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Structural study on few co-crystals and a salt of quinoline derivatives having amide bond

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ABSTRACT

The *N*-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide forms 1:1 co-crystals with aromatic diols namely 1,4-dihydroxybenzene, 1,5-dihydroxynaphthalene. In the later case co-crystal is formed in hydrated form. The hydrated form of co-crystal with 1,5-naphthalenediol has two symmetry independent host molecules in its unit cell, whereas such phenomenon in the co-crystal 1,4-dihydroxybenzene is not observed. The crystal structure of perchloric acid salt of (Quinolin-8-ylamino)-acetic acid is determined and this salt also shows two symmetry independent parent molecules in unit cell.

1. Introduction

The quinoline derivatives serve as template for guest binding and have interesting fluorescence properties [1]. The quinoline derivatives are acid sensitive and the understanding of the binding ability to guest molecule is of special interest [2]. It is also well known fact that the heterocyclic aromatic systems interact with hydroxy aromatics [3, 4] and can in turn effect the fluorescence emission [4]. Quinoline derivatives are also used as drugs for malaria, arthritis, and lupus [5–8]. Thus, the structural understanding on quinoline derivative having amide functionality is of importance. In this study we describe characterisation and structural aspects of two co-cystals (**2–3**) and a perchlorate salt of quinoline derivative (**4**) as shown in Fig. 1.

2. Experimental

The X-ray single crystal diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H atoms, except those attached to nitrogen and oxygen atoms were placed at their calculated positions and refined in the isotropic approximation; some of the H atoms attached to nitrogen and oxygen were located in the difference Fourier maps, and refined with isotropic displacement coefficients, while rest of the H atoms attached to N and O were placed in their calculated position and refined (Table 1).

2.1. Synthesis of N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide (*1*)

2-(4-Methoxyphenyl)ethylamine (1.51 g, 10 mmol) was dissolved in dry dichloromethane (20 ml) and triethylamine (1.01 g, 10 mmol) was added to it. The solution was stirred at 0 °C for 10 min after which bromoacetyl bromide (2.42 g, 12 mmol) was added dropwise to the stirred solution over a period of 30 min. The reaction mixture was then stirred overnight. Subsequently the reaction mixture was filtered to remove the hydrobromide salts, and the filtrate was collected. The filtrate was washed with water (10 ml), dried over sodium sulphate and then the solvent was removed under reduced pressure. The 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide was obtained as a brown solid, the crude product was recrystallised from dichloromethane. The 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide (2.72 g, 10 mmol), 8-hydroxyquinoline (1.45 g, 10 mmol) and K_2CO_3 (2.07 g, 15 mmol) was added to dry acetone (20 ml) in nitrogen atmosphere and the reaction mixture was stirred at 60 °C for 10 h. (The reaction

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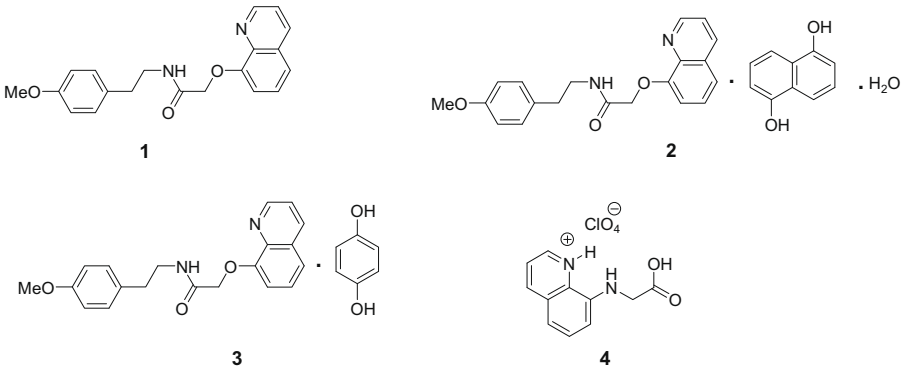


Fig. 1. Quinoline derivatives, co-crystals and a perchlorate salt.

