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Crystal and molecular structure of four 1:1 adducts from 2-methylquinoline and different acidic components

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ABSTRACT

Four 2-methylquinoline derived supramolecular complexes [2-methylquinoline: (2,4,6-trinitrophenol) [(HL)⁺ · (pic⁻), pic⁻ = picrate, L = 2-methylquinoline] (**1**), 2-methylquinoline: (5-nitrosalicylic acid) [(HL)⁺ · (5-nsa⁻), 5-nsa⁻ = 5-nitrosalicylate] (**2**), 2-methylquinoline: (5-sulfosalicylic acid): H₂O [(HL)⁺ · (5-ssa⁻). H₂O, 5-ssa⁻ = 5-sulfosalicylate] (**3**), and 2-methylquinoline: (trimesic acid) [(L)···(Tma), Tma = trimesic acid] (**4**) were synthesized and structurally characterized by X-ray crystallography.

All supramolecular architectures of **1–4** involve extensive classical hydrogen bonds as well as other noncovalent interactions. The results presented herein indicate that the strength and directionality of the N–H···O, O–H···N, and O–H···O hydrogen bonds (ionic or neutral) between acidic components and 2-methylquinoline are sufficient to bring about the formation of binary organic acid–base adducts. The role of weak and strong noncovalent interactions in the crystal packing is ascertained. These weak interactions combined, the complexes **1–4** displayed 2D–3D framework structure.

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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 extensively studied [4,5], with particular attention to their spectral [6], and structural [7,8] features.

Because of the predictable supramolecular properties and the ability to form strong hydrogen bonds, carboxylic acids were frequently chosen as building blocks for crystal engineering [9–11]. Numerous heterodimers composed of carboxylic acids and a variety of N-containing basic building blocks have been documented recently [12–16]. The hydrogen bonding between hydroxyl groups of carboxylic acids and heterocyclic nitrogen atoms has been proved to be a useful and powerful organizing force for the formation of supramolecules. It should be noted that these structures are normally held together by hydrogen-bonding, and in this regard, the most frequently used moieties with hydrogen bonding capability are pyridyl and carboxyl. As a pyridyl derivative, besides the methyl group, 2-methylquinoline bears more aromatic π electrons, which can be a better group 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 [17–19], herein we report the synthesis and crystal structure of four supramolecular complexes assembled through hydrogen bonding interactions between acidic synthons and 2-methylquinoline. In this study, we got four organic acid–base adducts composed of acidic units and 2-methylquinoline (Scheme 1), namely 2-methylquinoline: (2,4,6-trinitrophenol) [(HL)⁺ · (pic⁻), pic⁻ = picrate, L = 2-methylquinoline] (1), 2-methylquinoline: (5-nitrosalicylic acid) [(HL)⁺ · (5-nsa⁻), 5-nsa⁻ = 5-nitrosalicylate] (2), 2-methylquinoline: (5-sulfosalicylic acid): H₂O [(HL)⁺ · (5-ssa⁻). H₂O, 5-ssa⁻ = 5-sulfosalicylate] (3), and 2-methylquinoline: (trimesic acid) [(L) · (Tma), Tma = trimesic acid] (4).

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.





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Scheme 1. Hydrogen bond synthons discussed in this paper.

2.2. Preparation of supramolecular complexes

2.2.1. 2-Methylquinoline: $(2,4,6-trinitrophenol) [(HL)^+ \cdot (pic^-)]$ (1)

To a methanol solution (2 ml) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added 2,4,6-trinitrophenol (46 mg, 0.2 mmol) in 10 mL methanol. The solution was stirred for 10 min, then the solution was filtered into a test tube. The solution was left standing at room temperature for several days, yellow block crystals were isolated after slow evaporation of the solution in air. The crystals were dried in air to give the title compound $[(HL^+) \cdot (pic)^-]$ (1), yield 64 mg, 85.95%. mp 168–169 °C. Elemental analysis performed on crystals exposed to the atmosphere: Calc. for C₁₆H₁₂N₄O₇ (372.30): C, 51.57; H, 3.22; N, 15.04. Found: C, 51.52; H, 3.16; N, 14.94. Infrared spectrum (KBr disc, cm^{-1}): 3464s($v_{as}(NH)$), 3234s(v_s(NH)), 3188s, 3112s, 2936 m, 2870 m, 2822 m, 2376 m, 2322 m, 1740 m, 1666s, 1604s, 1556s, 1523s(v_{as}(NO₂)), 1474 m, 1438 m, 1354s, 1322s(v_s(NO₂)), 1256s, 1202 m, 1148 m, 1082 m, 1021 m, 974 m, 916 m, 876 m, 837 m, 786 m, 718 m, 676 m, 620 m.

