

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Title: **Single-crystal and Molecular Structures of Six Hydrogen-Bonding 3D Supramolecular Salts from 2-aminobenzoic Acid, 3-aminobenzoic Acid, 4-aminobenzoic Acid, and Acidic Components**

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Table 1. Summary of X-ray crystallographic data for complexes **1 - 6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{13}H_{13}NO_5S$	$C_{14}H_{15}NO_5S$	$C_{14}H_{15}NO_5S$	$C_{24}H_{22}N_2O_{10}S_2$	$C_{15}H_{12}N_2O_8$	$C_9H_8Cl_3NO_4$
Fw	295.30	309.33	309.33	562.56	348.27	300.51
T, K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P-1	P-1	P2(1)/c	C2/c	P2(1)/c	P2(1)/c
a, Å	5.6459(6)	6.3735(6)	32.236(3)	20.7219(18)	14.7057(12)	16.7245(14)
b, Å	9.8480(9)	9.099(9)	6.0514(6)	7.6610(7)	7.9661(5)	10.6570(9)
c, Å	12.9016(11)	12.0933(11)	15.0494(13)	16.2341(15)	13.4212(11)	6.9321(6)
α, deg.	100.265(2)	86.918(2)	90	90	90	90
β, deg.	92.8040(10)	89.500(3)	97.5480(10)	112.284(3)	109.317(2)	91.150(2)
γ, deg.	101.863(2)	86.979(2)	90	90	90	90
V, Å^3	688.05(11)	699.3(7)	2910.3(5)	2384.7(4)	1483.7(2)	1235.28(18)
Z	2	2	8	4	4	4
D_{calcd}, Mg/m^3	1.425	1.469	1.412	1.567	1.559	1.616
Absorption coefficient, mm^{-1}	0.253	0.253	0.243	0.288	0.129	0.742
F(000)	308	324	1296	1168	720	608
Crystal size, mm^3	0.40 x 0.24 x 0.15	0.41 x 0.35 x 0.27	0.15 x 0.13 x 0.04	0.41 x 0.30 x 0.13	0.41 x 0.40 x 0.17	0.26 x 0.17 x 0.04
θ range, deg	2.43 - 25.01	2.24 - 25.02	2.55 - 25.02	2.74 - 25.02	2.94 - 25.02	2.27 - 25.02
	$-6 \le h \le 6$	$-7 \le h \le 7$	$-38 \le h \le 38$	$-24 \le h \le 20$	$-17 \le h \le 16$	$-19 \le h \le 19$
Limiting indices	$-10 \le k \le 11$	$-10 \le k \le 10$	$-7 \le k \le 7$	$-9 \le k \le 8$	$-9 \le k \le 9$	$-12 \le k \le 5$
	$-10 \le l \le 15$	$-14 \le l \le 12$	$-16 \le l \le 17$	$-19 \le l \le 18$	$-15 \le l \le 15$	$-8 \le l \le 8$
Reflections collected	3491	3576	5116	5728	2595	6037
Reflections independent (R_{int})	2388 (0.0434)	2432 (0.0249)	5116 (0.0000)	2099 (0.0416)	2595 (0.0000)	2178 (0.1175)
Goodness-of-fit on F^2	1.025	0.983	0.944	1.018	1.163	0.900
R indices [$I > 2\sigma I$]	0.0787, 0.2183	0.0466, 0.1227	0.0964, 0.2257	0.0452, 0.1033	0.0695, 0.2273	0.0746, 0.1880
R indices (all data)	0.0877, 0.2286	0.0608, 0.1305	0.2060, 0.2730	0.0759, 0.1182	0.0931, 0.2444	0.1314, 0.2202
Largest diff. peak and hole, e.Å^{-3}	0.904, -1.022	0.313, -0.362	0.408, -0.341	0.273, -0.304	0.304, -0.367	0.323, -0.244

Table 2 Selected bond lengths [Å] and angles [°] for **1** - **6**.