progress was monitored at regular intervals using TLC). After completion of the reaction the solvent was removed under reduced pressure that gave a brown solid. The solids were washed with dilute sodium hydroxide solution (5%), and water and then extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulphate. Subsequent removal of the solvent gave the crude product, which was purified by chromatography (silica gel; hexane/ethyl acetate 3:2). Isolated yield 46%. IR (KBr, cm^{-1}): 3328(m), 2935(m), 1655(s), 1545(s), 1514(s), 1377(s), 1298(s), 1250(s), 1182(s), 1109(s), 1031(s), 819(s), 785(s), 614(s). Elemental analysis for $C_{20}H_{20}N_2O_3$: calculated C, 71.35; H, 5.95; N, 8.32; found C, 71.51; H, 5.39; N, 8.73. ^{1}H NMR ($CDCl_3$): 8.79(dd, J = 4 Hz,1.2 Hz, 1H), 8.15(dd, J = 8.4,1.6 Hz, 1H), 7.99(bs, 1H), 7.45(m, 3H), 7.08(dd, J = 6.8,1.6 Hz, 1H), 6.95(d, J = 8.4 Hz, 2H), 6.61(d, J = 8.8 Hz, 2H), 4.76(s, 2H), 3.73(s, 3H), 3.53(q, J = 13.2 Hz, 2H), 2.72(q, J = 13.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 168.6, 158.2, 153.8, 149.3, 140.0, 136.6, 131.1, 129.7, 127.0, 122.1, 121.5, 113.9, 111.6, 69.60, 55.3, 40.7, 34.8.

2.2. Co-crystal 2

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide (**1**) (0.1 g, 0.3 mmol) and 1,5-Naphthalenediol (0.05 g, 0.3 mmol) were dissolved in 10 ml of methanol. The resultant solution was then kept for crystallization. After 9 days reddish block type crystals were appeared. Yield: 61%. IR (KBr, cm^{-1}): 3472(bs), 3297(w), 2983(w), 1629(s), 1590(w), 1509(s), 1381(s), 1262(s), 1244(s), 1181(m), 1119(s), 937(w), 823(w), 780(s), 751(m). Elemental analysis for $C_{60}H_{58}N_4O_{11}$: calculated C, 71.21; H, 5.74; N, 5.54; found C, 71.56; H, 5.31; N, 5.36.^{1}H NMR($CDCl_3$): 9.36(s, 2H), 8.84(d, J = 4.4 Hz, 1H), 8.36(bs, 1H), 8.24(d, J = 8.4 Hz, 1H), 7.71(d, J = 8.4 Hz, 2H) 7.54(m, 3H), 7.21(m, 3H), 6.98(d, J = 7.2 Hz, 2H), 6.88(d, J = 7.2 Hz, 2H), 6.67(d, J = 8.4 Hz, 2H), 4.78(s, 2H), 3.74(s, 3H), 3.53(q, J = 14 Hz, 2H), 2.76(t, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 168.5, 158.1, 152.7, 148.9, 136.1, 134.2, 130.4, 129.2, 126.5, 126.1, 124.4, 121.6, 121.3, 113.4, 112.9, 111.8, 108.3, 69.6, 54.8, 40.2, 34.3.

Table 1
The crystallographic parameters of **2**, **3** and **4.**

Compound code	**2**	**3**	**4**
CCDC No.	727137	727136	727134
Empirical formula	$C_{60}H_{58}N_4O_{11}$	$C_{26}H_{26}N_2O_5$	$C_{11}H_{11}ClN_2O_6$
Formula weight	1011.10	446.49	302.67
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P-1$	$P2(1)2(1)2(1)$	$P2(1)/c$
Unit cell dimension	a = 10.8194(5) Å,	a = 5.6277(2) Å	
	b = 14.2801(7) Å,	b = 18.3147(6) Å,	a = 8.4382(2) Å,
	c = 17.6702(9) Å,	c = 22.0626(7) Å,	b = 32.4641(10) Å
	α = 79.482(4)°,	$\alpha = \beta = \gamma$ = 90.00°	c = 9.4498(3) Å,
	β = 88.028(3)°,		$\alpha = \gamma$ = 90.00°,
	γ = 74.127(3)°		β = 104.458(2)°
Volume (Å^3)	2581.5(2)	2273.98(13)	2506.68(13)
Z	2	4	8
Density (calculated)	1.301 mg/m^3	1.304 mg/m^3	1.604 mg/m^3
Absorption coefficient	0.090 mm^{-1}	0.091 mm^{-1}	0.334 mm^{-1}
F(000)	1068	944	1248
Crystal size	0.12 × 0.24 × 0.48 mm^3	0.16 × 0.21 × 0.28 mm^3	0.33 × 0.27 × 0.21 mm^3
Theta range for data collection (°)	1.73–25.00	1.45–28.33	1.25–24.99
Index ranges	$-12 \leqslant h \leqslant 12$	$-7 \leqslant h \leqslant 7$	$-9 \leqslant h \leqslant 10$
	$-16 \leqslant k \leqslant 15$	$-23 \leqslant k \leqslant 24$	$-35 \leqslant k \leqslant 38$
	$-21 \leqslant l \leqslant 21$	$-29 \leqslant l \leqslant 24$	$-10 \leqslant l \leqslant 11$
Reflections collected	23784	25648	19700
Independent reflections	8740	5630	4387
Completeness to theta	96.2%	99.3%	99.7%
Absorption correction	None	None	None
Data/restraints/parameters	8740/0/698	5630/0/305	4387/0/385
Goodness-of-fit on F^2	1.030	1.040	1.260
Final R indices [I > 2sigma(I)]	0.0471	0.0487	0.0541
R indices (all data)	0.0836	0.0713	0.0756