2.2.2. 2-Methylquinoline: $(5-nitrosalicylic acid) [(HL)^+ \cdot (5-nsa^-)]$ (2)

To a methanol solution (2 ml) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added 5-nitrosalicylic acid (36.6 mg, 0.2 mmol) in 4 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 57 mg, 87.34%. mp 192–193 °C. Elemental analysis: Calc. for $C_{17}H_{14}N_2O_5$ (326.30): C, 62.52; H, 4.29; N, 8.58. Found: C, 62.46; H, 4.22; N, 8.54. Infrared spectrum (KBr disc, cm⁻¹): 3646s (v(OH)), 3466s(multiple, v_{as} (NH)), 3348s(v_{s} (NH)), 3122 m, 3056 m, 2942 m, 2854 m, 2726 m, 2464w, 2366 m, 2224 m, 1982w, 1834w, 1782w, 1584s(v_{as} (COO⁻)), 1524s(v_{as} (NO₂)), 1486w, 1392s(v_{s} (COO⁻)), 1364 m, 1318s(v_{s} (NO₂)), 1268 m, 1189 m, 1121 m, 1068 m, 972 m, 904 m, 856 m, 808 m, 762 m, 694 m, 626 m.

2.2.3. 2-Methylquinoline: (5-sulfosalicylic acid): $H_2O[(HL)^+ \cdot (5\text{-ssa}^-) \cdot H_2O](\mathbf{3})$

To a methanol solution (2 ml) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added 5-sulfosalicylic acid (43.6 mg, 0.2 mmol) in

6 mL ethanol. Colorless crystals were afforded after several days of slow evaporation of the solvent, yield: 64 mg, 84.35%. mp 142–144 °C. Elemental analysis: Calc. for $C_{17}H_{17}NO_7S$ (379.38): C, 53.77; H, 4.48; N, 3.69; S, 8.43. Found: C, 53.72; H, 4.39; N, 3.64; S, 8.38. Infrared spectrum (KBr disc, cm⁻¹): 3596s(v(OH)), 3468s(multiple, v_{as}(NH)), 3366s(v_s(NH)), 3112 m, 3062 m, 2954 m, 2842 m, 2716 m, 2464w, 2368 m, 2216 m, 1972w, 1836w, 1786w, 1716s(v_{as}(C=O)), 1664w, 1532 m, 1476w, 1262s(v_s(C-O)), 1186 m, 1120 m, 1058 m, 956 m, 902 m, 855 m, 806 m, 748 m, 678 m, 616 m.

2.2.4. 2-Methylquinoline: (trimesic acid) [L · Tma] (4)

To a methanol solution (2 ml) of 2-methylquinoline (28.6 mg, 0.2 mmol) was added trimesic acid (42 mg, 0.2 mmol) in 8 mL ethanol. Colorless prisms were afforded after several days of slow evaporation of the solvent, yield: 50 mg, 70.76%. mp 204–206 °C. Elemental analysis: Calc. for $C_{19}H_{15}NO_6(353.32)$: C, 64.53; H, 4.24; N, 3.96. Found: C, 64.51; H, 4.22; N, 3.87. Infrared spectrum (KBr disc, cm⁻¹): 3576s(v(OH)), 3146 m, 3106 m, 3085 m, 3065 m, 2496w, 1898w, 1712s(v_{as}(C=O)), 1681 m, 1659 m, 1615 m, 1586 m, 1557 m, 1264s(v_s(C=O)), 1192 m, 1032 m, 986 m, 924 m, 872 m, 823 m, 786 m, 745 m, 707 m, 658 m, 618 m.

2.3. X-ray crystallography

Suitable crystals were performed on a Bruker SMART 1000 CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ 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 the four structures were generated geometrically. Further details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for complexes **1–4** are listed in Table 2, the relevant hydrogen bond parameters are provided in Table 3.

Table 1	
Summary of X-ray crystallographic data for con	nplexes 1-4.

