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Hydrogen bonded supramolecular framework in organic acid–base adducts: Crystal Structures of five cocrystals/salts assembled from 2-methylquinoline with monocarboxylic acid, dicarboxylic acid, and tricarboxylic acid

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ABSTRACT

Studies concentrating on noncovalent weak interactions between the organic base of 2-methylquinoline, and carboxylic acid derivatives have led to an increased understanding of the role 2-methylquinoline has in binding with carboxylic acid derivatives. Here anhydrous and hydrous multicomponent organic acid–base adducts of 2-methylquinoline have been prepared with carboxylic acids that ranged from monocarboxylic acid to tricarboxylic acid such as 3,5-dinitrobenzoic acid, 3-hydroxy-2-naphthoic acid, oxalic acid, fumaric acid, and citric acid.

The five crystalline complexes were characterized by X-ray diffraction analysis, IR, mp, and elemental analysis. These structures adopted homo or heterosupramolecular synthons or both. Analysis of the crystal packing of **1**–**5** suggests that there are N—H···O, O—H···N, and O—H···O hydrogen bonds (charge assisted or neutral) between acid and base components in the studied compounds. Except the classical hydrogen bonding interactions, the secondary propagating interactions also play an important role in structure extension. These weak interactions are responsible for the formation of 1D–3D frameworks.

1. Introduction

Hydrogen bonding plays a crucial role in chemical, catalytic, and biochemical processes, chemical and crystal engineering, as well as in supramolecular chemistry [1–3]. During the last few decades, new types of hydrogen bonding have been found, and all types of hydrogen bonds have been extensively studied [4,5], with particular attention to their spectral [6], and structural [7,8] features.

Carboxylic acids represent one of the most prevalent functional groups in crystal engineering because they possess a hydrogen bond donor and acceptor with a geometry that facilitates self-association through supramolecular homosynthons. Indeed, carboxylic acids are well-known to self-associate via centrosymmetric dimer or catemer [9–11]. Furthermore, it is now recognized that carboxylic acids are ideal candidates for multicomponent crystals since they form persistent supramolecular heterosynthons with a number of different N-containing components. It should be noted that these structures are normally held together by hydrogen-bonding synthons, and in this regard, the most frequently used moieties with hydrogen-bonding capability are pyridyl and carboxyl. Strong and specific recognition of the carboxylic acid group with pyridine (acid-pyridine synthon) is well studied [12–17].

As a pyridyl derivative, besides the methyl group, 2-methylquinoline bears more aromatic π electrons, which can be a better unit in creating aromatic stacking interactions. To the best of our knowledge there are very few reports involving the organic acid–base adduct concerning the Lewis base of 2-methylquinoline.

Following our previous works of acid–base adducts based on N-aromatic derivatives and carboxylic acids [18,19], herein we report the synthesis and crystal structure of five supramolecular complexes assembled through hydrogen bonding interactions between the carboxylic acid and 2-methylquinoline. In this study, we got five organic acid–base adducts composed of carboxylic acids and 2-methylquinoline (Scheme 1), namely 2-methylquinoline: (3,5-dinitrobenzoic acid): H_2O [$(HL^+)\cdots(dna^-)\cdots H_2O$, dna^- = 3,5-dinitrobenzoate, *L* = 2-methylquinoline] (**1**), 2-methylquinoline: (3-hydroxy-2-naphthoic acid) [$(HL)^+\cdots(npa^-)$, npa^- = 3-hydroxy-2-naphthoate] (**2**), 2-methylquinoline: (oxalic acid)$_{0.5}$: H_2O [$(HL)^+\cdots(oa^{2-})_{0.5}\cdots H_2O$, oa^{2-} = oxalate] (**3**), 2-methylquinoline: (fumaric acid)$_{0.5}$ [$(L)\cdots(H_2fum)_{0.5}$, H_2fum = fumaric acid] (**4**), and 2-methylquinoline: (citric acid) [$(HL)^+\cdots(H_2ctc^-)$, H_2ctc^- = dihydrogen citrate] (**5**) (Scheme 2).

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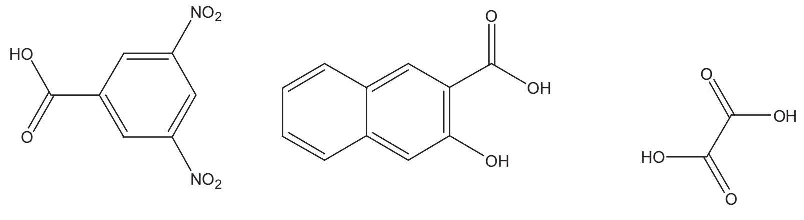
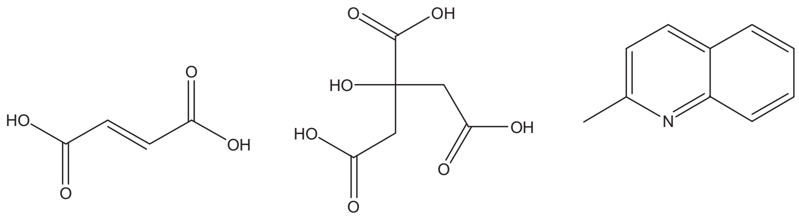
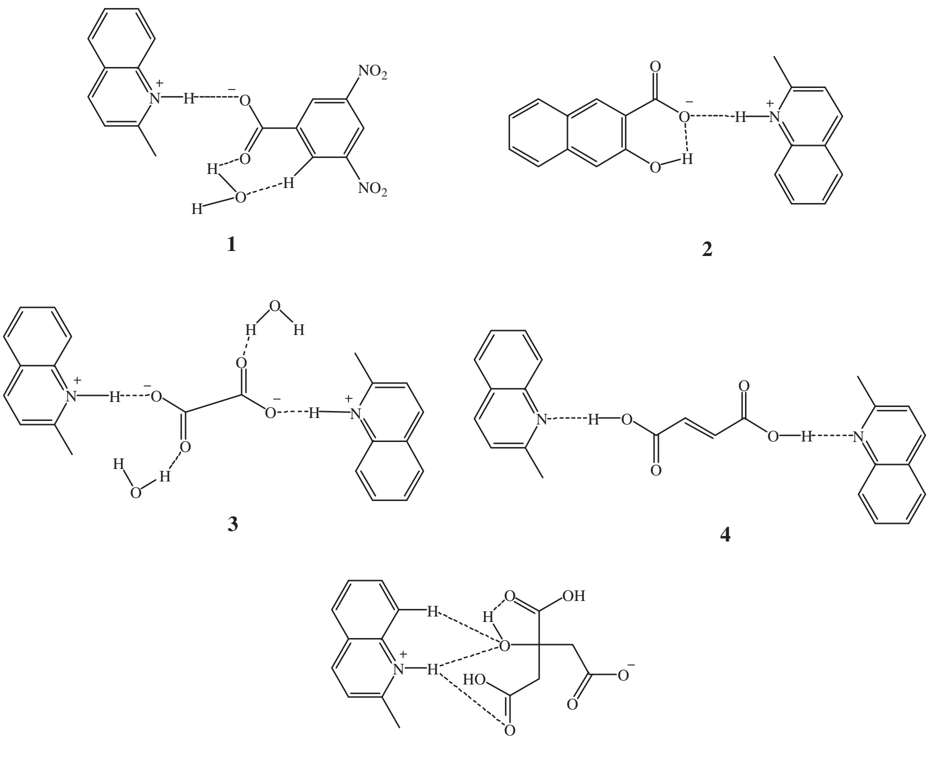