2.3. Co-crystal 3

N-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy) acetamide (**1**) (0.1 g, 0.3 mmol) and 1,4-dihydroxybenzene (0.03 g, 0.3 mmol) were dissolved in methanol (5 ml). The resultant solution was kept for crystallization. After 5 days colourless block type crystals were appeared. Yield: 54%. IR (KBr, cm^{-1}): 3309(bs), 2930(w), 1651(s), 1563(m), 1506(s), 1472(m), 1377(m), 1317(m), 1246(s), 1212(s), 1118(s), 1032(m), 824(s), 759(s), 515(w). Elemental analysis for $C_{26}H_{26}N_2O_5$: calculated C, 69.88; H, 5.82; N, 6.27; found C, 69.61; H, 5.61; N, 5.93. ^{1}H NMR($CDCl_3$): 8.79(d, J = 4.4 Hz, 1H), 8.33(bs, 1H), 8.20(d, J = 9.6 Hz, 1H), 7.48(m, 3H), 7.10(dd, J = 3.2, 5.6 Hz, 1H), 6.98(d, J = 8.8 Hz, 2H), 6.72(s, 1H), 6.67(d, J = 8.4 Hz, 2H), 4.73(s, 2H), 3.72(s, 3H), 3.51(q, J = 14 Hz, 2H), 2.73(t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): 167.8, 159.0, 153.8, 149.7, 148.4, 135.8, 132.2, 129.5, 127.0, 122.4, 121.5, 113.5, 116.7, 110.5, 68.8, 54.8, 40.3, 35.1.

2.4. Synthesis of (Quinolin-8-ylamino)-acetic acid (**4a**)

8-Aminoquinoline (0.72 g, 5 mmol) was dissolved in dry dichloromethane (20 mL) and triethylamine (0.69 mL, 5 mmol) was added to it. The solution was stirred at 0 °C for 15 min and then bromoacetylbromide (0.43 mL, 5 mmol) was added drop wise to the stirred solution. The reaction mixture was then stirred overnight at room temperature. It is them filtered to remove the hydrobromide salts, and the filtrate was removed under reduced pressure. The product obtained was further purified by recrystallization from dichloromethane. In the next step, the amide obtained (1.4 g, 5 mmol), 8-aminoquinoline (0.72 g, 5 mmol) and K_2CO_3 (1.03 g, 7.5 mmol) were added to dry acetone (20 mL) in nitrogen atmosphere and the reaction mixture was stirred at 60 °C for 9 h (progress of the reaction was monitored at regular intervals using TLC). After completion the solvent was removed under reduced pressure. The product obtained was purified by column chromatography. Yield: 58%. IR (KBr, cm^{-1}): 3353(s), 3303(m), 2922(m), 1667(s), 1577(m), 1515(s), 1486(m), 1423(w), 1384(m), 1315(s), 1127(m), 815(m), 782(s). ^{1}H NMR ($CDCl_3$): 10.9(s, 1H), 8.8 (d, J = 6 Hz, 2H), 8.4(d, J = 4 Hz, 1H), 8.1(d, J = 8.4 Hz,1H), 8.0 (d, J = 8.4 Hz, 1H), 7.5–7.4 (m, 3H), 7.3–7.2 (m, 2H), 7.1(d, J = 8 Hz, 1H), 7.0 (s, 1H), 6.7 (d, J = 7.6 Hz, 1H), 4.3(s, 2H).