1			
N(1)-C(3)	1.465(4)	O(1)-C(1)	1.207(4)
O(2)-C(1)	1.327(4)	O(3)-S(1)	1.456(2)
O(4)-S(1)	1.454(2)	O(5)-S(1)	1.463(2)
S(1)-C(8)	1.771(3)	O(4)-S(1)-O(3)	113.39(14)
O(4)-S(1)-O(5)	112.22(15)	O(3)-S(1)-O(5)	111.84(15)
O(1)-C(1)-O(2)	123.8(3)		
2			
N(1)-C(3)	1.463(3)	O(1)-C(1)	1.210(3)
O(2)-C(1)	1.315(3)	O(3)-S(1)	1.447(2)
O(4)-S(1)	1.4394(18)	O(5)-S(1)	1.4652(19)
S(1)-C(8)	1.771(2)	O(4)-S(1)-O(3)	112.98(11)
O(4)-S(1)-O(5)	110.78(11)	O(3)-S(1)-O(5)	112.78(12)
O(1)-C(1)-O(2)	122.9(3)		
3			
N(1)-C(5)	1.449(10)	N(2)-C(12)	1.452(9)
O(1)-C(1)	1.272(15)	O(2)-C(1)	1.257(15)
O(3)-C(8)	1.354(11)	O(4)-C(8)	1.206(10)
O(5)-S(1)	1.480(6)	O(6)-S(1)	1.443(6)
O(7)-S(1)	1.453(6)	O(8)-S(2)	1.462(6)
O(9)-S(2)	1.436(6)	O(10)-S(2)	1.446(7)
S(1)-C(15)	1.765(8)	S(2)-C(22)	1.775(9)
O(6)-S(1)-O(7)	112.5(4)	O(6)-S(1)-O(5)	111.2(4)
O(7)-S(1)-O(5)	112.2(4)	O(9)-S(2)-O(10)	114.6(5)
O(9)-S(2)-O(8)	110.9(5)	O(10)-S(2)-O(8)	111.0(4)
O(2)-C(1)-O(1)	123.9(11)	O(4)-C(8)-O(3)	121.8(8)
4			
S(1)-O(5)	1.448(2)	S(1)-O(3)	1.451(2)
S(1)-O(4)	1.452(2)	S(1)-C(10)	1.776(3)
O(1)-C(1)	1.302(3)	O(2)-C(1)	1.219(3)
C(3)-N(1)	1.457(3)	O(5)-S(1)-O(3)	111.67(13)
O(5)-S(1)-O(4)	113.25(13)	O(3)-S(1)-O(4)	111.64(13)
O(2)-C(1)-O(1)	123.6(3)		
5			
N(1)-C(5)	1.456(5)	N(2)-C(12)	1.468(6)
O(1)-C(1)	1.238(6)	O(2)-C(1)	1.293(6)
O(3)-C(8)	1.193(6)	O(4)-C(8)	1.310(6)
O(5)-C(9)	1.261(5)	O(6)-C(9)	1.250(5)
O(1)-C(1)-O(2)	123.7(4)	O(3)-C(8)-O(4)	124.0(4)
O(6)-C(9)-O(5)	125.7(4)		
6			
Cl(1)-C(2)	1.772(6)	Cl(2)-C(2)	1.749(6)
Cl(3)-C(2)	1.744(6)	N(1)-C(6)	1.460(5)

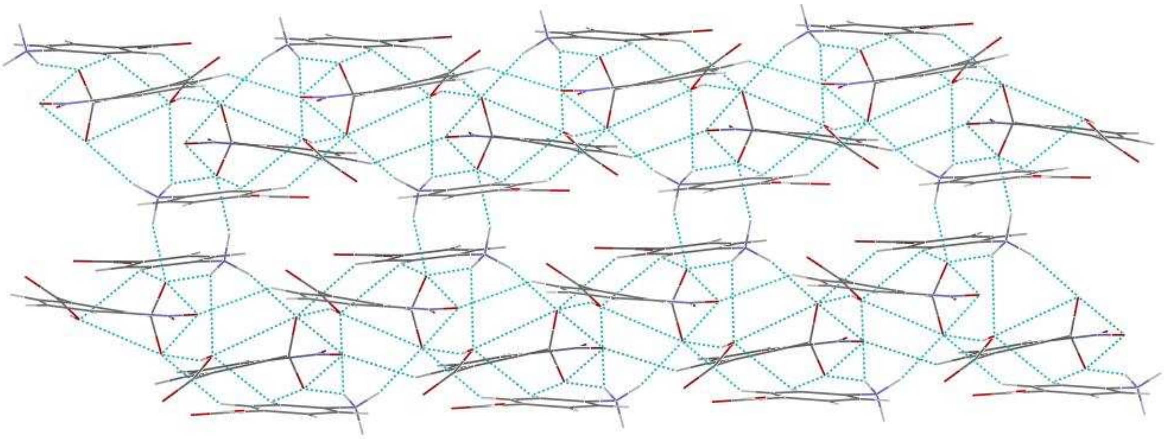
O(1)-C(1)	1.259(6)	O(2)-C(1)	1.226(6)
O(3)-C(3)	1.319(5)	O(4)-C(3)	1.223(5)
O(2)-C(1)-O(1)	128.4(5)	O(4)-C(3)-O(3)	124.2(5)

