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Five binary supramolecular organic salts constructed from 2-aminoheterocyclic compounds and carboxylic acid derivatives through strong and weak non-covalent interactions

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ABSTRACT

Studies concentrating on hydrogen bonding between the base of 2-aminoheterocyclic compounds 5,7-dimethyl-1,8-naphthyridine-2-amine, 4-phenylthiazol-2-amine, and carboxylic acid derivatives have led to an increased understanding of the role 2-aminoheterocyclic compounds have in binding with carboxylic acid derivatives. Here anhydrous and hydrous multicomponent adducts of 2-aminoheterocyclic compounds such as 5,7-dimethyl-1,8-naphthyridine-2-amine, and 4-phenylthiazol-2-amine have been prepared with 2-chloronicotinic acid, p-hydroxy benzoic acid, maleic acid, and phthalic acid. The five crystalline forms reported are organic salts of which the crystals and complexes were characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. All supramolecular architectures of salts **1**–**5** are stabilized by N—H···O hydrogen bonds as well as other non-covalent interactions. These weak interactions combined, all the complexes displayed 3D structure.

1. Introduction

The design and construction of multicomponent supermolecules or supramolecular arrays utilizing non-covalent bonding is a rapidly developing area in supramolecular synthesis. Thus, the supramolecular synthesis successfully exploits hydrogen bonding and other types of non-covalent interactions, in building supramolecular systems [1]. In this regard, there is great interest in co-crystals/organic salts in recent years [2–5].

Currently, H-bonding interactions have been widely developed in the area of crystal engineering, supramolecular chemistry, material science, and biological recognition [6–9]. The application of intermolecular hydrogen bonds is a well known and efficient tool in the field of organic crystal design because of its strength and directional properties [9]. Through hydrogen bonds cocrystals and organic salts can be generated. In pharmaceuticals, cocrystal/salt formation has also arouses great interest. This is primarily because cocrystals/salts have the potential to alter and optimize physical properties such as crystalline form, solubility, and stability of an active pharmaceutical ingredient (API) without detrimentally affecting its activity [10]. There are many interesting topological structures such as one-dimensional (1-D) tapes, two-dimensional (2-D) sheets, and three-dimensional (3-D) networks which have been constructed through hydrogen bonding interactions [11,12]. The carboxylic acid bears the important hydrogen bonding functional group COOH for crystal engineering [13]. Carboxylic acids aggregate in the solid state as dimer, catemer, and bridged motifs [14]. Besides the COOH group, the functional groups such as halogen and phenol OH groups are both good groups in forming organic solid through non-covalent interactions [15], thus we select some carboxylic acids bearing additional groups such as chloro and phenol OH. It is interesting to exploit the robust and directional recognition of carboxylic acids with nitrogen containing heterocyclic compounds [16].

Recently 2-aminoheterocyclic compounds have been reported to form supramolecular compounds with the carboxylic acid derivatives under the multiple hydrogen bonding action [17,18]. As the 2-aminoheterocyclic compounds 5,7-dimethyl-1,8-naphthyridine-2-amine, and 4-phenylthiazol-2-amine both may act as potentially tridentate ligands (NNN and NSN). The binary organic salts of the carboxylic acids and 2-aminoheterocyclic compounds may display the different hydrogen-bonding patterns from the three different donor atoms. As an extension of our study of weak interactions (hydrogen bonding, $\pi-\pi$ interaction, and halogen bonding) concerning aromatic N-containing derivatives [19], herein we report the preparation and structures of five organic salts assembled from

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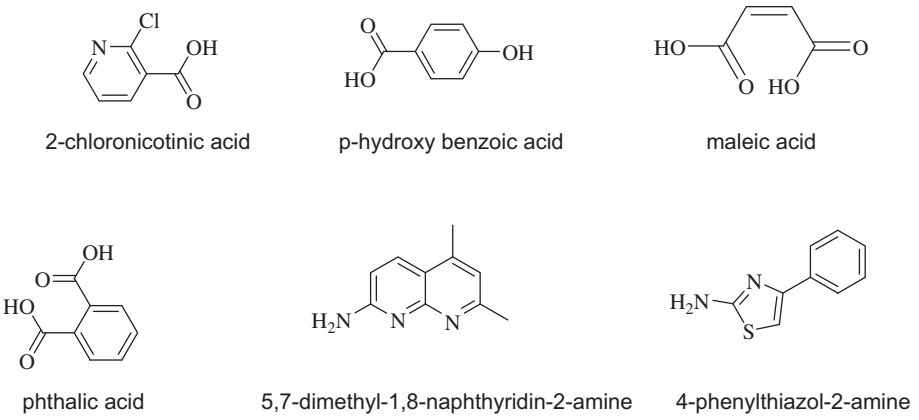
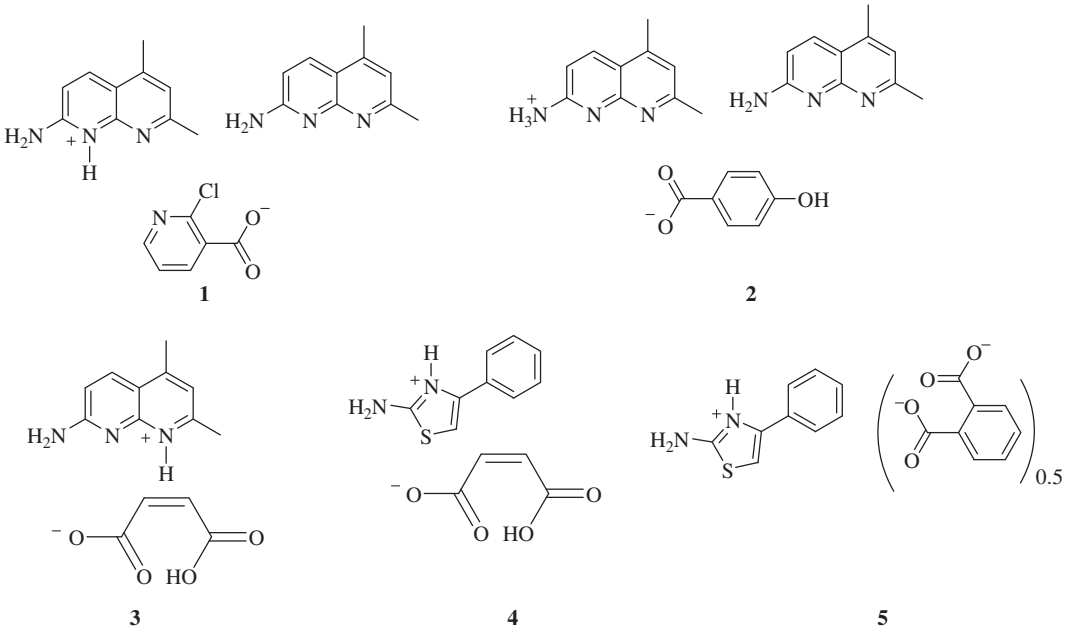


Scheme 1. Hydrogen bond synthons discussed in this paper.



Scheme 2. The five organic salts described in this paper, **1**–**5**.

5,7-dimethyl-1,8-naphthyridine-2-amine (L), 4-phenylthiazol-2-amine (L1) and the corresponding carboxylic compounds (Scheme 1), respectively. The five organic salts are (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: (2-chloronicotinic acid) (**1**) [$HL^+ \cdot L \cdot (cnic^-)$, cnic = 2-chloronicotinate], (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: (p-hydroxy benzoic acid): $2H_2O$ (**2**) [$HL^+ \cdot L \cdot (hbc^-) \cdot 2H_2O$, hbc = p-hydroxy benzoate], (5,7-dimethyl-1,8-naphthyridine-2-amine): (maleic acid) (**3**) [$HL^+ \cdot (Hmal^-)$, Hmal = hydrogen maleate], (4-phenylthiazol-2-amine): (maleic acid) (**4**) [$(HL1)^+ \cdot (Hmal^-)$], and (4-phenylthiazol-2-amine): (phthalic acid)$_{0.5}$ (**5**) [$(HL1)^+ \cdot (op^{2-})_{0.5}$, op^{2-} = phthalate] (Scheme 2).