	1	2	3	4
Formula	C ₁₆ H ₁₂ N ₄ O ₇	C ₁₇ H ₁₄ N ₂ O ₅	C ₁₇ H ₁₇ NO ₇ S	C ₁₉ H ₁₅ NO ₆
Fw	372.30	326.30	379.38	353.32
Т, К	298(2)	298(2)	298(2)	298(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P-1	P-1	P2(1)/c	P-1
a, Å	8.1184(9)	7.1158(6)	8.8164(6)	9.1239(8)
b, Å	9.2331(11)	9.5738(8)	14.3480(16)	13.4631(12)
<i>c</i> , Å	11.7013(16)	11.7604(12)	14.0002(13)	14.5106(16)
α, deg.	71.0570(10)	80.3870(10)	90	73.3720(10)
β , deg.	76.0760(10)	72.9660(10)	104.4390(10)	76.6220(10)
γ, deg.	84.359(2)	87.811(2)	90	88.549(2)
V, Å ³	805.03(17)	755.23(12)	1715.1(3)	1659.9(3)
Ζ	2	2	4	4
D_{calcd} , Mg/m ³	1.536	1.435	1.469	1.414
Absorption coefficient, mm ⁻¹	0.124	0.108	0.230	0.107
F(000)	384	340	792	736
Crystal size, mm ³	$0.42 \times 0.35 \times 0.13$	$0.49 \times 0.48 \times 0.45$	$0.47 \times 0.40 \times 0.25$	$0.47 \times 0.32 \times 0.21$
θ range, deg	1.89-25.02	2.60-25.02	2.39-25.02	1.51-25.02
	$-9\leqslant h\leqslant 9$	$-6 \leqslant h \leqslant 8$	$-8 \leqslant h \leqslant 10$	$-5 \leqslant h \leqslant 10$
Limiting indices	$-10 \leqslant k \leqslant 5$	$-11 \leqslant k \leqslant 11$	$-17 \leqslant k \leqslant 15$	$-15 \leqslant k \leqslant 16$
	$-13 \leqslant l \leqslant 12$	$-13 \leqslant l \leqslant 12$	$-16 \leqslant l \leqslant 16$	$-17 \leqslant l \leqslant 17$
Reflections collected	4229	3951	8351	8675
Reflections independent (R_{int})	2795 (0.0286)	2642 (0.0214)	3025 (0.0350)	5751 (0.0264)
Goodness-of-fit on F^2	1.006	1.016	1.023	0.993
R indices $[I > 2\sigma I]$	0.0517, 0.1122	0.0451, 0.1049	0.0428, 0.0998	0.0506, 0.1201
R indices (all data)	0.1309, 0.1469	0.0884, 0.1362	0.0690, 0.1185	0.1101, 0.1596
Largest diff. peak and hole, e.Å $^{-3}$	0.201, -0.191	0.203, -0.153	0.338, -0.301	0.265, -0.275

Table 2

Selected bond lengths [Å] and angles [°] for 1–4.

1			
N(1)-C(2)	1.325(4)	N(1)-C(6)	1.368(4)
O(1)-C(11)	1.243(3)	C(2) - N(1) - C(6)	124.1(3)
2			
N(1) - C(2)	1.324(3)	N(1) - C(6)	1.371(3)
N(2)-O(5)	1.218(3)	N(2)-O(4)	1.228(3)
N(2) - C(16)	1.459(3)	O(1) - C(11)	1.290(3)
O(2) - C(11)	1.224(3)	O(3)-C(13)	1.341(3)
C(2) - N(1) - C(6)	123.9(2)	O(5)-N(2)-O(4)	122.6(2)
O(2) - C(11) - O(1)	124.2(2)		
3			
S(1) - O(6)	1.4354(18)	S(1) - O(5)	1.4450(19)
S(1) - O(4)	1.4672(18)	S(1) - C(16)	1.759(3)
N(1) - C(1)	1.321(4)	N(1)-C(5)	1.370(4)
O(1) - C(11)	1.218(3)	O(2) - C(11)	1.311(3)
O(3)-C(13)	1.345(3)	O(6) - S(1) - O(5)	113.62(12)
O(6) - S(1) - O(4)	112.63(12)	O(5) - S(1) - O(4)	110.89(11)
C(1) - N(1) - C(5)	124.3(2)	O(1)-C(11)-O(2)	123.2(2)
4			
N(1) - C(1)	1.314(4)	N(1)-C(9)	1.377(4)
N(2) - C(11)	1.320(4)	N(2) - C(19)	1.374(4)
O(1) - C(21)	1.260(3)	O(2) - C(21)	1.261(3)
O(3) - C(22)	1.264(3)	O(4)-C(22)	1.263(3)
O(5) - C(23)	1.202(3)	O(6)-C(23)	1.305(3)
O(7)-C(30)	1.261(3)	O(8)-C(30)	1.270(3)
O(9)-C(31)	1.261(3)	O(10)-C(31)	1.264(3)
O(11)-C(32)	1.294(3)	O(12)-C(32)	1.203(3)
C(1) - N(1) - C(9)	119.7(3)	C(11)-N(2)-C(19)	120.1(3)
O(1)-C(21)-O(2)	123.9(2)	O(4) - C(22) - O(3)	123.9(3)
O(5)-C(23)-O(6)	125.4(3)	O(7)-C(30)-O(8)	123.0(3)
O(9)-C(31)-O(10)	123.9(3)	O(12)-C(32)-O(11)	125.3(3)

