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One-dimensional hydrogen-bonded structures in the 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid with 8-hydroxyquinoline, 8-aminoquinoline and quinoline-2-carboxylic acid (quinaldic acid)

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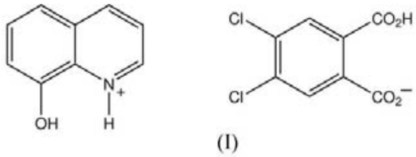
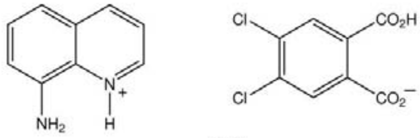
The structures of the 1:1 proton-transfer compounds of 4,5-dichlorophthalic acid with 8-hydroxyquinoline, 8-aminoquinoline and quinoline-2-carboxylic acid (quinaldic acid), namely anhydrous 8-hydroxyquinolinium 2-carboxy-4,5-dichlorobenzoate, $C_9H_8NO^+\cdot C_8H_3Cl_2O_4^-$, (I), 8-aminoquinolinium 2-carboxy-4,5-dichlorobenzoate, $C_9H_9N_2^+\cdot C_8H_3Cl_2O_4^-$, (II), and the adduct hydrate 2-carboxyquinolinium 2-carboxy-4,5-dichlorobenzoate quinolinium-2-carboxylate monohydrate, $C_{10}H_8NO_2^+\cdot C_8H_3Cl_2O_4^-\cdot C_{10}H_7NO_2\cdot H_2O$, (III), have been determined at 130 K. Compounds (I) and (II) are isomorphous and all three compounds have one-dimensional hydrogen-bonded chain structures, formed in (I) through $O-H\cdots O_{carboxyl}$ extensions and in (II) through $N^+-H\cdots O_{carboxyl}$ extensions of cation–anion pairs. In (III), a hydrogen-bonded cyclic $R_2^2(10)$ pseudo-dimer unit comprising a protonated quinaldic acid cation and a zwitterionic quinaldic acid adduct molecule is found and is propagated through carboxylic acid $O-H\cdots O_{carboxyl}$ and water $O-H\cdots O_{carboxyl}$ interactions. In both (I) and (II), there are also cation–anion aromatic ring π–π associations. This work further illustrates the utility of both hydrogen phthalate anions and interactive-group-substituted quinoline cations in the formation of low-dimensional hydrogen-bonded structures.

Comment

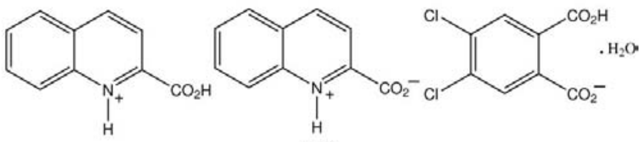
The crystal structures of the proton-transfer compounds of 4,5-dichlorophthalic acid (DCPA) are not common, being limited to tetramethylammonium hydrogen 4,5-dichlorophthalate (Bozkurt *et al.*, 2006), naphthalene-1,8-bis(dimethylammonium) 4,5-dichlorophthalate (Mallinson *et al.*, 2003), brucinium hydrogen 4,5-dichlorophthalate (Smith, Wermuth, Healy & White, 2007) and the 1:1 salts with 4-chloroaniline, 1,10-phenanthroline and the three isomeric monoaminobenzoic acids (Smith, Wermuth & White, 2008*b*). A non-transfer adduct with *trans*-cinnamamide is also known (Hosomi *et al.*, 2000). In the hydrogen 4,5-dichlorophthalates, as well as other substituted hydrogen phthalate salts (Glidewell *et al.*, 2003, 2005; Smith, Wermuth, Young & White, 2008), low-dimensional hydrogen-bonded structures are common. It was considered that, combined with the heteroaromatic Lewis bases derived from quinoline, namely the interactive functional-group-substituted analogues 8-hydroxyquinoline (quinolin-8-ol), 8-aminoquinoline and quinoline-2-carboxylic acid (quinaldic acid), DCPA would give one-dimensional 1:1 proton-transfer salts. This is found to be the case, with the determination of the structures of 8-hydroxyquinolinium 2-carboxy-4,5-dichlorobenzoate, (I), 8-aminoquinolinium 2-carboxy-4,5-dichlorobenzoate, (II), and the adduct hydrate 2-carboxyquinolinium 2-carboxy-4,5-dichlorobenzoate quinolinium-2-carboxylate monohydrate, (III), reported here.