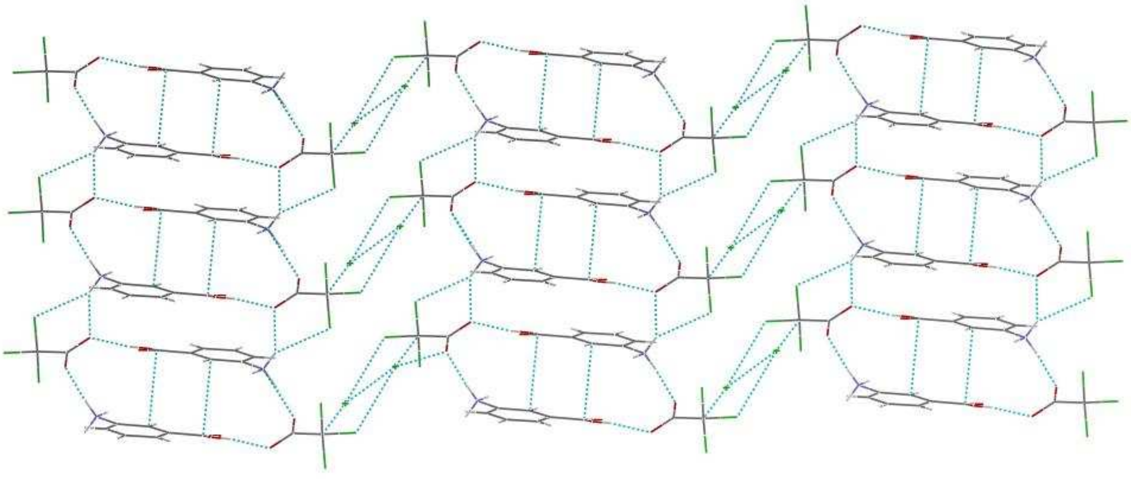
Table 3 H-bond distances and angles in **1** - **6**.