3. Results and discussion

3.1. Syntheses and general characterization

For the preparation of **1–4**, the acidic derivatives were mixed directly with 2-methylquinoline in methanol and/or ethanol

solvents in 1:1 ratio, which was allowed to evaporate at ambient conditions to give the final crystalline products. The molecular structures and their atom labelling schemes for the four structures are shown in Figs. 1, 3, 5, and 7, respectively.

The elemental analyses for the four compounds are in good agreement with their compositions. The infrared spectra of 1-4 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 3700–3200 cm⁻¹ arise from O-H or N-H stretching frequencies. Aromatic and guinoline ring stretching and bending are in the regions of 1500–1630 cm⁻¹ and 600-750 cm⁻¹, respectively. The intense peak at ca. 1710 cm⁻¹ was derived from the existence of the C=O stretches, and the band at ca. 1260 cm⁻¹ exhibited the presence of the C–O stretches of the COOH moieties. The presence of two broad bands at ca. 2500 cm⁻¹ and 1900 cm⁻¹ in compound **4**, characteristic of a neutral O–H \cdots N hydrogen-bond interaction, was viewed as evidence for co-crystal formation [23]. Except for the above bands, for 1, and 2, the bands at ca. 1520 and 1320 cm⁻¹ were attributed to the $v_{as}(NO_2)$ and $v_s(NO_2)$, 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 $1550-1610 \text{ cm}^{-1}$ and $1300-1420 \text{ cm}^{-1}$ in compound **2** [26].

3.2. X-ray structure of 2-methylquinoline: (2,4,6-trinitrophenol) (1)

Salt **1** was prepared by reacting of a methanol solution of 2,4,6trinitrophenol and 2-methylquinoline in 1:1 ratio, which crystallizes as triclinic pale yellow crystals in the centrosymmetric space group P-1. The asymmetric unit of **1** consists of one cation of 2-methylquinolinium and one anion of picrate, as shown in Fig. 1. In the compound, there is one pair of ion pair with no included solvent molecules, which is well agreement with the micro-analysis results.

Table 3

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

D—H…A	d(D—H) [Å]	d(H···A) [Å]	$d(D \cdots A)$ [Å]	<(DHA) [°]
1				
N(1)−H(1)···O(2)#1	0.86	2.29	2.857(3)	123.5
$N(1)-H(1)\cdots O(1)#1$	0.86	1.93	2.749(3)	158.2
2				
O(3) - H(3) - O(1)	0.82	1.76	2.494(2)	148.7
$N(1)-H(1)\cdots O(1)#1$	0.86	1.81	2.666(3)	173.6
3				
$O(7)-H(7D)\cdots S(1)$	0.85	2.80	3.492(2)	139.8
O(7)—H(7D) · · ·O(5)	0.85	1.91	2.751(3)	168.3
O(7) - H(7C) - S(1) = 1	0.85	3.00	3.754(2)	148.5
O(7)—H(7C)···O(4)#1	0.85	1.89	2.729(3)	168.2
O(3) - H(3) - O(1)	0.82	1.87	2.596(3)	146.3
$O(2)-H(2)\cdots O(4)#2$	0.82	1.83	2.629(2)	163.9
$N(1)-H(1)\cdots O(7)$	0.86	1.82	2.667(3)	168.0
4				
$O(11) - H(11) \cdots N(1) # 1$	0.82	1.82	2.572(3)	151.3
O(10)−H(10)···O(3)#2	0.82	1.85	2.650(3)	166.3
O(7) - H(7) - O(2)	0.82	1.78	2.588(3)	166.0
O(6)—H(6)···N(2)#3	0.82	1.84	2.602(3)	153.4
O(4)−H(4)···O(9)#4	0.82	1.79	2.593(3)	167.4
O(1)—H(1A)···O(8)	0.82	1.83	2.636(3)	167.5

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



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

This is a salt where the OH groups of 2,4,6-trinitrophenol are ionized by proton transfer to the nitrogen atom (N(1)) of the 2-methylquinoline moieties, which is also confirmed by the bond distance of O(1)–C(11) (1.243(3) Å) for phenolate $(1.24 \pm 0.01 \text{ Å})$ [27].