3,5-dinitrobenzoic acid 3-hydroxy-2-naphthoic acid oxalic acid



fumaric acid citric acid 2-methylquinoline

Scheme 1. Hydrogen bond synthons discussed in this paper.



1 2 3 4 5

Scheme 2. The five superamolecular compounds described in this paper, **1**–**5**.

2. Experimental section

2.1. Materials and methods

All reagents were commercially available and used as received. The C, H, and N microanalysis were carried out with a Carlo Erba 1106 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of supramolecular complexes

2.2.1. 2-Methylquinoline: (3,5-dinitrobenzoic acid): H_2O $[(HL^+)\cdot(dna^-)\cdot H_2O]$ (1)

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added 3,5-dinitrobenzoic acid (42.4 mg, 0.2 mmol) in 4 mL methanol. 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, light yellow block crystals were isolated after slow evaporation of the solution in

Table 1
Summary of X-ray crystallographic data for complexes **1**–**5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{17}H_{15}N_3O_7$	$C_{21}H_{17}NO_3$	$C_{11}H_{12}NO_3$	$C_{12}H_{11}NO_2$	$C_{16}H_{17}NO_7$
Fw	373.32	331.36	206.22	201.22	335.31
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	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*	*P2(1)/n*	*P2(1)/n*
a (Å)	12.5912(11)	13.0883(12)	6.9424(5)	7.4968(5)	7.5348(8)
b (Å)	7.2015(6)	6.7662(7)	12.1158(12)	11.5092(9)	12.8294(15)
c (Å)	18.8211(16)	18.8150(19)	11.7782(11)	12.6389(10)	16.9060(17)
α (°)	90	90	90	90	90
β (°)	99.3760(10)	93.7310(10)	93.0620(10)	105.7890(10)	94.0970(10)
γ (°)	90	90	90	90	90
V (Å^3)	1683.8(2)	1662.7(3)	989.28(15)	1049.37(14)	1630.1(3)
Z	4	4	4	4	4
D_{calcd} (Mg/m^3)	1.473	1.324	1.385	1.274	1.366
Absorption coefficient (mm^{-1})	0.117	0.089	0.102	0.087	0.108
F(000)	776	696	436	424	704
Crystal size (mm^3)	0.48 × 0.47 × 0.42	0.40 × 0.38 × 0.24	0.42 × 0.40 × 0.30	0.47 × 0.45 × 0.38	0.30 × 0.21 × 0.18
θ range (°)	2.52–25.02	2.59–25.02	2.41–25.01	2.44–25.02	2.42–25.01
Limiting indices	$-14 \le h \le 14$	$-10 \le h \le 15$	$-8 \le h \le 8$	$-8 \le h \le 8$	$-8 \le h \le 8$
	$-8 \le k \le 8$	$-7 \le k \le 7$	$-14 \le k \le 11$	$-13 \le k \le 13$	$-15 \le k \le 10$
	$-11 \le l \le 22$	$-22 \le l \le 22$	$-13 \le l \le 13$	$-13 \le l \le 15$	$-18 \le l \le 20$
Reflections collected	8008	7895	4811	5171	8053
Reflections independent (R_{int})	2972 (0.0377)	2903 (0.0639)	1733 (0.0370)	1847 (0.0437)	2863 (0.0690)
Goodness-of-fit on F^2	1.029	1.015	1.046	0.926	0.904
R indices [$I > 2\sigma I$]	0.0619, 0.1624	0.0565, 0.1301	0.0428, 0.1054	0.0466, 0.1222	0.0585, 0.1453
R indices (all data)	0.0961, 0.1984	0.1359, 0.1840	0.0785, 0.1344	0.0789, 0.1407	0.0998, 0.1694
Largest diff. peak and hole, *e*.Å^{-3}	0.379, −0.331	0.212, −0.207	0.219, −0.245	0.226, −0.146	0.280, −0.347

Table 2
Selected bond lengths (Å) and angles (°) for **1–5.**

1			
N(1)—C(2)	1.326(4)	N(1)—C(6)	1.361(4)
N(2)—C(14)	1.471(4)	N(3)—C(16)	1.458(4)
O(1)—C(11)	1.246(4)	O(2)—C(11)	1.215(4)
C(2)—N(1)—C(6)	123.6(3)		
2			
N(1)—C(13)	1.312(4)	N(1)—C(17)	1.369(4)
O(1)—C(1)	1.302(5)	O(2)—C(1)	1.231(4)
O(3)—C(4)	1.355(5)	C(13)—N(1)—C(17)	121.4(3)
O(2)—C(1)—O(1)	123.4(4)		
3			
N(1)—C(2)	1.324(3)	N(1)—C(6)	1.374(3)
O(1)—C(11)	1.238(3)	O(2)—C(11)	1.259(3)
C(2)—N(1)—C(6)	122.96(18)	O(1)—C(11)—O(2)	125.9(2)
4			
N(1)—C(4)	1.321(3)	N(1)—C(8)	1.383(2)
O(1)—C(1)	1.311(2)	O(2)—C(1)	1.224(3)
C(4)—N(1)—C(8)	119.93(17)	O(2)—C(1)—O(1)	124.4(2)
5			
N(1)—C(1)	1.337(4)	N(1)—C(5)	1.372(4)
O(1)—C(11)	1.205(3)	O(2)—C(11)	1.319(3)
O(3)—C(15)	1.262(3)	O(4)—C(15)	1.241(3)
O(5)—C(16)	1.316(3)	O(6)—C(16)	1.218(3)
O(7)—C(13)	1.431(3)	C(1)—N(1)—C(5)	124.7(3)
N(1)—C(1)—C(2)	118.0(3)	O(1)—C(11)—O(2)	123.4(3)
O(4)—C(15)—O(3)	123.0(3)	O(6)—C(16)—O(5)	125.2(2)

