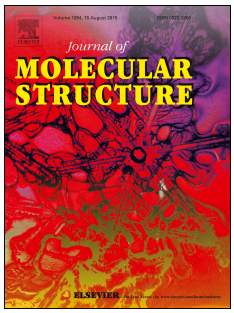
Accepted Manuscript



Crystal structures of seven molecular salts derived from benzylamine and organic acidic components

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Crystal Structures of Seven Molecular Salts Derived from Benzylamine and Organic Acidic Components

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Abstract:

Cocrystallization of the commonly available organic amine, benzylamine, with a series of organic acids gave a total of seven molecular salts with the compositions: (benzylamine) : (p-toluenesulfonic acid) **(1)** $[(HL)^+ \cdot (tsa^-)]$, (benzylamine) : (o-nitrobenzoic acid) **(2)** $[(HL^+) \cdot (onba)^-]$, (benzylamine) : (3,4-methylenedioxybenzoic acid) **(3)** $[(HL^+) \cdot (mdba^-)]$, (benzylamine) : (mandelic acid) **(4)** $[(HL^+) \cdot (mda^-)]$, (benzylamine) : $(5\text{-bromosalicylic acid})_2$ **(5)** $[(HL^+) \cdot (bsac^-) \cdot (Hbsac)]$, (benzylamine): (m-phthalic acid) **(6)** $[(HL^+) \cdot (Hmpta^-)]$, and $(benzylamine)_2$: (trimesic acid) **(7)** $[(HL^+)_2 \cdot (Htma^{2-})]$. The seven salts have been characterised by X-ray diffraction technique, IR, and elemental analysis, and the melting points of all the salts were also reported. And their structural and supramolecular aspects are fully analyzed.

The result reveals that among the seven investigated crystals the NH_2 groups in the benzylamine moieties are protonated when the organic acids are deprotonated, and the crystal packing is interpreted in terms of the strong charge-assisted N-H···O hydrogen bond formation between the ammonium and the deprotonated acidic groups. Except the N-H···O hydrogen bond, the O-H···O hydrogen bonds (charge assisted or neutral) were also found at the salts **4**-**7**.

Further analysis of the crystal packing of the salts indicated that a different family of additional CH-O/CH_2-O, CH-π/CH_2-π, O-O, and O-$C_π$ associations contribute to the stabilization and expansion of the total high-dimensional (2D-3D) framework structures. For the coexistence of the various weak nonbonding interactions these structures adopted homo or hetero supramolecular synthons or both. Some classical supramolecular synthons, such as $R_4^2(8)$, $R_4^3(10)$ and $R_4^4(12)$, usually observed in organic solids of organic acids with amine, were again shown to be involved in constructing most of these hydrogen bonding networks.

Keywords: Crystal structures; Nonbonding interactions; Benzylamine; Acidic components; Organic salts.

Introduction

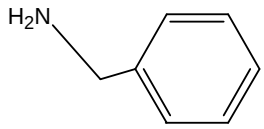
Noncovalent interactions such as electrostatic forces, hydrogen bonding, CH-π, π-π stacking, cation-π, anion-π, and lone pair-π hydrogen bonding, as well as other weak forces play significant roles in various fields ranging from molecular recognition, host-guest chemistry, crystal engineering, supramolecular chemistry, biochemistry, pharmaceutical chemistry, to materials science [1-4]. In the past few years, great efforts have been made to elucidate these interactions and their relationship to the final supramolecular structures [5]. Besides the noncovalent interactions, the supramolecular synthons are structural units within organic solids produced by these intermolecular interactions. And there existed two distinct categories of supramolecular synthons i.e. supramolecular homo- and heterosynthons, which was very important for the chemist to understand the synthons at the organic salt/cocrystal.

In the case of pharmaceutical ingredients, solid organic salts with such biopharmaceutical properties as solubility, stability and hygroscopicity have been studied systematically, and these properties are relevant to the noncovalent interactions [6-7]. The organic acids with the nice donor-acceptor groups are good blocks for the multi-component assembly [8], and they aggregate in the solid state as

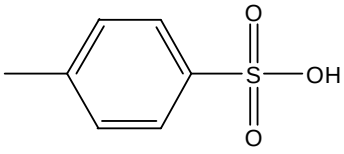
dimer, catemer, and bridged motifs [9], so they are frequently chosen as building blocks in the supramolecular crystal engineering.

A myriad of acid-base mediated supramolecular assemblies were explored through the powerful and directional recognition behavior between the organic acids and the basic components such as aromatic amine, aliphatic amine and pyridyl derivatives [10]. Amongst, a notable such studies were often directed towards systematic analysis on a kind of homologues series by varying the basic components for a given acid [11]. In order to create high-dimensional assemblies and elucidate molecular crystals especially the synthons between the benzylamine and the organic acids, we select some organic acids possessing methyl, nitro, halogen, OH and aromatic moieties which are all excellent groups in forming the organic crystalline solids through a wide variety of non-covalent interactions [12]. As an amine derivative, except the basic NH_2 group, benzylamine has the additional rigid phenyl ring and the somewhat flexible CH_2 linker, which can provide more complex noncovalent associations when it associated with the organic acids. To the best of our knowledge there are few reports dealing with the organic acid-base adducts concerning the Lewis base of benzylamine [13, 14].

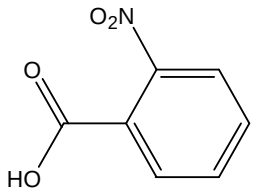
Recently, we have focused our continuing efforts on the systematic study of hydrogen bonding, π-π interaction, and halogen bonding concerning the given N-containing derivatives with varying the organic acids [15], we will report herein the preparation and structures of seven organic salts assembled from benzylamine (L) and the corresponding organic acids ranging from mono-acid to tri-acid (Scheme 1), respectively. The seven organic salts are (benzylamine) : (p-toluenesulfonic acid) **(1)** $[(HL)^+ \cdot (tsa^-)]$, (benzylamine) : (o-nitrobenzoic acid) **(2)** $[(HL^+) \cdot (onba)^-]$, (benzylamine) : (3,4-methylenedioxybenzoic acid) **(3)** $[(HL^+) \cdot (mdba^-)]$, (benzylamine) : (mandelic acid) **(4)** $[(HL^+) \cdot (mda^-)]$, (benzylamine) : $(5\text{-bromosalicylic acid})_2$ **(5)** $[(HL^+) \cdot (bsac^-) \cdot (Hbsac)]$, (benzylamine) : (m-phthalic acid) **(6)** $[(HL^+) \cdot (Hmpta^-)]$, and $(benzylamine)_2$: (trimesic acid) **(7)** $[(HL^+)_2 \cdot (Htma^{2-})]$ (Scheme 2). The supramolecular synthons of the salts **1**-**7** were listed at Scheme 3.



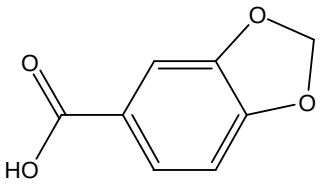
benzylamine



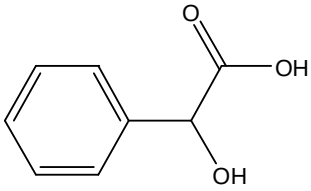
p-toluenesulfonic acid



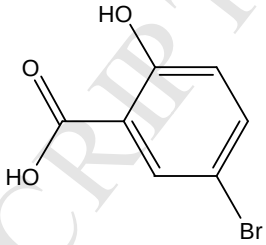
o-nitrobenzoic acid



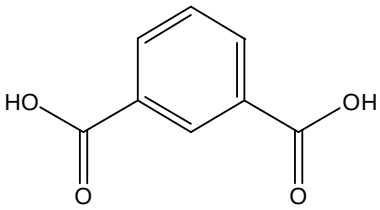
3,4-methylenedioxybenzoic acid



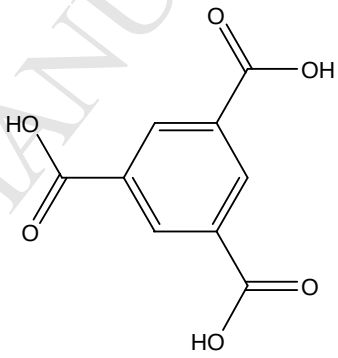
mandelic acid



5-bromosalicylic acid

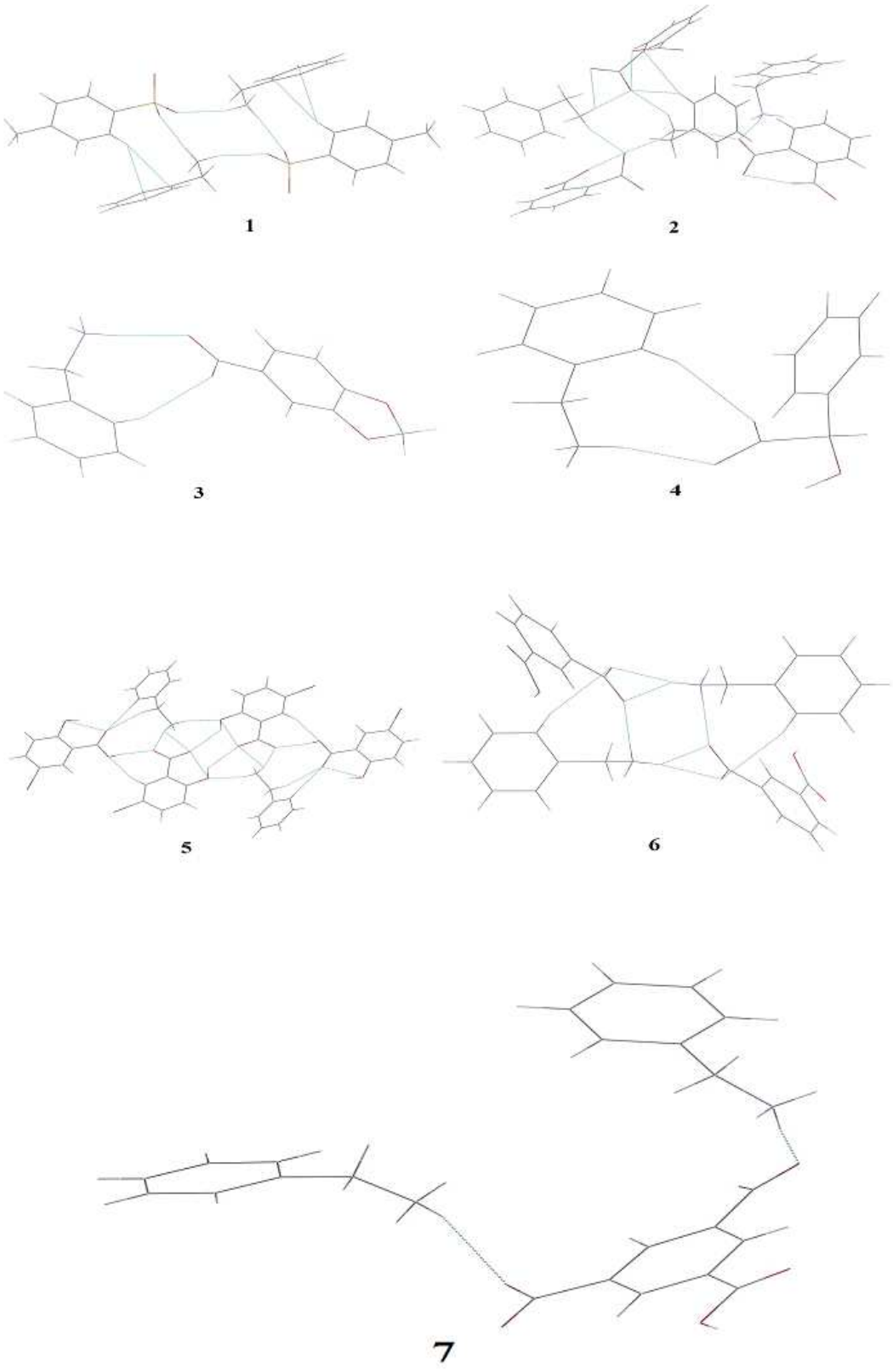


m-phthalic acid

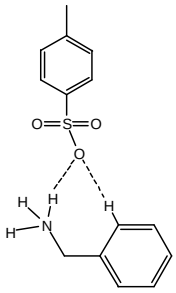


trimesic acid

Scheme 1 Molecular structures of the components present in salts **1**-**7**.



Scheme 2 The seven organic salts described in this paper, **1**-**7**.