Examination of the cationic moiety shows that the atoms C2–C10, and N1 of the quinolinium ring of the title compound have a good coplanarity and they form a conjugated plane with average deviation of 0.0152 Å. The benzene ring of the picrate is almost planar with r.m.s. deviation of 0.0066 Å. The dihedral angle between the aromatic ring of the cation and the benzene ring of the picrate is 95.9°, indicating an almost perpendicular arrangement of both rings. The ortho-nitro groups (N2–O2–O3, and N4–O6–O7) deviate from the benzene plane and have dihedral angles of 10.4 (2)°, and 115.4° respectively with the benzene ring of the anion, and the two ortho-nitro groups intersect at an angle of 116.4 (2)°. While the para-nitro group lies in the benzene plane [with dihedral angle of 0.9 (1)° between N3–O4–O5 group and the benzene ring of the picrate], which is similar to the organic salt concerning picrates [28].

The mean value of C—C and N—C bond lengths are 1.379 (4) and 1.346 (4) Å respectively, which are between that of a single bond and a double bond and agree with those values in the literature [29]. The C—N—C angles of pyridine are very sensitive to protonation [30,31]. A pyridinium cation always possesses an expanded angle of C—N—C in comparison with the parent pyridine. The angle of C(2)—N(1)—C(6) [124.1(3)] is consistent with a type of pyridinium cation. The hydrogen atom H(N1), which is deprived from its parent, attaches the nitrogen atom.

One 2-methylauinolinium cation and one 2.4.6-trinitrophenolate anion form a heterodimer through hydrogen bonding interactions. The NH⁺ group formed bifurcate N⁺—H···O hydrogen bonds with the picrate. One is the ionic $N^+-H\cdots O^-$ hydrogen bond produced between the NH⁺ cation of 2-methylquinolinium and the oxygen atom of the 2,4,6-trinitrophenolate ions with N–O distance of 2.749 Å, and $H \cdots O$ distance of 1.93 Å. The N^+ – $H \cdots O^-$ bond angle (158.2°), the N \cdots O and H \cdots O bond lengths are consistent with values reported from a study of N^+ –H···O⁻ hydrogen bonding in organic salts [32]. The other N–H⁺···O hydrogen bond is produced between the NH⁺ group and the NO₂ group with N–O distance of 2.857 Å, and H···O distance of 2.29 Å. Compared with the above ionic N^+ – $H^{\dots}O^-$ hydrogen bond, this hydrogen bond is more weaker. These two hydrogen bonding interactions generate a $R_1^2(6)$ ring motif according to Bernstein et al. [33]. There was also a CH₃—O interaction between the methyl group of the cation and the oxygen atom of the 2,4,6-trinitrophenolate anion in the same heterodimer with C–O distance of 3.443 Å. In compound 1, there also exist strong electrostatic interactions between charged cation units of NH⁺ and the picrate anions.

The adjacent heterodimers were connected together through the CH–O association between the CH of one anion and the NO₂ of its adjacent anion with C–O distance of 3.339 Å to form a chain running along the *a* axis direction. Adjacent chains were joined together through CH–O association between the 3-CH of the cation and the o-NO₂ group of the anion with C–O distance of 3.344 Å to form a 2D grid extending on the *ac* plane as shown in Fig. 2. In the grid the cations were protruded from the plane determined by the anion chain. In the grid there are 26-membered rings composed of three picrates and two cations and 13-membered rings composed



Fig. 2. 2D grid structure of 1 viewed down the b axis.

of two picrates and one cation. Two adjacent grids were connected together along the *b* axis direction through the CH—O interaction between the 8-CH of the cation at one grid and the o-NO₂ group of its neighboring grid with C—O distance of 3.168 Å, and O– π interactions between the o-nitro group and the aromatic ring of the cation with O—Cg distance of 3.131 Å to form a double layer structure. In the double layer structure the cations of the second grid were located just in the center of the 26-membered ring of the first grid. And the corresponding anions and cations of adjacent grids were antiparallelly arranged respectively. Such double grids were stacked along the *b* axis direction through the intergrid CH₃—O interaction between the 2-CH₃ of the cation and the p-NO₂ group of the anion with C—O distance of 3.627 Å to form a 3D layer network structure.