air. The crystals were dried in air to give the title compound [(HL$^+$)·(dna$^-$)·H_2O] (**1**), yield 64 mg, 85.72%. m. p. 168–170 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{17}H_{15}N_3O_7$ (373.32): C, 54.64; H, 4.02; N, 11.25. Found: C, 54.59; H, 3.92; N, 11.16. Infrared spectrum (KBr disk, cm^{-1}): 3638s(ν(OH)), 3456s(multiple, ν_{as}(NH)), 3323s(ν_s(NH)), 3112m, 3064m, 2960m, 1976w, 1836w, 1783w, 1662w, 1606s(ν_{as}(COO$^-$)), 1592m, 1526s(ν_{as}(NO$_2$)), 1466w, 1374s(ν_s(COO$^-$)), 1333s(ν_s(NO$_2$)), 1250m, 1195m, 1131m, 1079m, 952m, 903m, 853m, 806m, 757m, 726m, 680m, 635m.

Table 3
Hydrogen bond distances and angles in studied structures **1–5.**

D—H···A	d(D—H) (**Å**)	d(H···A) (**Å**)	d(D···A) (**Å**)	<(DHA) (°)
1				
O(7)—H(7D)···O(1)#1	0.85	1.89	2.708(4)	160.4
O(7)—H(7C)···O(2)	0.85	1.94	2.753(5)	160.6
N(1)—H(1)···O(1)	0.86	1.77	2.628(3)	173.2
2				
O(3)—H(3)···O(2)	0.82	1.86	2.592(4)	147.2
N(1)—H(1)···O(1)#1	0.86	1.72	2.575(3)	175.2
3				
O(3)—H(3D)···O(1)#1	0.85	2.05	2.892(3)	168.3
O(3)—H(3C)···O(1)#2	0.85	2.01	2.846(2)	168.4
N(1)—H(1)···O(2)	0.86	1.81	2.619(2)	156.7
4				
O(1)—H(1)···N(1)#2	0.82	1.80	2.603(2)	165.3
5				
O(7)—H(7)···N(1)#1	0.82	2.24	3.016(3)	156.9
O(7)—H(7)···O(6)	0.82	2.16	2.664(3)	119.8
O(5)—H(5)···O(3)#2	0.82	1.76	2.573(3)	168.6
O(2)—H(2)···O(4)#3	0.82	1.76	2.572(3)	171.4
N(1)—H(1)···O(7)#4	0.86	2.28	3.016(3)	143.7
N(1)—H(1)···O(6)#4	0.86	2.19	2.925(3)	143.1

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

2.2.2. 2-Methylquinoline : (3-hydroxy-2-naphthoic acid) [(HL)$^+$ ·(npa$^-$)] (2)

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added 3-hydroxy-2-naphthoic acid (36.4 mg, 0.2 mmol) in 8 mL ethanol. Colorless crystals were afforded after several days of slow evaporation of the solvent. The crystals were

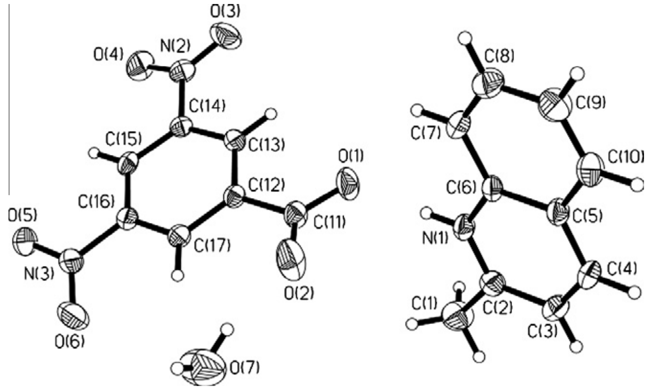


Fig. 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

dried in air to give the title compound $[(HL)^+\cdot(npa^-)]$ (**2**), yield: 64 mg, 96.57%. mp 192–194 °C. Elemental analysis: Calc. for $C_{21}H_{17}NO_3$ (331.36): C, 76.05; H, 5.13; N, 4.23. Found: C, 76.02; H, 5.06; N, 5.04. Infrared spectrum (KBr disk, cm^{-1}): 3596s(ν(OH), 3460s(ν_{as}(NH)), 3348s(ν_s(NH)), 3028m, 2928m, 1650m, 1616m, 1576s(ν_{as}(COO^-)), 1510m, 1480s, 1442m, 1368s(ν_s(COO^-)), 1296m, 1228s, 1180m, 1050m, 1016m, 967m, 882m, 818m, 740m, 688m, 622m.

2.2.3. 2-Methylquinoline: (oxalic acid)$_{0.5}$: H_2O $[(HL)^+\cdot(oa^{2-})_{0.5}\cdot H_2O]$ (3)

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added oxalic acid (25.4 mg, 0.2 mmol) in 3 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent. The crystals were dried in air to give the title compound $[(HL)^+\cdot(oa^{2-})_{0.5}]\cdot H_2O$ (**3**), yield: 32 mg, 77.59%(Based on L). mp 142–143 °C. Elemental analysis: Calc. for $C_{11}H_{12}NO_3$ (206.22): C, 40.09; H, 5.82; N, 6.79. Found: C, 40.02; H, 5.76; N, 6.74. Infrared spectrum (KBr disk, cm^{-1}): 3678s(ν(OH)), 3472s(ν_{as}(NH)), 3384s(ν_s(NH)), 2938m, 1642s, 1587s(ν_{as}(COO^-)), 1518m, 1401s, 1382s(ν_s(COO^-)), 1284m, 1232s, 1097s, 1036w, 962m, 848m, 792s, 728s, 662m, 614m.

