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

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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-

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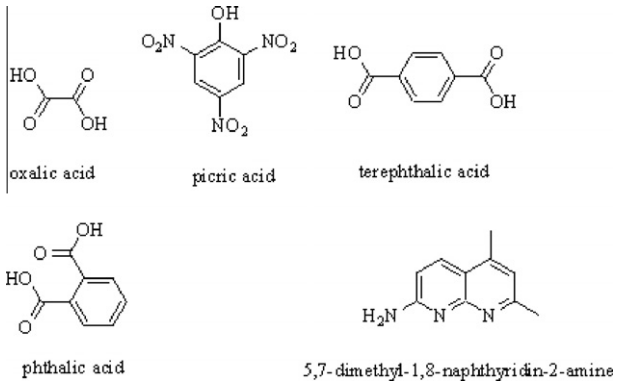


Scheme 1. Hydrogen bond synthons discussed in this paper.

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)**

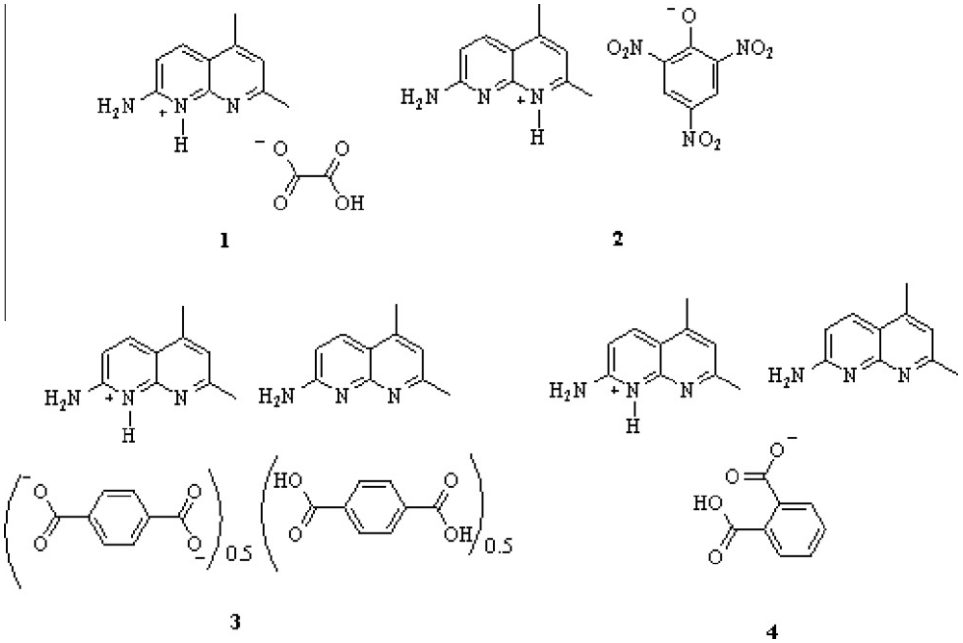
To an ethanol solution (8 ml) of 5,7-dimethyl-1,8-naphthyridine-2-amine (34.8 mg, 0.2 mmol) was added oxalic acid dihydrate (25.2 mg, 0.2 mmol). The solution was stirred for a few minutes, then the solution was filtered. The solution was left standing at room temperature for several days, colorless crystals 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**.