3.3. X-ray structure of 2-methylquinoline: $(5-nitrosalicylic acid) [(HL)^+ ... (5-nsa^-)] (2)$

The crystal structure of **2** consists of one monoanion of 5-nitrosalicylic acid, and one cation of 2-methylquinolinium in the asymmetric unit (Fig. 3). The proton of the COOH group has transferred to the ring N atom of the quinoline moiety. The assignment of **2** as a salt is based on successful refinement of the relevant H atoms using X-ray data also. This is confirmed by the C–O distances (O(1)-C(11), 1.29O(3) Å), O(2)-C(11), 1.224(3) Å with $\Delta =$ 0.066 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 without solvent molecules, which fits well with the micro-analysis results.

In the cation, the angle C(6)—N(1)—C(2) [123.9(2)°] is almost the same as that in **1** (124.1(3)°). Because of the presence of the intramolecular hydrogen bond between the carboxylate group and the phenol group (O(3)—H(3)···O(1), 2.494(2) Å), it is generally expected and found that the carboxylate group is essentially coplanar with the benzene ring [torsion angle C13—C12—C11—O2, 172.64°]. This feature is similar to that found in salicylic acid [34], and in the previously reported structure of proton-transfer



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

compound based on 5-nsa⁻ [35]. As expected the O–O separation is essentially in the range of the documented data [2.489–2.509 Å] [35] because of the planarity of the hydrogen bonded carboxylate unit, but it is slightly contracted compared with the nonproton transfer examples (2.547–2.604 Å, mean: 2.588 Å), as a result of deprotonation. The 5-nitro group also varies little conformationally [torsion angle C15–C16–N2–O5, 178.4°] compared with the reported data within this set of compounds (175.4–180°) [35].

The rms deviation of the quinoline ring excluding the CH_3 group is 0.0181 Å. The rms deviation of the benzene ring of the anion is 0.0094 Å. They make dihedral angle of 73.1° with each other.

One cation and one anion were held together by $N^+-H\cdots O^$ hydrogen bond between one O atom of the carboxylate group and the NH⁺ group to form a heterosynthon, the heterosynthons were joined together by CH-O interaction between the other O atom of the same carboxylate group and 5-CH of the cation with C–O distance of 3.301 Å to form a dimer. In this dimer the cations were antiparallelly arranged. And the two anions were inversionally located around the cations. There are no aromatic stacking interactions between the two antiparallelly arranged cations. The dimers were further joined together by the CH-O interaction between the 8-CH of the cation and the nitro group with C-O distance of 3.201 Å to form a 1D chain running along the diagonal direction of the *bc* plane. The adjacent 1D chains were linked together by $CH_3 - \pi$ interactions between the CH_3 of the cation and the benzene ring of the anion with C-Cg distance of 3.642 Å to form a 2D sheet extending on the bc plane (Fig. 4). These sheets were further stacked along the *a* axis direction to form a 3D network structure through CH₃–O interactions between the CH₃ of the cation and the carboxylate O atom with C-O distance of 3.426 Å, and CH–O interactions between the 3-CH of the cation and the NO₂ group with C–O distance of 3.301 Å. Here the adjacent sheets were slipped some distance from each other along the *b*, and *c* axis directions, respectively.

3.4. X-ray structure of 2-methylquinoline: (5-sulfosalicylic acid): H_2O [(HL)⁺...(5-ssa⁻)... H_2O] (**3**)

Similar to compound **2**, the compound **3** is also an organic salt. In **3** the asymmetric unit is occupied by one monoanion of 5-sulfosalicylic acid, one cation of 2-methylquinolinium (HL)⁺, and one water molecule (Fig. 5). Here only one proton of the 5-sulfosalicylic acid has transferred to the N atom of L. In this case it is the proton of the SO₃H group not other protons such as the phenol H and the carboxyl H that have been deprotonated. The reason could be that a sulfonic acid is a stronger acid than a carboxylic acid.

The S–O distances in SO₃⁻ are ranging from 1.4354(18) to 1.4672(18) Å (Δ is 0.0318 Å) which is in the range of the monodeprotonated 5-saa⁻ anion (1.435 (2)–1.4599 (17) Å) [36]. The C–O bond distance (O(3)–C(13) 1.345(3) Å) is in the range of the neutral C–O bond distance in the phenol derivatives (1.344 (3)– 1.357 (3) Å) [36]. In the COOH group, two C–O bond lengths are



Fig. 4. 2D sheet structure of 2 extending on the bc plane.