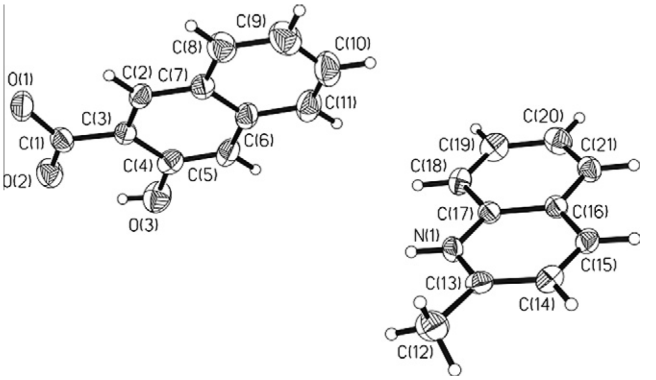


Fig. 3. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

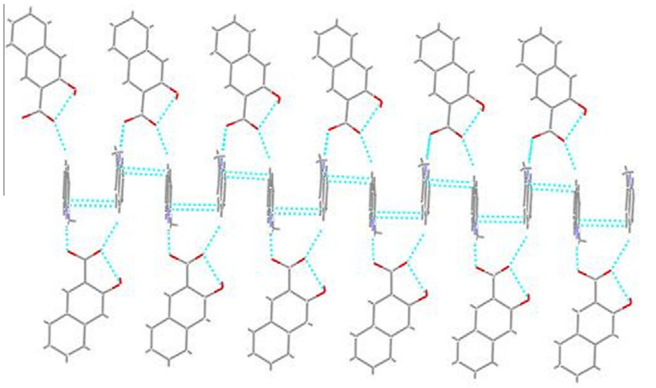


Fig. 4. The 1D chain structure of **2** running along the *b* axis direction formed by the cations via the π–π interaction, the anions were attached to the chain via N—H···O hydrogen bonds.

2.2.4. 2-Methylquinoline : (fumaric acid)$_{0.5}$ $[(L)\cdot(H_2fum)_{0.5}]$ (4)

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added fumaric acid (24 mg, 0.2 mmol) in 5 mL methanol. The solution was stirred for 10 min, then the solution

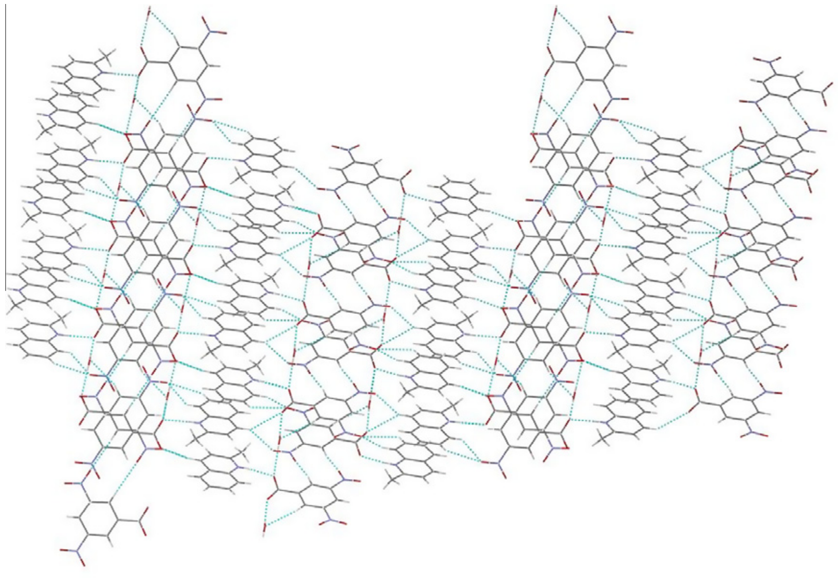


Fig. 2. 2D corrugated sheet structure of **1** extending parallel to the ab plane.

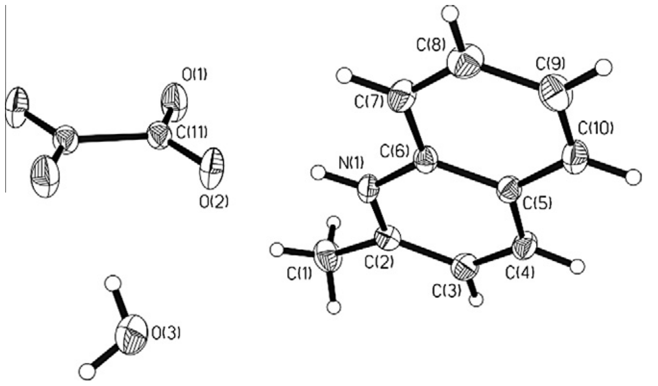


Fig. 5. The structure of **3**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

was filtered. The solution was left standing at room temperature for several days, colorless block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the title compound [(L)·(H_2fum)$_{0.5}$] (**4**), yield 34 mg, 84.48%(Based on L). m. p. 188–189 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for $C_{12}H_{11}NO_2$(201.22): C, 71.56; H, 5.47; N, 6.96. Found: C, 71.48; H, 5.44; N, 6.92. Infrared spectrum (KBr disk, cm^{-1}): 3518s(ν(OH)), 3064m, 2960m, 2492m(broad), 1976w, 1908m(broad), 1836w, 1783w, 1718s(v(C=O)), 1662w, 1596m, 1530m, 1486w, 1333m, 1286s(ν(C—O)), 1250m, 1195m, 1131m, 1079m, 952m, 903m, 853m, 806m, 757m, 726m, 692m, 654m, 606m.

2.2.5. 2-Methylquinoline: (citric acid) [(HL)$^+$·(H_2ctc$^-$)] (5)

To a methanol solution (2 mL) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added citric acid (42 mg, 0.2 mmol) in 6 mL ethanol. Colorless crystals were afforded after several days of slow evaporation of the solvent. The crystals were dried in air to give the title compound [(HL)$^+$·(H_2ctc$^-$)] (**5**), yield: 54 mg, 80.52%. mp 122–123 °C. Elemental analysis: Calc. for $C_{16}H_{17}NO_7$(335.31): C, 57.26; H, 5.07; N, 4.17. Found: C, 57.19; H, 4.94; N, 4.09. Infrared spectrum (KBr disk, cm^{-1}): 3624s(ν(OH)), 3462s(multiple, ν_{as}(NH)), 3346(br, ν_s(NH)), 3060m, 2990m, 2920m, 1964w, 1842w, 1776w, 1735m, 1672vs(v(C=O)), 1604s(ν_{as}(COO^-)), 1565m, 1522m, 1486s, 1424s, 1392s(ν_s(COO^-)), 1358m, 1300m, 1287s(ν(C—O)), 1244m, 1198m, 1134m, 1106m, 1054m, 1026m, 936m, 853m, 798m, 736m, 676m, 624m.

