

7-Carboxylato-8-hydroxy-2-methylquinolinium monohydrate and 7-carboxy-8-hydroxy-2-methylquinolinium chloride monohydrate at 100 K

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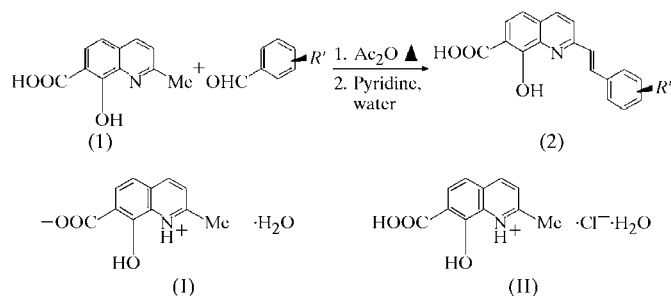
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Both 7-carboxylato-8-hydroxy-2-methylquinolinium monohydrate, $C_{11}H_9NO_3 \cdot H_2O$, (I), and 7-carboxy-8-hydroxy-2-methylquinolinium chloride monohydrate, $C_{11}H_{10}NO_3^+ \cdot Cl^- \cdot H_2O$, (II), crystallize in the centrosymmetric $P\bar{1}$ space group. Both compounds display an intramolecular O—H...O hydrogen bond involving the hydroxy group; this hydrogen bond is stronger in (I) due to its zwitterionic character [O...O = 2.4449 (11) Å in (I) and 2.5881 (12) Å in (II)]. In both crystal structures, the HN^+ group participates in the stabilization of the structure *via* intermolecular hydrogen bonds with water molecules [N...O = 2.7450 (12) Å in (I) and 2.8025 (14) Å in (II)]. In compound (II), a hydrogen-bond network connects the Cl^- anion to the carboxylic acid group [Cl...O = 2.9641 (11) Å] and to two water molecules [Cl...O = 3.1485 (10) and 3.2744 (10) Å].

Comment

8-Hydroxy-2-methylquinoline-7-carboxylic acid, (1), is used as a starting subunit in the syntheses of polyhydroxylated styrylquinoline derivatives, (2), which are potent HIV-1 integrase inhibitors that block the replication of HIV-1 in cell culture at non-toxic concentrations (Mekouar *et al.*, 1998). Zouhiri *et al.* (2000) have shown that, *in vitro*, the binding interactions between (2) and the HIV-1 integrase catalytic metallic sites (Mg^{2+} , Mn^{2+}) essentially involve the carboxylic acid group. Therefore, the crystallization of (1) and its metallic complexes is of particular interest in order to investigate the

interaction potency of such molecules. Compound (1) crystallizes from a mixture of water and acetic acid by slow evaporation at room temperature, giving rise to compound (I). Preliminary attempts to obtain a manganese complex of (1) by exchange with manganese chloride in the solid state failed and yielded 7-carboxy-8-hydroxy-2-methylquinolinium chloride monohydrate, (II). In the present study, we report the crystal structures of compounds (I) and (II) at 100 K.



Compound (1) crystallizes in the $P\bar{1}$ space group with either one water molecule in the asymmetric unit, giving (I), or one Cl^- anion and one water molecule, giving (II) (Fig. 1).

In compound (I), the carboxylate group is ionized giving a zwitterionic character in the solid state. This was also observed for the unsolvated 8-hydroxyquinaldic acid molecule reported by Okabe & Muranishi (2002). However, in (II), the carboxylic acid group is stabilized by an O—H...Cl hydrogen bond, with a donor–acceptor O1...Cl distance of 2.9641 (11) Å.

In both compounds, the quinoline N atom is protonated. Protonation of the N atom of (1) is characterized by the C2—N—C9 angle, which has a value of 123.14 (8)° in (I) and 123.14 (10)° in (II). This is in agreement with the angles obtained, for instance, for quinolinium-4-carboxylate [122.7 (2)°; Dobson & Gerkin, 1999] or for 8-hydroxyquinolinium-2-carboxylate [123.2 (3)°; Okabe & Muranishi, 2002]. Conversely, molecules with an unprotonated quinoline core exhibit smaller angles, *e.g.* 118.9 (2)° for 2-phenylquinoline-4-carboxylic acid (Blackburn *et al.*, 1996) and 119.3 (1)° for quinoline-4-carboxylic acid (Dobson & Gerkin, 1998). These typical C—N—C angles were reported recently in the structure of quinoline-2-carboxylic acid/quinolinium-2-carboxylate, where both tautomeric forms co-crystallize (Dobrzynska & Jerzykiewicz, 2004).