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

obviously different between O(1)—C(11) (1.218(3)Å) and O(2)—C(11) (1.311(3)Å) (\varDelta is 0.093Å) bearing the characteristic C—O bonds for the COOH groups, which are also confirming the reliability of adding H atoms experimentally by different electron density onto O atoms as mentioned above.

The angle $[124.3(2)^{\circ}]$ around the protonated N atom (N1) is similar to the corresponding angle in compound **1** [124.1(3)], **2** [123.9(2)^{\circ}], and the saccharate salt of 2-methylquinoline (123.7(3)^{\circ}) [37].

The rms deviation of the cation excluding the methyl group is 0.0055 Å. The rms deviation of the benzene ring of the anion is 0.0024 Å. Both planes make dihedral angle of $22.9(3)^\circ$, which is smaller than the corresponding value in **2**.

The 5-ssa⁻ anions formed a 1D chain along the *a* axis direction through O—H···O hydrogen bonding interactions between the OH group of the COOH and the SO₃⁻ with O—O distance of 2.629(2) Å. In the chain the 5-ssa⁻ anions were parallel to each other and arranged in head to tail fashion. Adjacent chains were linked together along the *c* axis direction by C(carbonyl)– π interaction

with C—Cg distance of ca. 3.330 Å and CH—O interactions between the SO₃⁻ group and 3-CH of the anion with C—O distance of 3.333 Å to form a double chain structure. Unlike the anions in the same chain, here the anions in these two chains were antiparallelly arranged. The cations were bound to the anion chain through three CH—O contacts, of which two are formed between the same sulfonyl O atom and 4-CH, and 5-CH of the same cation to produce a $R_2^2(6)$ ring motif with C—O distances of 3.328 and 3.470 Å respectively, the other is produced between OH of the carboxyl group and 3-CH of the cation with C—O distance of 3.392 Å.

The lattice water molecules (acceptor) were bound to the cations through N^+ –H···O hydrogen bond with N–O distance of 2.667(3) Å, thus there are no direct classical hydrogen bond interactions between the cations and the anions (the water molecule blocked the donor position of the cation so that the NH⁺ groups have no classical hydrogen bonding interaction with the anion). Besides as acceptors, the water molecules also formed two hydrogen bonds in bifurcate mode via the same OH group (donor), one is the O–H···O hydrogen bond formed between the OH group of the water and the sulfonyl group of the neighboring anion chain at the *c* axis direction with O–O distance of 2.751(3) Å, the other is the O-H···S interaction formed between the same OH unit and the S atom of the sulfonyl group of the neighboring anion chain at the c axis direction with O–S distance of 3.492(2) Å. Under these interactions, the water molecules linked the double anion chains and the cations together to give a 2D double layer sheet structure (Fig. 6). The double layer sheets were further stacked along the *c* axis direction through the π - π stacking interactions between the cation aromatic ring and the anion benzene ring with the centroid-centroid separation of 3.313 Å to form a 3D layer network structure. Like 2, the usual intramolecular hydrogen bond is found between the phenol OH group and a carboxyl O atom [O(3)-H(3)-O(1); O-O=2.596(3)Å], essentially giving coplanarity of the carboxylic acid group and the benzene ring [torsion angle O(2)–C(11)–C(12)–C(13); –177.48(3)°]. For the presence of this hydrogen bond, compound **3** also bears the $S_1^{(1)}(6)$ loop motif. This hydrogen bond geometries were similar to the documented data [36], and the data in compound 2 also.

3.5. X-ray structure of 2-methylquinoline: (trimesic acid) (4)

Cocrystallization of 2-methylquinoline and trimesic acid in a 1:1 ratio from methanol gave single crystals suitable for X-ray



Fig. 6. 2D double layer sheet structure of 3.

diffraction. Structure determination (Table 1) revealed that 2-methylquinoline and trimesic acid are present in a 1:1 ratio in the molecular complex **4**, and the asymmetric unit is shown in Fig. 7. Unlike the salts **1–3**, no protons from the trimesic acid have been deprotonated and transferred to the ring N atoms of the 2-methylquinoline. Thus **3** is a cocrystal instead of a salt, it is the same as the adduct of trimesic acid tris(pyridine) solvate [38].

