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Hydrogen bonded supramolecular architectures of organic salts based on 5,7-dimethyl-1,8-naphthyridine-2-amine and acidic compounds

Shouwen Jin [a,*], Wenbiao Zhang [b], Li Liu [a], Hongfang Gao [c], Daqi Wang [d], Rongpo Chen [a], Xiaolei Xu [a]

[a] Faculty of Science ZheJiang Forestry University, Lin'An 311300, PR China
[b] School of Engineering ZheJiang Forestry University, Lin'An 311300, PR China
[c] Middle School of JinShan, Shanyin Road 1268 XiaoShan, Hangzhou ZheJiang 311203, PR China
[d] Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

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ABSTRACT

Studies concentrating on hydrogen bonding between the base of 5,7-dimethyl-1,8-naphthyridine-2-amine and acidic compounds have led to an increased understanding of the role 5,7-dimethyl-1,8-naphthyridine-2-amine has in binding with acidic compounds. Here anhydrous and hydrated multicomponent crystals of 5,7-dimethyl-1,8-naphthyridine-2-amine have been prepared with oxalic acid, 2,4,6-trinitrophenol, terephthalic acid, and phthalic acid. The four crystalline forms reported are organic salts of which the crystal structures have all been determined by X-ray diffraction. All products were formed in solution and obtained by the slow evaporation technique. The role of weak and strong hydrogen bonding in the crystal packing is ascertained.

1. Introduction

Nowadays, hydrogen bonding has been widely developed in the area of crystal engineering, supramolecular chemistry, material science, and biological recognition [1–4]. The application of intermolecular hydrogen bonds is a well known and efficient tool to regulate the molecular arrangement in a crystal structure [4]. Through hydrogen bonds we can form co-crystals and organic salts. In pharmaceuticals, salt formation is often used in order to modify the properties of the compounds [5]. Salt formation can be used to increase or decrease solubility, to improve stability and to reduce hygroscopicity of a drug product. There are many interesting hydrogen bonded topological structures from infinite 1D chain to 3D supramolecular framework [6,7]. The carboxylic acid contains the important hydrogen bonding functional group for crystal engineering [8]. Carboxylic acids aggregate in the solid state as dimer, catemer, and bridged motifs [9]. It is interesting to exploit the robust and directional recognition of carboxylic acids with N-heterocyclic moieties [10].

Recently 1,8-naphthyridine derivatives have been reported to form supramolecular compounds under the multiple hydrogen bonding action [11]. The derivatives of 1,8-naphthyridine have also been widely utilized as molecular recognition receptors for urea, carboxylic acids and guanine [12], in which the major driving force is intermolecular hydrogen bonding. As the 1,8-naphthyridine core (N^C^N) has similar dimensions to those of carboxylate (O^C^O), the 5,7-dimethyl-1,8-naphthyridine-2-amine may act as a potentially tridentate ligand. The binary organic salts of the carboxylic acids and 5,7-dimethyl-1,8-naphthyridine-2-amine may display the different hydrogen-bonding patterns from the three different N atoms. As an extension of our study of weak interactions (hydrogen bonding, π–π interaction, and halogen bonding) concerning 1,8-naphthyridine derivatives [13], herein we report the preparation and structures of four organic salts assembled from 5,7-dimethyl-1,8-naphthyridine-2-amine (L) and the corresponding acidic compounds (Scheme 1), respectively. The four organic salts are 5,7-dimethyl-1,8-naphthyridine-2-amine: (oxalic acid)$_{0.5}$ (**1**) [HL·(ox^{2-})$_{0.5}$·H$_2$O, ox = oxalate], 5,7-dimethyl-1,8-naphthyridine-2-amine: picric acid (**2**) [HL·(pic), pic = picrate], (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: terephthalic acid (**3**) [HL$^+$·L·(tp^{2-})$_{0.5}$·(H$_2$tp)$_{0.5}$, tp = terephthalate], and (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: phthalic acid (**4**) [HL$^+$·L·(Hop$^-$), Hop$^-$ = hydrogen phthalate] (Scheme 2).

2. Experimental section

2.1. Materials and physical measurements

The chemicals and solvents used in this work are of analytical grade and available commercially and were used without further purification. 5,7-Dimethyl-1,8-naphthyridine-2-amine was pre-

* Corresponding author. Tel./fax: +86 571 6374 0010.
E-mail address: Jinsw@zjfc.edu.cn (S. Jin).

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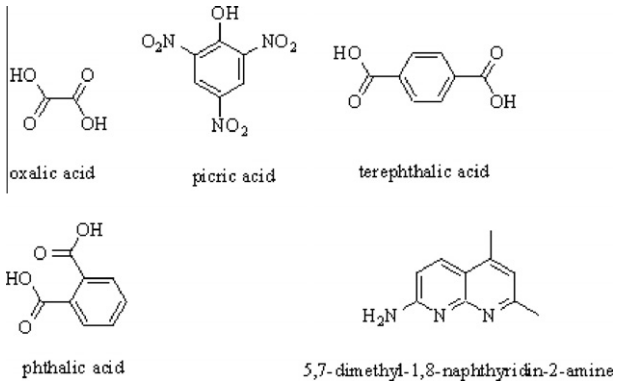


Scheme 1. Hydrogen bond synthons discussed in this paper.

pared by the method described in the literature [14]. 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) data were obtained with a Perkin-Elmer Model 2400II elemental analyzer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of the compounds 1–4

2.2.1. a. 5,7-Dimethyl-1,8-naphthyridine-2-amine: (oxalic acid)$_{0.5}$: H_2O **(1)**