2. Experimental

2.1. Materials and physical measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. 5,7-Dimethyl-1,8-naphthyridine-2-amine and 4-phenylthiazol-2-amine were prepared by the method described in the literature [20,21]. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N, S) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Melting points of new complexes were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of the organic salts ***1*–*5***

2.2.1. (5,7-Dimethyl-1,8-naphthyridine-2-amine)$_2$: (2-chloronicotinic acid) [$HL^+ \cdot L \cdot (cnic^-)$] (1)

To an ethanolic solution (8 ml) of 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was added 2-chloronicotinic acid (31.4 mg, 0.2 mmol). 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 ethanolic solution in air. The crystals were collected and dried in air to give the

title compound [$HL^+ \cdot L \cdot (cnic^-)$] (**1**). Yield: 39 mg, 77.38% (based on L). m.p. 189–191 °C. Anal. Calcd. for $C_{26}H_{26}ClN_7O_2$ (503.99): C, 61.91; H, 5.16; N, 19.44. Found: C, 61.87; H, 5.11; N, 19.38. Infrared spectrum (KBr disc, cm^{-1}): 3306s(ν_{as}(NH)), 3144s(ν_s(NH)), 3070s, 2980s, 2920s, 2380m, 2320m, 2080w, 1760w, 1668w, 1620m, 1580s($\nu_{as}(COO^-)$), 1540m, 1500m, 1487m, 1448m, 1400m, 1380s($\nu_s(COO^-)$), 1295m, 1240m, 1200m, 1160m, 1080m, 1000m, 930m, 850m, 744m, 700m, 646m, 606m, 540m, 480m, 440m.

2.2.2. (5,7-Dimethyl-1,8-naphthyridine-2-amine)$_2$: (p-hydroxy benzoic acid): 2H_2O [$HL^+ \cdot L \cdot (hbc^-) \cdot 2H_2O$] (2)

To a methanolic solution (5 ml) of 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was added p-hydroxy benzoic acid (27.6 mg, 0.2 mmol). The solution was stirred for three 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 methanolic solution in air. The crystals were dried in air to give the title compound [$HL^+ \cdot L \cdot (hbc^-) \cdot 2H_2O$]. Yield: 42 mg, 80.67% (Based on L). m.p. 206–208 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calcd. for $C_{27}H_{32}N_6O_5$(520.59): C, 62.24; H, 6.15; N, 16.14; Found: C, 62.18; H, 6.10; N, 16.06. Infrared spectrum (KBr disc, cm^{-1}): 3560s(ν(OH)), 3440s(multiple, ν_{as}(NH)), 3320s(ν_s(NH)), 3140m, 3060m, 2990m, 2920m, 2812m, 2720m, 2360m, 2190m, 1960w, 1840w, 1775w, 1730m, 1670w, 1628m, 1598s($\nu_{as}(COO^-)$), 1542m, 1488s, 1426s, 1382s($\nu_s(COO^-)$), 1358m, 1300m, 1240m, 1196m, 1130m, 1100m, 1060m, 1020m, 936m, 853m, 800m, 738m, 680m, 620m, 580m, 542m, 510m, 470m, 443m.

2.2.3. (5,7-Dimethyl-1,8-naphthyridine-2-amine): (maleic acid) [$(HL)^+ \cdot (Hmal^-)$] (3)

5,7-Dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was dissolved in 5 mL of ethanol. To this solution was added maleic acid (23.2 mg, 0.2 mmol) in 3 mL ethanol. Colorless prisms were afforded after 1 week of slow evaporation of the solvent. The crystals were collected and dried in air to give the title compound [$HL^+ \cdot (Hmal^-)$] (**3**), yield 45 mg, 77.78%. m.p. 197–198 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{14}H_{15}N_3O_4$(289.29) C, 58.07; H, 5.18; N, 14.52. Found: C, 58.02; H, 5.09; N, 14.46. Infrared spectrum (KBr disc, cm^{-1}): 3530s(ν(OH)), 3410s(multiple, ν_{as}(NH)), 3316s(ν_s(NH)), 3130m, 2988m, 2837m, 2722m, 2390w, 2196m, 1988w, 1773w, 1719s(ν(COOH)), 1658w, 1602s($\nu_{as}(COO^-)$), 1588m, 1536m, 1476m, 1436m, 1378s($\nu_s(COO^-)$), 1350s, 1310m, 1269m, 1172m, 1134m, 1072m, 1026m, 927m, 848m, 780m, 740m, 674m, 630mm, 567m, 452m.

2.2.4. (4-Phenylthiazol-2-amine): (maleic acid) [$(HL1)^+ \cdot (Hmal^-)$] (4)

4-Phenylthiazol-2-amine (35.2 mg, 0.2 mmol) was dissolved in 5 mL of ethanol. To this solution was added maleic acid (23.2 mg, 0.2 mmol) in 5 mL ethanol. Colorless prisms were afforded after several weeks of slow evaporation of the solvent. The crystals were dried in air to give the title compound [$(HL1)^+ \cdot (Hmal^-)$] (**4**), yield 42 mg, 71.84%. m.p. 212–214 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{13}H_{12}N_2O_4S$ (292.31): C, 53.37; H, 4.10; N, 9.58; S, 10.95. Found: C, 53.29; H, 4.01; N, 9.56; S, 10.88. Infrared spectrum (KBr disc, cm^{-1}): 3456s(multiple, ν_{as}(NH)), 3323s(ν_s(NH)), 3112m, 3064m, 2960m, 2842m, 2718m, 2468w, 2374m, 2213m, 1976w, 1836w, 1783w, 1713s(ν(COOH)), 1662w, 1606s($\nu_{as}(COO^-)$), 1596m, 1530m, 1486w, 1374s($\nu_s(COO^-)$), 1333m, 1250m, 1195m, 1131m, 1079m, 952m, 903m, 853m, 806m, 757m, 726m, 680m, 637m, 558m, 470m.

2.2.5. (4-Phenylthiazol-2-amine): (phthalic acid)$_{0.5}$ [$(HL1)^+ \cdot (op^{2-})_{0.5}$] (5)

4-Phenylthiazol-2-amine (35.2 mg, 0.2 mmol) was dissolved in 5 mL of ethanol. To this solution was added phthalic acid (34 mg, 0.2 mmol) in 5 mL ethanol. Colorless prisms were afforded after several weeks of slow evaporation of the solvent. The crystals were dried in air to give the title compound [$H(L1)^+ \cdot (op^{2-})_{0.5}$] (**5**), yield 42 mg, 80.98%. m.p. 240–241 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for

Table 1
Summary of X-ray crystallographic data for complexes **1**, **2**, **3**, **4**, and **5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{26}H_{26}ClN_7O_2$	$C_{27}H_{32}N_6O_5$	$C_{14}H_{15}N_3O_4$	$C_{13}H_{12}N_2O_4S$	$C_{13}H_{11}N_2O_2S$
Fw	503.99	520.59	289.29	292.31	259.30
T, K	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	P2(1)	P-1	C2/c	Pbca	P4(3)2(1)2
a, Å	7.4939(8)	8.597(2)	17.1529(16)	12.7241(14)	9.3377(11)
b, Å	22.9214(19)	12.554(3)	7.3086(8)	7.3388(6)	9.3377(11)
c, Å	7.7690(9)	12.762(3)	23.442(2)	29.109(2)	27.079(2)
α, °	90	96.008(2)	90	90	90
β, °	114.214(2)	107.332(2)	104.722(2)	90	90
γ, °	90	91.396(2)	90	90	90
V, Å^3	1217.1(2)	1305.4(5)	2842.3(5)	2718.2(4)	2361.1(4)
Z	2	2	8	8	8
D_{calcd}, Mg/m^3	1.375	1.324	1.352	1.429	1.459
Absorption coefficient, mm^{-1}	0.196	0.094	0.101	0.253	0.269
F(0 0 0)	528	552	1216	1216	1080
Crystal size, mm^3	0.18 × 0.16 × 0.10	0.42 × 0.39 × 0.17	0.42 × 0.39 × 0.20	0.42 × 0.39 × 0.38	0.49 × 0.45 × 0.29
θ range, °	1.78–25.01	1.68–25.01	2.46–25.01	2.13–25.02	2.31–25.01
Limiting indices	$-8 \le h \le 8$ $-27 \le k \le 17$ $-9 \le l \le 9$	$-9 \le h \le 10$ $-14 \le k \le 14$ $-15 \le l \le 9$	$-12 \le h \le 20$ $-8 \le k \le 8$ $-27 \le l \le 27$	$-15 \le h \le 14$ $-4 \le k \le 8$ $-34 \le l \le 34$	$-11 \le h \le 11$ $-7 \le k \le 11$ $-32 \le l \le 21$
Reflections collected	6459	6424	7063	10,403	10,117
Reflections independent (R_{int})	3071 (0.0794)	4353 (0.2638)	2502 (0.0583)	2398 (0.0477)	2079 (0.0377)
Goodness-of-fit on F^2	0.946	0.815	1.032	1.026	1.058
R indices [$I > 2\sigma I$]	0.0583, 0.1474	0.0948, 0.1631	0.0552, 0.1356	0.0403, 0.0895	0.0344, 0.0772
R indices (all data)	0.1095, 0.1756	0.2543, 0.2266	0.1279, 0.1769	0.0808, 0.1137	0.0480, 0.0859
Largest diff. peak and hole, e Å^{-3}	0.172, −0.198	0.282, −0.294	0.223, −0.194	0.183, −0.204	0.166, −0.198