The O–C bond distances of the carboxyl group were ranging from 1.202(3) to 1.305(3). The pair of O–C bond distances in the four carboxyl groups concerning the C(21), C(22), C(30), and C(31) atoms are almost equal to each other, suggesting that there are strong p– π conjugated effect between the O atom of the OH unit and the carbonyl group. The C–N–C angles at the neutral 2-methylquinoline are 119.7(3)°, and 120.1(3)° respectively. Compared with the above protonated 2-methylquinoline, these angles are significantly smaller than the corresponding angles in the above salts **1–3**, which also confirms our correct assignment of **4** as a cocrystal.

The rms deviation of the ring containing atoms C30–C38–O7–O12 is 0.0205 Å, the rms deviation of the ring bearing the atoms C21–C29–O1–O6 is 0.0434 Å, the dihedral angle between the two rings is 1.2° indicating the parallel arrangement

of both rings. The rms deviation of the ring with the N2 atom is 0.0044 Å, the dihedral angles between this ring and the above two benzene rings of the trimesic acids are 3.1°, and 2.3° respectively. The rms deviation of the ring with the N1 atom is 0.0038 Å, the dihedral angle between the two quinoline rings is 2.7°. The quinoline ring with the N1 atom makes dihedral angles of 5°, and 3.8° with the above two aromatic rings of the trimesic acid moieties respectively.

Every 2-methylquinoline is bonded to one trimesic acid through one neutral O—H…N (between the OH group of one COOH and the ring N atom of 2-methylquinoline with N—O distance of 2.602(3) Å), one CH₃—O (between the 2-CH₃ of the 2-methylquinoline molecule and the OH group with C—O distance of 3.105 Å), and one CH—O (between 8-CH of the 2-methylquinoline and the C=O group with C—O distance of 3.496 Å) associations to form a bicomponent heteroadduct. In the heteroadduct there are $R_2^2(8)$ and $R_2^2(6)$ ring motifs according to Bernstein et al. [33], and this two kinds of ring motifs were fused together by the neutral O—H…N hydrogen bond. The adjacent heteroadducts were connected together via two CH—O associations to form a 1D chain running along the direction that formed an angle of ca. 60° with the *bc* plane. Of the two CH—O associations, one is between the 5-CH of



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



Fig. 8. 2D sheet structure of 4.

the 2-methylquinoline and the C=O group of the second COOH group with C–O distance of 3.594 Å and the other is between 6-CH of the 2-methylquinoline and the C=O group of the third COOH group with C–O distance of 3.622 Å. In the same chain the heteroadducts formed between 2-methylquinoline and trimesic acid were parallel to each other, while the heteroadducts at the neighboring chains were antiparallel to each other. The corresponding heteroadducts at the third chain have the same projects as the heteroadducts at the first chain when viewed from the *c* axis direction, so do the heteroadducts at the second chain and the heteroadducts at the fourth chain. Adjacent such chains were joined together through the homomeric carboxylic acid-carboxylic acid $R_2^2(8)$ synthon (cyclic hydrogen bonded carboxylic acid ring motif $R_2^2(8)$). And there are also CH–O interactions between the 3-CH of 2-methylquinoline in one chain and the C=O of the COOH unit of its adjacent chain with C–O distance of 3.448 Å, in this case the OH group in this COOH unit is involved in O—H…N interaction. Under these interactions the complex **4** displays a 2D sheet structure extending along the direction that formed an angle of ca. 60° with the *bc* plane, which is shown in Fig. 8. Such 2D sheets were further stacked along the *a* axis direction through π - π interactions between the trimesic acids with centroid-centroid separation of 3.348 Å to form a double sheet structure. Here the aromatic rings of the 2-methylquinoline units are not involved in this kind of interactions.

4. Conclusion

Four complexes with 2D–3D network structure have been synthesized and structurally characterized. Despite variations in molecular shape on the acidic components, there all exist strong inter-molecular hydrogen bonds between the acidic moieties and the 2-methylquinoline.

In the compounds **1–3**, 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 study has demonstrated that the O-H···N hydrogen bond is the primary intermolecular force in a family of structures containing the OH···N_{2-methylquinoline} synthons, in addition two types of secondary C-H···O hydrogen bond (intra- and interchain C-H···O contacts) were also observed. There are found CH₃-O interactions in compounds **1**, **2**, and **4**. Compound **2** possesses CH₃- π interaction, while there are π - π interactions in compound **3**. There are O- π interactions in compound **1**.

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 acidic units and 2-methylquino-line are sufficient to bring about the formation of binary organic salts or cocrystals.

5. Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data center, CCDC Nos. 765311 for **1**, 809893 for **2**, 809677 for **3**, and 792910 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.

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