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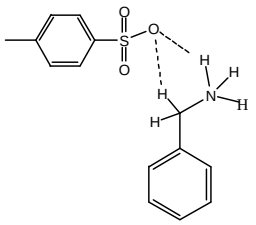

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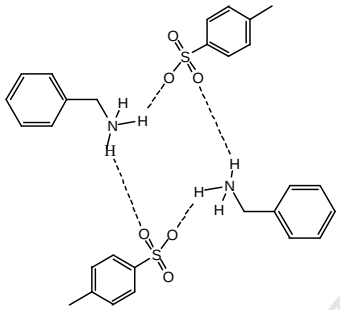

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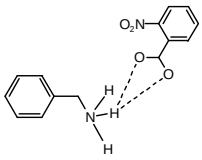

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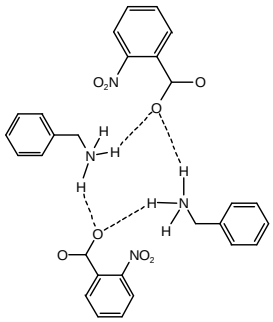

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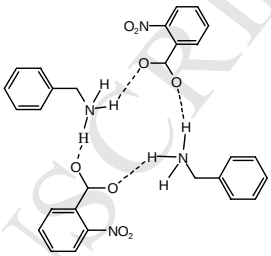

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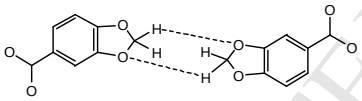

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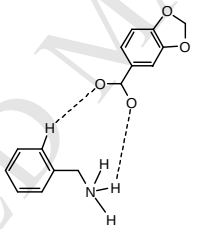

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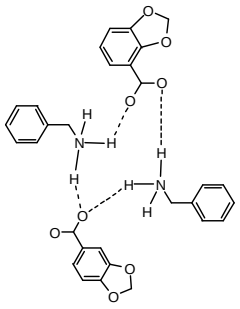

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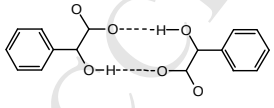

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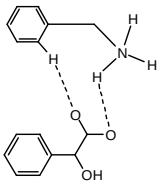

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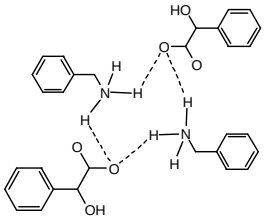

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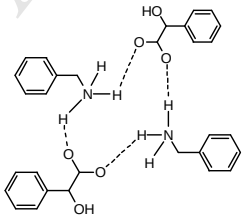

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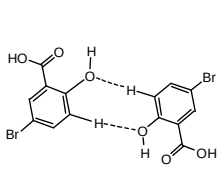

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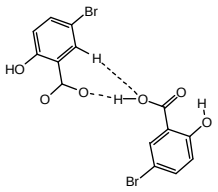

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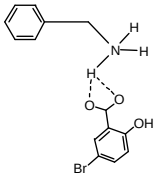

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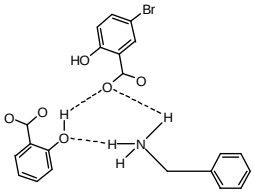

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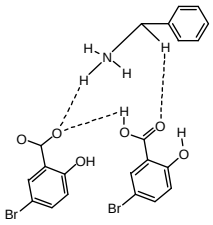

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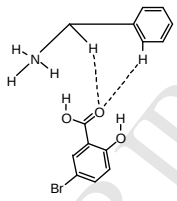

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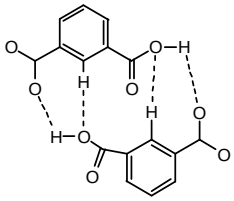

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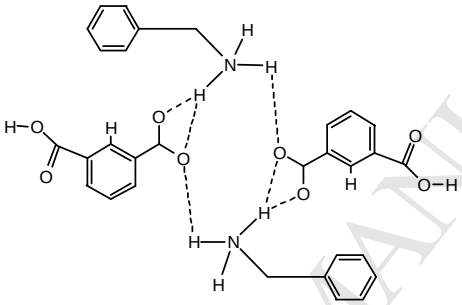

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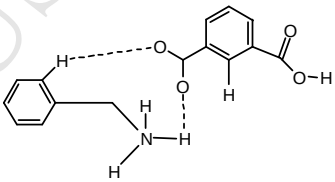

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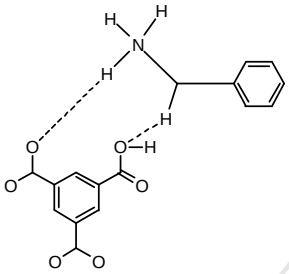

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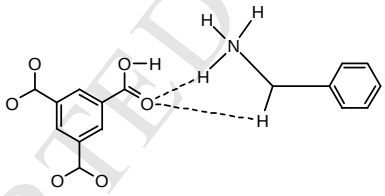

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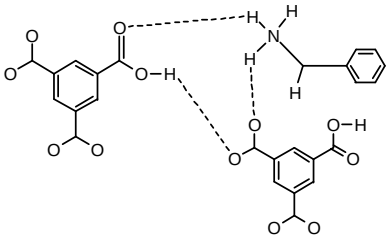

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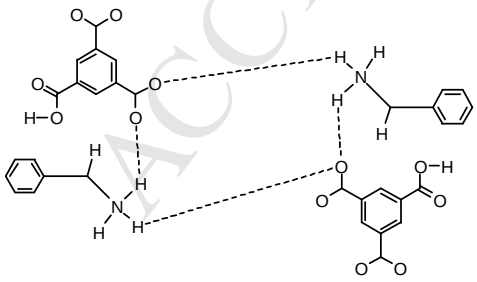

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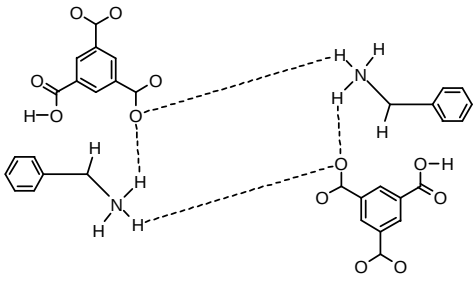

XXVII

Scheme 3 Supramolecular synthons of salts **1**-**7**.

Experimental section

Materials and Physical Measurements

The chemicals and solvents used in this work were of analytical grade commercial products and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer, and the IR bands were marked as strong (s), medium (m), and weak (w) at the preparation part. The asymmetrical and symmetrical IR vibration bands of the corresponding groups were shown as ν_{as} and ν_s, respectively. The carbon, hydrogen, nitrogen, and sulfur data were obtained microanalytically on a Perkin-Elmer elemental analyzer (with Model 2400II). The melting points of the new compounds were measured by an XT-4 thermal apparatus without correction.

Preparation of the salts 1-7

a. (benzylamine) : (p-toluenesulfonic acid) $[(HL)^+ \cdot (tsa^-)]$ (1)

To a methanol solution (8 mL) of p-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the methanol solution in air. The crystals were collected and dried in air to give the title compound $[(HL)^+ \cdot (tsa^-)]$ **(1)**. Yield: 46 mg, 82.33% (based on benzylamine L). m. p. 76-78 °C. Anal. Calcd for $C_{14}H_{17}NO_3S$ (279.35): C, 60.14; H, 6.08; N, 5.01; S, 11.46. Found: C, 60.08; H, 6.03; N, 4.97; S, 11.42. Infrared spectrum (KBr disc, cm^{-1}): 3446s(ν_{as}(NH)), 3368s(ν_s(NH)), 3230m, 3139m, 3045m, 2962m, 2870m, 2825m, 2770m, 2729m, 1628m, 1589m, 1547m, 1505m, 1462m, 1417m, 1374m, 1333m, 1279m, 1236m, 1188m, 1145m, 1099m, 1051m, 1008m, 969m, 920m, 879m, 832m, 789m, 742m, 700m, 666m, 630m, 605m.

b. (benzylamine) : (o-nitrobenzoic acid) $[(HL^+) \cdot (onba)^-]$ (2)

To a methanol solution (5 mL) of o-nitrobenzoic acid (33.4 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after two weeks from the solution at room temperature in air. The crystals

were collected and dried in air to give the title compound [$(HL^+)\cdot(onba)^-$] **(2)**. Yield: 46 mg, 83.86%. m. p. 146-147°C. Anal. Calcd for $C_{14}H_{14}N_2O_4$ (274.27): C, 61.25; H, 5.10; N, 10.21. Found: C, 61.22; H, 5.04; N, 10.17. Infrared spectrum (KBr disc, cm^{-1}): 3411m(ν_{as}(NH)), 3326w(ν_s(NH)), 3214m, 3015m, 2976m, 2928w, 2824w, 2724w, 2630m, 2420m, 1627m, 1585s($\nu_{as}(COO^-)$), 1544m, 1515s($\nu_{as}(NO_2)$), 1472m, 1438m, 1395s($\nu_s(COO^-)$), 1355m, 1315s($\nu_s(NO_2)$), 1272m, 1229m, 1187m, 1141m, 1100m, 1055m, 1012m, 971m, 928m, 882m, 840m, 797m, 755m, 712m, 670m, 635m, 610m.

c. (benzylamine) : (3,4-methylenedioxybenzoic acid) [$(HL^+)\cdot(mdba^-)$] (3)

To a methanol solution (10 mL) of 3,4-methylenedioxybenzoic acid (33.2 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after several weeks from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [$(HL^+)\cdot(mdba^-)$] **(3)**. Yield: 38 mg, 69.52% (based on L). m. p. 189-191°C. Anal. Calcd for $C_{15}H_{15}NO_4$ (273.28): C, 65.87; H, 5.49; N, 5.12. Found: C, 65.82; H, 5.44; N, 5.07. Infrared spectrum (KBr disc, cm^{-1}): 3412m(ν_{as}(NH)), 3327w(ν_s(NH)), 3240m, 3164m, 2926m, 2844w, 2785w, 2670w, 2631w, 1611s($\nu_{as}(COO^-)$), 1566m, 1523m, 1480m, 1439m, 1397s($\nu_s(COO^-)$), 1356m, 1313m, 1271m, 1228m, 1186m, 1142m, 1098m, 1056m, 1012m, 968m, 923m, 882m, 839m, 795m, 749m, 706m, 663m, 624m.

d. (benzylamine) : (mandelic acid) [$(HL^+)\cdot(mda^-)$] (4)

To a methanol solution (10 mL) of mandelic acid (33.2 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after several weeks from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [$(HL^+)\cdot(mda^-)$] **(4)**. Yield: 35 mg, 67.49% (based on L). m. p. 83-85°C. Anal. Calcd for $C_{15}H_{17}NO_3$ (259.30): C, 69.42; H, 6.56; N, 5.40. Found: C, 69.38; H, 6.51; N, 5.35. Infrared spectrum (KBr

disc, cm^{-1}): 3688w(ν(HO), 3440m(ν_{as}(NH)), 3367w(ν_{s}(NH)), 3271m, 3162m, 2991m, 2844w, 2783w, 2671w, 2625w, 1620s($\nu_{as}(COO^-)$), 1578m, 1533m, 1491m, 1450m, 1406s($\nu_{s}(COO^-)$), 1364m, 1320m, 1276m, 1233m, 1189m, 1145m, 1099m, 1057m, 1016m, 970m, 927m, 884m, 843m, 800m, 757m, 714m, 672m, 631m, 604m.

e. (benzylamine) : (5-bromosalicylic acid)$_2$ [(HL^+) · ($bsac^-$) · (Hbsac)] (5)

To a methanol solution (10 mL) of 5-bromosalicylic acid (43.4 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after several weeks from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [(HL^+) · ($bsac^-$) · (Hbsac)] **(5)**. Yield: 78 mg, 72.06% (based on L). m. p. 141-142°C. Anal. Calcd for $C_{21}H_{19}Br_2NO_6$ (541.19): C, 46.56; H, 3.51; N, 2.59. Found: C, 46.50; H, 3.44; N, 2.55. Infrared spectrum (KBr disc, cm^{-1}): 3702w(ν(HO), 3440m(ν_{as}(NH)), 3380w(ν_{s}(NH)), 3264m, 3149m, 2988m, 2846w, 2784w, 1597s($\nu_{as}(COO^-)$), 1554m, 1515m, 1474m, 1433m, 1391s($\nu_{s}(COO^-)$), 1346m, 1304m, 1263m, 1220m,, 1179m, 1136m, 1094m, 1053m, 1009m, 965m, 917m, 875m, 833m, 787m, 746m, 700m, 656m, 621m, 600m.

f. (benzylamine) : (m-phthalic acid) [(HL^+) · ($Hmpta^-$)] (6)

To a methanol solution (10 mL) of m-phthalic acid (33.2 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after several weeks from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [(HL^+) · ($mpta^-$)] **(6)**. Yield: 46 mg, 84.16% (based on L). m. p. 241-242°C. Anal. Calcd for $C_{15}H_{15}NO_4$ (273.28): C, 65.87; H, 5.49; N, 5.12. Found: C, 65.84; H, 5.469; N, 5.09. Infrared spectrum (KBr disc, cm^{-1}): 3655w(br, ν(HO), 3431m(ν_{as}(NH)), 3333w(ν_{s}(NH)), 3245m, 3166m, 2990m, 2844w, 2785w, 1656s(ν(C=O)), 1609s($\nu_{as}(COO^-)$), 1563m, 1520m, 1478m, 1437m, 1405s($\nu_{s}(COO^-)$), 1361m, 1295s(ν(C-O)), 1253m, 1212m, 1169m, 1127m,

1085m, 1039m, 996m, 957m, 914m, 872m, 828m, 788m, 746m, 704m, 660m, 619m, 604m.

g. (benzylamine)$_2$: (trimesic acid) [(HL$^+$)$_2$ · (Htma^{2-})] (7)

To a methanol solution (10 mL) of trimesic acid (42 mg, 0.2 mmol), benzylamine (21.4 mg, 0.2 mmol) was added. The solution was stirred for a few minutes, then the solution was filtered into a test tube. Colorless block crystals were isolated after several weeks from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [(HL$^+$)$_2$ · (Htma^{2-})] **(7)**. Yield: 34 mg, 80.10% (based on L). m. p. 253-254°C. Anal. Calcd for $C_{23}H_{24}N_2O_6$ (424.44): C, 65.03; H, 5.65; N, 6.60. Found: C, 64.97; H, 5.62; N, 6.57. Infrared spectrum (KBr disc, cm^{-1}): 3644w(br, ν(HO), 3451m(ν_{as}(NH)), 3347w(ν_s(NH)), 3260m, 3143m, 2982m, 2824w, 2781w, 1643s(ν(C=O)), 1599s(ν_{as}(COO$^-$)), 1556m, 1413m, 1471m, 1430m, 1388s(ν_s(COO$^-$)), 1346m, 1302s(ν(C-O)), 1259m, 1217m, 1174m, 1133m, 1091m, 1048m, 1004m, 961m, 919m, 877m, 834m, 792m, 745m, 703m, 662m, 631m, 611m.