$C_{13}H_{11}N_2O_2S$(259.30): C, 60.16; H, 4.24; N, 10.79; S, 12.34. Found: C, 60.06; H, 4.12; N, 10.71; S, 12.32. Infrared spectrum (KBr disc, cm^{-1}): 3454s(multiple, ν_{as}(NH)), 3332s(ν_s(NH)), 3140m, 3032m, 2979m, 2926m, 2842m, 2724m, 2580w, 2356m, 2179m, 1998w, 1812w, 1769w, 1721m, 1676w, 1638m, 1586m, 1551s(ν_{as}(COO^-)), 1470m, 1426m, 1368s(ν_s(COO^-)), 1304m, 1232m, 1196m, 1126m, 1073m, 1020m, 930m, 888m, 802m, 716m, 656m, 614m, 574m, 510m, 464m.

2.3. X-ray crystallography and data collection

Suitable crystals were mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo Kα radiation (0.71073 Å). Data collection and reduction were performed using the SMART and SAINT software [22]. 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 [23].

Hydrogen atom positions for all of the structures were located in a difference map and refined independently. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for the salts **1**, **2**, **3**, **4**, and **5** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **3**, **4**, and **5**.

1			
Cl(1)—C(2)	1.725(4)	N(1)—C(2)	1.330(5)
N(1)—C(6)	1.334(6)	N(2)—C(7)	1.314(16)
N(2)—C(11)	1.387(14)	N(3)—C(12)	1.322(16)
N(3)—C(11)	1.352(16)	N(4)—C(7)	1.271(16)
N(5)—C(21)	1.357(14)	N(5)—C(17)	1.371(16)
N(6)—C(21)	1.337(15)	N(6)—C(22)	1.348(15)
N(7)—C(17)	1.353(17)	O(1)—C(1)	1.176(16)
O(2)—C(1)	1.293(18)	O(2′)—C(1)	1.199(17)
C(2)—N(1)—C(6)	116.0(4)	C(7)—N(2)—C(11)	121.1(10)
C(12)—N(3)—C(11)	114.4(10)	C(21)—N(5)—C(17)	120.0(10)
C(21)—N(6)—C(22)	120.4(10)	O(1)—C(1)—O(2′)	113.9(11)
O(1)—C(1)—O(2)	125.1(5)	O(2′)—C(1)—O(2)	50.3(10)
2			
N(1)—C(8)	1.334(7)	N(1)—C(15)	1.341(7)
N(2)—C(9)	1.330(7)	N(2)—C(8)	1.411(7)
N(3)—C(9)	1.327(7)	N(4)—C(25)	1.332(7)
N(4)—C(18)	1.372(7)	N(5)—C(19)	1.330(7)
N(5)—C(18)	1.361(7)	N(6)—C(19)	1.340(7)
O(1)—C(1)	1.255(7)	O(2)—C(1)	1.275(8)
O(3)—C(5)	1.356(6)	C(1)—C(2)	1.493(8)
C(2)—C(7)	1.379(8)	C(2)—C(3)	1.393(8)
C(3)—C(4)	1.382(7)	C(4)—C(5)	1.381(8)
C(8)—N(1)—C(15)	117.8(5)	C(9)—N(2)—C(8)	121.1(5)
C(25)—N(4)—C(18)	118.5(5)	C(19)—N(5)—C(18)	117.3(5)
O(1)—C(1)—O(2)	122.6(6)	O(1)—C(1)—C(2)	119.6(7)
O(2)—C(1)—C(2)	117.8(6)	C(7)—C(2)—C(3)	116.8(6)
C(7)—C(2)—C(1)	123.4(6)	C(3)—C(2)—C(1)	119.8(6)
C(4)—C(3)—C(2)	121.3(6)	O(3)—C(5)—C(4)	118.4(7)
O(3)—C(5)—C(6)	122.7(6)	C(4)—C(5)—C(6)	118.9(6)
N(1)—C(8)—N(2)	114.6(5)	N(3)—C(9)—N(2)	119.1(5)
N(5)—C(18)—N(4)	114.0(5)	N(5)—C(19)—N(6)	118.5(5)
3			
N(1)—C(5)	1.333(4)	N(1)—C(9)	1.339(4)
N(2)—C(10)	1.341(4)	N(2)—C(9)	1.369(4)
N(3)—C(5)	1.320(4)	O(1)—C(1)	1.268(4)
O(2)—C(1)	1.241(4)	O(3)—C(4)	1.281(5)
O(4)—C(4)	1.206(4)	C(5)—N(1)—C(9)	117.1(3)
C(10)—N(2)—C(9)	123.5(3)	O(2)—C(1)—O(1)	123.4(3)
O(4)—C(4)—O(3)	121.4(4)	N(3)—C(5)—N(1)	118.7(3)
N(1)—C(9)—N(2)	115.8(3)		
4			
N(1)—C(1)	1.333(3)	N(1)—C(2)	1.389(3)
N(2)—C(1)	1.310(3)	O(1)—C(10)	1.214(3)
O(2)—C(10)	1.295(3)	O(3)—C(13)	1.273(3)
O(4)—C(13)	1.238(3)	S(1)—C(1)	1.719(3)
S(1)—C(3)	1.720(3)	C(1)—N(1)—C(2)	114.8(2)
C(1)—S(1)—C(3)	89.68(14)	N(2)—C(1)—N(1)	123.7(3)
N(2)—C(1)—S(1)	125.0(2)	N(1)—C(1)—S(1)	111.2(2)
O(1)—C(10)—O(2)	120.1(3)	O(4)—C(13)—O(3)	123.7(3)
5			
N(1)—C(1)	1.329(3)	N(1)—C(2)	1.395(3)
O(1)—C(10)	1.252(3)	O(2)—C(10)	1.256(3)
S(1)—C(1)	1.723(3)	S(1)—C(3)	1.724(3)
N(2)—C(1)	1.313(3)	C(1)—N(1)—C(2)	114.6(2)
C(1)—S(1)—C(3)	89.82(12)	N(2)—C(1)—N(1)	124.6(2)
N(2)—C(1)—S(1)	123.97(19)	N(1)—C(1)—S(1)	111.46(19)

3. Results and discussion

3.1. Preparation and general characterization

5,7-Dimethyl-1,8-naphthyridine-2-amine and 4-phenylthiazol-2-amine both have good solubility in common organic solvents, such as CH_3COCH_3, CH_3OH, C_2H_5OH, CH_2Cl_2, $CHCl_3$, and CH_3CN. The crystals were grown by slow evaporation of the corresponding polar hydroalcoholic solution at room temperature.

The preparation of compounds **1**–**5** were carried out with 2-aminoheterocyclic compounds and the corresponding carboxylic acid derivatives in 1:1 ratio. In all of the structures the base molecules are protonated therefore the structures can be classified as salts. The five salts are not hygroscopic, and they all crystallized with no solvent molecules accompanied except salt **2**. The molec-

Table 3
Hydrogen bond distances and angles in studied structures of **1**, **2**, **3**, **4**, and **5**.