In both title compounds, the hydroxyl and carboxyl groups are linked by an O—H...O intramolecular hydrogen bond involving atom H31 (Fig. 1). However, there is a significant difference in the donor–acceptor distances [O3...O2 = 2.4449 (11) Å in (I) and 2.5881 (12) Å in (II)], relating to the zwitterionic character of (I). In (I), the hydrogen bond is actually a resonance-assisted hydrogen bond (RAHB), leading to an intramolecular ring formed by atoms H31, O3, C8, C7, C12 and O2 (Fig. 1). As predicted from theoretical quantum calculations by Wojtulewski & Grabowski (2003), a significant change in the molecular geometry is expected since RAHBs belong to the strongest hydrogen-bonded systems: a short donor–acceptor O...O distance is combined with an

equalization of the C—O and C=O bond lengths. This is not the case for compound (II), which exhibits a rather longer O2···O3 distance [2.5881 (12) Å]. Moreover, significant differences in the C—O and C=O bond lengths are found between (I) [C8—O3 = 1.3328 (11) Å and C12=O2 = 1.2951 (12) Å] and (II) [C8—O3 = 1.3401 (13) Å and C12=O2 = 1.2280 (14) Å].

The crystal structures of the title compounds are stabilized by intermolecular N—H···O hydrogen bonds [$N\cdots O_w$ = 2.7450 (12) Å in (I) and 2.8025 (14) Å in (II)] involving the HN^+ group and the water molecules. Carboxylate atoms O1 and O2 in (I) also participate in intermolecular hydrogen bonds with water molecules (Table 2). In compound (II), the Cl^- anion is engaged in three hydrogen bonds, *viz.* with O1 [$\text{Cl}\cdots\text{O1}$ = 2.9641 (11) Å] and two water molecules [$\text{Cl}\cdots\text{O}_w$ = 3.1485 (10) and 3.2744 (10) Å] (Table 4). The differences in the interactions between molecules in the crystal lattices of (I) and (II) can also explain the slight distortion of the carboxyl groups with respect to the planar quinoline moiety, characterized by the C8—C7—C12—O2 torsion angles [-3.9 (1)° in (I) and -0.5 (2)° in (II)].

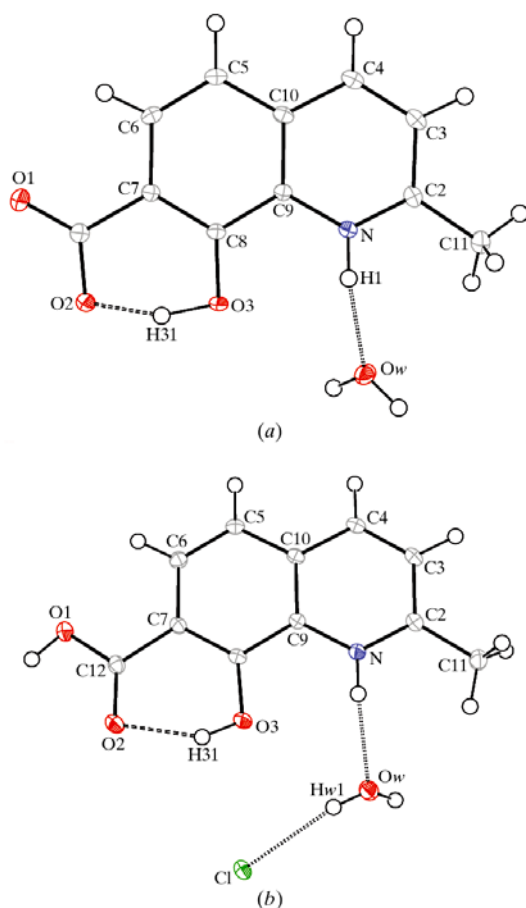


Figure 1

The molecular structures of (a) (I) and (b) (II), shown with 50% probability displacement ellipsoids for non-H atoms. Double-dashed and dotted lines indicate intramolecular and intermolecular hydrogen bonds, respectively.