X-ray Crystallography and Data Collection

Single-crystal X-ray diffraction studies for the seven compounds were carried out *via* a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo Kα radiation (λ = 0.71073 Å, monochromator graphite). Data collection and reduction were completed using the SMART and SAINT softwares [16]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXTL package [17].

All H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation. Data collection and structure refinement parameters along with crystallographic data for all compounds are given in Table 1 and Table 2, while selected bond lengths, bond angles, and hydrogen bond geometries are listed in Tables 3, and 4.

Table 1. should be inserted here.

Table 2. should be inserted here.

Results and Discussion

Preparation and General Characterization

All salts **1-7** were prepared by the same method of mixing the acids with the benzylamine with 1:1 ratio in methanol solvents, and the crystals were obtained at ambient conditions *via* the common solvent evaporating technique. All compounds crystallized without water or methanol molecules accompanied, and the seven crystalline products are not hygroscopic. Fig. 1, Fig. 3, Fig. 5, Fig. 7, Fig. 9, Fig. 11, and Fig. 13 exhibit the molecular structures and their atom labelling schemes for the seven structures, respectively.

The O-H or N-H stretching frequencies were found at approximately 3688-3326 cm^{-1} as strong and broad bands in the IR spectra of the seven compounds. The medium intensity bands occurred in the regions of 1500-1630 cm^{-1} and 600-750 cm^{-1} are attributed to the aromatic ring stretching and bending, respectively. IR spectroscopy is very useful for the diagnosis of proton transfer compounds [18], for in the proton transfer compounds **2-7**, the most distinct feature in the IR spectrum are the presence of strong asymmetrical (1580-1620 cm^{-1}) and symmetrical (1388-1406 cm^{-1}) carboxylate stretching frequencies [19], respectively.

Table 3. should be inserted here.

Table 4. should be inserted here.

Structural descriptions

X-ray structure of (benzylamine) : (p-toluenesulfonic acid) $[(HL)^{+} \cdot (tsa^{-})]$ (1)

Fig. 1 should be inserted here.

Fig. 2 should be inserted here.

The analysis of the XRD data indicated the title compound crystallized as triclinic colorless crystals in the centrosymmetric space group P-1. The compound **1** is a salt with the SO_3H groups of the p-toluenesulfonic acids fully donated its H to the NH_2 of the benzylamine molecules, which is also verified by the O-S bond lengths

(1.4425(19)-1.4533(18) Å) at the deprotonated SO_3H. These O-S bond lengths are comparable to those in other documented 4-toluenesulfonate salt [20]. Fig. 1 shows the asymmetric unit of the compound **1** that contains the benzylaminium cation and the p-toluenesulfonate anion. The rms (root mean square) deviations of the phenyl rings of the cation and the anion are 0.0048 Å and 0.0024 Å, respectively, and both phenyl rings subtended at an angle of 53.9° with each other. The plane composed of the N group and the CH_2 spacer at the same cation was roughly perpendicular to the phenyl plane that they are attached.

One anion was bonded to one cation *via* the N-H···O hydrogen bond between the NH_3^+ and one O atom of the SO_3^- group with N-O distance of 2.861(3) Å, and CH-π association between the phenyl CH of the anion and the phenyl ring of the cation with C-Cg (Cg is the gravity centre of the phenyl ring of the cation) distance of 3.646 Å to form a heteroadduct. Two such heteroadducts generate a tetracomponent aggregate by a pair of N-H···O hydrogen bonds between the NH_3^+ of the cation and the oxygen atom of the SO_3^- group with N-O distance of 2.884(3) Å, and CH_2-O association from the CH_2 spacer of the cation and the SO_3^- with C-O separation of 3.177 Å, generating the close joint synthons II $R_2^1(5)$, and III $R_4^4(12)$. Similar with the documented ammonium sulfonate salts [21], here the most common III $R_4^4(12)$ synthon was also produced by two sulfonate O atoms and two H of each NH_3^+ *via* the bridging amino-sulfonate hydrogen bonds.

In the tetracomponent aggregate the corresponding cations and anions were inversionally related with the inversion centre located at the middle point of the two SO_3^- groups. The tetracomponent aggregates were linked together to form 1D chain running along the *a* axis direction with the assistance of two CH-O associations. Of the two CH-O associations one is between the phenyl CH of the anion and the SO_3^- group with C-O distance of 3.424 Å, and the other exists between the phenyl CH of the cation and the SO_3^- group with C-O distance of 3.496 Å. Within the crystal structure, neighboring chains are linked through additional interchain N-H···O hydrogen bond between the NH_3^+ and the oxygen atom of the SO_3^- group with N-O distance of 2.918(3) Å to give an overall 2D hydrogen bonded network running

parallel to the *ab* plane (Fig. 2). In addition, the crystal lattice is stabilized further through interchain CH-O association between the phenyl CH of the cation and the SO_3^- with C-O distance of 3.454 Å, and O-O contact between the O atoms of the SO_3^- groups with O-O distance of 3.010 Å. It is noteworthy to be pointed out that the O-O distance in the O-O contact was in accordance with the published value of 2.965(4) Å [22]. The above interchain N-H···O and CH-O associations produced the I ($R_2^1(7)$) synthon.

X-ray structure of (benzylamine) : (o-nitrobenzoic acid) [(HL^+) · ($onba)^-$] (2)

Fig. 3 should be inserted here.

Fig**.** 4 should be inserted here.

Compound **2** crystallizes as monoclinic colorless crystals in the space group P2(1)/c with Z =12. Although there was a documented salt of the same formula [14d], the differences between the two salts were the temperatures that the X-ray analysis were performed (298(2)/100(2)), and the Z values (12/4). The most important fact was that the crystal structure of the documented salt was not described in detail, so we described the structure again in depth. The asymmetric unit of **2** contains three thirds cation of benzylaminium, and three thirds of o-nitrobenzoate, as depicted in Fig. 3.

From the bond distances of the O(1)-C(22) (1.257(3) Å), O(2)-C(22) (1.248(3) Å), O(5)-C(29) (1.242(4) Å), O(6)-C(29) (1.251(3) Å), O(9)-C(36) (1.228(4) Å), and O(10)-C(36) (1.246(4) Å) at the carboxylates (Table 3), it can be decided that the compound **2** was also an organic salt. The differences (Δ are 0.009 Å, 0.009 Å, and 0.018 Å) in bond distances between the pair of O-C bonds in the same COO^- group in the compound **2** are in the range of the deprotonated COOH (Table 3). In the salt **2**, there were strong electrostatic interactions between the charged units of NH^+ and the o-nitrobenzoate.

One anion and one cation form a heteroadduct A by the N-H···O hydrogen bond between the NH_3^+ and one O atom of the COO^- group with N-O distance of 2.764(3) Å. The other anion was associated with the other cation *via* the bifurcated N-H···O hydrogen bonds between the NH_3^+ and both O atoms of the COO^- with N-O distances

of 2.715(3)-3.276(4) Å to form a heteroadduct B with the synthon IV ($R_1^2(4)$). The heteroadduct A and B were joined together by the N-H···O hydrogen bonds between the NH_3^+ and the oxygen atoms of the carboxylate with N-O distances of 2.817(3)-2.819(3) Å, CH-O association between the phenyl CH of the cation and the O atom of the carboxylate with C-O distance of 3.360 Å, and CH-π association between the phenyl CH of the cation and the phenyl nucleus of the anion with C-Cg distance of 3.703 Å to generate a tetracomponent aggregate. The N-H···O hydrogen bonds between heteroadduct A and B formed the V $R_4^2(8)$ synthon. Two tetracomponent aggregates were further connected together to produce an eight-component aggregate by the N-H···O hydrogen bond between the NH_3^+ and the oxygen atoms of the carboxylate with N-O distance of 2.706(4) Å. The third anion was bonded to the third cation by the N-H···O hydrogen bond between the NH_3^+ and one oxygen atom of the carboxylate with N-O distance of 2.783(3) Å to form a heteroadduct C. Two heteroadduct C produced a tetracomponent aggregate C by the N-H···O hydrogen bond between the NH_3^+ and the oxygen atom of the carboxylate with N-O distance of 2.761(3) Å exhibiting the VI ($R_4^4(12)$) ring motif. The VI ($R_4^4(12)$) ring motif was also frequently found at other ammonium carboxylate salts of the general formula ($R\text{-}NH_3^+$) · ($R'\text{-}CO_2^-$) [23].

Salt **2** exhibited 1-D chain running along the *a* axis direction based on the interlinked tetracomponent aggregate C and the eight-component aggregate by the N-H···O hydrogen bonds between the NH_3^+ and the carboxylate with N-O distances of 2.768(3)-2.819(3) Å. Herein the tetracomponent aggregate C and the eight-component aggregate alternated along the chain. Furthermore the CH-O associations between the phenyl CH of the anion, the carboxylate, and the nitro group with C-O distances of 3.433-3.634 Å, and CH-π association between the phenyl CH of the anion and the phenyl ring of the cation with C-Cg separation of 3.530 Å connected the neighboring 1D chains to form 2D corrugated sheet extending at the direction that made an angle of *ca*. 60° with the *ab* plane (Fig. 4). In this regard the phenyl rings of the anions at two neighboring chains were perpendicular with each other, so did the phenyl rings of the cations belonging to two neighboring chains. The

phenyl rings of the cations at the first chain were parallel to the phenyl rings of the cations at the third chain, so did the phenyl rings of the anions at the first chain and the phenyl rings of the anions at the third chain. In the third dimension, the 2D corrugated sheets were interlinked through CH-O associations between the phenyl CH of the anion, the carboxylate, and the nitro group with C-O distances of 3.329-3.634 Å to form the final 3-D network where the neighboring sheets were glided some distance from each other along the extending directions.

X-ray structure of (benzylamine) : (3,4-methylenedioxybenzoic acid) [(HL^+) · ($mdba^-$)] (3)

Fig. 5 should be inserted here.

Fig**.** 6 should be inserted here.

As depicted in Fig. 5, the molecular structure of **3** which belongs to the monoclinic P2(1)/c space group, crystallizes with one molecule of 3,4-methylenedioxybenzoic acid which is absolutely deprotonated and one molecule of protonated benzylamine. The C-O bond lengths in the carboxylate are 1.268(4) Å (O(1)-C(8)) and 1.258(4) Å (O(2)-C(8)) with the Δ value of 0.01 Å, supporting the ionization of the COOH at the 3,4-methylenedioxybenzoic acid.

The rms deviation of the rings containing C2-C7 atoms and C9-C14 atoms are 0.0040 Å and 0.0033 Å, and the dihedral angle between the both rings is 119.9º. The rms deviation of the 5-membered ring of the 1,3-dioxole is 0.0186 Å, which forms dihedral angles of 119.4º, and 0.5º with the phenyl rings containing C2-C7 and C9-C14 atoms, respectively. The carboxylate group twisted out of the phenyl ring plane with C9-C14 atoms only by 9.0˚, indicating the almost coplanarity of both units.

One cation was bonded to one anion through the strong N-H···O hydrogen bond between the NH_3^+ and one O atom of the carboxylate with H-O and N-O distances of 1.83 Å and 2.705(4) Å to form a heteroadduct. There also existed weak CH-O association between the phenyl CH of the cation and the other O of the carboxylate with C-O distance of 3.584 Å, which formed a graph-set motif of VIII ($R_2^2(9)$) together with the just mentioned N-H···O hydrogen bond. The heteroadducts extend

in the form of infinite chains through the N-H···Ohydrogen bonds along the *b* axis direction [N(1)-H(1A)···O(1)#3, 2.789(5) Å, 169.2°,#3 -x+1, y-1/2, -z+3/2] formed between the NH_3^+ and the carboxylate. With the help of the N-H···Ohydrogen bond between the NH_3^+ cation and the O atom of the carboxylate with N-O distance of 2.786(4) Å, two 1D chains were joined together to form a double chain. Between the two chains at the double chain there generated the IX ($R_4^3(10)$) ring motif, which was also one of the frequently found supramolecular heterosynthons at the ammonium carboxylate [24].