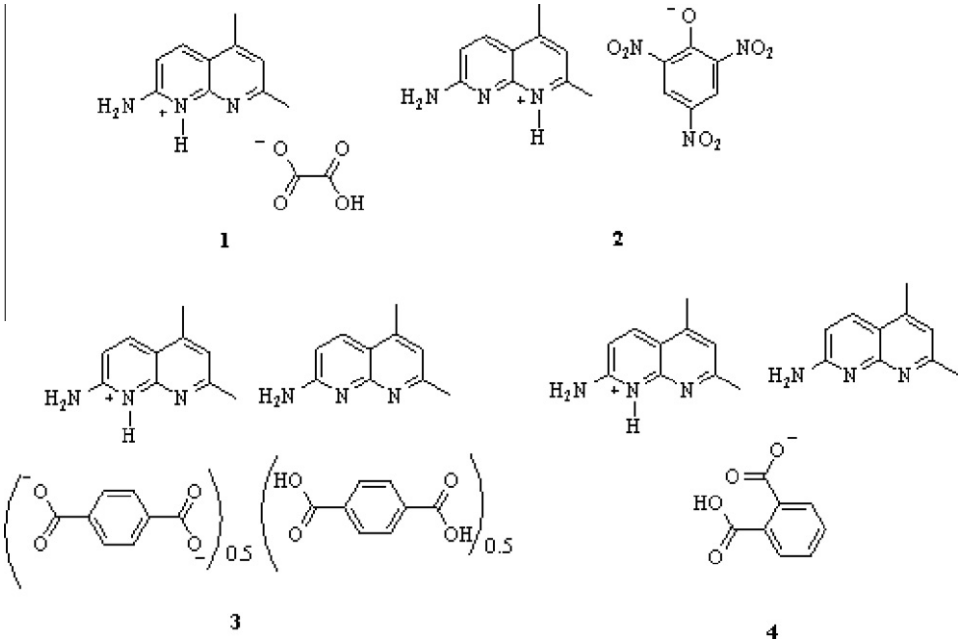
To an ethanol solution (8 ml) of 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was added oxalic acid dihydrate (25.2 mg, 0.2 mmol). The solution was stirred for a few minutes, then the solution was filtered. The solution was left standing at room temperature for several days, colorless crystals were isolated after slow evaporation of the ethanol solution in air. The crystals were collected and dried in air to give the title compound [HL·(ox^{2-})$_{0.5}$·H_2O] (**1**) Yield: 39 mg, 82.54%. m. p. 189–191 °C. Anal. calcd for $C_{11}H_{14}N_3O_3$: C, 55.87; H, 5.93; N, 17.78. Found: C, 55.82; H, 5.91; N, 17.73. Infrared spectrum (KBr disc, cm^{-1}): 3360s(ν(H_2O), broad), 3306s(ν_{as}(NH)), 3140s(ν_s(NH)), 3070s, 2980s, 2920s, 2380m, 2320m, 2080w, 1760w, 1670s, 1640s(ν(C═O)), 1620s, 1602m, 1580s(ν_{as}(COO)), 1540s, 1500m, 1487m, 1448m, 1400m, 1380s(ν_s(COO)), 1295m, 1288s(ν(C—O)), 1240m, 1200m, 1160m, 1080m, 1000m, 930m, 850m, 740s, 700m, 646s, 610m, 540m, 480m, 440m.

2.2.2. b. 5,7-Dimethyl-1,8-naphthyridine-2-amine: (2,4,6-trinitrophenol) **(2)**

To a methanol solution (5 ml) of 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was added 2,4,6-trinitrophenol (46 mg, 0.2 mmol) in 10 ml methanol. The solution was filtered immediately. Pale yellow block crystals were isolated after several minutes from the solution at room temperature in air. The crystals were collected and dried in air to give the title compound [HL·(pic)] (**2**) Yield: 72 mg, 89.92%. m. p. 202–203 °C. Anal. calcd for $C_{16}H_{14}N_7O_6$: C, 47.96; H, 3.50; N, 24.48. Found: C, 47.90; H, 3.44; N, 24.46. Infrared spectrum (KBr disc, cm^{-1}): 3440s(ν_{as}(NH)), 3240s(ν_s(NH)), 3190s, 3100s, 2940m, 2880m, 2848m, 2820m, 2370m, 2330m, 1740m, 1665s, 1614s, 1600s, 1560s, 1520s(ν_{as}(NO_2)), 1480m, 1440m, 1360s, 1320s(ν_s(NO_2)), 1260s, 1240m, 1210m, 1160m, 1080m, 1020m, 980m, 920m, 880m, 840m, 820m, 790m, 720m, 680m, 660m, 620m, 540m, 460m.

2.2.3. c. (5,7-Dimethyl-1,8-naphthyridine-2-amine)$_2$: (terephthalic acid) **(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 terephthalic acid (34 mg, 0.2 mmol) in 3 ml DMSO. 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^+·L·(tp^{2-})$_{0.5}$·(H_2tp)$_{0.5}$] (**3**) yield 70 mg, 68.28%. m. p. 196–198 °C. Elemental analysis performed on crystals exposed to the atmosphere: calc. for $C_{28}H_{28}N_6O_4$: C, 65.55; H, 5.46; N, 16.39. Found: C, 65.54; H, 5.41; N, 16.32. Infrared spectrum (KBr disc, cm^{-1}): 3460m (broad, ν(OH)), 3340s(ν_{as}(NH)), 3160s(ν_s(NH)), 3064m, 2950m, 2880m, 2810m, 2720m, 2560w, 2380m, 1940w, 1860w, 1820w, 1700w, 1660s, 1645s(ν(C═O)), 1620s, 1580s(ν_{as}(COO)), 1560m, 1530s, 1460m, 1420m, 1380s(ν_s(COO)), 1300m, 1284m(ν(C—O)), 1240m, 1200m, 1160m, 1080m, 1020m, 960m,



Scheme 2. The four organic salts described in this paper, **1**–**4**.

920m, 890m, 820m, 800m, 780m, 760m, 740m, 660m, 620m, 560m, 520m, 460m, 440m, 420m.

2.2.4. d. (5,7-Dimethyl-1,8-naphthyridine-2-amine)$_2$: (phthalic acid) (4)

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 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 [HL^+·L·(Hop^-)] (**4**), yield 72 mg, 70.24%. m. p. 180–182 °C. Elemental analysis performed on crystals exposed to the atmosphere: calc. for $C_{28}H_{28}N_6O_4$: C, 65.55; H, 5.46; N, 16.39. Found: C, 65.52; H, 5.44; N, 16.37. Infrared spectrum (KBr disc, cm^{-1}): 3560s(ν(OH)), 3440s (multiple, ν_{as}(NH)), 3320s(ν_s(NH)), 3140m, 3060m, 2990m, 2920m, 2812m, 2720m, 2540w, 2360m, 2190m, 1960w, 1840w, 1800w, 1775w, 1730m, 1670s, 1648s(ν(C═O)), 1628s, 1580s(ν_{as}(COO)), 1500s, 1460s, 1426s, 1380s(ν_s(COO)), 1350s, 1300m, 1280s(ν(C—O)), 1240m, 1196m, 1130m, 1100m, 1060m, 1020m, 930m, 888m, 800m, 780m, 740m, 680m, 660m, 620m, 580m, 540m, 510m, 470m, 450m.

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 [15]. 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 [16].