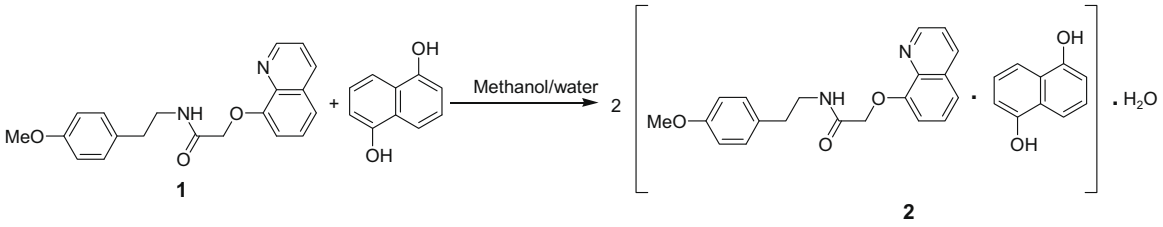
2.5. Synthesis of perchloric acid salt of (Quinolin-8-ylamino)-acetic acid (**4**)

Compound **4a** was dissolved in dilute $HClO_4$ solution (3 M) and the reaction mixture was warmed for 30 min to obtain a homogeneous solution. The solution was kept undisturbed and brown colored crystal appeared after14 days. Yield: 52%; IR (KBr, cm^{-1}): 3401(b), 3323(m), 2926(m), 2800(m), 1747(s), 1626(s), 1591(m), 1569(m), 1473(m),1378(m), 1341(m), 1217(m), 1180(m), 1147 (s), 1120(s), 1080(s), 808(s), 753(s), 625(s). ^{1}H NMR ($CDCl_3$): 8.9 (d, J = 4.8, 1H), 8.5(d, J = 8, 1H), 7.7 (m, 1H), 7.5 (t, J = 7.6, 1H), 7.2(m, 1H), 6.8(d, J = 7.6), 5.1(bs, 1H), 4.0(s, 2H).

3. Results and discussion

The *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy) acetamide forms 1:1 co-crystal (**2**) with 1,5-dihydroxynaphthalene which is isolated as colorless crystals and characterized by spectroscopic techniques (Scheme 1). A relatively strong absorption in 3472 cm^{-1} in the IR spectra of co-crystal **2** is attributed to the hydrogen bonded phenolic –OH groups of 1,5-dihydroxy naphthalene.

The carbonyl stretching of amide appears at 1629 cm^{-1}. ^{1}H NMR spectrum of the **1** shows the N–H proton as broad singlet



Scheme 1.

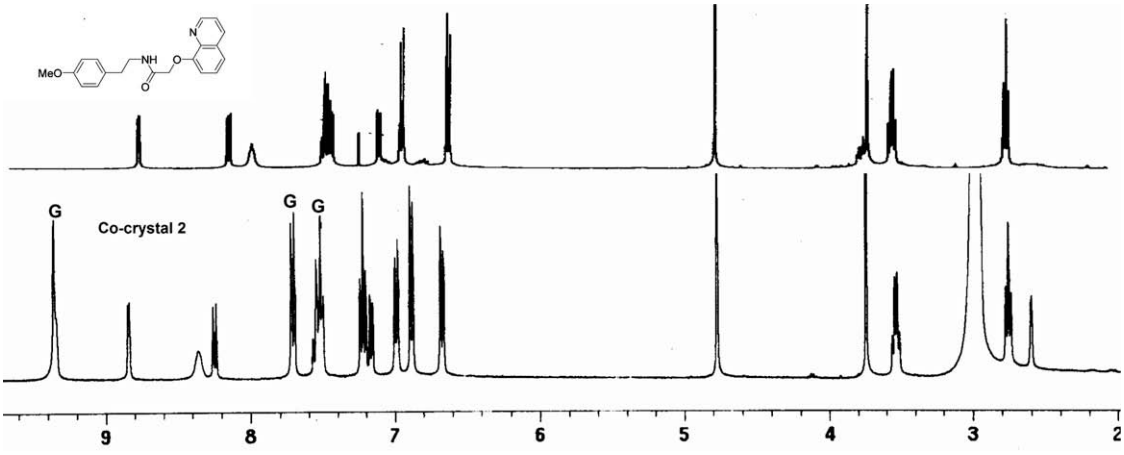


Fig. 2. ^{1}H NMR spectra of compound **1** and the co-crystal **2** (The peak due to guest molecule are indicated by G).

at 8.0 ppm in $CDCl_3$. After formation of co-crystals with 1,5-naphthalenediol the N–H peak gets shifted to 8.3 ppm, which indicates that the N–H proton participate in a strong hydrogen bonding interaction (Fig. 2).

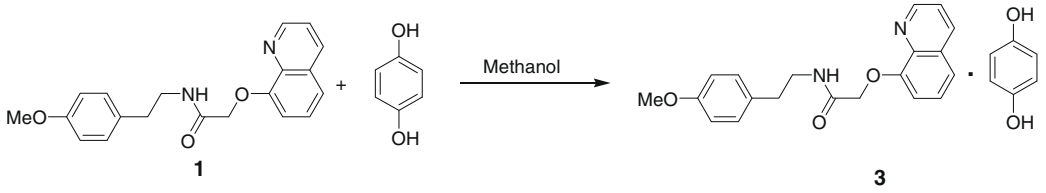
The phenolic –OH proton is not observed in the ^1H NMR spectra of the co-crystal **2** in $CDCl_3$ at room temperature**.** This probably occurs due to proton exchange with water present in the solvent. Moreover, no appreciable changes in the chemical shift of the protons of the host molecule are observed upon co-crystal formation.