The cations belonging to the same chain were parallel to each other, and the cations belonging to two different chains at the double chain were antiparallel to each other. The adjacent double chains were bridged together through the additional weak CH_2-O associations between the CH_2 of the O-CH_2-O and the O at the O-CH_2-O with C-O separation of 3.096 Å to form the extending 2D sheet running at the direction that made an angle of *ca*. 60° with the *ab* plane (Fig. 6). The CH_2-O associations produced the VII ($R_2^2(6)$ ring) synthon. In the third dimension, the crystal lattice is propagated further through the independent CH-O association between the phenyl CH of the cation and the carboxylate with C-O distance of 3.329 Å, giving a complex 3D layer network structure.

X-ray structure of (benzylamine) : (mandelic acid) [(HL^+) · (mda^-)] (4)

Fig. 7 should be inserted here.

Fig**.** 8 should be inserted here.

In the compound **4** the N group in the L molecule was assumed to be protonated with H atom from the COOH group in mandelic acid, thus **4** was an organic salt also. In the asymmetric unit of **4** there existed one cation of HL, and one mandelate (Fig. 7), generating one pair of ion pair. The C-O bond lengths of the carboxylate group C8-O1-O2 were 1.239(4) Å, and 1.255(3) Å, respectively, with the difference (0.016 Å) between the pair of C-O bonds greatly smaller than the corresponding Δ value found in the crystal of the unionized (*RS*)-mandelic acid [25]. The rms deviations of the phenyl rings C2-C3-C4-C5-C6-C7 and C10-C11-C12-C13-C14-C15 are 0.0040 Å,

and 0.0055 Å, respectively, in which the two rings inclined at an angle of 51.1° with each other. The carboxylate O1-O2-C8 underwent an approximate 108.8° rotation from the phenyl ring plane (C10-C11-C12-C13-C14-C15), which is due to the flexible linker between the COO^- group and the phenyl ring. The plane defined by the N group and the CH_2 spacer of the cation lied nearly orthogonal to the phenyl plane to which they are attached.

The N-H···O hydrogen bond between the NH_3^+ and one O of the carboxylate with N-O distance of 2.767(3) Å, and CH-O association between the phenyl CH of the cation and the other O of the carboxylate with C-O distance of 3.404 Å united one anion and one cation into a bicomponent adduct exhibiting the XI $R_2^2(9)$ synthon which was similar with the VIII synthon at the salt **3**. Two bicomponent adducts were held together by the N-H···O hydrogen bond between the NH_3^+ and the O of the carboxylate that was involved in the CH-O association with N-O distance of 2.838(3) Å to form a tetracomponent aggregate with XIII ($R_4^4(12)$) synthon as found at **1**-**2**. Along the *a* axis direction, the tetracomponent aggregates were linked to each other by the N-H···O hydrogen bond from the NH_3^+ and the O atom of the carboxylate that had the CH-O association with N-O distance of 2.728(3) Å to form 1D chain along the *a* axis direction. In the chain the N-H···O hydrogen bonds between the tetracomponent aggregates found the XII ($R_4^2(8)$) synthon which was the same as the V synthon at **2**. Further connection through O-H···O hydrogen bond between the alcohol group and the COO^- with O-O distance of 2.855(3) Å generates an overall 2D sheet extending parallel to the *ab* plane (Fig. 8), in which the neighboring chains were moved some distance from each other along the *a* axis direction. Herein the O-H···O hydrogen bonds produced a ring with X ($R_2^2(10)$) synthon.

X-ray structure of (benzylamine) : (5-bromosalicylic acid)$_2$ [(HL^+) · ($bsac^-$) · (Hbsac)] (5)

Fig. 9 should be inserted here.

Fig**.** 10 should be inserted here.

Crystallization of benzylamine and 5-bromosalicylic acid in a 1:1 ratio from the

solvent of methanol gave single crystals suitable for X-ray diffraction. The compound **5** belongs to triclinic block crystals in the space group P-1, in which only the proton at the COOH was fully transferred to the N atom of the L molecule forming an organic salt. In an asymmetric unit of **5** there existed entire ions of HL cation, 5-bromosalicylic acid monoanion, and 5-bromosalicylic acid molecule, as shown in Fig. 9. Herein the composition of the compound **5** was similar to the published compound of $[(C_3H_5N_2)^+ \cdot (C_7H_4O_3Cl)^-] \cdot C_7H_5O_3Cl$($C_7H_5O_3Cl$ = 5-chlorosalicylic acid) [26]. Structural and conformational features like those previously observed are found at the $bsac^-$ anion in **5** also [26]. The anticipated intramolecular hydrogen bond is established between the phenol group and a carboxyl O atom (O(3)-H(3)···O(2), 2.512(7) Å, 147.6º) which has comparable strength as those found in the salt $[(C_3H_5N_2)^+ \cdot (C_7H_4O_3Cl)^-] \cdot C_7H_5O_3Cl$ from the imidazole and the 5-chlorosalicylic acid [26]. Due to the planarity of the hydrogen bonded carboxylate unit, the O-O separation is in the range of the archived results [2.489-2.509 Å] [27], but it is slightly shortened when it is compared with the unproton transfer examples (2.547-2.604 Å, mean: 2.588 Å). The C-O bond distances of the carboxylate varied from 1.252(9) Å (O(1)-C(8)) to 1.260(8) Å (O(2)-C(8)) with the Δ value of 0.008 Å, lending strong support to the suggested ionic character of **5**. The C-O bond distances of the O4-C15-O5 were 1.302(10) Å, and 1.215(9) Å with the Δ value of 0.087 Å, the significantly difference of the Δ values at the COO^- and COOH groups further verifies our correct assignment of the H atom at the COOH. The rms deviation of the phenyl ring with C2-C7 is 0.0044 Å. The rms deviation of the phenyl ring of the anion is 0.0101 Å. The dihedral angle between the two phenyl ring planes is 80.5°. The rms deviation of the ring with C16-C21 is 0.0034 Å, this ring subtended at dihedral angles of 82.3°, and 1.9° with the rings C2-C7 and C16-C21, respectively.

Two anions were held together by the O-H···O hydrogen bond between the phenol unit and the COO^- with O-O distance of 3.128(7) Å to form an anion dimer. At the anion dimer there were bonded two 5-bromosalicylic acid molecules by the O-H···O hydrogen bond between the COOH unit and theCOO^- with O-O distance of 2.599(7) Å, and CH-O association between the phenyl CH of the anion and the OH of

the COOH with C-O distance of 3.303 Å to form a tetracomponent adduct. The same with the salicylic acid derivatives [26, 27], the intramolecular O-H···O hydrogen bonds displaying the $S_1^1(6)$ rings were also occurred at both the anion and the 5-bromosalicylic acid molecule. At the tetracomponent adduct there were attached two cations *via* the N-H···O hydrogen bonds from the NH_3^+, the phenol group, and both O atoms of the carboxylate with N-O distances of 2.772(9)-3.156(8) Å, CH-O association between the phenyl CH of the cation and the carbonyl unit of the COOH with C-O distance of 3.428 Å, and CH_2-O association between the CH_2 spacer of the cation and the carbonyl unit of the COOH with C-O distance of 3.452 Å to generate a six-component assembly with an inversion centre located at the middle point of the two anions.

The six-component assemblies are further mediated by the CH-O association between the phenyl CH of the 5-bromosalicylic acid and the phenol group of the 5-bromosalicylic acid with C-O distance of 3.506 Å to form 1D chain. The discrete 1D parallel chains formed a sheet extending at the direction that made an angle of *ca*. 60° with the *bc* plane (Fig. 10), but there were not found any bonding interactions between these chains. At the chain the synthons XIV $R_2^2(8)$, XIX $R_2^1(6)$, XV $R_2^2(7)$, XVI $R_1^2(4)$, XVII $R_3^2(6)$, and XVIII $R_3^3(9)$ were found. Different from **1**, **2**, and **4**, there were neither $R_4^4(12)$ nor $R_4^2(8)$ synthons produced by the $NH_3^+\cdots^-OOC$ at **5**, which may be caused by the presence of the phenol units participating in multiple O-H···O hydrogen bond which blocked the COO^- from bridging the NH_3^+. Within the crystal structure, neighboring sheets are linked through additional intersheet N-H···O hydrogen bonds between the NH_3^+ and the carboxylate with N-O distances of 2.907(8)-3.245(8) Å to give an overall 3D hydrogen bonded network. In this case the discrete chains belonging to two neighboring sheets were slide some distance from each other along the running direction of the chain.

X-ray structure of (benzylamine) : (m-phthalic acid) [(HL^+) · ($Hmpta^-$)] (6)

Fig. 11 should be inserted here.

Fig**.** 12 should be inserted here.

In the asymmetric unit of **6** there occupied one cation of benzylamine, and one monoanion of m-phthalic acid, which is shown in Fig. 11. In the compound, there is a pair of ion pair with no included solvent molecules accompanied, either. Different from the published adduct [28], here only one COOH of the m-phthalic acid is deprotonated to maintain the charge balance. The rms deviations of the rings with C2-C7 and C10-C15 are 0.0061 Å, and 0.0099 Å, respectively, and both rings made an angle of 122.2° with each other. The carboxylates twisted only by 4.4 (for O(1)-C(8)-O(2)), and 12.8° (for O3-C9-O4) from the phenyl ring plane of the m-phthalate, respectively, which is similar to the reported adduct from the phthalate in which the carboxylates are almost coplanar with the phenyl ring also [29]. Both carboxyl units intersected at an angle of 16.7° with each other. It is very clear that the difference in bond lengths of the C-O within the C9-O3-O4 group (0.108 Å) is much greater than the one found in the C8-O1-O2 anion (0.009 Å). Also the average bond length for C-O (1.258 Å) in the COO^- (C8-O1-O2) is less than the C-O single bond (C9-O3, 1.314(3) Å) and greater than the C=O double bond (C9-O4, 1.206(3) Å) in the COOH group of the anion, this further supports our correct assignment of the m-phthalate monoanion.

One anion and one cation form a bicomponent adduct $[(HL^+) \cdot (Hmpta^-)]$ by the bifurcated N-H···O hydrogen bond between the NH_3^+ and both O atoms of the carboxylate with N-O distances of 2.839(2)-3.197(2) Å. Two bicomponent adducts $[(HL^+) \cdot (Hmpta^-)]$ were linked together by the N-H···O hydrogen bond between the NH_3^+ and the O atom of the carboxylate with N-O distance of 2.805(2) Å, and CH-O association between the phenyl CH of the cation and the O of the carboxylate with C-O distance of 3.552 Å to generate a tetramer having an inversion centre located at the middle point of the two carboxylates.

Along *a* axis direction, the resulting tetramers were linked together by the N-H···O hydrogen bond between the NH_3^+ and the O atoms of the carboxylate with N-O distance of 2.777(2) Å to produce a 1D chain running along the *a* axis direction. Further connection through the interchain O-H···O hydrogen bond between the COOH and the COO^- groups with O-O separation of 2.595(2) Å generates an overall

2D sheet extending parallel to the *ac* plane (Fig. 12). The 2D sheets displayed the XXI $R_4^4(12)$ (composed of the close joint $R_1^2(4)$ and $R_4^2(8)$ synthons), XX $R_2^2(16)$ (composed of the close joint $R_2^2(7)$, and $R_2^2(10)$ synthons), and XXII $R_2^2(9)$ ring motifs. The interchain CH-O association between the p-CH of the anion and the OH unit at the COOH with C-O distance of 3.245 Å, and CH_2-O association between the CH_2 spacer of the cation and the carbonyl unit of the COOH with C-O distance of 3.476 Å were also found, which contribute also to the formation and stabilization of the final 2D sheet structure.

X-ray structure of (benzylamine)$_2$: (trimesic acid) [(HL$^+$)$_2$ · (Htma^{2-})] (7)

Fig. 13 should be inserted here.

Fig**.** 14 should be inserted here.

Compound **7** is a 1:2 salt composed of two cations of benzylaminium, and an anion of hydrogen trimesate (Fig. 13), which crystallizes as triclinic block crystals in the space group P-1. In the COOH (O(3)-C(16)-O(4)) group, two pairs of C-O bond lengths (O(3)-C(16), 1.312(3) Å, and O(4)-C(16), 1.203(3) Å) are significantly different with the large Δ value of 0.109 Å which is anticipated between the neutral C-O and C=O bond distances [30]. The C-O bond lengths of the O2-C15-O1 group are 1.242(3) Å, and 1.261(3) Å, respectively. The C-O bond lengths of the O5-C17-O6 group are 1.264(3) Å, and 1.223(3) Å, respectively. The longer bond O(2)-C(15) (1.261(3) Å) has almost the same length as that of the longer bond of O5-C17 (1.264(3) Å). But there is relative significant difference between the shorter bonds O(1)-C(15) (1.242(3) Å) and O(6)-C(17) (1.223(3) Å), the reason is that O(1) takes part in more strong hydrogen bond than that of O(6) (Table 4). The rms deviations of the rings C2-C7 and C9-C14 were 0.0017 Å and 0.0038 Å, respectively, and both rings made a dihedral angle of 63.9° with each other. The rms deviation of the ring with C18-C23 was 0.0098 Å. The phenyl ring C18-C23 of the anion subtended the dihedral angles of 80°, and 24.4° with the above two rings, respectively. The mean planes of the three carboxylate groups underwent slight twist from the anion benzene ring with dihedral angles of 4.9(1)° for C15-O1-O2, 8.2(1)° for

C16-O3-O4, and 20.2(1)° for C17-O5-O6, which are smaller than those corresponding dihedral angles in the benzene-1,3,5-tricarboxylate trianion [31].