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**, and **4** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3. The IR bands which indicate chemical functionalities in the resulting compounds are given in Table 4.

3. Results and discussion

3.1. Preparation and general characterization

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

The preparation of compounds **1**–**4** were carried out with 5,7-dimethyl-1,8-naphthyridine-2-amine and the corresponding acidic component in 1: 1 ratio. The four compounds are not hygroscopic, and they all crystallized with no solvent molecules accompanied except compound **1**. The molecular structures and their atom labelling schemes for the four structures are illustrated in Figs. 1, 3, 5 and 7, respectively.

In the preparation of the organic salts **1**, **2**, **3**, and **4**, the acidic compounds 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 four compounds are in good agreement with their compositions. The infrared spectra of the four 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 acidic molecule have transferred to the 5,7-dimethyl-1,8-naphthyridine-2-amine molecules. In **3**, both protons of one carboxylic acid have transferred to the base, while another carboxylic acid remains protonized. In **4**, only one proton of the phthalic acid has transferred to the 5,7-dimethyl-1,8-naphthyridine-2-amine molecule, thus **3** and **4** form 2:1 salts. But the acid presents a different valence number in these two situations, −2 for compound **3**, and −1 for compound **4**.

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

	1	2	3	4
Formula	$C_{11}H_{14}N_3O_3$	$C_{16}H_{14}N_7O_6$	$C_{28}H_{28}N_6O_4$	$C_{28}H_{28}N_6O_4$
Fw	236.25	400.34	512.56	512.56
T, K	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2(1)/*n*	P-1	P-1	P-1
a, Å	7.3486(14)	7.9058(10)	7.7530(10)	7.8990(10)
b, Å	10.4028(18)	8.0659(11)	12.3651(13)	11.4371(14)
c, Å	14.739(2)	14.0204(17)	13.5561(15)	14.5669(16)
α, deg.	90	83.3330(10)	100.946(2)	97.7550(10)
β, deg.	89.8960(10)	84.249(2)	100.291(2)	100.522(2)
γ, deg.	90	83.9670(10)	92.5200(10)	103.618(2)
V, Å^3	1126.7(3)	879.6(2)	1251.3(3)	1235.5(3)
Z	4	2	2	2
D_{calcd}, Mg/m^3	1.393	1.512	1.360	1.378
Absorption coefficient, mm^{-1}	0.104	0.119	0.094	0.095
F(0 0 0)	500	414	540	540
Crystal size, mm^3	0.42 × 0.40 × 0.39	0.46 × 0.43 × 0.30	0.41 × 0.33 × 0.26	0.41 × 0.18 × 0.16
θ Range, deg	2.40–25.02	1.47–25.02	1.56–25.02	1.86–25.02
Limiting indices	$-8 \leqslant h \leqslant 8$ $-12 \leqslant k \leqslant 11$ $-17 \leqslant l \leqslant 9$	$-9 \leqslant h \leqslant 9$ $-9 \leqslant k \leqslant 7$ $-15 \leqslant l \leqslant 16$	$-7 \leqslant h \leqslant 9$ $-12 \leqslant k \leqslant 14$ $-16 \leqslant l \leqslant 16$	$-9 \leqslant h \leqslant 9$ $-13 \leqslant k \leqslant 13$ $-15 \leqslant l \leqslant 17$
Reflections collected	5220	4598	6510	6535
Reflections independent (R_{int})	1976 (0.0395)	3061 (0.0197)	4335 (0.0255)	4309 (0.0276)
Goodness-of-fit on F^2	1.018	1.008	1.010	0.864
R indices [$I > 2\sigma I$]	0.0507, 0.1168	0.0464, 0.1143	0.0519, 0.1167	0.0554, 0.1243
R indices (all data)	0.0917, 0.1440	0.0882, 0.1457	0.1135, 0.1571	0.1287, 0.1499
Largest diff. peak and hole, e.Å^{-3}	0.203, −0.260	0.164, −0.187	0.198, −0.170	0.203, −0.248

Table 2
Selected bond lengths [Å] and angles [°] for compounds **1**, **2**, **3**, and **4**.

1			
N(1)—C(2)	1.340(3)	N(1)—C(6)	1.378(3)
N(2)—C(6)	1.336(3)	N(2)—C(7)	1.345(3)
N(3)—C(2)	1.312(3)	O(1)—C(1)	1.251(3)
O(2)—C(1)	1.232(3)	C(2)—N(1)—C(6)	123.9(2)
C(6)—N(2)—C(7)	116.5(2)	O(2)—C(1)—O(1)	125.7(3)
N(3)—C(2)—N(1)	119.9(2)	N(2)—C(6)—N(1)	115.8(2)
2			
N(1)—C(1)	1.335(3)	N(1)—C(5)	1.341(3)
N(2)—C(6)	1.340(3)	N(2)—C(5)	1.354(3)
N(3)—C(1)	1.332(3)	N(4)—O(3)	1.205(3)
N(4)—O(2)	1.212(3)	N(4)—C(12)	1.463(3)
N(5)—O(4)	1.220(3)	N(5)—O(5)	1.221(3)
N(5)—C(14)	1.442(3)	N(6)—O(7)	1.201(3)
N(6)—O(6)	1.215(3)	N(6)—C(16)	1.450(3)
O(1)—C(11)	1.256(3)	C(1)—N(1)—C(5)	116.8(2)
C(6)—N(2)—C(5)	123.7(2)	O(3)—N(4)—O(2)	123.7(3)
O(3)—N(4)—C(12)	117.6(3)	O(2)—N(4)—C(12)	118.7(3)
O(4)—N(5)—O(5)	122.3(2)	O(4)—N(5)—C(14)	118.3(3)
O(5)—N(5)—C(14)	119.5(3)	O(7)—N(6)—O(6)	122.4(3)
O(7)—N(6)—C(16)	119.5(3)	O(6)—N(6)—C(16)	118.0(3)
N(3)—C(1)—N(1)	117.7(3)	N(1)—C(5)—N(2)	116.5(2)
3			
N(1)—C(9)	1.333(4)	N(1)—C(13)	1.368(4)
N(2)—C(14)	1.334(4)	N(2)—C(13)	1.351(4)
N(3)—C(9)	1.331(4)	N(4)—C(19)	1.341(4)
N(4)—C(23)	1.377(4)	N(5)—C(24)	1.339(4)
N(5)—C(23)	1.344(4)	N(6)—C(19)	1.316(4)
O(1)—C(1)	1.278(3)	O(2)—C(1)	1.229(3)
O(3)—C(5)	1.276(4)	O(4)—C(5)	1.222(3)
C(9)—N(1)—C(13)	119.5(3)	C(14)—N(2)—C(13)	118.0(3)
C(19)—N(4)—C(23)	120.6(3)	C(24)—N(5)—C(23)	117.3(3)
O(2)—C(1)—O(1)	124.9(3)	O(4)—C(5)—O(3)	124.6(3)
N(3)—C(9)—N(1)	118.6(3)	N(2)—C(13)—N(1)	115.5(3)
N(5)—C(23)—N(4)	114.9(3)		
4			
N(1)—C(9)	1.336(3)	N(1)—C(13)	1.375(3)
N(2)—C(14)	1.332(3)	N(2)—C(13)	1.359(3)
N(3)—C(9)	1.337(3)	N(4)—C(19)	1.345(3)
N(4)—C(23)	1.381(3)	N(5)—C(23)	1.340(3)
N(5)—C(24)	1.350(3)	N(6)—C(19)	1.313(3)
O(1)—C(1)	1.213(4)	O(2)—C(1)	1.281(4)
O(3)—C(2)	1.257(4)	O(4)—C(2)	1.224(4)
C(9)—N(1)—C(13)	117.7(2)	C(14)—N(2)—C(13)	117.8(2)
C(19)—N(4)—C(23)	122.7(2)	C(23)—N(5)—C(24)	116.4(2)
O(1)—C(1)—O(2)	121.8(4)	O(4)—C(2)—O(3)	122.4(4)
N(1)—C(9)—N(3)	118.0(2)	N(2)—C(13)—N(1)	114.5(2)
N(6)—C(19)—N(4)	120.3(2)	N(5)—C(23)—N(4)	115.1(2)