2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data collections and reductions were performed using the SMART and SAINT software [20,21]. 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 [22]. 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 complexes **1**–**5** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

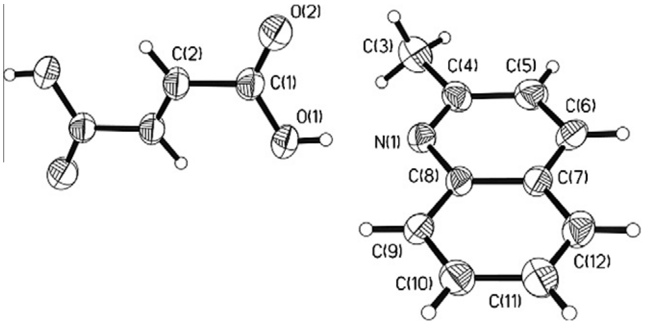


Fig. 7. The structure of **4**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

3. Results and discussion

3.1. Syntheses and general characterization

For the preparation of **1**–**5**, the carboxylic acids were mixed directly with the 2-methylquinoline in 1:1 ratio in methanol and/or ethanol solvents, which was allowed to evaporate at ambient conditions to give the final crystalline products. The molecular structures and their atom labeling schemes for the five structures are shown in Figs. 1, 3, 5, 7, and 9, respectively.

The elemental analyses for the five compounds are in good agreement with their compositions. The infrared spectra of **1**–**5** are consistent with their chemical formulas determined by elemental analysis and further confirmed by X-ray diffraction analysis. The very strong and broad features at 3700–3300 cm^{-1} arise from O—H or N—H stretching frequencies. Aromatic and quinoline ring stretching and bending are in the regions of 1500–1630 cm^{-1} and 600–750 cm^{-1}, respectively. All of the compounds except **4** show the characteristic bands for COO^-, and compounds **4**, and **5** display strong IR peaks for COOH groups. The presence of two broad bands at ca. 2500 cm^{-1} and 1900 cm^{-1} in compound **4**, characteristic of a neutral O—H···N

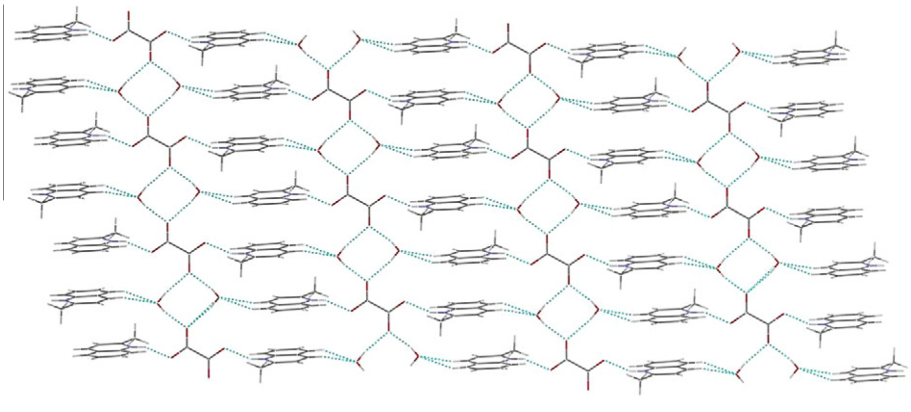


Fig. 6. 2D sheet structure of **3** which was extending on the ac plane.

hydrogen-bond interaction, was viewed as evidence for co-crystal formation [23]. Except for the above bands, for **1**, the bands at ca. 1526 and 1333 cm^{-1} were attributed to the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively [24].

IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds [25]. The most distinct feature in the IR spectrum of proton transfer compounds is the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1550–1610 cm^{-1} and 1300–1420 cm^{-1} [26].

3.2. X-ray structure of 2-methylquinoline: (3,5-dinitrobenzoic acid): H_2O [$(HL^+)\cdot(dna^-)\cdot H_2O$] (1)

The compound **1** of the composition [$(HL^+)\cdot(dna^-)\cdot H_2O$] was prepared by reaction equal mol of 2-methylquinoline and 3,5-dinitrobenzoic acid, in which the proton of 3,5-dinitrobenzoic acid was transferred to the ring N atom of the quinoline. This structure is a solvate. The asymmetric unit of **1** contains one cation of 2-methylquinolinium, an anion of 3,5-dinitrobenzoate, and a water molecule as shown in Fig. 1.

The r.m.s deviations of the aromatic rings in the cation and the anion from the mean planes of the corresponding rings are 0.0147 Å, and 0.0057 Å, respectively. The dihedral angle between the benzene ring of the anion and the quinoline ring of the cation is 113.4°. The carboxylate deviated by 14° from the benzene ring of the anion. The two nitro groups deviated by 172.4° (for the group N2—O3—O4), and 9.2° (for the group N3—O5—O6) from the mean plane of the anion benzene ring unit, respectively.

The C—O distances of COO^- of the 3,5-dinitrobenzoate are ranging from 1.215(4) (O(2)—C(11)) to 1.246(4) Å (O(1)—C(11)). The difference (Δ is 0.031 Å) in bond distances between O(1)—C(11) and O(2)—C(11) in the carboxylate group in compound **1** is expected for ionized carboxyl group. The angle C(2)—N(1)—C(6) around the protonated N atom is 123.6(3)°, which is similar to the value in the protonated L [27].

The ionic N—H···O hydrogen bond is formed between the oxygen atom of the carboxylate and the NH^+ group (N(1)—H(1)···O(1), 2.628(3) Å). Two anions formed a dimer via a pair of intermolecular CH—O associations between the benzene CH and the nitro group with C—O distance of 3.487 Å. For the presence of such interactions the two anions generated a $R_2^2(8)$ ring motif according to Bernstein [28].