D—H···A	d(D—H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
1				
N(7)—H(7B)···O(1)#1	0.86	1.89	2.722(16)	164.0
N(7)—H(7A)···N(3)	0.86	1.98	2.838(13)	172.4
N(4)—H(4B)···O(2)#2	0.86	2.03	2.878(17)	167.9
N(4)—H(4B)···O(2′)#2	0.86	1.93	2.757(19)	159.9
N(4)—H(4A)···N(6)	0.86	2.06	2.915(14)	174.2
N(2)—H(2)···N(5)	0.86	2.11	2.971(5)	176.6
2				
O(5)—H(31)···O(1)#1	0.85	1.97	2.813(6)	168.7
O(5)—H(30)···O(1)#2	0.85	1.82	2.671(6)	176.1
O(4)—H(29)···O(5)#3	0.85	1.91	2.728(6)	162.0
O(4)—H(28)···O(2)#4	0.85	1.90	2.712(6)	159.6
O(3)—H(3)···O(4)	0.82	1.83	2.645(6)	170.1
N(6)—H(6C)···O(5)#5	0.89	2.41	2.894(7)	114.8
N(6)—H(6A)···N(1)#6	0.89	2.10	2.961(6)	164.0
N(3)—H(3B)···O(2)#7	0.86	1.95	2.799(7)	170.1
N(3)—H(3A)···N(4)#8	0.86	2.02	2.868(6)	168.1
3				
O(3)—H(3)···O(1)	0.82	1.62	2.437(3)	177.8
N(3)—H(3B)···O(1)	0.86	2.01	2.859(4)	168.3
N(3)—H(3A)···O(4)#1	0.86	2.15	2.936(4)	152.6
N(2)—H(2)···O(2)#2	0.86	1.92	2.766(3)	168.5
4				
O(2)—H(2)···O(3)	0.82	1.61	2.429(3)	179.0
N(2)—H(2B)···O(1)#1	0.86	2.40	3.181(3)	151.8
N(2)—H(2B)···O(2)#1	0.86	2.17	2.956(3)	151.2
N(2)—H(2A)···O(3)#2	0.86	1.96	2.815(3)	174.1
N(1)—H(1)···O(4)#2	0.86	1.89	2.742(3)	172.9
5				
N(2)—H(2B)···O(2)#2	0.86	2.01	2.810(3)	154.8
N(2)—H(2A)···O(2)#1	0.86	2.07	2.828(3)	147.1
N(1)—H(1)···O(1)#1	0.86	1.81	2.654(2)	167.6

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1$, $y+1/2$, $-z$; #2 x, y, $z+1$. Symmetry transformations used to generate equivalent atoms for **2**: #1 $-x+1$, $-y+1$, $-z+1$; #2 x, $y-1$, $z+1$; #3 x, y, $z-1$; #4 $-x$, $-y+1$, $-z$; #5 $x+1$, y, z; #6 $x+1$, $y-1$, z; #7 $-x$, $-y+2$, $-z$; #8 $x-1$, $y+1$, z. Symmetry transformations used to generate equivalent atoms for **3**: #1 $-x+1$, y, $-z+3/2$; #2 $x+1/2$, $y-1/2$, z. Symmetry transformations used to generate equivalent atoms for **4**: #1 $x-1/2$, $-y+3/2$, $-z+1$; #2 $x-1$, $y+1$, z. Symmetry transformations used to generate equivalent atoms for **5**: #1 y, x, $-z+2$; #2 $y-1/2$, $-x+3/2$, $z+1/4$.

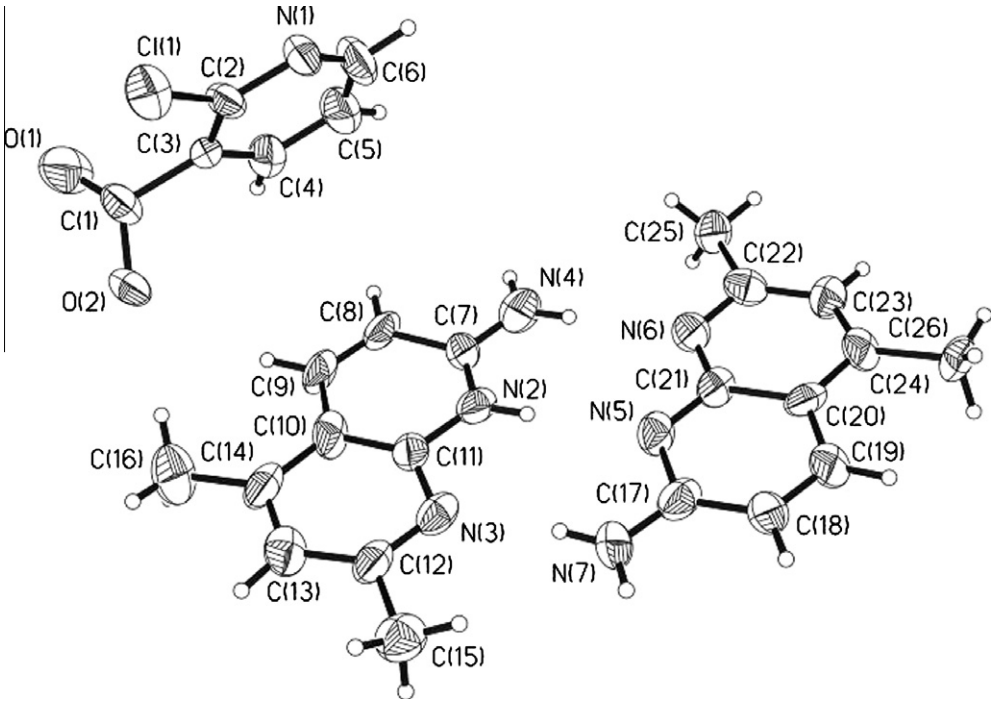


Fig. 1. Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

ular structures and their atom labelling schemes for the five structures are illustrated in Figs. 1, 3, 5, 7 and 9, respectively. In the preparation of the organic salts **1**, **2**, **3**, **4**, and **5** the carboxylic acids were mixed directly with the base in the corresponding solution, which was allowed to evaporate at ambient conditions to give the final crystalline products. The elemental analysis data for the five compounds are in good agreement with their compositions. The infrared spectra of the five compounds are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. H atoms connected to O or N atoms were well found from the difference electron density map, which also indirectly confirms the proton transfer.

In **1** and **2**, the protons of each monoacids have transferred to the 5,7-dimethyl-1,8-naphthyridine-2-amine molecules. In **3** and **4**, one proton of the maleic acid has transferred to the base, while another carboxylic acid group remains protonized, thus **3** and **4** form 1:1 salts. In **5**, both protons of the phthalic acid have transferred to two 4-phenylthiazol-2-amine molecules to form 1:2 adduct, thus the acid in **5** presents a valence number of −2.

The very strong and broad features at approximately 3600–3100 cm^{-1} in the IR spectra of the five compounds arise from O—H or N—H stretching frequencies. Aromatic, naphthyridic, and phenylthiazolic ring stretching and bending are attributed to the medium intensity bands in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively. All of the five salts show the characteristic bands for COO^{-}, and compounds **3**, and **4** display strong IR peaks for COOH groups. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [24]. The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical

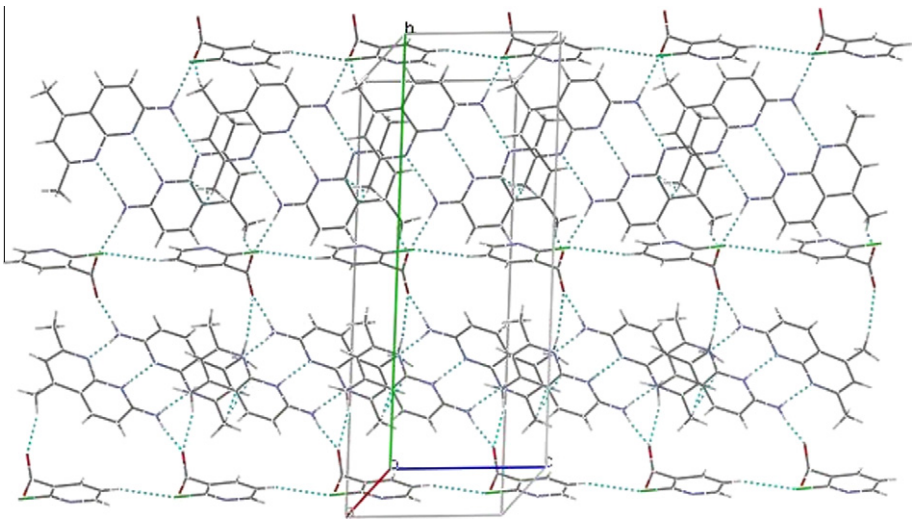


Fig. 2. 2D sheet structure of **1** which is viewed along the *a* axis.

carboxylate stretching frequencies at 1550–1610 cm^{-1} and 1300–1420 cm^{-1} in compounds **1**, **2**, **3**, **4**, and **5**, respectively [25].

4. Structural descriptions

4.1. X-ray structure of (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: (2-chloronicotinic acid) [$HL^+ \cdot L \cdot (cnic^-)$] (1)

The compound **1** of the composition [$HL^+ \cdot L \cdot (cnic)^-$] was prepared by reaction equal mol of 5,7-dimethyl-1,8-naphthyridine-2-amine and 2-chloronicotinic acid, in which the proton of 2-chloronicotinic acid was transferred to the N atom adjacent to the NH_2 group on the naphthyridine ring. This structure is not a solvate. In the asymmetric unit of **1** there existed one molecule of 5,7-dimethyl-1,8-naphthyridine-2-amine, one cation of 5,7-dimethyl-1,8-naphthyridinium-2-amine, and an anion of 2-chloronicotinate, as shown in Fig. 1. The oxygen atom O(2) was disordered over two positions both with occupancies of 0.5.