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

D—H···A	d(D—H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
1				
O(3)—H(3F)···N(2)	0.85	2.16	2.972(3)	159.3
O(3)—H(3E)···O(2)#1	0.85	2.52	3.117(3)	127.9
O(3)—H(3E)···O(1)	0.85	1.88	2.690(3)	158.4
N(3)—H(3B)···O(3)#2	0.86	1.94	2.738(3)	154.5
N(3)—H(3A)···O(1)	0.86	2.65	3.285(3)	132.1
N(3)—H(3A)···O(2)	0.86	1.99	2.840(3)	170.7
N(1)—H(1)···O(1)	0.86	1.81	2.656(3)	167.6
2				
N(3)—H(3B)···O(1)#1	0.86	2.29	2.887(3)	126.5
N(3)—H(3A)···N(1)#2	0.86	2.23	3.079(4)	171.8
N(2)—H(2)···O(1)#3	0.86	2.00	2.801(3)	154.4
3				
O(3)—H(3)···O(1)#3	0.82	1.65	2.447(3)	163.9
N(6)—H(6B)···O(2)#3	0.86	1.97	2.831(3)	173.8
N(6)—H(6A)···N(2)#3	0.86	2.03	2.887(4)	171.8
N(4)—H(4)···N(1)#3	0.86	2.14	3.004(4)	177.6
N(3)—H(3B)···O(4)#4	0.86	2.01	2.841(4)	163.8
N(3)—H(3A)···N(5)#5	0.86	2.07	2.925(4)	176.3
N(1)—H(1)···N(4)#5	0.86	2.15	3.004(4)	175.6
4				
O(3)—H(3)···O(2)	0.82	1.57	2.383(4)	167.7
N(6)—H(6B)···O(4)#1	0.86	2.04	2.875(3)	163.2
N(6)—H(6A)···N(2)#2	0.86	1.99	2.848(3)	175.1
N(4)—H(4)···N(1)#2	0.86	2.13	2.994(3)	178.0
N(3)—H(3B)···O(3)#3	0.86	2.13	2.925(3)	153.1
N(3)—H(3A)···N(5)#4	0.86	2.07	2.928(3)	176.8

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

The very strong and broad features at approximately 3400–3100 cm^{-1} in the IR spectra of the four compounds arise from O—H or N—H stretching frequencies. Aromatic and naphthyridic 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. Except for the above bands for **2**, the bands at 1520 and 1320 cm^{-1} were attributed to the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively [17]. The intense peak at ca. 1642 cm^{-1} was derived from the existence of the C=O stretches, and the band at ca. 1284 cm^{-1} exhibited the presence of the C—O stretches of the carboxylate in compounds **1**, **3**, and **4** [18]. The absence of two broad bands at ca. 2500 cm^{-1} and 1900 cm^{-1} which is characteristic of a neutral O—H···N hydrogen-bond interaction was interpreted as a lack of co-crystal formation in compounds **1**, **2**, **3**, and **4** [19]. IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [20]. The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1550–1610 cm^{-1} and 1300–1420 cm^{-1} in compounds **1**, **3**, and **4**, respectively [21].

3.2. Structural descriptions

3.2.1. X-ray structure of 5,7-dimethyl-1,8-naphthyridine-2-amine: (oxalic acid)$_{0.5}$: $H_2O{\cdot}[HL{\cdot}(ox^{2-})_{0.5}{\cdot}H_2O]$ (1)

The compound **1** of the composition $[HL{\cdot}(ox^{2-})_{0.5}{\cdot}H_2O]$ was prepared by reaction equal mol of 5,7-dimethyl-1,8-naphthyridine-2-amine and oxalic acid, in which both protons of oxalic acid were transferred to the N atoms on the naphthyridine ring. In the asymmetric unit of **1** there existed one cation of 5,7-dimethyl-1,8-naphthyridinium-2-amine, half an anion of oxalate, and one water molecule, as shown in Fig. 1. The C—O distances of the COO^- of oxalate are ranging from 1.232(3) to 1.251(3) Å, which suggests that the carboxylic group is deprotonated, and the N atom adjacent to the amine group on the naphthyridine ring is protonated. The significant difference in bond distances between O(1)—C(1) (1.251(3) Å) and O(2)—C(1) (1.232(3) Å) in the carboxylate group in compound **1** is caused by the fact that O(1) is involved in forming more hydrogen bonds than that of O(2).

The N—H···O hydrogen bond is formed between the naphthyridinium cation and the oxygen atom of the oxalate, in which the N(1)···O(1) distance in these contacts is 2.656(3) Å, which is considerably less than the sum of the van der Waals radii for N and O (3.07 Å) [22]. Thus in the solid state, there is consistently ionic hydrogen bonds formed between the naphthyridinium NH^+ and the oxalate ions, which is to be expected [23]. In compound **1**, there also exist strong electrostatic interactions between charged cation units of NH^+ and the di-anion oxalates.