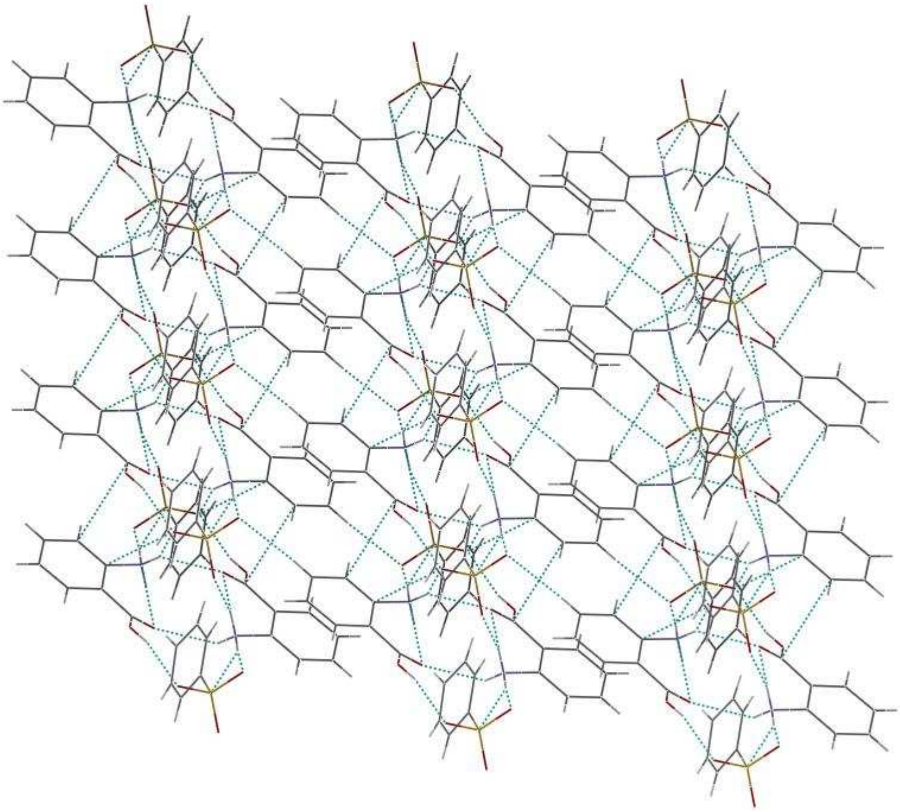
D-H···A	d(D-H) **[Å]**	d(H···A)**[Å]**	d(D···A)**[Å]**	<(DHA)[°]
1				
O(2)-H(2)···O(5)#1	0.82	1.90	2.693(3)	163.8
N(1)-H(1C)···O(1)	0.89	2.27	2.725(3)	111.2
N(1)-H(1C)···O(4)#2	0.89	2.03	2.828(3)	148.8
N(1)-H(1B)···O(1)#3	0.89	2.34	2.909(3)	122.2
N(1)-H(1B)···O(5)#4	0.89	2.14	2.912(4)	145.2
N(1)-H(1A)···S(1)#5	0.89	2.89	3.713(3)	155.4
N(1)-H(1A)···O(3)#5	0.89	1.95	2.816(3)	163.5
2				
O(2)-H(2)···O(5)#1	0.82	1.83	2.641(3)	168.4
N(1)-H(1C)···S(1)#2	0.89	2.98	3.821(2)	157.8
N(1)-H(1C)···O(4)#2	0.89	2.00	2.859(3)	162.3
N(1)-H(1A)···O(3)#4	0.89	1.90	2.778(3)	171.2
3				
O(3)-H(3)···O(4)#1	0.82	1.86	2.660(8)	164.0
O(1)-H(1)···O(2)#2	0.82	1.82	2.636(10)	169.9
N(2)-H(2C)···O(5)#3	0.89	1.98	2.734(9)	141.2
N(2)-H(2B)···S(2)	0.89	3.02	3.878(7)	163.7
N(2)-H(2B)···O(9)	0.89	1.96	2.830(9)	164.3
N(2)-H(2A)···S(1)	0.89	3.03	3.633(7)	126.8
N(2)-H(2A)···O(8)#4	0.89	2.18	2.913(9)	138.7
N(1)-H(1C)···S(1)#5	0.89	2.94	3.403(7)	114.6
N(1)-H(1C)···O(5)#5	0.89	2.09	2.854(9)	143.0
N(1)-H(1B)···O(8)	0.89	1.99	2.811(10)	153.5
N(1)-H(1A)···O(7)	0.89	1.96	2.778(9)	152.8
4				
N(1)-H(1C)···O(3)#1	0.89	1.85	2.729(3)	171.7
N(1)-H(1B)···O(2)#2	0.89	2.45	2.968(3)	117.4
N(1)-H(1B)···O(2)	0.89	1.91	2.652(3)	140.0
N(1)-H(1A)···S(1)#3	0.89	2.81	3.600(2)	148.0
N(1)-H(1A)···O(5)#3	0.89	1.84	2.727(3)	174.4
O(1)-H(1)···S(1)#4	0.82	2.84	3.641(2)	166.1
O(1)-H(1)···O(4)#4	0.82	1.83	2.639(3)	167.2
5				
O(4)-H(4)···O(5)#1	0.82	1.81	2.590(4)	158.7
O(2)-H(2)···O(1)#2	0.82	1.78	2.599(5)	176.7
N(1)-H(1C)···O(6)#3	0.89	1.87	2.712(5)	157.1
N(1)-H(1B)···O(4)	0.89	2.50	2.935(5)	110.6
N(1)-H(1B)···O(6)#1	0.89	2.04	2.878(5)	156.2
N(1)-H(1A)···O(5)	0.89	2.01	2.885(5)	165.7
6				
O(3)-H(3)···O(1)	0.82	1.81	2.613(4)	165.9