The C—O distances of COO^- of the 2-chloronicotinate are ranging from 1.176(16) to 1.293(18) Å. The significant difference (Δ is 0.117 Å) in bond distances between O(1)—C(1) (1.176(16) Å) and O(2)—C(1) (1.293(18) Å) in the carboxylate group in compound **1** is caused by the fact that O(2) is involved in forming more strong hydrogen bonds than that of O(1).

The N—H···O hydrogen bond is formed between the oxygen atom of the carboxylate and the amine group (N(7)—H(7B)···O(1)#1, 2.722(16) Å; N(4)—H(4B)···O(2)#2, 2.878(17) Å; N(4)—H(4B)···O(2′)#2, 2.757(19) Å), there does not exist ionic N^+—H···O^- hydrogen bonds.

Two naphthyridines formed dimers through intermolecular hydrogen bonding (N—H···N) interaction of the type DDA–AAD (D represents the donor group NH, and A represents the acceptor group N respectively) between HL^+ and L. Two naphthyridinium dimers and two 2-chloronicotinate anions self-assembled via N—H···O hydrogen bonds to form bis-2-chloronicotinate terminated moiety, in which the two terminal 2-chloronicotinates exist in trans conformation. When viewed along the *a* axis, the corresponding 2-chloronicotinate ions in the adjacent bis-2-chloronicotinate terminated moieties are parallel to each other. Adjacent naphthyridine dimers are extended along the *c* axis direction through CH_3–π interaction in which the C—C_g distance is ca. 3.409 Å to exhibit 1D ladder structure.

As expected, the naphthyridine rings are planar (the r.m.s deviations of the naphthyridine ring atoms from the mean plane of the ring are 0.0176 and 0.0153 Å within the HL^+ cation and L molecule respectively). And the dihedral angle between the two naphthyridine rings in the same dimer is 0.9°, indicating that they are roughly coplanar. The r.m.s deviation of the pyridine ring atoms of the anion in **1** from the mean plane of the ring is 0.0103 Å. While the dihedral angles between the anion and the pair of naphthyridine rings of the naphthyridine dimer are both 112.6°.

The anions formed 1D chain structure along the *c* axis direction through C—H···Cl hydrogen bonds with the C—Cl distance of 3.654 Å which is in the upper limit of the reported C—H···Cl bonds [26]. The cationic naphthyridine dimers were suspended between the two chains through N—H···O (between the amine group of the naphthyridine dimer and the O atom of 2-chloronicotinate chains with N—O distance in the range of 2.722–2.877 Å) and CH_3—O (between 5-CH_3 of the naphthyridine dimer and the carboxylate O with the C—O distance of 3.387, and 3.150 Å) hydrogen bonds to form one-dimensional grid structure. The grids extended in the bc plane to form 2D sheet which is shown in Fig. 2. And the 2D sheets were further stacked along the *a* axis direction through CH_3–π interaction to form 3D layer network structure.

4.2. X-ray structure of (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: (p-hydroxy benzoic acid): 2H_2O [$HL^+ \cdot L \cdot (hbc^-) \cdot 2H_2O$] (2)

The compound **2** was also prepared by reaction of 5,7-dimethyl-1,8-naphthyridine-2-amine with p-hydroxybenzoic acid in 1:1 ratio, which crystallizes as triclinic block crystals in the centrosymmetric space group P-1.

The compound consists of one 5,7-dimethyl-1,8-naphthyridine-2-amine molecule, one 5,7-dimethyl-1,8-naphthyridinium-2-amine cation, one p-hydroxybenzoate anion, and two water molecules (Fig. 3). The compound is also an organic salt. The present investigation clearly shows that the positive charge (coming from the carboxylate H of p-hydroxybenzoic acid) in the title compound is on the amino group not on the ring nitrogen atom, forming an ion pair, which is different from that of the compound 2-aminopyridinium salicylate [27] and also different from compound **1**. As shown in Table 2, all the bond angles and bond distances are in the normal range. The O—C bond distances of the carboxylate group are 1.255(7), and 1.275(8) Å respectively. The difference between the two C—O bonds is 0.020 Å which is in the range of the

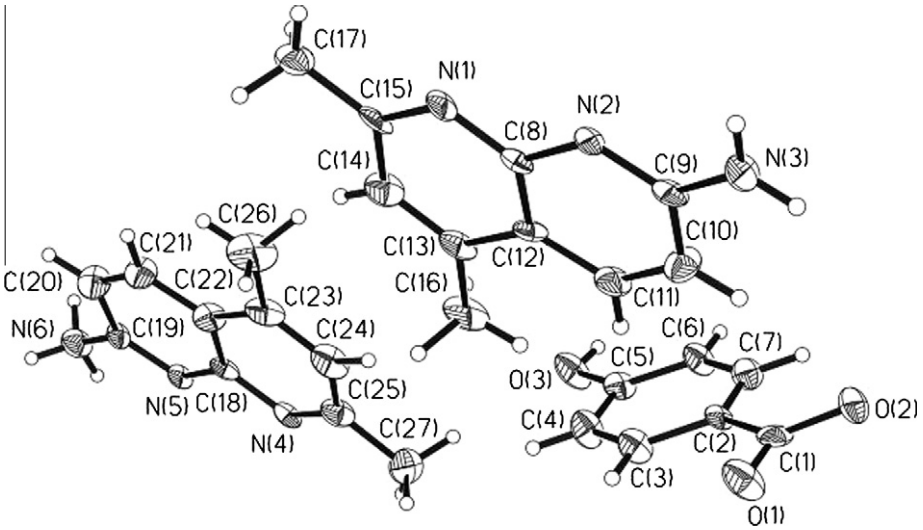


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. The water molecules were omitted.

reported Δ value for organic salts formed between the carboxylic acid and the N-containing base [28], which is also expected for ionic C—O bond distances.

The C19—N5 bond length is 1.330(7) Å, and is approximately equal to a C=N double-bond length [29], indicating that atom N6 of the amino group must also be sp^3 hybridized. This is also supported by the angles around C(19), (N(5)—C(19)—C(20), 123.5(6)°), and also verified by the bond angles concerning N(6) i.e. C(19)—N(6)—H(6A), C(19)—N(6)—H(6B), H(6A)—N(6)—H(6B), C(19)—N(6)—H(6C), H(6A)—N(6)—H(6C), and H(6B)—N(6)—H(6C) are all 109.5°.

The r.m.s deviation of the protonated naphthyridine ring atoms from the mean plane of the ring is 0.0162 Å, the r.m.s deviation of the neutral naphthyridine ring atoms from the mean plane of the ring is 0.0169 Å. The dihedral angle between these two naphthyridine rings is 3.6° indicating the coplanarity of both rings. The anions are also planar with a r.m.s deviation of 0.017 Å. The anions form dihedral angles of 104°, and 102° with the protonated L cation and neutral L molecule respectively.

In the compound, there is consistently a hydrogen bond (N(3)—H(3B)···O(2)#7, 2.799(7) Å, 170.1°) formed between the amine group NH_2 and the CO_2^- anions, which is to be expected [30].

The two water molecules formed water dimers through O—H···O (O(4)—H(29)···O(5)#3, 2.728(6) Å) hydrogen bonds. The water dimers connect the p-hydroxybenzoate anions in head to tail fashion along the *b* axis direction to form a 1D chain structure. Two adjacent chains were connected by two O—H···O hydrogen bonds between the water molecules in one chain and the carboxylate group in another chain to form 1D ladder structure. Adjacent ladders were further connected through O—H···O hydrogen bonds (between the water molecules and the carboxylate group) along the *a* axis direction to form 2D corrugated sheet structure. Two naphthyridines formed dimers through two N—H···N hydrogen bonds of the type DA-AD between HL^+ and L, adjacent dimers were connected by N—H···π interactions between the NH_3^+ cations and the naphthyridine rings to form naphthyridine tetramers. The tetramers were further connected by CH_3–π interaction (between the 7-CH_3 of the naphthyridine of one tetramer and the naphthyridine ring of the adjacent tetramer with the C—C_g distance of 3.839 Å) to form one-dimensional cationic chain extending along the *b* axis direction. Such chains were sandwiched between two anionic sheets through N—H···O hydrogen bonds between the NH_3^+ cation and the O atom of carboxylate and the water molecules with N—O distance in the range of 2.799–2.893 Å. There are also CH_3–π (between the 5-CH_3 of the naphthyridine and the anion ring with C—C_g distance of ca. 3.583 Å) and CH_3—O interaction (between the phenol OH of the anions and the 7-CH_3 of the naphthyridine with C—O distance of 3.329 Å) between the cation chain and the anion sheet. The anionic sheet and the cationic chains were stacked alternatively along the *c* axis direction to form 3D ABAB layer structure, as shown in Fig. 4.