In the framework of **1**, there are 5,7-dimethyl-1,8-naphthyridine-2-amine dimers formed through π–π interaction between adjacent parallel naphthyridine rings with the closest two rings

Table 4
Character IR bands of chemical functionalities of the four organic salts **1**–**4**.

Compound	ν(OH)	ν_{as}(NH)	ν_s(NH)	ν(C=O)	ν_{as}(COO)	ν_s(COO)	ν(C—O)
1	3360s (broad)	3306s	3140s	1640s	1580s	1380s	1288s
2		3440s	3240s				
3	3460m (broad)	3340s	3160s	1645s	1580s	1380s	1284m
4	3560s	3440s (multiple)	3320s	1648s	1580s	1380s	1280s

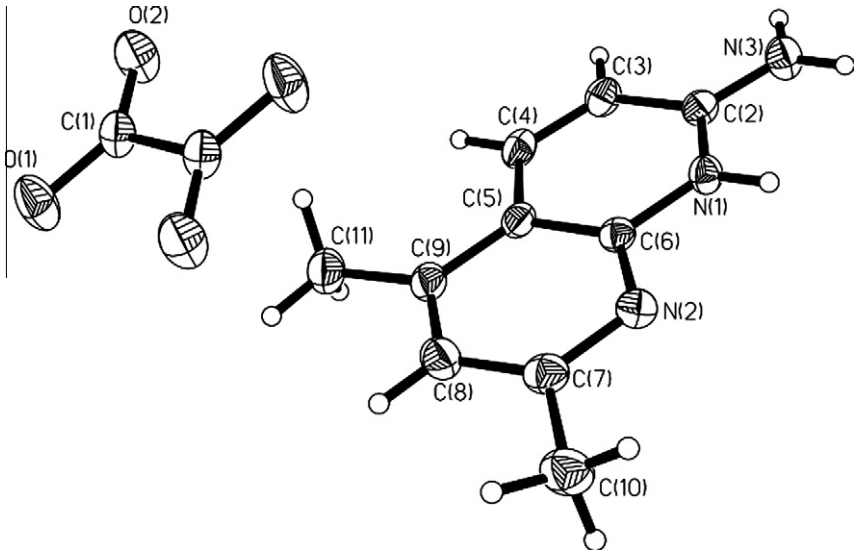


Fig. 1. Molecular structure of **1** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

distance of 3.386 Å. In addition there are also 1D chains formed by 5,7-dimethyl-1,8-naphthyridine-2-amine dimers through N^+—H···O^- hydrogen bonds between the N^+—H of 5,7-dimethyl-1,8-naphthyridinium-2-amine and the oxygen atom of the oxalate. These chains extended along the directions that slipped from the *b* and *c* axis direction with angles of about 67°, respectively. The chains extending in the two crossed directions were connected through the lattice water molecules to form 3D network structure, which is shown in Fig. 2. The lattice water formed two hydrogen bonds with the naphthyridine amine group and the ring N atom. The lattice water also formed two H bonds with the oxalate in which only one hydrogen atom of the water is involved in forming two hydrogen bonds with the oxalate in bifurcate mode. In the compound the oxalate formed eight hydrogen bonds, of which

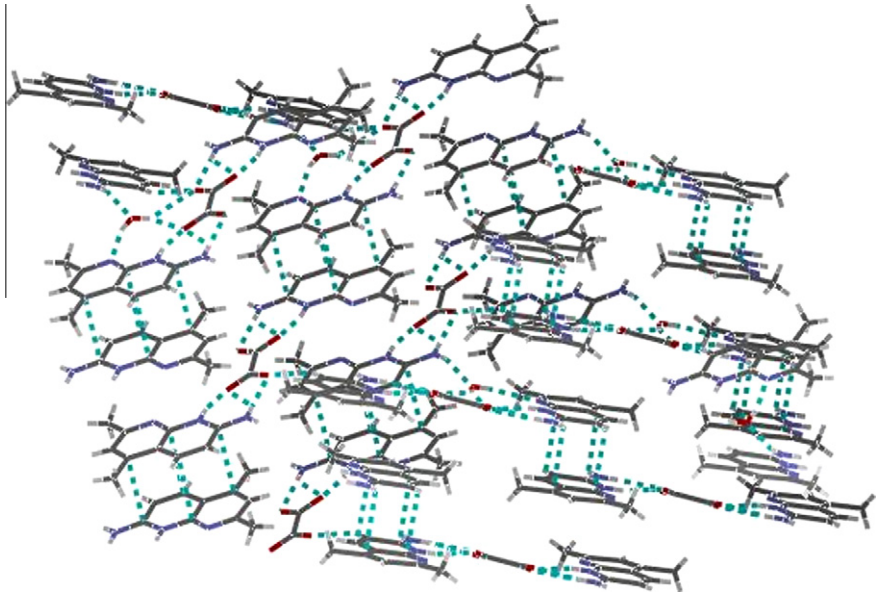


Fig. 2. 3D network structure of **1** which is viewed along the *c* axis.

six hydrogen bonds connect with the naphthyridine moiety, and two with the lattice water. Two oxygen atoms of the oxalate both formed two hydrogen bonds with the naphthyridine in bifurcate fashion. Each of the other two oxygen atoms formed one hydrogen bond with the amine group of the naphthyridine, respectively.

The deprotonated carboxyl group acts as hydrogen bond acceptor for the formation of hydrogen bonds with protonated N atoms on the naphthyridine rings, and the amine group also. The hydrogen bond involves N(1) on naphthyridine rings and O(1) on the COO^- carbonyl oxygen atom in which the naphthyridine-carboxylate moieties are almost coplanar (the torsion angle O(1)—C(1)—O(2)—N(3) is 2.34 (2)°). In addition, there are also C—H···O (C—O distance is 3.478 Å) hydrogen bonds between crossed chains formed between 3—CH of naphthyridine and O atom of oxalate.

3.2.2. X-ray structure of 5,7-dimethyl-1,8-naphthyridine-2-amine: (2,4,6-trinitrophenol) [HL·(pic)] **(2)**

Salt **2** was prepared by reaction of a methanol solution of 2,4,6-trinitrophenol and 5,7-dimethyl-1,8-naphthyridine-2-amine in 1:1 ratio, which crystallizes as triclinic pale yellow crystals in the centrosymmetric space group P-1. The structure of **2** with the atom-numbering scheme is shown in Fig. 3. This is a salt where the OH groups of 2,4,6-trinitrophenol are ionized by proton transfer to one nitrogen atom (N(2)) of the naphthyridine moieties, which is also confirmed by the bond distance of O(1)—C(11) (1.256(3) Å) for phenolate (1.24 ± 0.01 Å) [24]. In this case the less basic nitrogen atom close to the methyl group is protonated which is similar to the published result [25], but it is different from the compound **1**. In the compound, there is one ion pair without solvent molecules, which is well agreement with the micro-analysis results.