On the other hand the co-crystal **3** is prepared by mixing **1** and 1,4-dihydroxybenzene in stoichiometric amounts in methanol as colorless plates (Scheme 2). Elemental analysis shows that **3** show it to have 1:1 ratio between host and guest.

In the co-crystal **3**, the O–H stretching appears as broad absorption at 3309 cm^{-1} and the amide carbonyl stretching frequency appears at 1651 cm^{-1}. A broad singlet appears at 2930 cm^{-1} due to the N–H stretching frequency. The N–H proton of the host is shifted from 8.0 ppm to 8.3 ppm after the formation of co-crystal. A singlet appears at 6.7 ppm due to the aromatic protons of 1,4-dihydroxybenzene. The other aromatic protons are not affected significantly upon formation of co-crystal.

The 1:1 co-crystal of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy) acetamide with 1,5-dihydroxynaphthalene and it crystallizes in the triclinic P-1 space group. From the crystal structure it is observed that two units of *N*-[2-(4-methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy) acetamide co-crystal with 1,5-dihydroxynaphthalene molecule forms assembly with one molecule of water of crystallization (Fig. 3A). The structure is decided by weak interactions between 1,5-dihydroxynaphthalene molecule and amide derivatives in which the diols are in two different environments. A chain like structure is formed, in which water along with diol molecules act as bridges between the amides on one side and diols as bridges on the other side. This makes two different environments around the diols and enables one to distinguish two amide hosts in terms of their symmetry. The dihydroxy molecules are held by the receptor through N1–H···O8 [$d_{N1\cdots O8}$ 3.05 Å,<D–H···A 147.3°], N3–H···O7 [$d_{N3\cdots O7}$ 2.96 Å,<D–H···A 151.5°], O7–H···N4 [$d_{O7\cdots N4}$ 2.67 Å,<D–H···A 173.2°] and O8–H···N2 [$d_{O8\cdots N2}$ 2.70 Å,<D–H···A 171.2°] hydrogen bonding interactions, where the N-H protons of amide behave as hydrogen bond donor but the phenolic -OH group serve as donor as well as acceptor atom. It was earlier showed that the N-(2,6-dimethylphenyl)-2-(quinolin-8-yloxy)acetamide forms 1:1 co-crystal with 1,5-dihydroxynaphthalene in that case there were no water of crystallisation [9]. It has a chain like structure where symmetry non-equivalent molecules of the same compounds were not observed. This indicates clearly the role of water molecule in this crystal on generating symmetry non-equivalent molecules. It is worth noting that the crystal structure of hydrated and anhydrous form of the receptor **1** is already determined [9]; which does not show symmetry non-equivalence. This result also suggests the origin of symmetry non-equivalent molecules in the case of **2,** to a combined role of all the three components by formation of assemblies.

The water molecule with the host molecule in a bridging fashion is held by the oxygen atoms of two symmetry non-equivalent



Scheme 2.

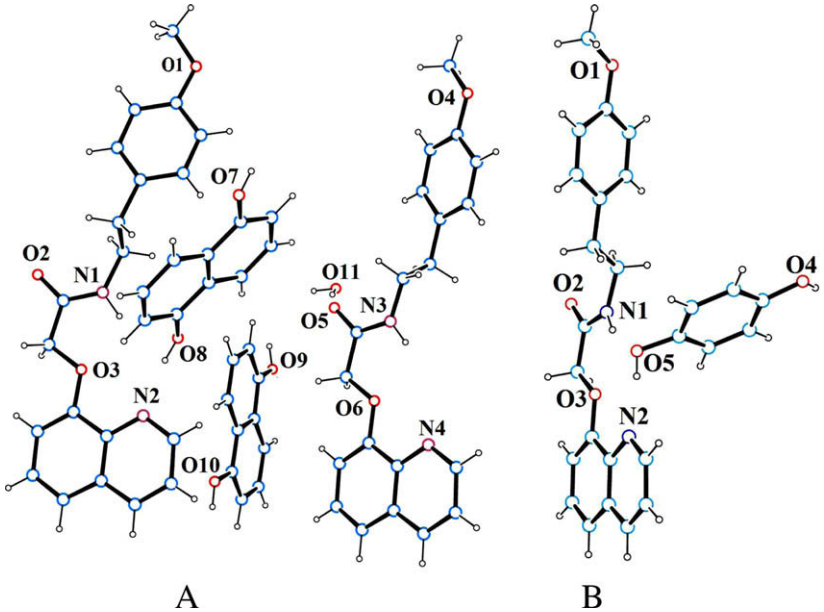


Fig. 3. (A) Crystal structure of co-crystal **2**, (B) Structure of compound **3.**