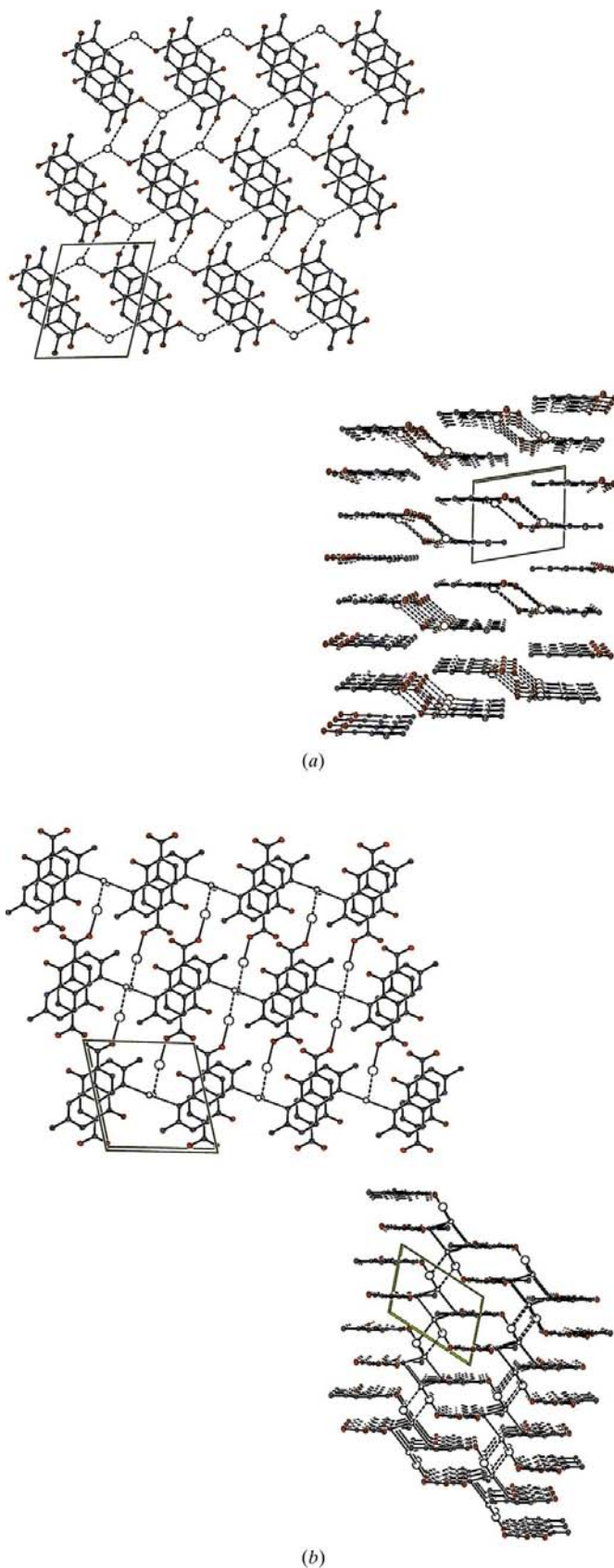


Figure 2

Packing diagrams for (a) (I) and (b) (II). The views on the left are down *a* and those on the right are down *c*. H atoms have been omitted for clarity. Dashed lines indicate the intermolecular donor–acceptor networks.

Fig. 2 shows how the molecules stack along the crystallographic *a* axis, with layers parallel to the *bc* plane. For both compounds, the distance between layers is 3.6 Å. The water molecules and Cl[−] anions occupy the empty space and constitute a three-dimensional hydrogen-bond network connecting the quinoline rings. Due to centers of inversion, the molecules have a head-to-tail arrangement. However, facing quinoline moieties are longitudinally shifted with respect to each other in both (I) and (II) because of *pπ*–*pπ* electronic repulsion (Fig. 2).

Experimental

Acid (I) was synthesized using the Kolbe reaction, as described by Meek & Fuchsmann (1969) and Polanski *et al.* (2002). Crystals of (I) were obtained by slow evaporation of a water–acetic acid solution (1:4 *v/v*) at room temperature. Crystals of (II) were obtained by slow evaporation at room temperature of a solution in methanol containing MnCl₂·4H₂O. Both crystal samples are very unstable in air and were mounted in glass capillaries before the data collections, which were carried out at 100 K.