At every COO^- of the dianion there was bonded a cation by the N-H···O hydrogen bonds from the NH_3^+ with N-O distances of 2.704(3)-2.909(3) Å to form a tricomponent adduct. Two tricomponent adducts were united into a six-component aggregate through the N-H···O hydrogen bond from the NH_3^+, the COO^- and the carbonyl unit of the COOH with N-O distances of 2.783(3) Å-2.953(3) Å, CH_2-O association between the CH_2 linker of the cation, the carbonyl and the OH units of the COOH with C-O distances of 3.105 Å-3.477 Å, and O-C_π association between the carbonyl unit of the COOH and the π-C of the COO^- with O-C distance of 3.196 Å, in which the two tricomponent adducts at the six-component aggregate were antiparallel to each other. It is worthy to point out that the O-C separation is slightly longer than the archived value of 3.019(4) Å [32].

There were O-H···O hydrogen bonds between the COOH and the COO^- with O-O separation of 2.565(3) Å which joined the six-component aggregates into 1D chain running along the *a* axis direction, together with the N-H···O hydrogen bond between the NH_3^+ and the carboxylate with N-O distance of 2.709(3) Å. The 1D chains were linked into 2D sheet extending parallel to the *ab* plane (Fig. 14) under the assistance of the N-H···O hydrogen bonds, CH-π and CH_2-π associations. Herein the N-H···O hydrogen bonds were from the NH_3^+ and the carboxylate with N-O distances of 2.713(3)-2.844(3) Å, CH-π associations existed between the phenyl CH of the cation and the phenyl ring of the cation with C-Cg distances of 3.497-3.748 Å, and CH_2-π association is established between the CH_2 spacer of the cation and the phenyl ring of the cation with C-Cg distance of 3.728 Å. The 2D sheets displayed XXIV $R_2^1(5)$, XXIII $R_2^2(11)$, XXVII $R_4^2(8)$, XXV $R_3^3(10)$, and XXVI $R_4^3(10)$ rings. The 2D sheets were further expanded along the *c* axis direction to form 3D layer network structure, where the neighboring sheet layers were slipped some distances from each other along the *a* and *b* axis directions, respectively.

Conclusions

Seven benzylaminium salts with different anions have been synthesized and characterized by X-ray diffraction analysis. The structure analysis confirms that the N atoms in the benzylamine are protonated in all the seven salts. Robust hydrogen bonds in combination with other weak nonbonding associations led to the final generation of distinct 2D-3D supramolecular networks. Although the organic acids utilized in this work were different from each other, their structures display some certain common structural features: in all of the crystal packing, the building blocks of **1**-**7** are self-assembled *via* proton-transferred N-H···O hydrogen bonds, salts **4**-**7** possess the additional O-H···O hydrogen bonds. The weak CH-O/CH_2-O, CH-π/CH_2-π, O-O, and O-C_π associations also become prominent in the construction of the final supramolecular networks. All structures have the 1D substructure (1D chain), from an inspection of the function exhibited by each set of interactions, it seems that the intra- and interchain noncovalent bonding interactions played equal importance in structure propagation.

In this study, an intricate array of homosynthons and hetersynthons with small and large sized ring motifs were observed including $R_1^2(4)$, $R_2^1(5)$, $R_2^1(6)$, $R_2^1(7)$, $R_2^2(6)$, $R_2^2(7)$, $R_2^2(8)$, $R_2^2(9)$, $R_2^2(10)$, $R_2^2(11)$, $R_2^2(16)$, $R_3^2(6)$, $R_3^3(9)$, $R_3^3(10)$, $R_4^2(8)$, $R_4^3(10)$, and $R_4^4(12)$. But not all of them were observed repeatedly, as most of them occurred only in some structures. Nevertheless $R_4^2(8)$, $R_4^3(10)$ and $R_4^4(12)$ motifs have been the most recurrently occurring ones in the present study and previous reports. The seven structures discussed here further tell that the benzylaminium cation is a good build block to be incorporated into organic salts so as to produce diversiform and stable hydrogen-bonded structures.

Supporting Information Available: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 1029026 for **1**, 1029027 for **2**, 1029028 for **3**, 1029029 for **4**, 1029030 for **5**, 1029031 for **6**, and 1029032 for **7**. Copies of this information may be obtained free of charge from the +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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Figure captions

Fig. 1. Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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

Fig. 3. Molecular structure in crystal of **2** according to XRD study (Due to the crowded nature of the structure, the atomic numbering is not shown). Displacement ellipsoids were drawn at the 30% probability level.

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

Fig. 5. Molecular structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

Fig. 6. 2D sheet structure of **3** formed by the interchain CH_2-O association extending at the direction that made an angle of ca. 60° with the *ab* plane.

Fig. 7. Molecular structure of **4** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Fig. 8. 2D sheet structure of **4** extending parallel to the *ab* plane.

Fig. 9. Molecular structure of **5** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Fig. 10. 2D sheet structure of **5** extending at the direction that made an angle of ca. 60° with the *bc* plane.

Fig. 11. Molecular structure of **6** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Fig. 12. 2D sheet structure of **6** extending parallel to the *ac* plane.

Fig. 13. Molecular structure of **7** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Fig. 14. 2D sheet structure of **7** extending parallel to the *ab* plane.

Covering information sheet

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Table 1. Summary of X-ray crystallographic data for salts **1** - **4**.

	1	**2**	**3**	**4**
Formula	$C_{14}H_{17}NO_3S$	$C_{14}H_{14}N_2O_4$	$C_{15}H_{15}NO_4$	$C_{15}H_{17}NO_3$
Fw	279.35	274.27	273.28	259.30
T, K	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	P2(1)/c	P2(1)/c	P-1
a, Å	5.6416(5)	16.9163(16)	13.773(12)	6.0499(4)
b, Å	7.3677(6)	18.7587(17)	6.469(6)	7.4999(5)
c, Å	16.1213(12)	13.0003(12)	15.644(14)	15.0126(15)
α, deg.	90.124(2)	90	90	97.590(2)
β, deg.	89.4540(10)	95.1840(10)	103.735(13)	97.514(2)
γ, deg.	89.964(2)	90	90	91.5650(10)
V, Å^3	670.06(9)	4108.5(7)	1354(2)	668.72(9)
Z	2	12	4	2
D_{calcd}, Mg/m^3	1.385	1.330	1.341	1.288
Absorption coefficient, mm^{-1}	0.245	0.099	0.098	0.090
F(000)	296	1728	576	276
Crystal size, mm^3	0.48 x 0.32 x 0.16	0.46 x 0.43 x 0.43	0.41 x 0.31 x 0.18	0.41 x 0.37 x 0.23
θ range, deg	2.76 - 25.02	2.34 - 25.02	2.68 - 28.45	2.74 - 25.01
	$-6 \le h \le 6$	$-20 \le h \le 16$	$-18 \le h \le 18$	$-7 \le h \le 7$
Limiting indices	$-8 \le k \le 8$	$-20 \le k \le 22$	$-7 \le k \le 8$	$-7 \le k \le 8$
	$-19 \le l \le 14$	$-15 \le l \le 15$	$-20 \le l \le 10$	$-17 \le l \le 16$
Reflections collected	3311	20440	8171	3372
Reflections independent (R_{int})	2298 (0.0212)	7222 (0.0501)	3284 (0.1143)	2307 (0.0316)
Goodness-of-fit on F^2	1.057	1.001	0.881	0.957
R indices [$I > 2\sigma I$]	0.0435, 0.1092	0.0543, 0.1267	0.0610, 0.1489	0.0572, 0.1345
R indices (all data)	0.0614, 0.1201	0.1410, 0.1667	0.2222, 0.2244	0.1193, 0.1596
Largest diff. peak and hole, e.Å^{-3}	0.284, -0.296	0.319, -0.201	0.220, -0.243	0.321, -0.210

Table 2. Summary of X-ray crystallographic data for salts **5** - **7**.

	5	**6**	**7**
Formula	$C_{21}H_{19}Br_2NO_6$	$C_{15}H_{15}NO_4$	$C_{23}H_{24}N_2O_6$
Fw	541.19	273.28	424.44
T, K	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1
a, Å	4.6374(3)	6.4023(4)	9.5898(7)
b, Å	13.9282(9)	10.0924(8)	10.5101(8)
c, Å	17.0681(13)	11.0536(9)	11.0182(9)
α, deg.	79.0940(10)	92.7740(10)	102.765(2)
β, deg.	88.744(2)	96.864(2)	92.4220(10)
γ, deg.	84.7700(10)	96.490(2)	105.594(2)
V, $Å^3$	1078.01(13)	703.17(9)	1037.08(14)
Z	2	2	2
D_{calcd}, Mg/m^3	1.667	1.291	1.359
Absorption coefficient, mm^{-1}	3.797	0.094	0.099
F(000)	540	288	448
Crystal size, mm^3	0.40 x 0.32 x 0.11	0.41 x 0.37 x 0.15	0.41 x 0.27 x 0.15
θ range, deg	2.43 - 25.02	2.67 - 25.02	2.45 - 25.02
	$-5 \le h \le 5$	$-7 \le h \le 7$	$-11 \le h \le 10$
Limiting indices	$-16 \le k \le 13$	$-9 \le k \le 12$	$-12 \le k \le 12$
	$-18 \le l \le 20$	$-13 \le l \le 13$	$-9 \le l \le 13$
Reflections collected	5313	3578	5208
Reflections independent (R_{int})	3666 (0.0444)	2438 (0.0252)	3572 (0.0253)
Goodness-of-fit on F^2	0.925	0.881	1.000
R indices [$I > 2\sigma I$]	0.0717, 0.1783	0.0521, 0.1198	0.0597, 0.1395
R indices (all data)	0.1640, 0.2219	0.0912, 0.1348	0.1172, 0.1670
Largest diff. peak and hole, $e.Å^{-3}$	0.776, -0.613	0.208, -0.192	0.276, -0.230

Table 3 Selected bond lengths [Å] and angles [°] for **1** - **7**.

1			
S(1)-O(3)	1.4425(19)	S(1)-O(1)	1.4496(17)
S(1)-O(2)	1.4533(18)	S(1)-C(8)	1.769(2)
N(1)-C(1)	1.478(3)	O(3)-S(1)-O(1)	113.08(13)
O(3)-S(1)-O(2)	113.27(12)	O(1)-S(1)-O(2)	111.12(11)
2			
N(1)-C(1)	1.484(4)	N(2)-C(8)	1.480(4)
N(3)-C(15)	1.479(4)	N(4)-O(4)	1.221(3)
N(4)-O(3)	1.223(3)	N(4)-C(24)	1.456(4)
N(5)-O(8)	1.216(3)	N(5)-O(7)	1.219(3)
N(5)-C(31)	1.461(4)	N(6)-O(11)	1.191(4)
N(6)-O(12)	1.207(4)	N(6)-C(38)	1.452(5)
O(1)-C(22)	1.257(3)	O(2)-C(22)	1.248(3)
O(5)-C(29)	1.242(4)	O(6)-C(29)	1.251(3)
O(9)-C(36)	1.228(4)	O(10)-C(36)	1.246(4)
O(2)-C(22)-O(1)	125.4(3)	O(5)-C(29)-O(6)	126.4(3)
O(9)-C(36)-O(10)	125.7(3)		
3			
N(1)-C(1)	1.474(5)	O(1)-C(8)	1.268(4)
O(2)-C(8)	1.258(4)	O(3)-C(11)	1.381(4)
O(3)-C(15)	1.418(5)	O(4)-C(12)	1.374(4)
O(4)-C(15)	1.409(5)	C(11)-O(3)-C(15)	105.4(3)
C(12)-O(4)-C(15)	105.7(3)	O(2)-C(8)-O(1)	123.0(4)
O(4)-C(15)-O(3)	109.4(3)		
4			
N(1)-C(1)	1.471(3)	O(1)-C(8)	1.255(3)
O(2)-C(8)	1.239(4)	O(3)-C(9)	1.422(3)
O(2)-C(8)-O(1)	125.1(3)		
5			
Br(1)-C(13)	1.903(7)	Br(2)-C(20)	1.924(9)
N(1)-C(1)	1.494(10)	O(1)-C(8)	1.252(9)
O(2)-C(8)	1.260(8)	O(3)-C(10)	1.350(8)
O(4)-C(15)	1.302(10)	O(5)-C(15)	1.215(9)
O(6)-C(17)	1.364(10)	O(1)-C(8)-O(2)	121.5(8)
O(5)-C(15)-O(4)	123.4(7)		
6			
N(1)-C(1)	1.487(3)	O(1)-C(8)	1.254(2)
O(2)-C(8)	1.263(3)	O(3)-C(9)	1.314(3)
O(4)-C(9)	1.206(3)	O(1)-C(8)-O(2)	121.7(2)
O(4)-C(9)-O(3)	123.6(2)		
7			
N(1)-C(1)	1.486(4)	N(2)-C(8)	1.477(4)
O(1)-C(15)	1.242(3)	O(2)-C(15)	1.261(3)