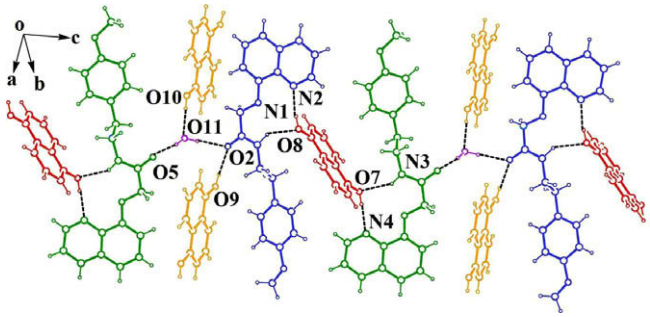


Fig. 4. Hydrogen bonded one dimensional assembly in co-crystal **2.**

Table 2
Hydrogen bond geometry (Å,°) for co-crystal **2.**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<D–H···A
N(1)–H(1 N)···O(8)	0.98(3)	2.18(3)	3.05(3)	147.3(2)
N(3)–H(2 N)···O(7) [1–*x*, 1–*y*, 1–*z*]	0.89(3)	2.15(3)	2.96(3)	151.5(2)
O(7)–H(7A)···N(4) [1–*x*, 1–*y*, 1–*z*]	0.82	1.86	2.67(2)	173.2
O(8)–H(8)···N(2)	0.82	1.89	2.70(2)	171.2
O(9)–H(9)···O(2) [1–*x*, 1–*y*, –*z*]	0.82	1.92	2.74(2)	178.8
O(11)–H(11O)···O(2) [1–*x*, 1–*y*, –*z*]	0.86(5)	2.04(5)	2.89(3)	175.9(1)
O(11)–H(12O)···O(5)	0.87(4)	1.94(4)	2.81(3)	170.0(3)
O(10)–H(10)···O(11) [–1 + *x*, *y*, *z*]	0.82	1.87	2.69(3)	174.2

receptors through O11–H···O2 [$d_{O11\cdots O2}$ 2.89 Å,<D–H···A 175.9°] and O11–H···O5 [$d_{O11\cdots O5}$ 2.81 Å,<D–H···A 170.0°] intermolecular hydrogen bonding interactions (Fig. 4).

The water molecule is also hydrogen bonded with 1,5-naphthalenediol by intermolecular O10–H···O11 [$d_{O10\cdots O11}$ 2.69 Å,<D–H···A 174.2°] interaction, where the oxygen atom of water acts as acceptor and the –OH group as donor. One of the dihydroxy molecules is held by the receptor through O9–H···O2 [$d_{O9\cdots O2}$ 2.74 Å,<D–H···A 178.8°] interaction and the amide carbonyl act as a bifurcated acceptor (Table 2). A two dimensional hydrogen bonded molecular assembly is formed in the lattice.

The compound **1** and 1,4-dihydroxybenezene form a 1:1 co-crystal (**3**) of host and guest and it crystallizes in the orthorhombic $P2_12_12_1$ space group. The crystal structure of the co-crystal is shown in Fig. 3. The N–H proton of the host molecule binds the guest molecule through N1–H···O5 [$d_{N1\cdots O5}$ 2.99 Å,<D–H···A

Table 3
Hydrogen bond geometry (Å,°) for co-crystal **3.**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<D–H···A
N(1)–H(1 N)···O(5) [1–*x*, –1/2 + *y*, 1/2–*z*]	0.92(3)	2.12(3)	2.99(3)	159.1(2)
O(4)–H(4A)···O(2) [1 + *x*, *y*, *z*]	0.82	1.90	2.71(3)	169.8
O(5)–H(5)···N(2) [1–*x*, 1/2 + *y*, 1/2–*z*]	0.82	1.91	2.72(2)	166.8