Compound (I)

Crystal data

C₁₁H₉NO₃·H₂O
M_r = 221.21
 Triclinic, *P* $\bar{1}$
a = 6.6556 (7) Å
b = 7.8062 (8) Å
c = 9.6690 (10) Å
 α = 75.043 (2)°
 β = 86.534 (2)°
 γ = 79.042 (2)°
V = 476.45 (9) Å³
Z = 2
D_x = 1.542 Mg m^{−3}

Mo *K*α radiation
 Cell parameters from 2110 reflections
 θ = 2.2–30.1°
 μ = 0.12 mm^{−1}
T = 100 (2) K
 Prism, yellow
 0.40 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 3364 measured reflections
 2364 independent reflections
 2052 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.008
 θ _{max} = 30.1°
h = −9 → 9
k = −10 → 10
l = 0 → 13

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.037
wR(*F*²) = 0.109
S = 1.05
 2364 reflections
 189 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.0491P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

C2–N	1.3352 (12)	C8–C9	1.4253 (13)
C2–C11	1.4889 (14)	C9–N	1.3735 (12)
C7–C8	1.3969 (13)	C12–O1	1.2379 (12)
C7–C12	1.5019 (13)	C12–O2	1.2951 (12)
C8–O3	1.3328 (11)		
N–C2–C11	118.88 (9)	O1–C12–O2	124.27 (9)
C8–C7–C12	119.18 (8)	O2–C12–C7	115.29 (8)
O3–C8–C7	122.93 (9)	C2–N–C9	123.14 (8)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O3–H31...O2	1.08 (2)	1.42 (2)	2.4449 (11)	157 (2)
N–H1...Ow	0.91 (2)	1.85 (2)	2.7450 (12)	170 (2)
Ow–Hw1...O1 ⁱ	0.87 (2)	1.91 (2)	2.7746 (12)	168 (2)
Ow–Hw2...O2 ⁱⁱ	0.87 (2)	1.92 (2)	2.7863 (12)	176 (2)

Symmetry codes: (i) *x*, *y*, 1 + *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*.

Compound (II)

Crystal data

C₁₁H₁₀NO₃⁺·Cl[−]·H₂O
M_r = 257.67
 Triclinic, *P* $\bar{1}$
a = 7.1089 (4) Å
b = 9.4102 (5) Å
c = 9.6230 (5) Å
 α = 96.7190 (10)°
 β = 110.1840 (10)°
 γ = 107.9410 (10)°
V = 556.57 (5) Å³
Z = 2
D_x = 1.538 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 2975 reflections
 θ = 2.3–30.2°
 μ = 0.35 mm^{−1}
T = 100 (2) K
 Prism, white
 0.60 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 3978 measured reflections
 2904 independent reflections
 2627 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.010
 θ _{max} = 30.3°
h = −9 → 9
k = −12 → 8
l = −13 → 12

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.030
wR(*F*²) = 0.086
S = 1.08
 2904 reflections
 202 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.1462P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

C2–N	1.3312 (14)	C8–C9	1.4200 (14)
C2–C11	1.4892 (16)	C9–N	1.3746 (14)
C7–C8	1.3919 (15)	C12–O2	1.2280 (14)
C7–C12	1.4812 (15)	C12–O1	1.3209 (14)
C8–O3	1.3401 (13)		
N–C2–C11	119.09 (10)	O2–C12–O1	123.77 (10)
C8–C7–C12	118.07 (10)	O2–C12–C7	122.80 (10)
O3–C8–C7	124.50 (10)	C2–N–C9	123.14 (10)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N–H1...Ow	0.86 (2)	1.97 (2)	2.8025 (14)	164 (2)
O1–H11...Cl ⁱ	0.90 (2)	2.12 (2)	2.9641 (11)	155 (2)
O3–H31...O2	0.88 (2)	1.80 (2)	2.5881 (12)	149 (2)
Ow–Hw1...Cl	0.82 (2)	2.47 (2)	3.2744 (10)	169 (2)
Ow–Hw2...Cl ⁱⁱ	0.80 (2)	2.35 (2)	3.1485 (10)	177 (2)

Symmetry codes: (i) 1 − *x*, 2 − *y*, 2 − *z*; (ii) −*x*, 1 − *y*, 1 − *z*.

For both compounds, all H atoms were found in difference Fourier maps and refined with isotropic displacement parameters.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE-Plus* (Bruker, 1998); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1072). Services for accessing these data are described at the back of the journal.

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