4.3. X-ray structure of (5,7-dimethyl-1,8-naphthyridine-2-amine): (maleic acid) [$HL^+ \cdot (Hmal^-)$] (3)

The asymmetric unit of **3** consists of one cation of 5,7-dimethyl-1,8-naphthyridin-1-ium-2-amine, and an anion of hydrogen maleate, as shown in Fig. 5. In this case the less basic nitrogen atom close to the methyl group is protonated which is similar to the published result [31], but it is different from the compounds **1** and **2**. There exist two N—H···O hydrogen bonds between the oxygen atom of the carboxylate and the amine group (N(3)···O(1), 2.859(4) Å, and N(3)···O(4)#1, 2.936(4) Å), there also exists one strong ionic N^+—H···O^- hydrogen bond of N(2)—H(2)···O(2)#2 with the N(2)···O(2)#2 distance of 2.766(3) Å. Unlike **1**, and **2**, there does not exist N—H···N hydrogen bond so in **3** there are no naphthyridine dimers. The singly deprotonated maleic acid has intramolecular hydrogen bonded structure through strong hydrogen bond $S_1^1(7)$ O(3)—H(3)···O(1) interaction, which is similar to the monoanion of maleic acid in forming intramolecular hydrogen bonds [32].

The maleates were bonded to the naphthyridine core through hydrogen bonds of N—H···O (between the amine protons of the NH_2 group and the carboxylate O atom with N—O distance of 2.859 Å) and C—H···O (between 3-CH of the naphthyridine ring and the carboxylate O atom with C—O distance of 3.583 Å) to exhibit a $R_2^2(8)$ ring motif which agrees well with the published results of Bernstein [33].

In the COOH group, two C—O bond lengths are obviously different between O(3)—C(4) (1.281(5) Å) and O(4)—C(4) (1.206(4) Å) with the Δ value of 0.075 Å. The relatively larger Δ value which is expected for neutral C—O and C=O bond distances [34] are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms as mentioned above. But for the COO^- group, two C—O bond lengths (The C—O distances of COO^- of the hydrogen maleate are ranging from 1.241(4) to 1.268(4) Å) are basically not equal with an average value of 1.254 Å, which is shorter than that of the single bond of O(3)—C(4) (1.281(5) Å) but longer than that of the double bond

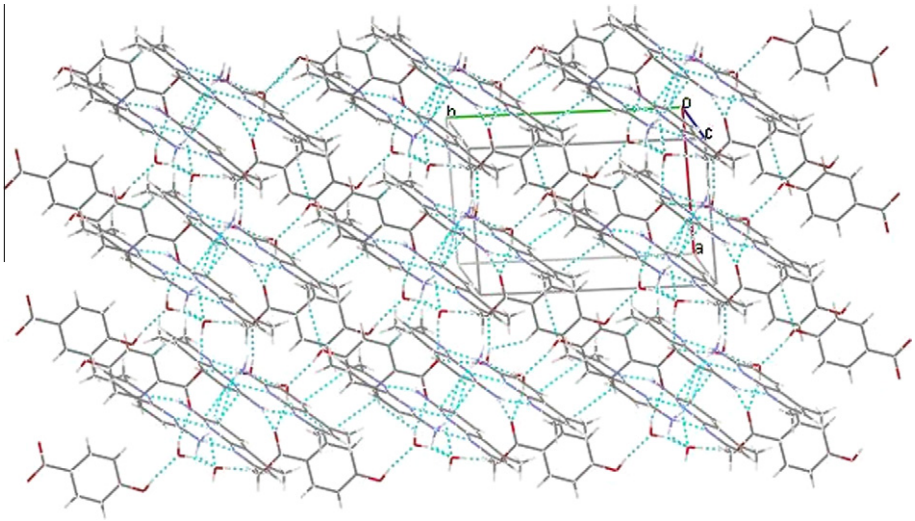


Fig. 4. 3D ABAB layer structure of **2** viewed along the *c* axis direction.

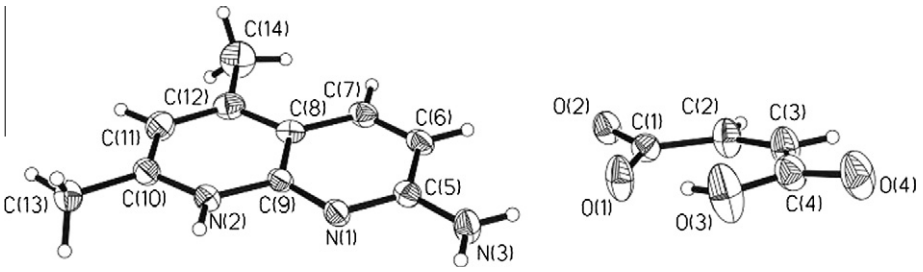


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

of O(4)—C(4) (1.206(4) Å) in the carboxylic group of hydrogen maleate. This also supports our correct assignment of the hydrogen maleate anion. It is clear that the difference in bond lengths of C—O within the carboxylic acid group (0.075 Å) is larger than the one found in the hydrogen maleate anion (0.027 Å), which also confirms the deprotonation of one carboxylic H.

The carboxylate and the naphthyridine units connect alternatively through N—H···O and C—H···N (between the olefinic CH of the maleate and the ring N atom with C—N distance of 3.525 Å) interactions along the direction that slipped by ca. 30° from the bc plane to form one-dimensional chain structure. There are also one-dimensional chain formed by the carboxylate and the naphthyridine which extended along the direction that forms angle of ca. 30° with the ac plane. Such crossed chains were connected by N—H···O and C—H···O bonds to form 3D network structure which is shown in Fig. 6. There are also π–π and CH_3–π interactions between adjacent parallel chains with the centroid separation and C—C_g distance of 3.385 Å, and 3.564 Å respectively. Obviously, the three-dimensional structure is stabilized by these weak interactions.

4.4. X-ray structure of (4-phenylthiazol-2-amine): (maleic acid) [$(HL1)^+ \cdot (Hmal^-)$] (4)

Similar to compound **3**, in **4** the asymmetric unit is occupied by one monoanion of maleic acid and one cation of 4-phenylthiazol-1-ium-2-amine $(HL1)^+$ (Fig. 7). Here only one proton of the maleic acid has transferred to the N atom of the thiazole ring. The same as that in the compound **3**, the monoanion of maleic acid also forms intramolecular hydrogen bonded structure through strong hydrogen bond $S_1^1(7)$ O(3)—H(3)···O(2) interaction, which agrees well with the reported results [32].

The C—O distances of COO^- of the hydrogen maleate are ranging from 1.238(3) to 1.273(3) Å (Δ is 0.035 Å). The angle C3—S1—C1 (89.68(14)°) is larger than the corresponding angle in the neutral molecule (88.7 (2)°) [35], yet it is smaller than that in compound 2-amino-4-phenylthiazole hydrobromide monohydrate (90.17°) [36]. This may be due to the difference of the hydrogen bonding strength in the corresponding compound. The dihedral angle between the planes of the phenyl and thiazole rings in the same cation of **4** is 18.4 (3)°, which is also smaller than the value (19.23°) in 2-amino-4-phenylthiazole hydrobromine monohydrate. But compound **4** is less planar than the neutral L1 in which the dihedral angle between the phenyl ring and the thiazole ring is (6.2(3)°). The planarity of **4** is further verified by the shorter C(2)—C(4) bond distance [1.476(4) Å] in **4** compared with the value of 1.506 Å found in 2-amino-4-phenylthiazole hydrobromine monohydrate [35].

Three N—H···O hydrogen bonds are formed between the oxygen atom of the carboxylate and the amine group (N(2)···O(1)#1, 3.181(3) Å, N(2)···O(2)#1, 2.956(3) Å, and N(2)···O(3)#2, 2.815(3) Å). There is also one ionic N^+—H···O^- hydrogen bond (N(1)—H(1)···O(4)#2) with the N(1)···O(4)#2 distance of 2.742(3) Å.