159.1°] hydrogen bonding (Fig. 5). The phenolic –OH group of 1,4-dihydroxybenzene molecule is also hydrogen bonded with quinolinic nitrogen through O5–H···N2 [$d_{O5\cdots N2}$ 2.72 Å,<D–H···A 166.8°] interaction. The carbonyl of amide group is involved in O4–H···O2 [$d_{O4\cdots O2}$ 2.71 Å,<D–H···A 169.8°] hydrogen bonding interaction with the hydroxyl group of 1,4-dihydroxybenzene (Table 3). The aromatic ring protons participate in weak C13–H···π [$d_{C13\cdots\pi}$ 3.77 Å] and C18–H···π [$d_{C18\cdots\pi}$ 3.70 Å] hydrogen bonding interactions with quinoline rings. Absence of water of crystallisation makes the system symmetric in terms of the 1,4-dihydroxybenzene bridges and the co-crystals are placed symmetrically in the lattice with respect to each other. The structure has similarity to the reported structure of co-crystal of 1,4-dihydroxybenzene with *N*-(2,6-dimethylphenyl)-2-(quinolin-8-yloxy) acetamide [9].

The above example shows the occurrence of symmetry non-equivalent molecules in lattice is by a combined effect of binding of a host to water molecules through a guest molecule. However, symmetry equivalence may arise in system without a solvent molecule but by self assembling process [10]. The crystal structure of the salt **4** (Scheme 3) shows symmetry non-equivalent cations in the lattice. The perchlorate salt of quinoline containing carboxylic acid **4** is formed from a hydrolytic reaction as shown in Scheme 3.

The crystal structure of **5** (Fig. 6a) has two symmetry non-equivalent cations and anions in each asymmetric unit ($Z' = 2$). Recently, we have shown that in the crystal structure of carbamates and urea derivatives of amino or hydroxy-quinolines have symmetry non-equivalent molecules in lattice on formation of perchlorate salts [11]. However, in those cases water of crystallisation had also a role on the symmetry non-equivalence. In the present case the perchlorate salt without water of crystallisation leads to assembly formation, in which pairs of symmetry non-equivalent carboxylic acids are placed in head to tail orientations. The packing pattern of the molecule is governed by C–H···O and N–H···O interactions (Table 4). The structure does not posses direct O–H···O hydrogen

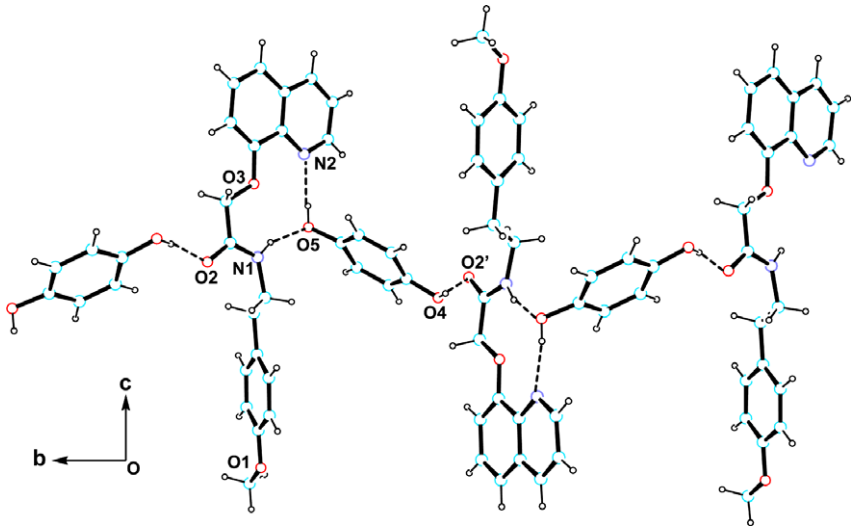
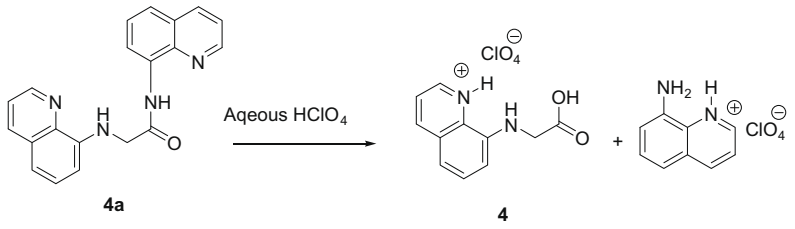


Fig. 5. One dimensional hydrogen bonded assembly of host and guest in co-crystal **3.**



Scheme 3.