Two naphthyridines formed dimers through intermolecular hydrogen bonds of N—H···N. In the dimers two naphthyridinium cations and two 2,4,6-trinitrophenolate anions self-assembled via N^+—H···O^- hydrogen bonds to form bis-2,4,6-trinitrophenolate terminated moiety, in which the two terminated 2,4,6-trinitrophenolates exist in trans conformation. When viewed along the *a* axis, the corresponding 2,4,6-trinitrophenolate ions in the adjacent bis-2,4,6-trinitrophenolate terminated moieties are antiparallel. The planes formed by the terminated 2,4,6-trinitrophenolates are

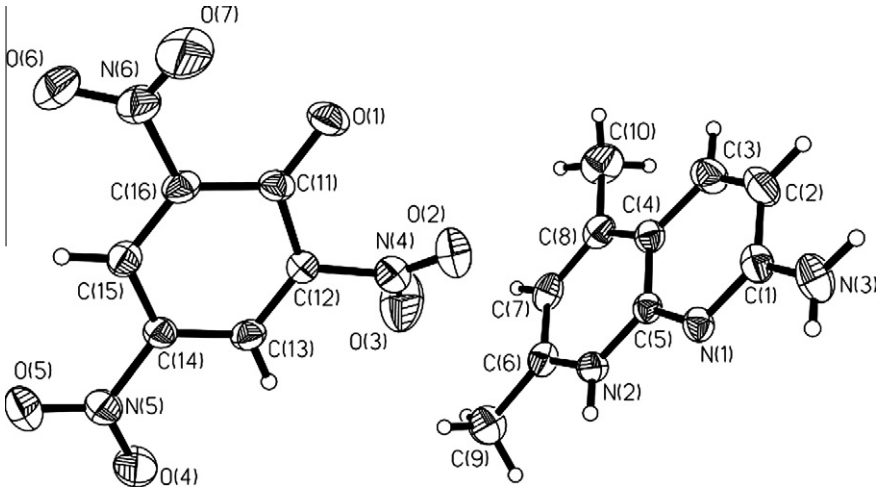


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

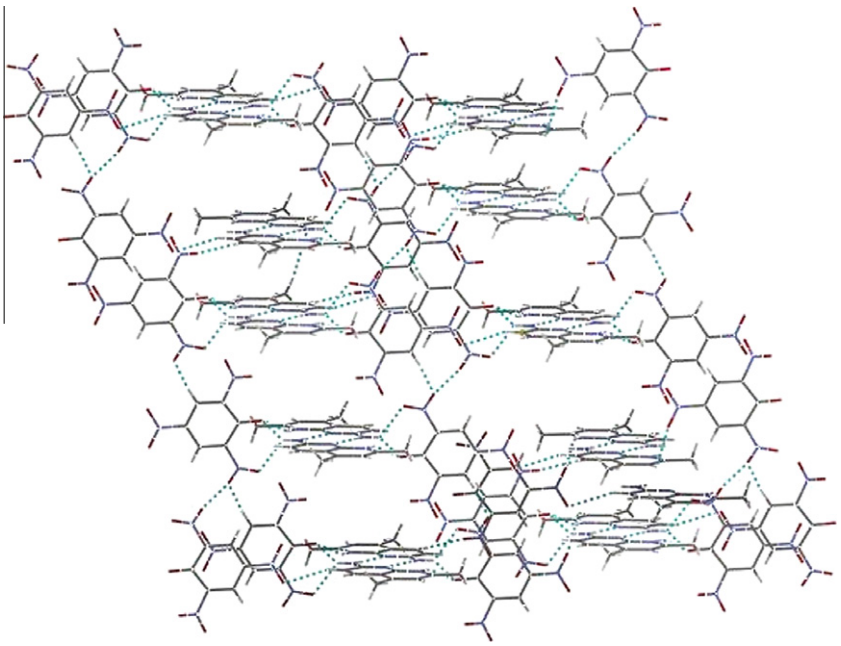


Fig. 4. 2D grid structure of **2** viewed along the *a* axis.

almost perpendicular to the planes formed by the naphthyridine dimers which are formed through hydrogen bonds.

In the solid state, there are consistently hydrogen bonds formed between the naphthyridinium NH^+, and the 2,4,6-trinitrophenolate ions. Each naphthyridinium NH^+ forms one hydrogen bond with the oxygen atom of the 2,4,6-trinitrophenolate ions. The N^+ —H···O^- bond angles and the N···O and H···O bond lengths are consistent with the values reported from a statistical analysis of N—H···O hydrogen bonds involving imidazolium residues [26], and from a study of N^+—H···O^- hydrogen bonding in salts of imidazole with monocarboxylic acids [27].

Two naphthyridine dimers and four picrates form closed loop structure through C—H···O interaction. Adjacent closed loops connect through O—O (NO_2—NO_2), and C—H···O (between 3—CH on naphthyridine and NO_2 of picrate with the C—O distance of 3.495 Å) interactions to form 2D grid structure (Fig. 4) when viewed along the *a* axis. There are also C—H···O hydrogen bonds between two picrates of which the O atom comes from NO_2 of one picrate of one closed loop, and the phenyl C—H comes from picrate of another adjacent parallel closed loop. These 2D grids were connected further by C—H···O, and O—O contacts to form 3D layer structure.