The parallel anion dimers were stacked along the *a* axis direction and joined together via the water molecules by the O—H···O hydrogen bond between the water molecule and the carboxylate with O—O separation of 2.708(4) and 2.753(5) Å respectively, and CH—O interaction between the benzene CH of the anion and the Ow atom with C—O distance of 3.532 Å to form a 1D ladder structure. The cations were bonded to the ladders by the N—H···O and CH—O interactions to form 2D corrugated sheet extending parallel to the ab plane (Fig. 2). In the sheet the anion ladders and the cations alternate, the adjacent ladders were not parallel to each other, and they made an angle of ca 30° with each other, while the third ladder is parallel to the first ladder, so does the second ladder and the fourth ladder. The adjacent cations intercalated between the same pair of anion ladders are antiparallelly arranged, while the cations intercalated between different pairs of ladders were parallel to each other. The corrugated sheets were further stacked along the *c* axis direction through the O–π interaction between the nitro group and the benzene ring of the anion with O—Cg distance of 3.033 Å, and CH_3—O interaction between the methyl group of the cation and the Ow atom with C—O distance of 3.261 Å to form 3D layer network structure.

3.3. X-ray structure of 2-methylquinoline: (3-hydroxy-2-naphthoic acid) [$(HL)^+\cdot(npa^-)$] (2)

Similar to compound **1**, the compound **2** is also an organic salt. In **2** the asymmetric unit is occupied by one anion of 3-hydroxy-2-naphthoate, and one cation of 2-methylquinolinium $(HL)^+$ (Fig. 3).

The rms deviation of the cation excluding the methyl group is 0.0073 Å. The rms deviation of the benzene ring of the anion is 0.00146 Å. Both planes make dihedral angle of 109.5(3)°. The C—O bond distance (O(3)—C(4) 1.355(5) Å) is in the range of the neutral C—O bond distance in the phenol derivatives (1.344 (3) – 1.357 (3) Å) [29].

In the COO^- group, the two C—O bond lengths are significantly different between O(2)—C(1) (1.231(4) Å) and O(1)—C(1) (1.302(5) Å) (Δ is 0.071 Å) The relative large Δ value is attributed to the fact that the O1 atom involves more strong hydrogen bond than that of O2 (Table 3). The angle [121.4(3)°] around the protonated N atom (N1) is smaller than the corresponding angle in compound **1** [123.6(3)°], and the saccharate salt of 2-methylquinoline (123.7(3)°) [30]. This may be due to the difference of the hydrogen bonding strength in the corresponding compound.

The cations formed a 1D chain along the *b* axis direction via the π–π interaction between the aromatic rings with centroid separation of 3.394 Å. In the cation chain, the neighboring cations were antiparallelly arranged, while the third cation is parallel to the first cation. So does the second cation and the fourth cation. The anions were bonded to the cation chain through the N—H···O hydrogen bond between one O atom of the carboxylate and the NH^+ of one cation and CH—O association between the other O atom of the same carboxylate and the 5-CH of the neighboring cation with C—O distance of 3.449 Å (Fig. 4). The carboxylate also made an intramolecular O—H···O contact to form a ring with descriptor of $S_1^1(6)$. It is worthy to note that the anions at the same side of the cation chain were parallel to each other, while the anions at different sides of the cation chain intersect at an angle of ca. 60° with each other.

3.4. X-ray structure of 2-methylquinoline: (oxalic acid)$_{0.5}$: H_2O [$(HL)^+\cdot(oa^{2-})_{0.5}\cdot H_2O$] (3)

The crystal structure of **3** consists of half a dianion of oxalic acid, one cation of 2-methylquinolinium, and one water molecule in the asymmetric unit (Fig. 5). The proton of the COOH group has transferred to the ring N atom of the quinoline moiety. The assignment of **3** as a salt is based on successful refinement of the relevant H atoms using X-ray data. This is further verified by the C—O distances [(O(1)—C(11), 1.238(3) Å), O(2)—C(11), 1.259(3) Å with Δ = 0.021 Å] in the carboxylate group, which is in the range for the O—C distances concerning the deprotonated carboxyl groups. In the compound, there is one ion pair with one water molecule, which fits well with the micro-analysis results.

The C—N—C angles of pyridine are very sensitive to protonation [31,32]. A pyridinium cation always possesses an expanded angle of C—N—C in comparison with the parent pyridine. The hydrogen atom H(N1), which is deprived from its parent, attaches the nitrogen atom. In the cations, the angle C(6)—N(1)—C(2) [122.96(18)°] is similar to the value in its hydrochloride salt (123.6) [27]. Yet it is slightly larger than the corresponding CNC angle in the compound **2** (121.4(3)°).

The anions and the water molecules were joined together through the O—H···O hydrogen bond between the water molecules (donor) and the carboxylate group (acceptor) with O—O separations of 2.846(2) Å, and 2.892(3) Å, respectively to form a 1D chain running along the *a* axis direction. Herein the anions at adjacent chains were slipped some distance from each other along the *a* axis direction, while the anions at the third chain and the anions at the first

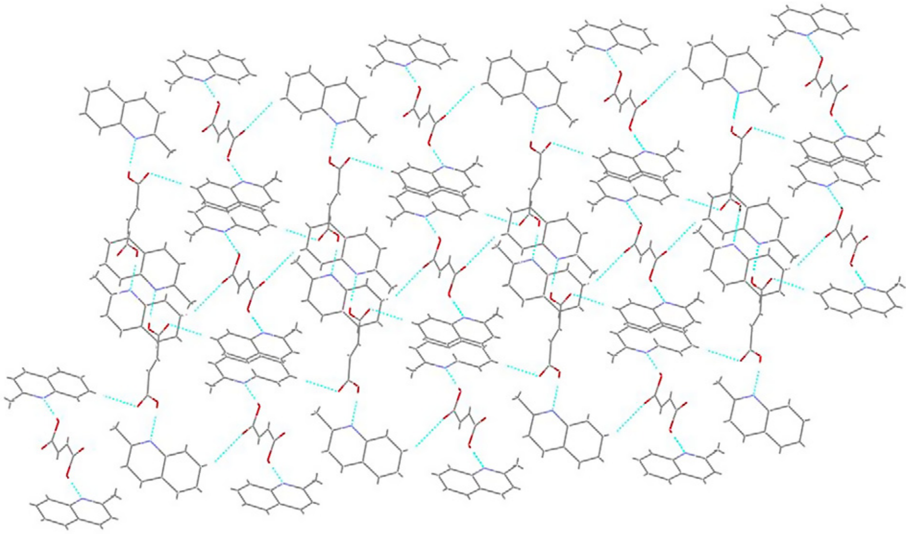


Fig. 8. 2D corrugated sheet structure of **4**.

chain were almost in the same line when viewed from the *c* axis direction. Such kind of discrete chains were arranged parallelly on the ac plane. Between the two neighboring chains the cations are intercalated through the ionic $N—H^{+}\cdots O^{-}$ hydrogen bond (N(1)—H(1)···O(2), 2.619(2) Å) between the NH^{+} cation and the carboxylate and CH—O interactions between the water molecule and the 4-CH, and 5-CH of the cation with C—O distance of 3.298–3.417 Å to form a 2D sheet structure extending on the ac plane (Fig. 6). Here the water molecule acts as bidentate acceptor forming two CH—O contacts in bifurcate mode. At the same sheet the adjacent cations intercalated between the same pair of anion chains were antiparallelly arranged, while the third cation and the first cation between the same pair of anion chains were parallelly arranged. In the sheet there are four-membered O rings composed by two water molecules and two O atoms of two adjacent oxalates.