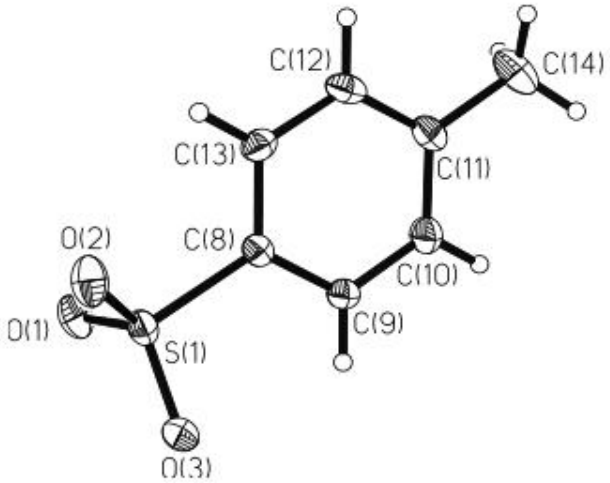
O(3)-C(16)	1.312(3)	O(4)-C(16)	1.203(3)
O(5)-C(17)	1.264(3)	O(6)-C(17)	1.223(3)
O(1)-C(15)-O(2)	124.1(3)	O(4)-C(16)-O(3)	124.2(3)
O(6)-C(17)-O(5)	125.1(3)		

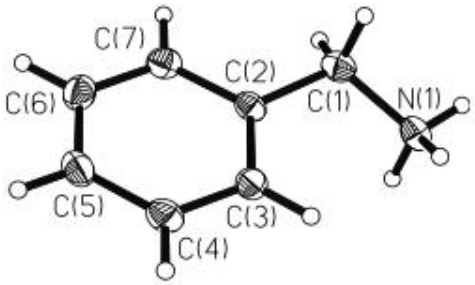
Table 4 Hydrogen bond distances and angles in studied structures **1** - **7**.

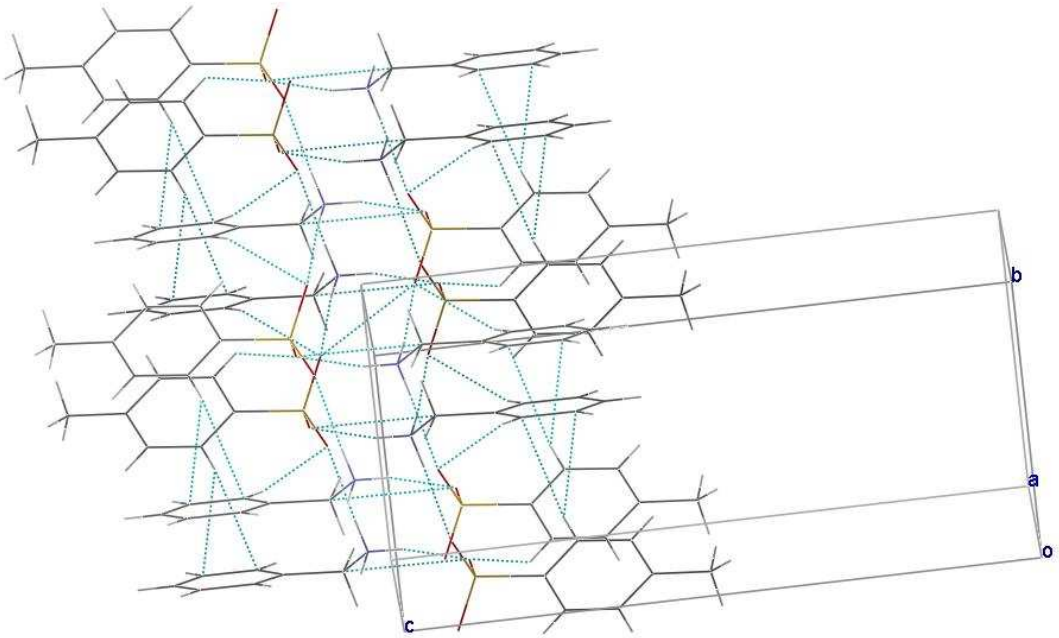
D-H···A	d(D-H) **[Å]**	d(H···A)**[Å]**	d(D···A)**[Å]**	<(DHA)[°]
1				
N(1)-H(1C)···O(1)#1	0.89	1.98	2.861(3)	173.6
N(1)-H(1B)···O(3)#2	0.89	2.09	2.884(3)	148.5
N(1)-H(1A)···O(2)#3	0.89	2.03	2.918(3)	172.8
2				
N(3)-H(3C)··O(1)#1	0.89	1.90	2.781(3)	170.1
N(3)-H(3B)··O(6)#2	0.89	1.89	2.764(3)	165.5
N(3)-H(3A)··O(10)	0.89	2.05	2.817(3)	143.8
N(2)-H(2C)··O(9)	0.89	1.82	2.706(4)	175.0
N(2)-H(2B)··O(9)#2	0.89	2.62	3.276(4)	131.0
N(2)-H(2B)··O(10)#2	0.89	1.85	2.715(3)	164.9
N(2)-H(2A)··O(6)	0.89	1.98	2.819(3)	157.2
N(1)-H(1C)··O(1)	0.89	1.90	2.783(3)	170.5
N(1)-H(1B)··O(2)#3	0.89	1.87	2.761(3)	177.2
N(1)-H(1A)··O(5)	0.89	1.89	2.768(3)	168.4
3				
N(1)-H(1C)···O(2)#1	0.89	1.83	2.705(4)	168.1
N(1)-H(1B)··O(1)#2	0.89	1.94	2.786(4)	157.3
N(1)-H(1A)···O(1)#3	0.89	1.91	2.789(5)	169.2
4				
O(3)-H(3)··O(2)	0.82	2.18	2.656(3)	117.3
O(3)-H(3)··O(2)#1	0.82	2.13	2.855(3)	146.7
N(1)-H(1C)··O(2)#2	0.89	1.90	2.767(3)	165.3
N(1)-H(1B)··O(1)#3	0.89	1.97	2.838(3)	164.5
N(1)-H(1A)··O(1)#4	0.89	1.87	2.728(3)	161.3
5				
O(6)-H(6)··O(5)	0.82	1.88	2.596(8)	145.1
O(4)-H(4)··O(1)#1	0.82	1.78	2.599(7)	171.9
O(3)-H(3)··O(2)#2	0.82	2.51	3.128(7)	133.4
O(3)-H(3)··O(2)	0.82	1.78	2.512(7)	147.6
N(1)-H(1C)··O(2)#1	0.89	2.66	3.156(8)	116.5
N(1)-H(1C)··O(1)#1	0.89	1.91	2.772(9)	162.6
N(1)-H(1B)··O(2)#2	0.89	2.51	3.245(8)	139.7
N(1)-H(1B)··O(2)	0.89	2.12	2.907(8)	146.3
N(1)-H(1A)··O(3)#3	0.89	2.13	3.005(8)	165.6
6				
O(3)-H(3)··O(2)#1	0.82	1.86	2.595(2)	148.7
N(1)-H(1C)··O(2)#2	0.89	1.92	2.805(2)	178.8
N(1)-H(1B)··O(2)	0.89	2.51	3.197(2)	134.8
N(1)-H(1B)··O(1)	0.89	1.96	2.839(2)	167.3
N(1)-H(1A)··O(1)#3	0.89	1.90	2.777(2)	167.1
7				

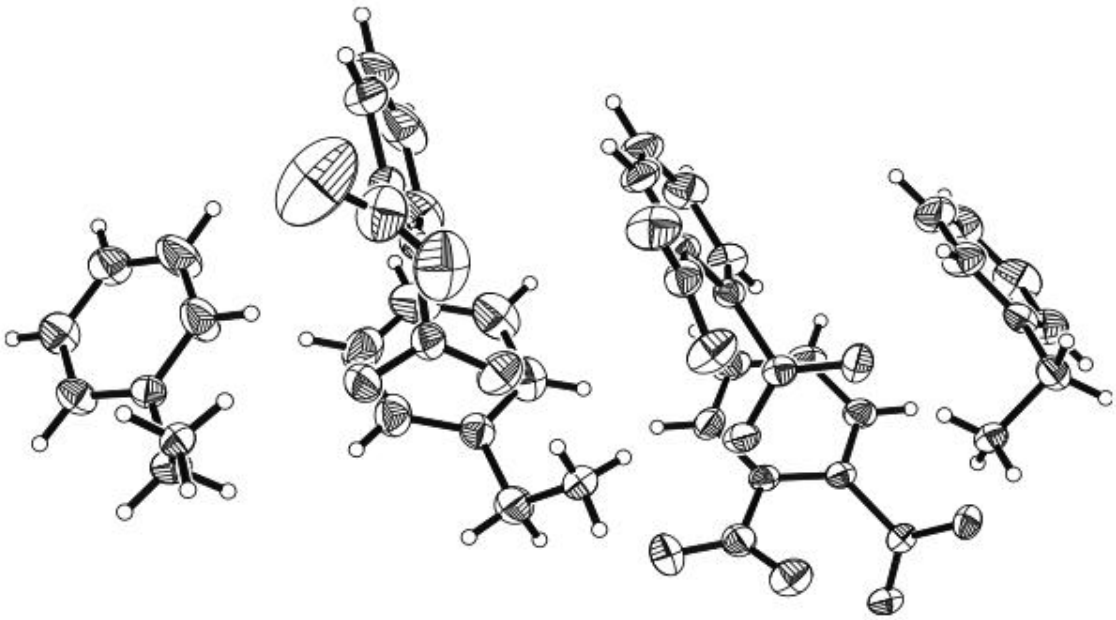
O(3)-H(3)···O(6)#1	0.82	1.83	2.565(3)	147.6
N(2)-H(2C)···O(5)#2	0.89	1.84	2.709(3)	165.4
N(2)-H(2B)···O(1)#3	0.89	2.29	2.909(3)	126.8
N(2)-H(2B)···O(4)#4	0.89	2.24	2.953(3)	136.3
N(2)-H(2A)···O(1)	0.89	1.96	2.844(3)	171.7
N(1)-H(1C)···O(2)#5	0.89	1.83	2.713(3)	168.7
N(1)-H(1B)···O(5)	0.89	1.84	2.704(3)	162.6
N(1)-H(1A)···O(2)#6	0.89	1.94	2.783(3)	158.6

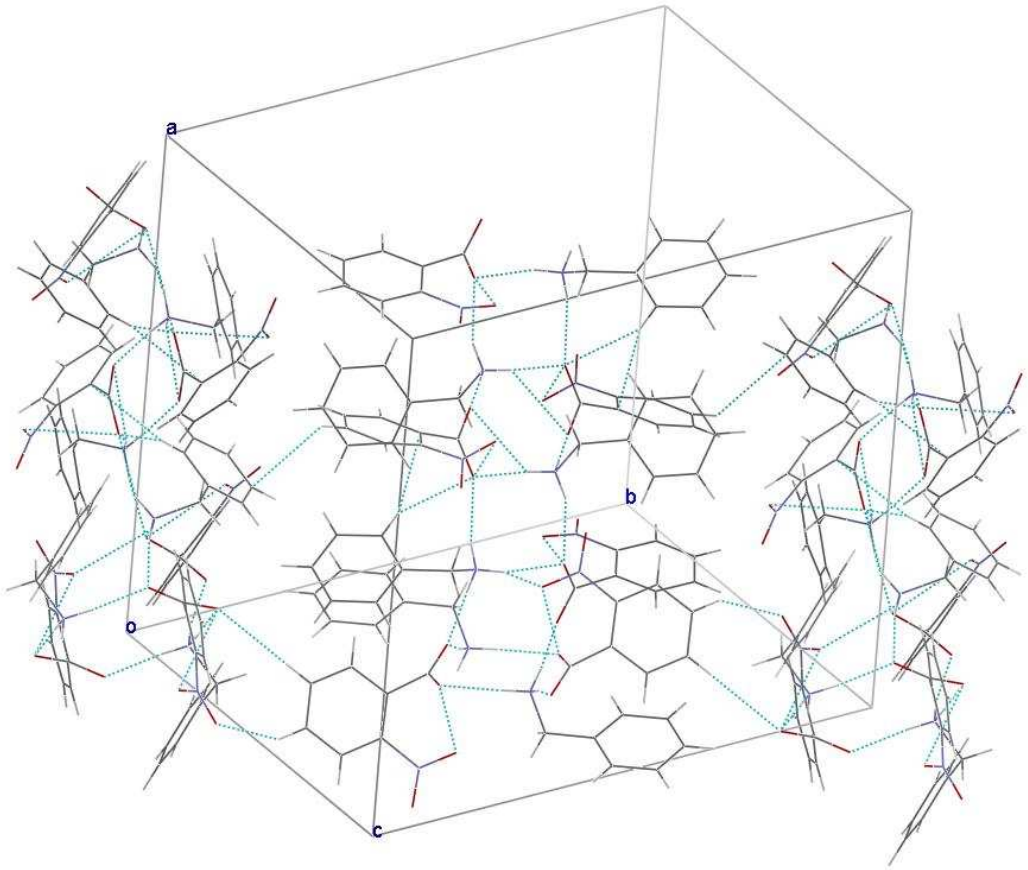
Symmetry transformations used to generate equivalent atoms for **1**: #1 -x+1, -y+1, -z+1; #2 x+1, y, z+1; #3 -x+1, -y+2, -z+1. Symmetry transformations used to generate equivalent atoms for **2**: #1 x-1, y, z; #2 -x+1, -y+1, -z+1; #3 -x+2, -y+1, -z+1. Symmetry transformations used to generate equivalent atoms for **3**: #1 -x+1, y-3/2, -z+3/2; #2 x, y-1, z; #3 -x+1, y-1/2, -z+3/2. Symmetry transformations used to generate equivalent atoms for **4**: #1 -x+1, -y+1, -z+2; #2 -x+1, -y+1, -z+1; #3 x, y-1, z-1; #4 -x, -y+1, -z+1. Symmetry transformations used to generate equivalent atoms for **5**: #1 x-1, y, z; #2 -x+2, -y+1, -z; #3 -x+1, -y+1, -z. Symmetry transformations used to generate equivalent atoms for **6**: #1 -x, -y+1, -z+2; #2 -x, -y+1, -z+1; #3 -x+1, -y+1, -z+1. Symmetry transformations used to generate equivalent atoms for **7**: #1 x+1, y, z; #2 x, y-1, z; #3 -x, -y, -z+1; #4 x-1, y-1, z; #5 x, y+1, z; #6 -x+1, -y+1, -z+1.