3.2.3. X-ray structure of (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$:(terephthalic acid) [$(HL)^+ \cdot L \cdot (tp)_{0.5} \cdot (H_2tp)_{0.5}$] **(3)**

The asymmetric unit of **3** consists of one molecule of 5,7-dimethyl-1,8-naphthyridine-2-amine, one cation of 5,7-dimethyl-1,8-naphthyridin-1-ium-2-amine, half a molecule of terephthalic acid, and half an anion of terephthalate, as shown in Fig. 5. The C—O distances of COO^- of the terephthalate are ranging from 1.229(3) to 1.278(3) Å, which suggests that the carboxylate group is partially deprotonated, while the N atom of 5,7-dimethyl-1,8-

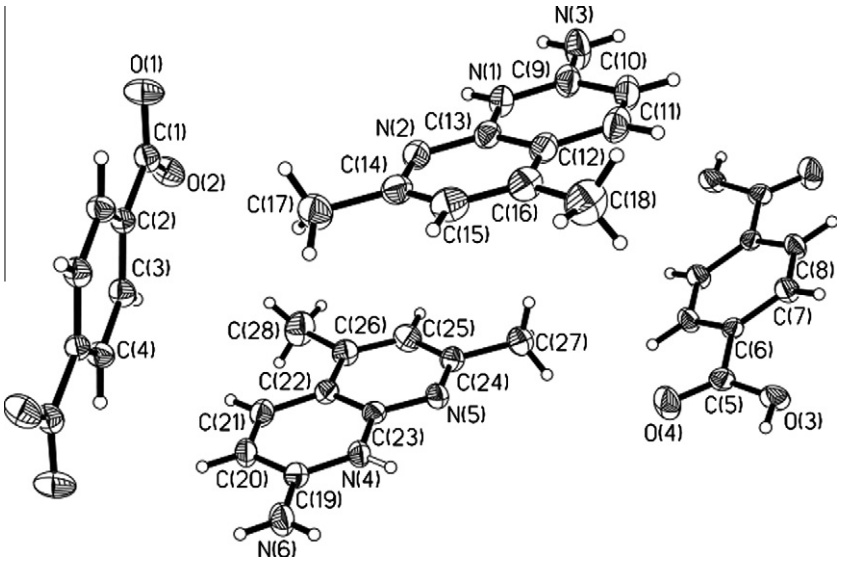


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

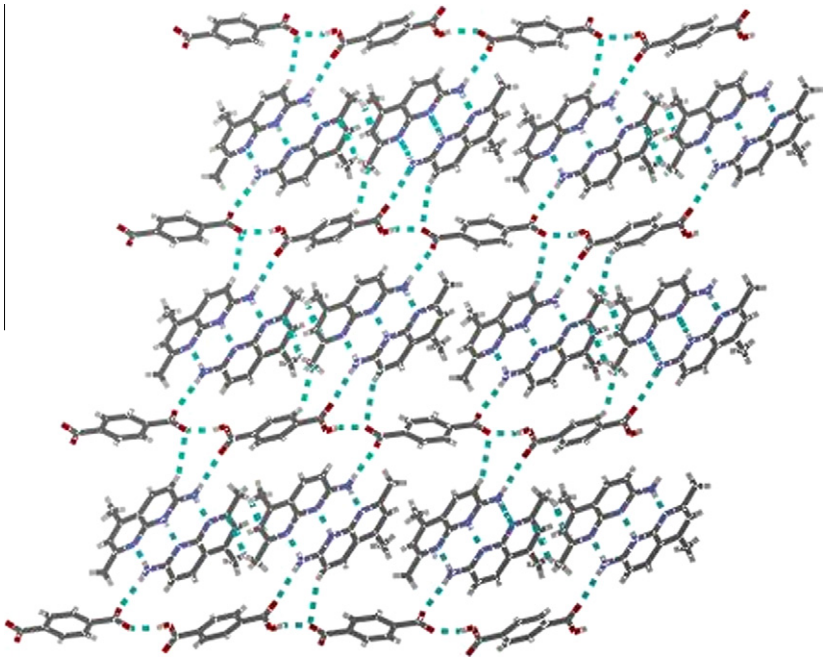


Fig. 6. 2D grid structure of **3** viewed from the *c* axis.

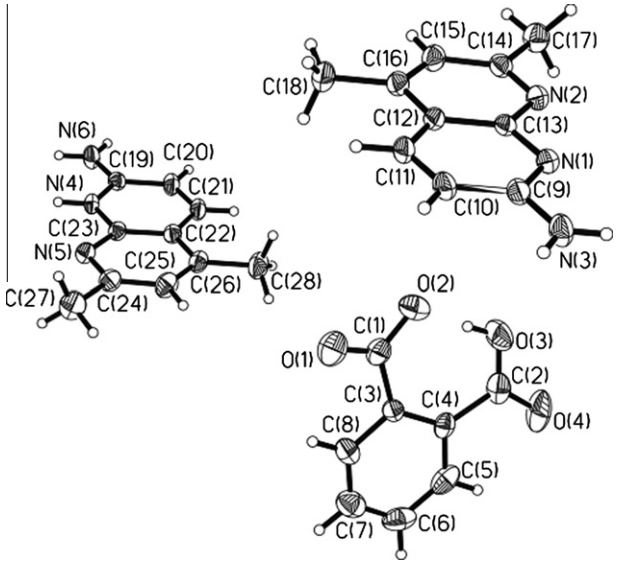


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

naphthyridine-2-amine is partially protonated. The neutral N—H···O hydrogen bond is formed between the oxygen atom of the carboxylate and the amine group (N(6)···O(2)#3, 2.831(3) Å), there does not exist ionic N^+—H···O^- hydrogen bonds. In the COOH group, two C—O bond lengths are obviously different between O(3)—C(5) (1.276(4) Å) and O(4)—C(5) (1.222(3) 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 1.2535 Å, which is shorter than that of the single bond of O(3)—C(5) (1.276(4) Å) but longer than that of the double bond of O(4)—C(5) (1.222(3) Å) in terephthalic acid. This supports our assignment of the terephthalate anions. It is clear that the difference in bond lengths of C—O within the carboxylic acid group (0.054 Å) is almost the same with the one found in the terephthalate anions (0.049 Å).

In the structure, there are chains of terephthalate moieties linked via COO^-···COOH hydrogen bonds along the *a* axis, with naphthyridinium ions suspended between the two chains through N—H···O hydrogen bonds. The carboxylate O atom of one terephthalate forms hydrogen bond with the carboxyl group of the terephthalic acid in head to tail fashion. The OH group of the terephthalic acid only acts as hydrogen bond donor for one O atom of the carboxylate anion of the terephthalate, while another O atom of the carboxylate functioned as hydrogen bond acceptor forms one hydrogen bonds with the amine group of the naphthyridine. The same as the carbonyl group in the terephthalic acid, the deprotonated carboxyl group in the terephthalate acts as hydrogen bond acceptor for the amine group of the naphthyridine dimer also. There are also C—H···O hydrogen bonds formed between the carbonyl group of the terephthalate and 3—CH of naphthyridine with C—O distance of 3.557 Å. In compound **3**, there do not exist strong electrostatic interactions between charged cation units of NH^+ and the di-anion terephthalates. One-dimensional grid structure is formed through naphthyridine dimers forming hydrogen bonds to di-ion carboxylate groups of two parallel terephthalate chains along the *a* axis, in which the naphthyridine dimers are almost perpendicular with the plane composing of two parallel terephthalate chains (Fig. 6).