Such kind of sheets were further stacked along the *b* axis direction via the intersheet CH—O association between 3-CH of the cation and the carboxylate with C—O distance of 3.524 Å and CH_3—O interactions between the 2-CH_3 of the cation and the carboxylate with C—O distance of 3.556 Å to form a 3D ABAB layer network structure. Here the third sheet layer has the same projection on the ac plane as the first sheet layer, so does the second sheet layer and the fourth sheet layer.

3.5. X-ray structure of 2-methylquinoline: (fumaric acid)$_{0.5}$ [(L)·(H_2fum)$_{0.5}$] (4)

Similar to the above compounds, compound **4** was prepared by reaction of a methanol solution of fumaric acid and 2-methylquinoline in 1:1 ratio, which crystallizes as Monoclinic colorless crystals in the centrosymmetric space group *P2(1)/n*. The asymmetric unit of **4** consists of one molecule of 2-methylquinoline and half a molecule of fumaric acid, as shown in Fig. 7.

This is a cocrystal where the COOH groups of fumaric acid are not ionized by proton transfer to the nitrogen atom (N(1)) of the 2-methylquinoline moieties, which is also confirmed by the bond distances of O(1)—C(1) (1.311(2) Å) and O(2)—C(1) (1.224(3) Å) which are typical bond distances for protonated carboxyl groups.

The mean values of the C—C and N—C bond lengths in the ring of the 2-methylquinoline are 1.394 (3) and 1.352 (2) Å respectively, which are between that of a single bond and a double bond and agree with those values in the literature [33].

The angle of C(4)—N(1)—C(8) [119.93(17)°] is smaller than the corresponding angle (123.6°) in the protonated L [27], and the corresponding value in compounds **1**–**3**, which also conforms our correct assignment of **4** as a cocrystal.

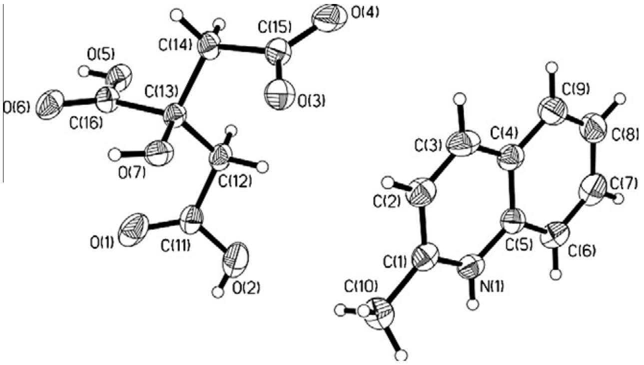


Fig. 9. The structure of **5**, showing the atom-numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

At each fumaric acid there are bonded two 2-methylquinoline through the neutral O—H···N hydrogen bond with N—O distance of 2.603(2) Å, which is considerably less than the sum of the van der Waals radii for N and O (3.07 Å) [34]. One of the shortest known O—H···N hydrogen bonds was observed in the crystal structure of 4-methylpyridine and pentachlorophenol [35] with the O···N distance of 2.506 (3) Å at 20 K. Similarly, the title crystal is also an example of a system with short O···H···N hydrogen bond (with the O···N distance being 2.603(2) Å).

Two 2-methylquinoline and one fumaric acid form a heteroadduct. In the heteroadducts there are inversion centers located at the middle point of the olefinic group in the fumaric acid. So the two 2-methylquinoline molecules are antiparallelly arranged. Such kind of heteroadducts were linked together via CH—O associations between the 7-CH of the 2-methylquinoline and the carbonyl moiety of the fumaric acid with C-O distance of 3.457 Å to form 2D corrugated sheet structure (Fig. 8).

3.6. X-ray structure of 2-methylquinoline: (citric acid) $[(HL)^{+}\cdot(H_2ctc^{-})]$ (5)

Similar to **1**–**4**, the compound $[(HL)^{+}$ $(H_2ctc^{-})]$ **(5)** was also prepared by reaction of 2-methylquinoline with citric acid in 1:1 ratio, which crystallizes as monoclinic block crystals in the centrosymmetric space group *P2(1)/n*. The compound consists of one

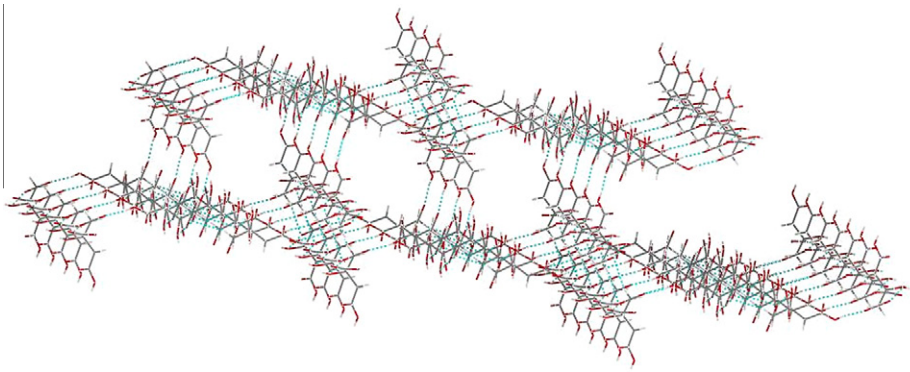


Fig. 10. 2D corrugated anionic sheet structure of **5** which is extending along the direction that made an angle of ca. 45° with the ac plane.