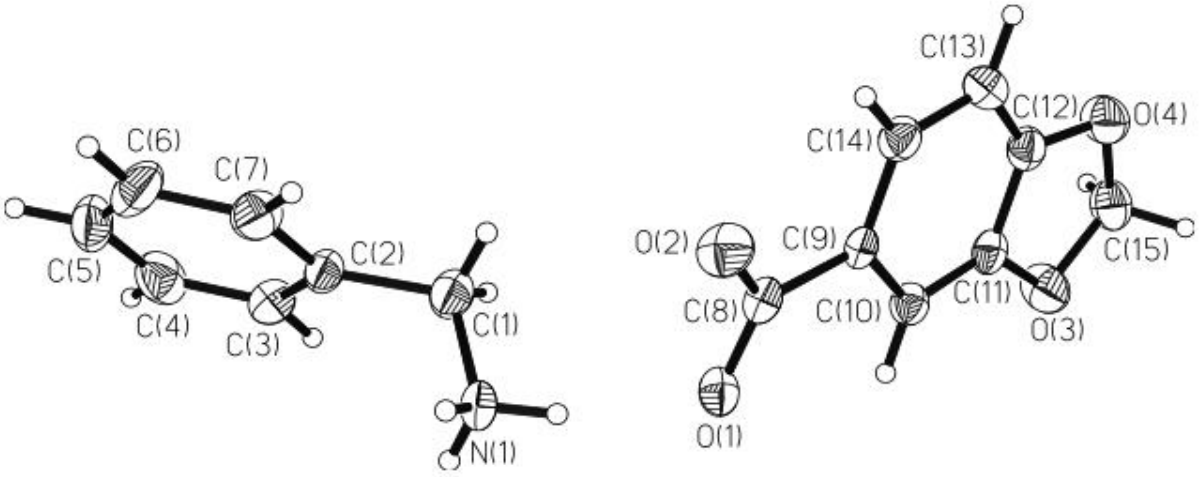


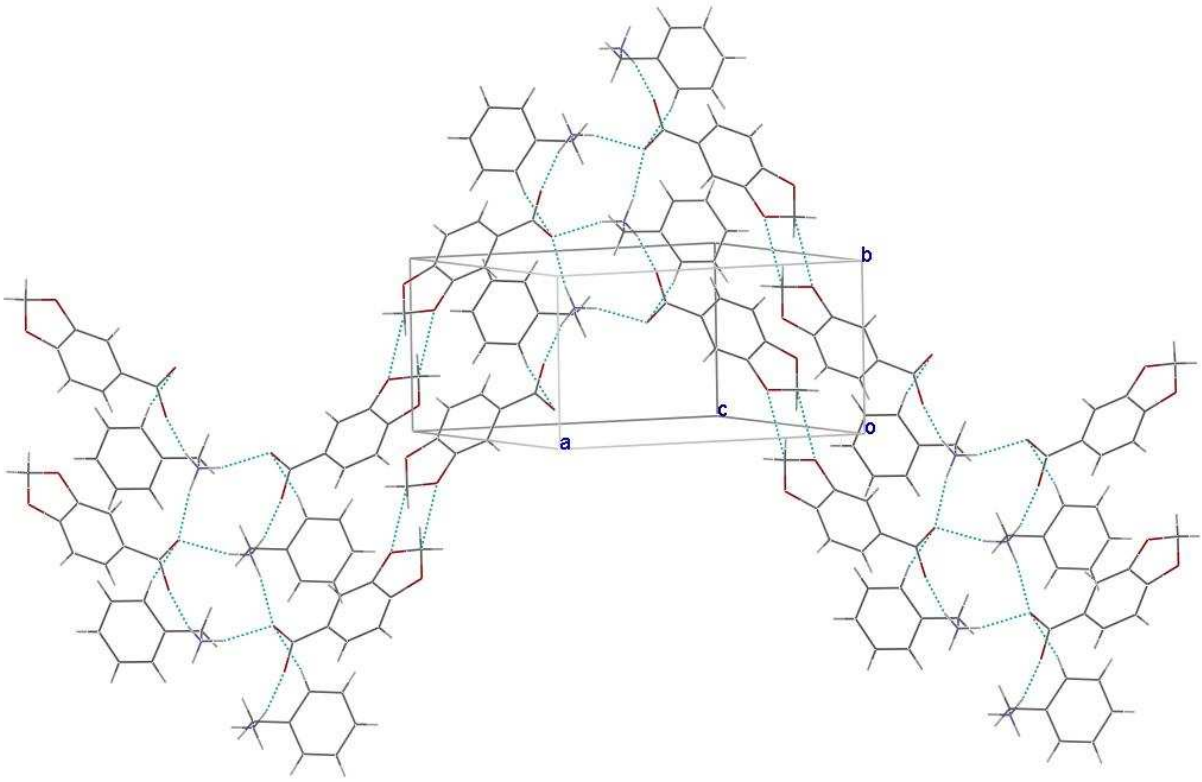


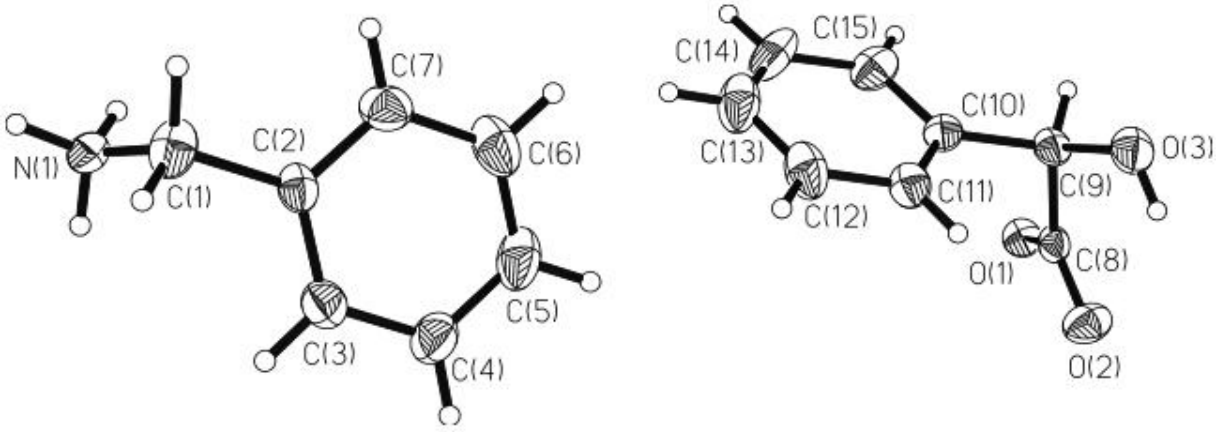


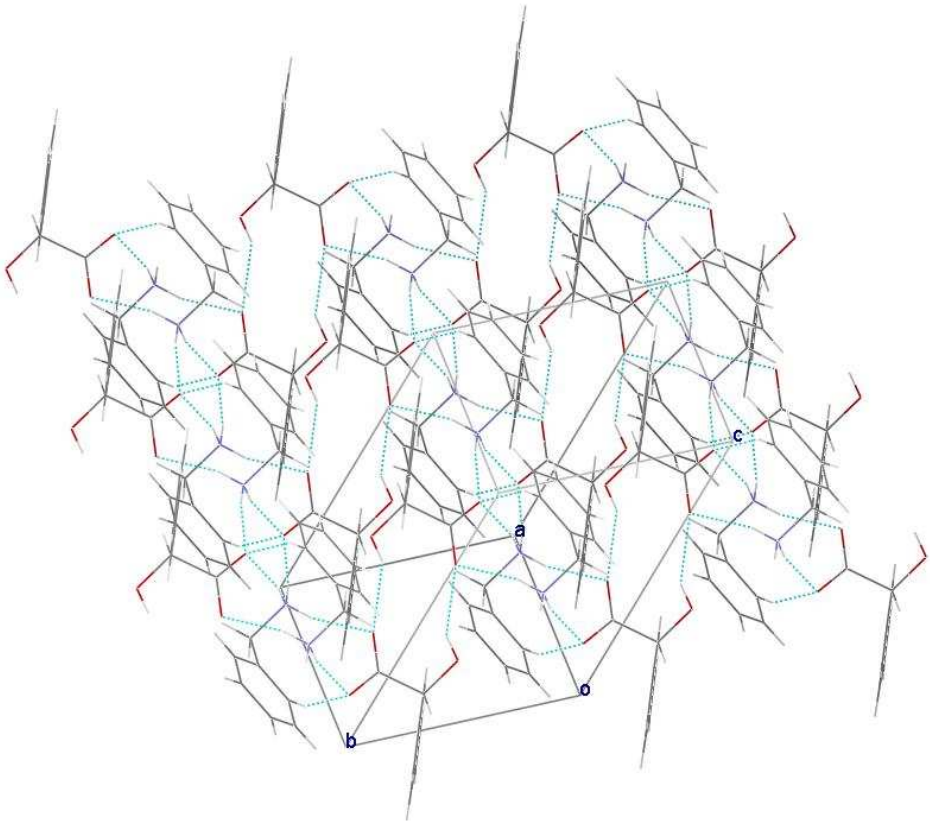


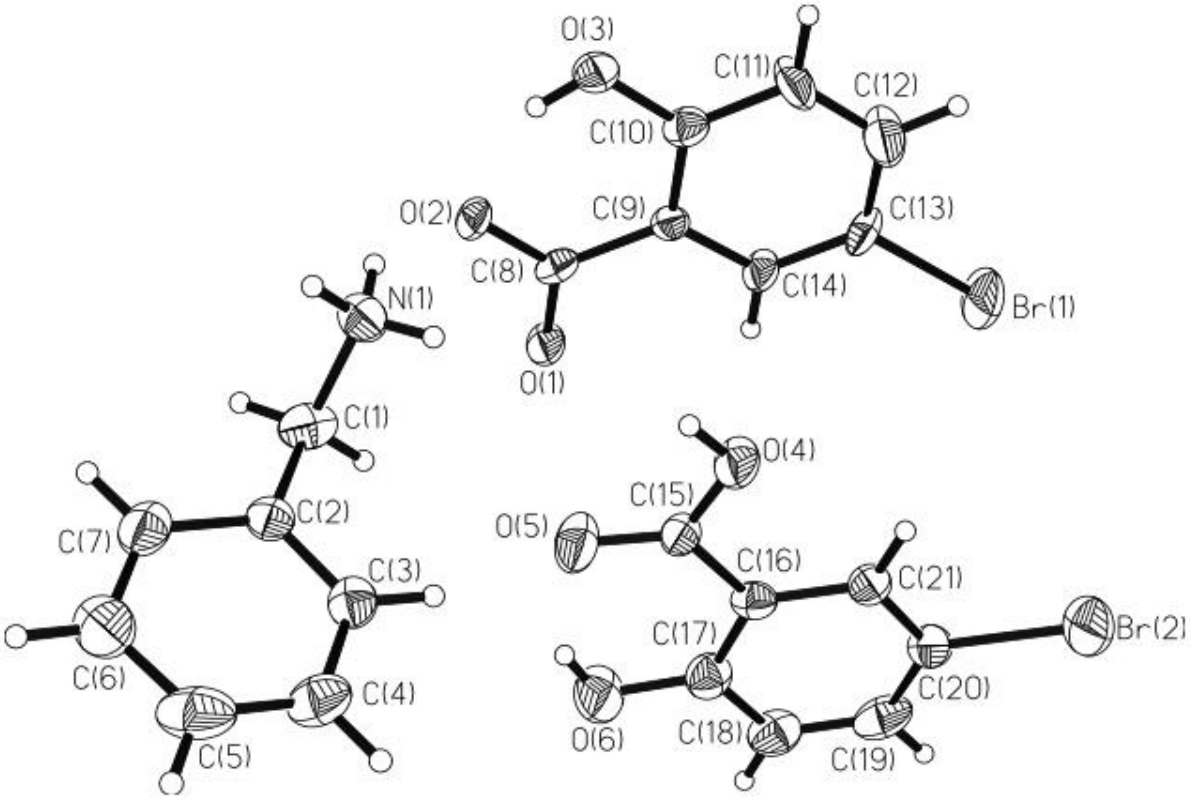








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C(9)
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O(1)
C(1)
O(4)
C(15)
C(2)
O(5)
C(7)
C(16)
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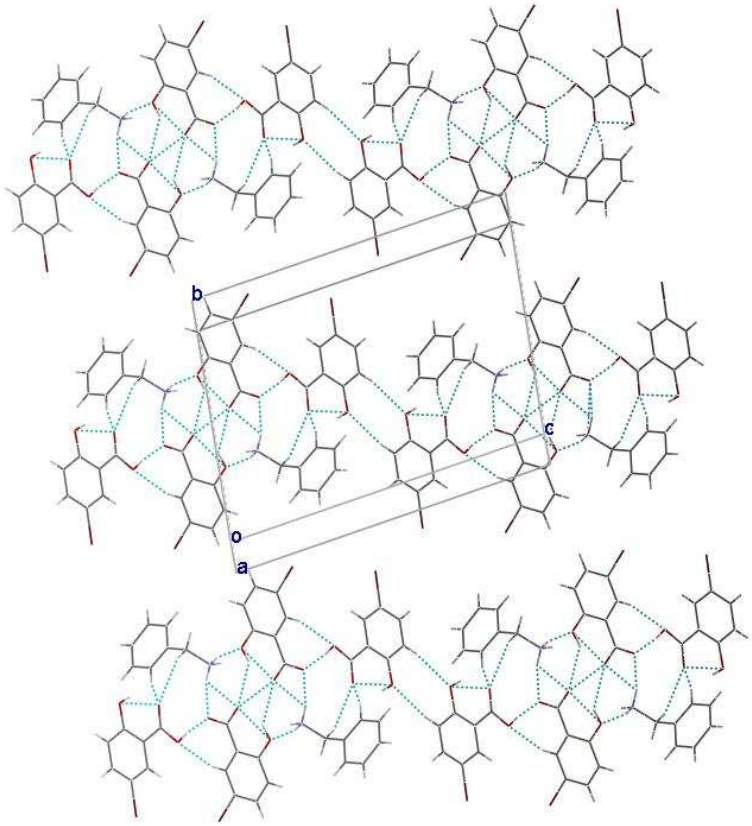

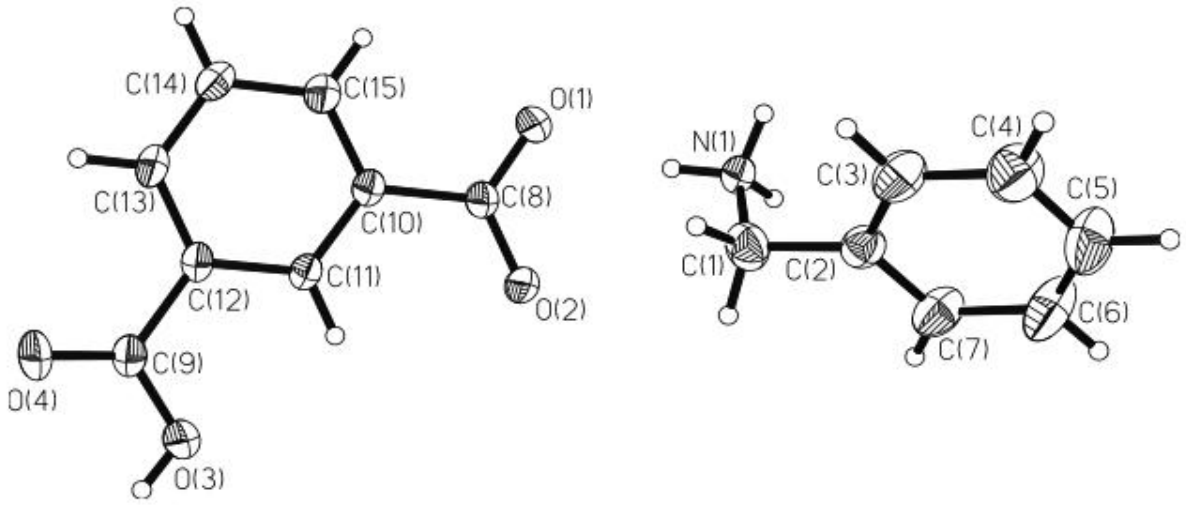

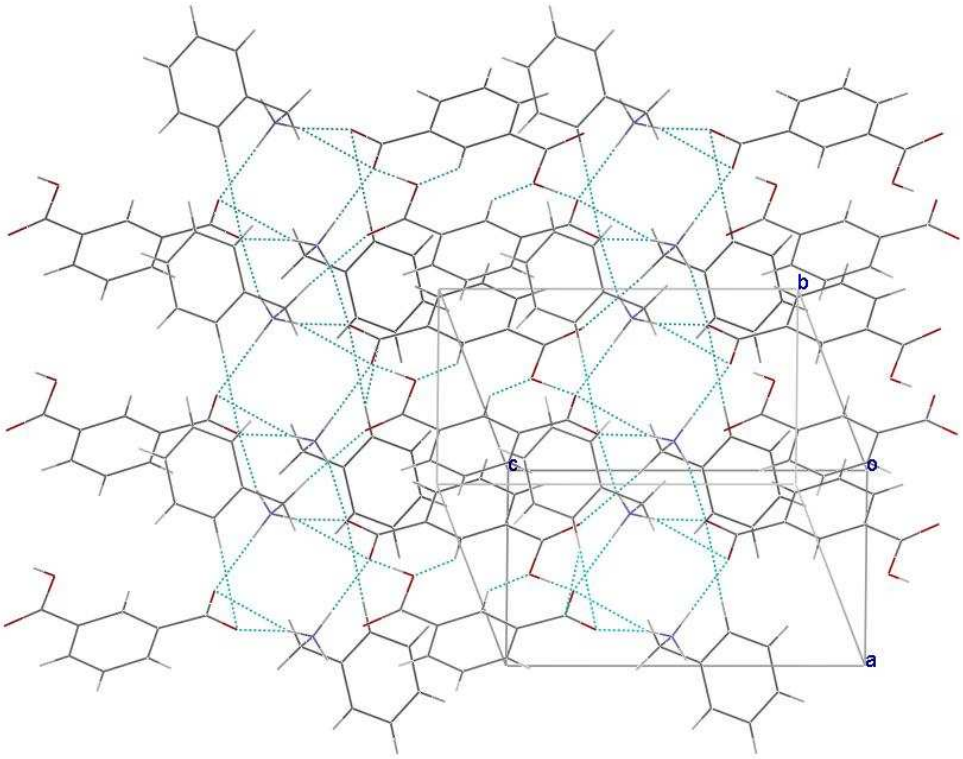

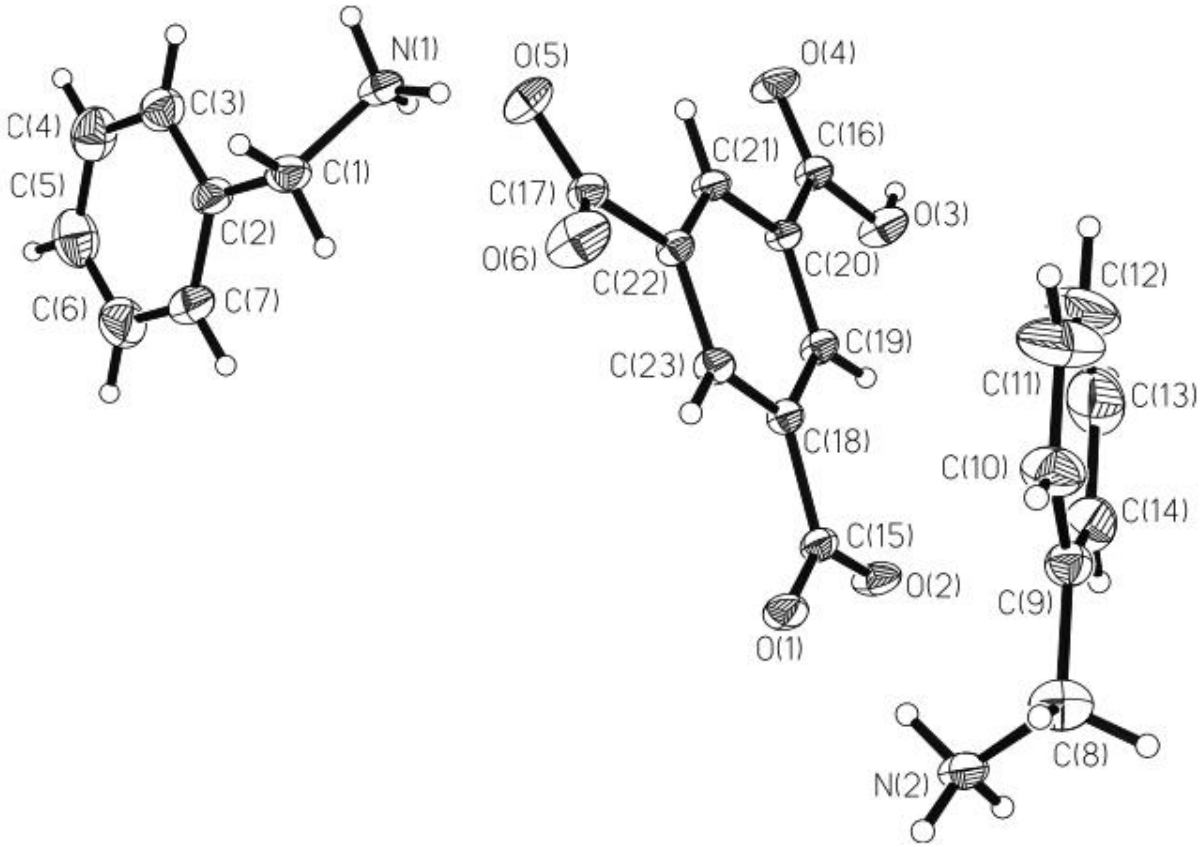
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C(4)
C(5)