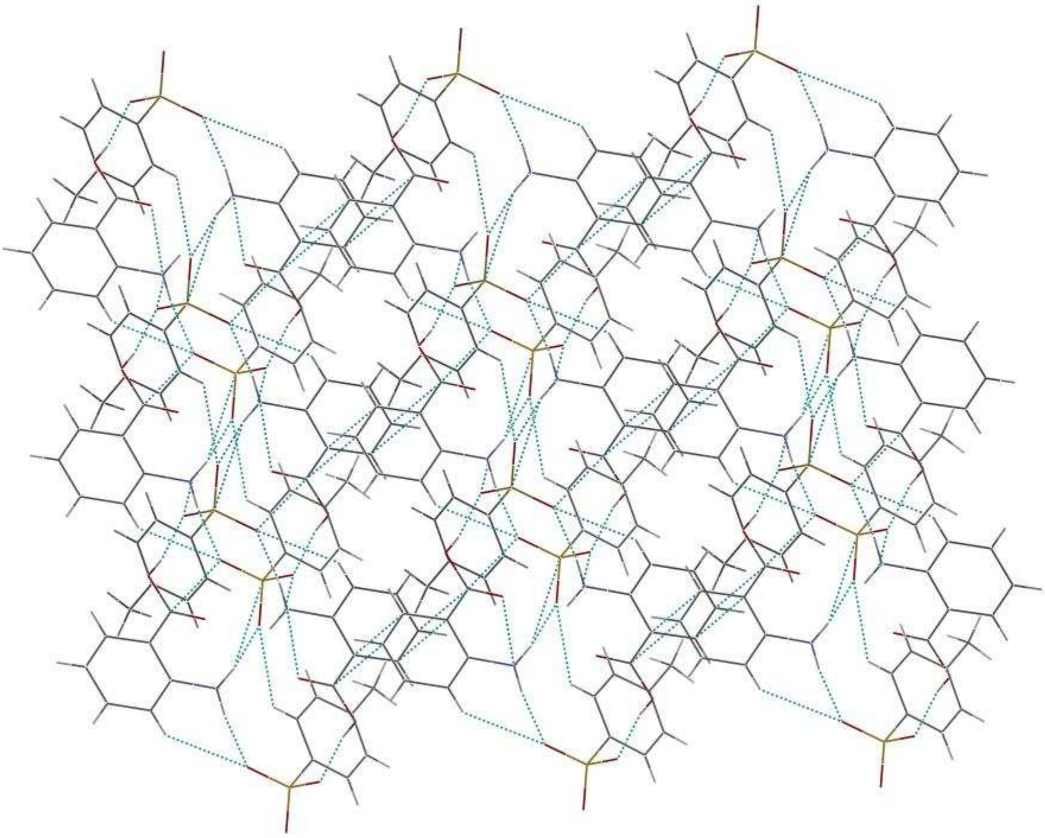
N(1)-H(1C)···O(1)#1	0.89	2.04	2.799(5)	142.7
N(1)-H(1B)···O(2)#2	0.89	1.87	2.746(5)	165.6
N(1)-H(1A)···O(4)#3	0.89	1.92	2.790(5)	164.3