The terephthalate chains were also extended along the *c* axis direction through the C—H···O (C—O distances are 3.549 and 3.409 Å respectively) interactions to form 2D grid structure. The C—H···O interactions were formed between the phenyl C—H and the oxygen atoms belonging to COO^- of terephthalate or OH group of terephthalic acid, respectively. The naphthyridine dimers were bound to the terephthalate grids through N—H···O and C—H···O hydrogen bonds to form 3D ABAB layer structure when viewed along the *c* axis direction.

3.2.4. X-ray structure of (5,7-dimethyl-1,8-naphthyridine-2-amine)$_2$: (phthalic acid) [(HL)$^+$·L·(Hop$^-$)] ***(4)***

The crystal structure of **4** consists of one monoanion of phthalic acid, one molecule of 5,7-dimethyl-1,8-naphthyridine-2-amine, and one cation of 5,7-dimethyl-1,8-naphthyridin-1-ium-2-amine in the asymmetric unit (Fig. 7). Only one proton of the phthalic acid has transferred to the N atom of the naphthyridine ring. Of the two naphthyridines there is only one naphthyridine that has been protonated, while the other naphthyridine remains neutral. The monoanion of phthalic acid has

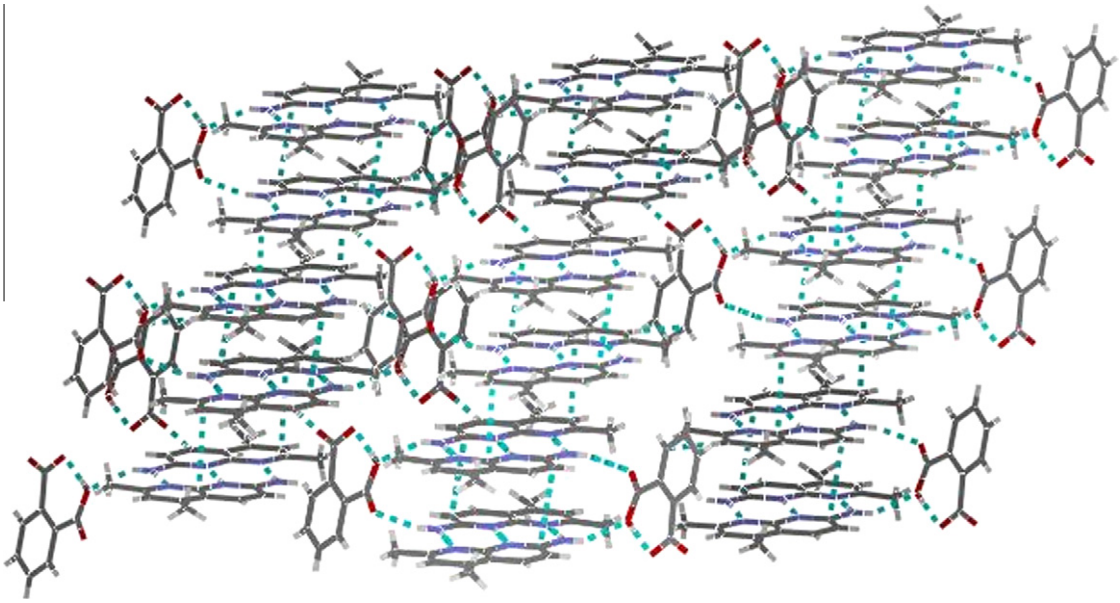


Fig. 8. 3D network structure of **4** viewed along the *c* axis.

intramolecular hydrogen bonded structure through strong hydrogen bond $S_1^1(7)$ O(3)—H(3)···O(2) interactions, which agrees well with the reported results [28]. Two naphthyridines formed dimers through complementary hydrogen bonds of N—H···N. In every dimer there is an anti-ion of hydrogen phthalate, which forms two hydrogen bonds of O···H—N with the amine group of two different naphthyridine dimers. The two dimers further formed donut structure through π–π interaction of which the closest approach of the ring centers between the naphthyridine ring in adjacent parallel dimers is 2.994(3) Å. The adjacent donuts were further connected by 6-CH···π interaction (between 6—CH of naphthyridine and the phthalate ring) along the *b* axis to form a 1D chain structure, in addition the donuts along the *a* axis were connected through C—H···O hydrogen bonds between the carbonyl group of phthalate and the 4—CH of the naphthyridine. And there are also π–π interactions in parallel naphthyridine rings between adjacent donuts in which the closest distance between the ring centers is 3.390(3) Å. All these interactions combined the compound showed 3D network structure, which is shown in Fig. 8.

4. Conclusions

A series of organic salts with different topologies have been synthesized and structurally characterized. The different hydrogen bond interaction modes of the carboxylate anions and 5,7-dimethyl-1,8-naphthyridinium-2-amine cation lead to a wide range of different structures (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). These interactions are responsible for the high-yielding supramolecular assembly of 1,8-naphthyridine and acidic components into salts, with desire connectivities.

From this study it can be seen that the 5,7-dimethyl-1,8-naphthyridine-2-amine will form salts with the acidic molecule. All the salts are formed by the proton transfer process resulting in a 5,7-dimethyl-1,8-naphthyridinium-2-amine ion with a single positive charge. With the exception of compound **2**, for the other three salts the nitrogen atoms in the naphthyridine ring adjacent to the amine group are protonated as this is the most basic nitrogen atom in the naphthyridine ring (for the NH_2 group is a more strong electron-donating group than that of the CH_3 group). In all these cases the NH_2 groups are not protonated which fits well with the Ref. [28], the reason is that the aromatic amines are less basic than the pyridine.

In addition all products possess weak C—H···O hydrogen bonds. Two types of secondary C—H···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 interactions are of equal structural importance. There are also π–π interactions in compounds **1** and **4** in which the closest separations between centers of aromatic rings ranged from 2.994 to 3.390 Å.

In conclusion, we have shown that 3D structures containing strong hydrogen bond interactions or mixture of strong and weak hydrogen bond interactions can be constructed and the structure may be modulated to have nonplanar structure by functional groups on planar system.

5. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 739,932 for **1**, 746,307 for **2**, 746,308 for **3**, and 746,465 for **4**. 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.

Acknowledgment

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