In the COOH group, two C—O bond lengths are obviously different between O(1)—C(10) (1.214(3) Å) and O(2)—C(10) (1.295(3) Å) (Δ is 0.081 Å) which are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms as mentioned above. But for the COO^- group, two C—O bond lengths are basically not equal with an average value of 1.255 Å, which is shorter than that of the single bond of O(2)—C(10) (1.295(3) Å) but longer than that of the double bond of O(1)—C(10) (1.214(3) Å) in the maleic acid. This supports our assignment of the maleate anion. It is clear that the Δ value in

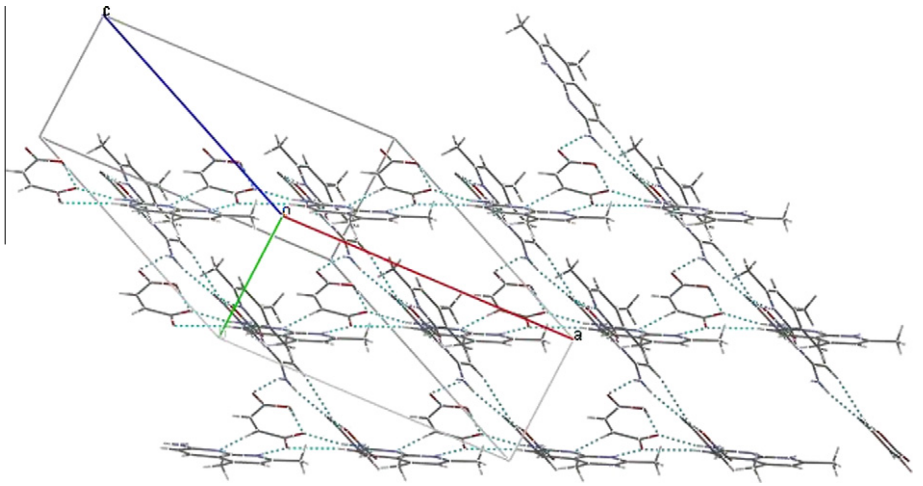


Fig. 6. 3D network structure of **3**.

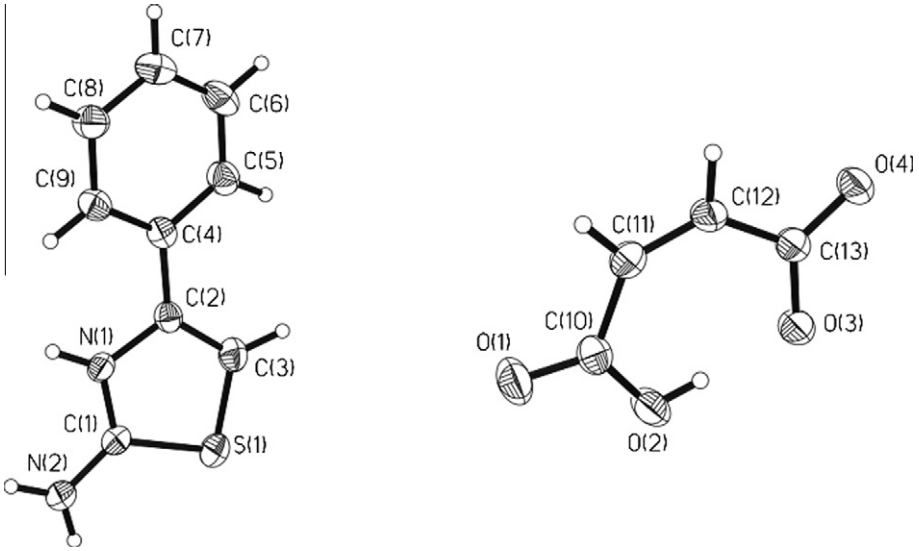


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

bond lengths of C—O within the carboxylic acid group (0.081 Å) is larger than the one found in the maleate anion (0.035 Å), which also confirms the monoionization of the dicarboxylic acid.

One hydrogen maleate anion is bound to one 4-phenylthiazol-1-ium-2-amine cation to form the adduct unit of $[(HL1)^+ \cdot (Hmal^-)]$. In the adduct unit one hydrogen atom of the amine group forms two neutral N—H···O hydrogen bonds with the oxygen atom of COOH of the maleate in bifurcate mode. The adduct units were connected by C—H···π hydrogen bond between olefinic CH of the maleate and the phenyl ring of the $(HL1)^+$ cation to form 1D corrugated chain along the *c* axis direction. Adjacent corrugated chains were further connected by N—H···O hydrogen bonds. There are also two kinds of C—H···O interactions between the neighboring corrugated chains, one is between the phenyl CH of $(HL1)^+$ and the carboxylate group of the maleate with C—O distance of 3.271 Å, the other is between the 4-CH on the thiazole ring and the COOH of the anion with C—O distance of 3.163 Å. For the above weak interactions every carboxylate of the maleate formed $R_2^2(7)$ and $R_2^2(8)$ motifs with the 4-phenylthiazol-1-ium-2-amine cation, in which the two kinds of hydrogen bonding motifs were fused together. Under these weak interactions the chains were connected together to form two-dimensional corrugated sheet structure along the ac plane which is shown in Fig. 8. The 2D sheets were further stacked along the *b* axis direction to form 3D layer structure.

4.5. X-ray structure of (4-phenylthiazol-2-amine): (phthalic acid)$_{0.5}$ [(HL1)$^+$ · (op^{2-})$_{0.5}$] (5)

The crystal structure of **5** consists of half a di-anion of phthalic acid, and one cation of 4-phenylthiazol-1-ium-2-amine in the asymmetric unit (Fig. 9). Both protons of the phthalic acid have transferred to the ring N atom of two equivalent thiazole molecules. The assignment of **5** as a salt is based on successful refinement of the relevant H atoms using X-ray data. This is also supported by equivalence of the C—O distances in the carboxylate group, and a relatively low energy C=O stretch in the IR band. In the compound, there is one ion pair without solvent molecules, which is well agreement with the micro-analysis results.

The C—O distances of COO^- of the phthalate are roughly equal with each other (which are ranging from 1.252(3) to 1.256(3) Å), indicating that the carboxylic groups are completely deprotonated. And the ring N atom of 4-phenylthiazol-1-ium-2-amine is also completely protonated. There are N—H···O hydrogen bonds arising from the oxygen atom of the carboxylate and the amine group (N(2)···O(2)#2, 2.810(3) Å; N(2)···O(2)#1, 2.828(3) Å). There is also strong ionic N^+—H···O^- hydrogen bond (N(1)—H(1)···O(1)#1) with N(1)···O(1) distance of 2.654(2) Å, which is considerably less than the sum of the van der Waals radii for N and O (3.07 Å) [37]. Thus in the solid state, there is consistently ionic hydrogen bond formed

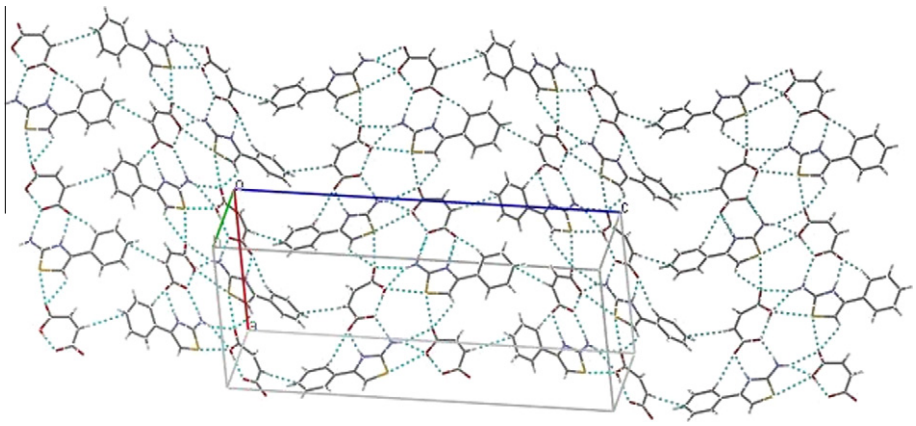


Fig. 8. 2D corrugated sheet structure of **4** viewed along the *a* axis.