2-methylquinolin-1-ium cation, and one dihydrogen citrate anion (Fig. 9). In **5** the citric acid is singly deprotonated to exhibit valence number of -1. The present investigation clearly shows that the compound is also an organic salt. The proton coming from the carboxylic H of the citric acid in compound **5** is on the ring nitrogen atom, forming an ion pair, which is similar to that of the proton transfer compound assembled from citric acid and 2,4,6-triamine-1,3,5-triazine [36]. Unlike the adduct of citric acid and 2,4,6-triamine-1,3,5-triazine [36], in **5** only one terminal COOH carboxyl group is ionized. And in this case the order of ionization of the citric acid [37] does not agree with the previous published results that the central carboxyl group is the first ionized carboxyl group.

As shown in Table 3, all the bond angles and bond distances are in the normal range. The O—C bond distances of the carboxylate group were 1.262(3) (O(3)—C(15)), and 1.241(3) Å (O(4)—C(15)) respectively. The difference between the two C—O bonds is 0.021 Å which is in the range of the reported Δ value for organic salts formed between the carboxylic acid and the N-containing base [38], which is also expected for ionic C—O bond distances. The two carboxyl groups both have C=O and C—O bond distances indicative of an unionized character, in which no Hs transfer has occurred to the quinoline N atom. The ratio of C—O(long) to C=O (short) bond distances are 1.0804, and 1.0946, respectively, for the two carboxyl groups on C(16), and C(11). These values are characteristic for unionized COOH (ionized COOH groups have a lower ratio of about 1.030, here it is 1.0169 for the deprotonated COOH) [39]. It is clear that the Δ value in bond lengths of C—O within the COOH group (Δ are 0.098, and 0.114 Å) is larger than the one found in the carboxylate group (0.021 Å), which also confirms the monoionization of the tricarboxylic acid.

The plane defined by the central hydroxyl and carboxyl groups is almost perpendicular to the plane of the C atom backbone (82.7(2)°), yet the dihedral angle between these two planes is somewhat smaller than what was found for the 1:1 adduct of trimethylglycine and citric acid [40].

The planes of the two end carboxyl groups lie at angles of 16.4 (for C11—O1—O2) and 76.7° (for C15—O3—O4) respectively with the C atom backbone, and they made a dihedral angle of 74.1° with each other. The dihydrogen citrate anion assumes a conformation not previously observed in the solid, with one terminal carboxyl (C11—O1—O2) and the middle carboxyl group (C16—O5—O6) almost perpendicular to each other (the dihedral angle between the two groups is 88.5°). While another carboxylate group (C15—O3—O4) and the middle carboxyl group (C11—O1—O2) intersect at an angle of ca. 149.9° with each other. In this case the dihedral angle is significantly larger than the corresponding angle in anhydrous 1:1 cocrystal of citric acid and caffeine (17.5°) [41].

The anions were connected together by the intermolecular O—H⋯O interaction between the middle carboxyl unit of one anion and the terminal carboxylate of its adjacent anion with O—O separation of 2.573(3) Å to form a 1D chain running along the *a* axis direction. Two neighboring chains were linked together via the interchain O—H⋯O associations between the terminal carboxylate group of one chain and the terminal carboxyl group of its neighboring chain to form a double chain structure. Such double chains were further combined together via the CH_2—O interaction between the CH_2 group of the anion and the carboxylate with C—O distance of 3.500 Å to form a tetrachain structure running along the *a* axis direction. In the tetrachain the middle two chains are almost in the same plane, while the outer two chains were protruded from the plane defined by the middle two chains. Such kinds of tetrachains were joined together along the *c* axis direction via CH_2—O interactions with C—O distance of 3.500 Å to form 2D corrugated sheet structure extending along the direction that made an angle of ca. 45° with the ac plane (Fig. 10). Such kind of sheets were further stacked along the *b* axis direction via the intersheet O—H⋯O interactions between the terminal carboxyl group of one sheet layer and the terminal carboxylate group of its neighboring sheet layer with O—O distance of 2.575(3) Å to form 3D network structure with channels. In the channels there are cations which is bound to the anion network through N—H⋯O hydrogen bond (between the NH^+ cation and the carbonyl unit of the middle carboxyl group in the anion with N—O distance of 2.925(3) Å, and between the alcohol hydroxyl group of the anion and the same NH^+ cation with N—O distance of 3.016(3) Å), CH—O interaction (between the 8-CH of the cation and the alcohol hydroxyl moiety with C—O distance of 3.256 Å), and CH_3—O interaction (between the 2-CH_3 of the cation and the carboxylate with C—O distance of 3.298 Å) to form 3D network structure with reduced channels.

4. Conclusion

Single crystal X-ray diffraction has enabled the elucidation of five examples of 2-methylquinoline-carboxylic acid adducts, novel contributions to the extensive research into the occurrence of carboxylic acid-quinoline compound motifs in organic salts or cocrystal. In their place are a series of motifs in which extensive strong classical N—H⋯O/O—H⋯N hydrogen bonds (ionic or neutral) combine with weaker interactions (CH—O, CH_2—O, and CH_3—O). This variety, coupled with the varying geometries and number of COOH groups of the carboxylic acids employed, has led to the creation of a range of supramolecular arrays, from 1D chain structure, to 2D sheet structure, and 3D network structure.

In the compounds **1**, **2**, **3**, and **5**, the 2-methylquinolinium cations function as acceptors for ionic hydrogen bonds that organize and orient the anions, while in compound **4** 2-methylquinoline fragments function as acceptors for neutral hydrogen bonds. This phenomenon may be explained by the rule “strongest donor to strongest acceptor". For the carboxylic acids present in **1**–**4**, the fumaric acid has the relatively larger Pka (Pka_1) which may led the ΔPka (between the L and the carboxylic acid) to be out of the range for salt formation. Although citric acid in **5** has the similar Pka (Pka_1) with the fumaric acid in **4**, this molecule (citric acid) may be too flexible introducing factors that result more important than the small difference between the donors to decide the preferred molecular interactions.

This study has demonstrated that the N—H···O/O—H···N hydrogen bond is the primary intermolecular force in a family of structures containing the $OH \cdots N_{quinoline}$ synthons. The secondary C—H···O hydrogen bonds were observed in all compounds. CH_3—O interactions are found in compounds **1**, **3**, and **5**. Compound **1** possesses O–π interaction, while there are π–π interactions in compound **2**.

The results presented herein indicate that the strength and directionality of the N^+—H···O^-, O—H···O, and O—H···N hydrogen bonds (ionic or neutral) between carboxylic acids and 2-methylquinoline are sufficient to bring about the formation of binary organic salts or cocrystals.

5. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 851592 for **1**, 836676 for **2,** 836679 for **3**, 835832 for **4**, and 841400 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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