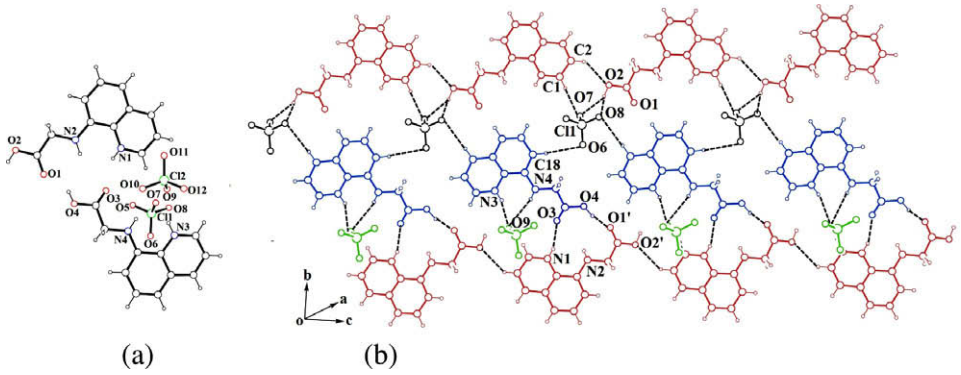


Fig. 6. (a) Crystal structure of salt **4**, (b) the weak interactions in its crystal lattice.

Table 4
Hydrogen bonds in the salt **4.**

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1 N)···O(3) [*x*, 1/2–*y*, 1/2 + *z*]	0.80(4)	2.04(4)	2.781(4)	154.2(4)
O(2)–H(2C)···O(7) [−1 + *x*, 1/2–*y*, −1/2 + *z*]	0.82	2.22	2.981(5)	154.6
O(2)–H(2C)···O(8) [−1 + *x*, 1/2–*y*, −1/2 + *z*]	0.82	2.38	3.030(5)	137.2
N(3)–H(3 N)···O(9) [*x*, *y*, −1 + *z*]	0.81(3)	2.17(3)	2.908(4)	152.5(3)
O(4)–H(4)···O(1) [*x*, 1/2–*y*, −1/2 + *z*]	0.82	1.87	2.624(4)	151.6
N(4)–H(4A)···O(9) [*x*, *y*, −1 + *z*]	0.86	2.57	3.371(4)	154.8
C(1)–H(1)···O(7) [*x*, 1/2–*y*, 1/2 + *z*]	0.93	2.37	3.283(5)	168.4
C(2)–H(2)···O(2) [1 + *x*, *y*, 1 + *z*]	0.93	2.59	3.352(5)	149.8
C(7)–H(7)···O(11) [−1 + *x*, *y*, −1 + *z*]	0.93	2.60	3.525(5)	174.2
C(14)–H(14)···O(8) [2–*x*, –*y*, 1–*z*]	0.93	2.58	3.494(5)	167.5

bonding interactions among the carboxylic acid group but they form cyclic hydrogen bonded network with the NH^+ and C=O of the quinolinium and carboxylic acid functional group of the parent compound. The dimeric units formed, are associated with a perchlorate anion through N–H···O interactions and leads to a chain like structure along crystallographic *c*-axis (Fig. 6b). The chain like structures are further held by intervening perchlorate anions. The packing pattern is such that the parent compounds in each layer along *c*-axis are not symmetrically equivalent.

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References

[1] A. Karmakar, R.J. Sarma, J.B. Baruah, CrystEngComm 9 (2007) 378–388.
[2] J. Ouyang, L. Li, Z. Tai, Z. Lu, G. Wang, Chem. Lett. (1997) 815–816.
[3] P. Vishweshwar, A. Nangia, V.M. Lynch, CrystEngComm 5 (2003) 164–168.
[4] C. Tamuly, N. Barooah, M. Laskar, R.J. Sarma, J.B. Baruah, Supramol. Chem. 18 (2006) 605–613.
[5] L. Tilley, P. Loria, M. Foley, Antimalarial Chemother. (2001) 87–121.
[6] R.G. Ridley, A.T. Hudson, Expert Opin. Ther. Pat. 8 (1998) 121–136.
[7] H. Maud, B. Sebastien, F. Albin, M. Joel, B. Eric, A. Remy, F. Thierry, F. Laurent, R. Christophe, P. Bruno, Antimicrob. Agents Chemother. 52 (2008) 2755–2759.
[8] P.R. Graves, J.J. Kwiek, P. Fadden, R. Ray, K. Hardeman, A.M. Coley, M. Foley, T.A.J. Haystead, Mol. Pharmacol. 62 (2002) 1364–1372.
[9] A. Karmakar, J.B. Baruah, Supramol. Chem. 20 (2008) 667–674.
[10] G.J. Perpetuo, J. Janczak, Acta Cryst. C63 (2007) o301–o302.
[11] D. Kalita, R. Sarma, J.B. Baruah, CrystEngComm 11 (2009) 803–810.