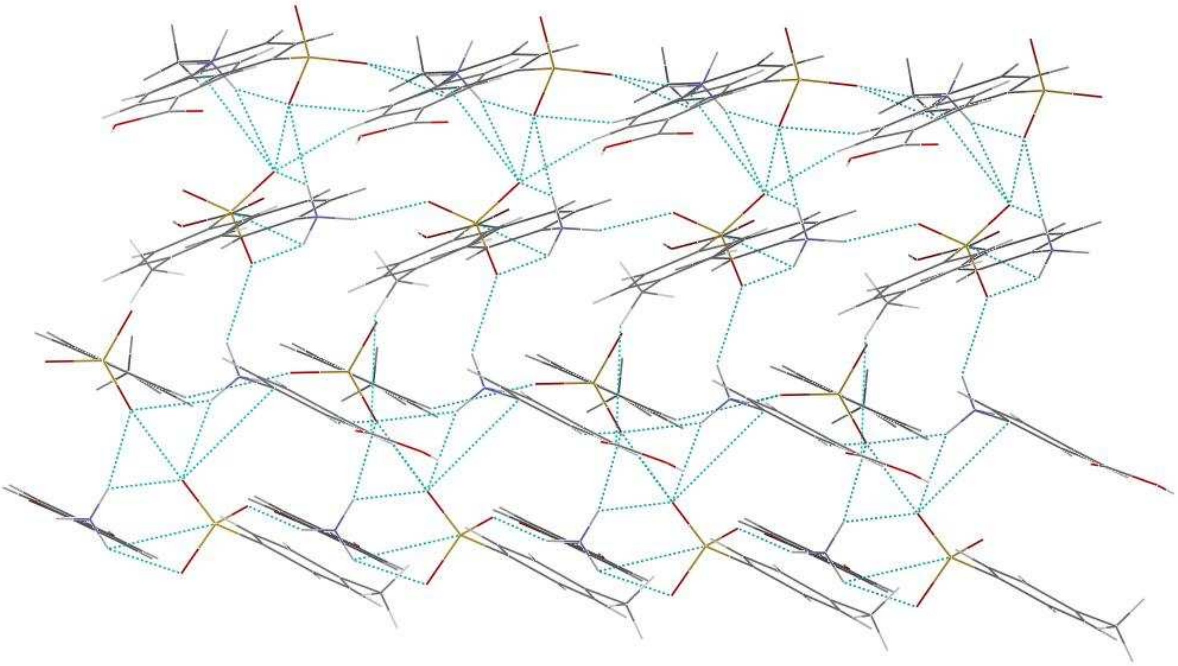
Symmetry transformations used to generate equivalent atoms for **1**: #1 -x, -y+2, -z+1; #2 x, y, z-1; #3 -x+1, -y+2, -z; #4 -x+1, -y+2, -z+1; #5 x+1, y, z-1. Symmetry transformations used to generate equivalent atoms for **2**: #1 x, y, z+1; #2 -x+2, -y+1, -z+1; #4 -x+1, -y+1, -z+1. Symmetry transformations used to generate equivalent atoms for **3**: #1 -x, y+1/2, -z+3/2; #2 -x+1, -y+1, -z+2; #3 x, -y-1/2, z-1/2; #4 x, y-1, z; #5 x, y+1, z. Symmetry transformations used to generate equivalent atoms for **4**: #1 -x+3/2, -y+1/2, -z+1; #2 -x+1, -y, -z+1; #3 x-1/2, -y+1/2, z-1/2; #4 -x+3/2, y-1/2, -z+3/2. Symmetry transformations used to generate equivalent atoms for **5**: #1 -x, y+1/2, -z+1/2; #2 -x+1, -y+2, -z+1; #3 x, -y+1/2, z+1/2. Symmetry transformations used to generate equivalent atoms for **6**: #1 -x+1, -y+1, -z+2; #2 -x+1, -y+1, -z+1; #3 -x+1, y+1/2, -z+3/2.

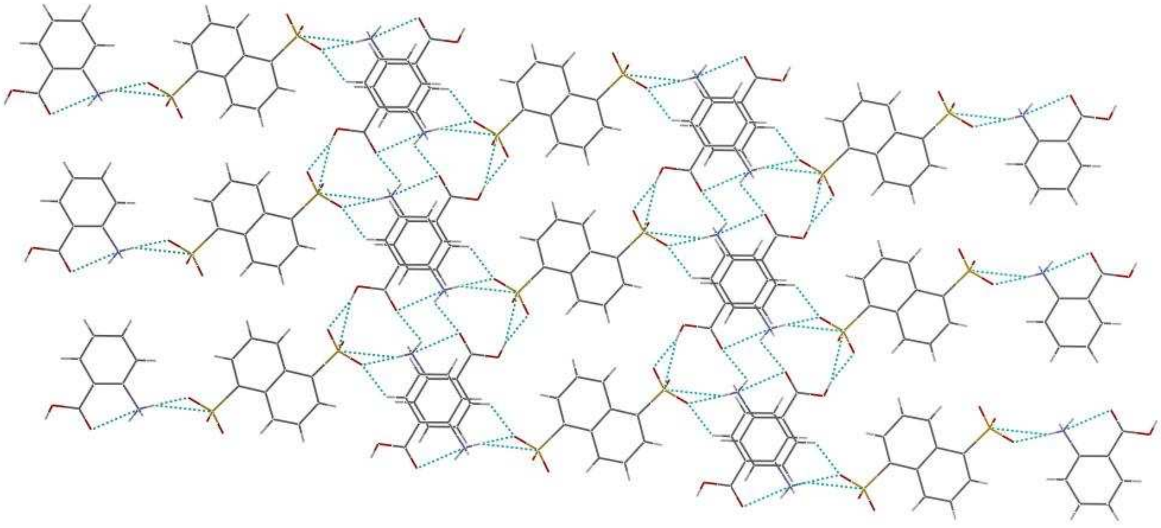












Highlights

Six organic salts have been prepared and structurally characterized.

The H-bonds in the salts have been ascertained.

Classical H-bonds are the primary forces in these salts.

Secondary interactions also play important role in structure extension.