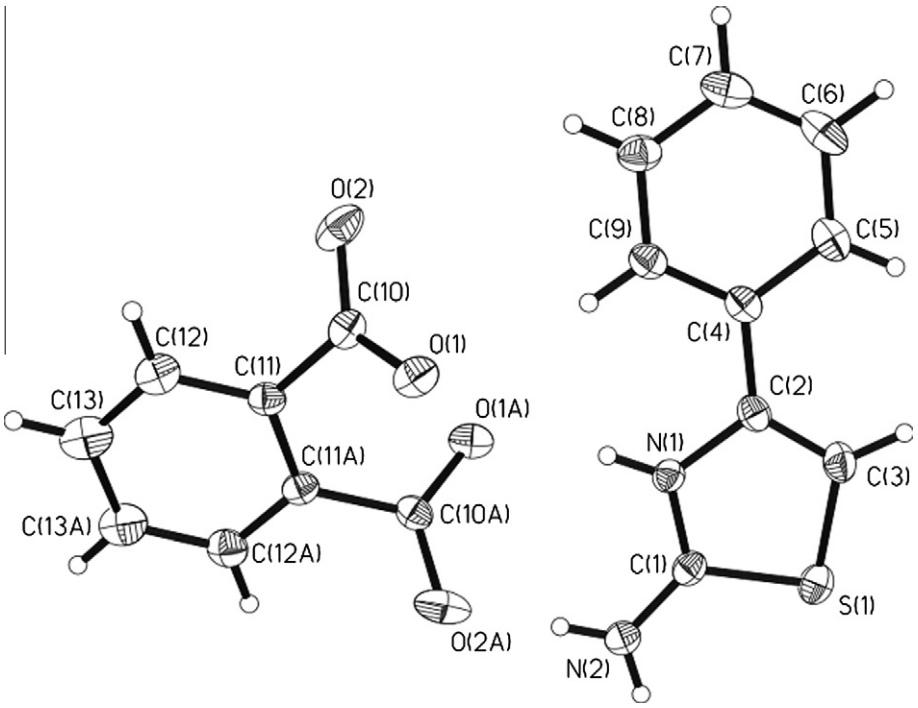


Fig. 9. The structure of **5**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

between the thiazole NH^+ and the phthalate ion, which is to be expected [38]. In compound **5**, there also exist strong electrostatic interactions between charged cation units of NH^+ and the di-anion phthalates.

The angle C3—S1—C1 (89.82(12)°) is similar to that in compound **4** (89.68(14)°), and it is larger than the corresponding angle in the neutral molecule (88.7 (2)°) [35]. But it is smaller than that in compound 2-amino-4-phenylthiazole hydrobromide monohydrate (90.17°) [36]. This may be due to the difference of the hydrogen bonding strength also. The dihedral angle between the planes of the phenyl and thiazole rings in **5** is 3.3 (3)°, so **5** is more planar than both neutral L1(6.2(3)°) and ionic compounds such as compound **4** (18.4 (3)°) and 2-amino-4-phenylthiazole hydrobromine monohydrate (19.23°).

In the whole structure there exist strong intermolecular S–π interactions between the S atom at the thiazole ring and the phenyl ring of the cation with the closest S–C contact of ca. 3.414 Å, which is similar to the previously published literature data [39]. But the S–C contact is in the lower limit of the recently reported S–C contact values [3.390–3.888 Å] [40].

Each phthalate is hydrogen bonded with six 4-phenylthiazol-1-ium-2-amine cations through N—H···O and C—H···O hydrogen bonds. Every carboxylate O atom forms five hydrogen bonds in which one oxygen atom forms two N—H···O hydrogen bonds with the amine group of two L1 in bifurcate mode with N—O distances ranged from 2.810 to 2.829 Å. While another O atom formed two C—H···O hydrogen bonds (the C—O distances are 3.196 Å, and 3.306 Å respectively) and one ionic N^+—H···O^- hydrogen bond (with N—O distance of 2.654 Å) in trifurcate fashion. For the above weak interactions every carboxylate of the phthalate formed $R_2^2(7)$ and $R_2^2(8)$ motifs with the 4-phenylthiazol-1-ium-2-amine cation. The same as the compound **4** the two kinds of hydrogen bonding motifs were also fused together. The r.m.s deviation of the ring atoms of the cation in **5** from the mean plane of the ring is 0.0291 Å, the phthalate excluding the two carboxylate groups is also plane with the r.m.s deviation of 0.1625 Å. The dihedral angle between the cation and the phthalate ring excluding the two carboxylate groups is 161.6°. However the carboxylate [O(1)—C(10)—O(2)] deviates by 48.5° from the phenyl ring plane of the phthalate which is different from the reported adduct of phthalate in which the carboxylates are almost coplanar with the phenyl ring [41]. All of the interactions combined, the compound displays 3D network structure, as shown in Fig. 10.

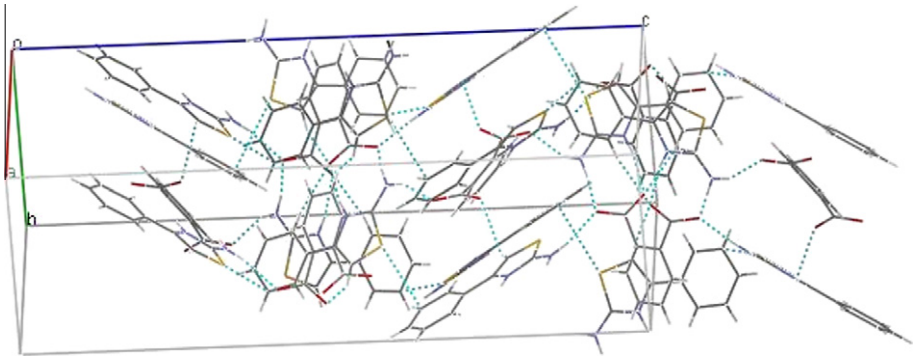


Fig. 10. 3D network structure of organic salt **5** when viewed down the *b* axis.

5. Conclusions

Five organic salts with different topologies have been prepared and structurally characterized. The different hydrogen bond interaction modes of the carboxylate anions and the 2-aminoheterocyclic cations lead to a wide range of different structures such as 3D layer structure, 3D network structure, and 3D ABAB layer structure. Despite variations in molecular shape on the carboxylic acids, there all existed strong intermolecular N—H···O hydrogen bonds (ionic or neutral). In naphthyridine salts **1**, and **2** there are also ionic and neutral N—H···N hydrogen bonds between HL^+ and L, so both form the most commonly observed naphthyridine dimers.

From this study it can be seen that the 2-aminoheterocyclic compounds such as 5,7-dimethyl-1,8-naphthyridine-2-amine and 4-phenylthiazol-2-amine will form salts with the acidic molecules. All the salts are formed by the proton transfer process resulting in a 2-aminoheterocyclic ion with a single positive charge. For the three compounds (**1**, **2**, and **3**) concerning 5,7-dimethyl-1,8-naphthyridine-2-amine, the positive charges are in different N atoms. Only in the salt **1** the most basic nitrogen atom adjacent to the amine group (for the NH_2 group is a more strong electron-donating group than that of the CH_3 group) in the naphthyridine ring is protonated. But in **2** the least basic NH_2 group is protonated. This phenomenon may be explained by the rule "strongest donor to strongest acceptor", for the carboxylic acids present in **1**–**2**, the 2-chloronicotinic acid has the relatively smaller Pk_a than the p-hydroxybenzoic acid discussed in this manuscript. Although maleic acid with the lowest Pk_{a1} among 2-chloronicotinic acid, p-hydroxybenzoic acid, and maleic acid, this molecule may be too flexible introducing factors that result more important than the small difference between the donors to decide the preferred molecular interactions.

Only in **3**, **4**, and **5**, the most common hydrogen-bonded $R_2^2(8)$ graph sets for 2-aminoheterocyclic derivatives have been observed. There are also $R_2^2(7)$ and $R_2^2(8)$ fused hydrogen bond graph sets in salts **4**, and **5**.

In addition all products possess weak C—H···O or CH_3—O hydrogen bonds. Two types of secondary C—H···O (CH_3—O) hydrogen bonds were observed based upon their geometric preferences, intra- and interchain interactions. Based upon an analysis of the metrics displayed by each set of interactions, it seems that intra- and interchain C—H···O (CH_3—O) interactions are of equal structural importance. There are also CH_3–π interactions in compounds **1**–**3**. Organic salt **4** possesses CH–π interaction. There exists strong intermolecular S–π interaction in **5**.

In conclusion, we have shown that 3D structures can be constructed by the collective weak interactions such as strong directional hydrogen bond, mixture of strong and weak hydrogen bond and some other non-covalent interactions.

Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 765440 for **1**, 673181 for **2**, 765438 for **3**, 766264 for **4**, and 765309 for **5**. 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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