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C(6)
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O(5)
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C(16)
C(17)
O(3)
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C(12)
C(19)
C(23)
C(11)
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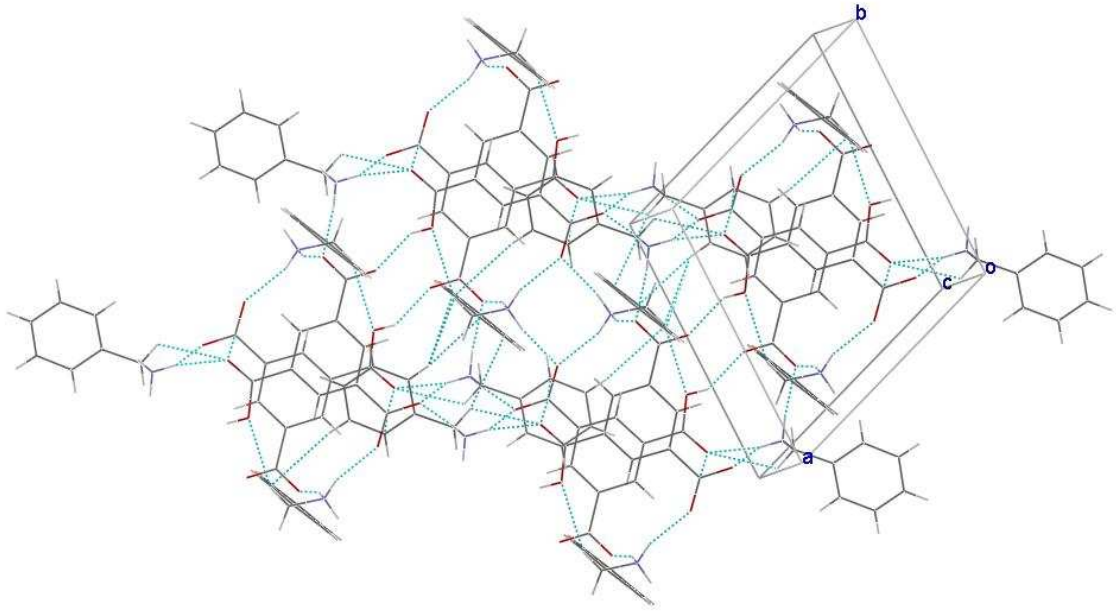
C(9)
O(1)
C(8)
N(2)



Highlights

Seven organic salts have been prepared and structurally characterized. The noncovalent interaction modes in the salts have been ascertained. The classical hydrogen bonds are the driving forces in producing the OH···benzylamine synthon. Other weak interactions also play important role in structure propagation.