(I)



(II)



(III)

In all three compounds, proton transfer has occurred, with the quinolinium group giving a primary $N^+-H\cdots O_{carboxyl}$ hydrogen-bonding interaction (Tables 1–3). However, in (I) and (II), which are isomorphous, the association is heteromeric (Figs. 1 and 2), whereas in (III), the primary association is homomeric, forming a cation–adduct molecule pseudo-dimer (Fig. 3). All three compounds are extended into one-dimensional chain structures [graph set *C*(11) in (I) and (II), and *C*(13) in (III) (Etter *et al.*, 1990)] by secondary hydrogen bonding involving the second functional groups of both the cation and anion, as well as, in the case of (III), the water molecule of solvation (Figs. 3–6). In (I), the single intermolecular cation–anion $N^+-H\cdots O$ association is extended through the 8-hydroxy group of the cation, giving zigzag chains analogous to those found in other proton-transfer compounds of 8-hydroxyquinoline (Smith, Wermuth & White, 2001; Smith, Wermuth & Healy, 2004). There is also a short intramolecular $N1A-H\cdots O8A$ contact [2.689 (3) Å], which is common in these compounds. In (II), duplex asymmetric N^+-

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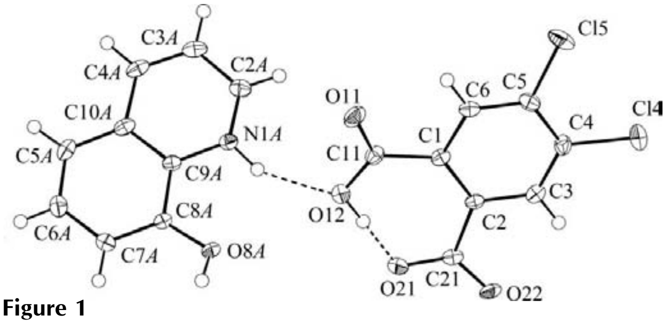

Figure 1
The molecular configuration and atom-numbering scheme for the 8-hydroxyquinolinium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (I). The interspecies hydrogen bond is shown as a dashed line. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

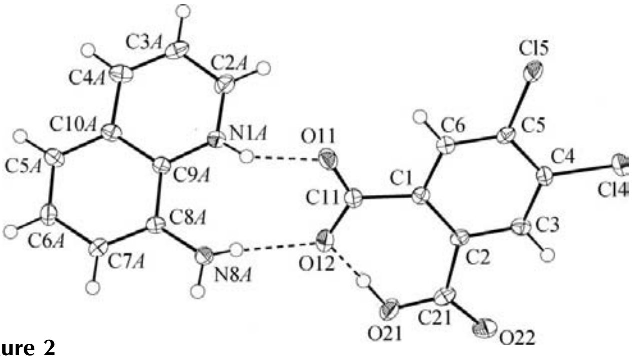

Figure 2
The molecular configuration and atom-numbering scheme for the 8-aminoquinolinium cation and the 2-carboxy-4,5-dichlorobenzoate anion in (II). The interspecies cyclic $R_2^2(9)$ hydrogen-bonding interaction and the intramolecular hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

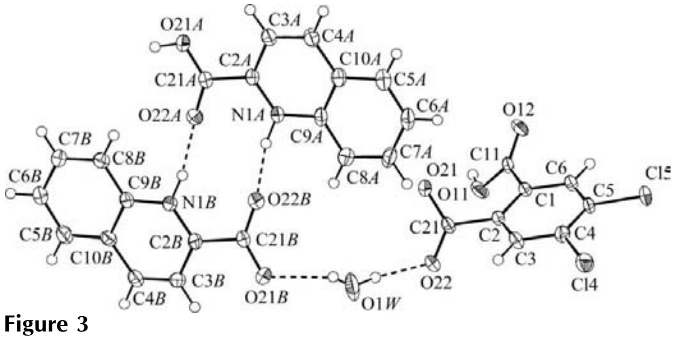

Figure 3
The molecular configuration and atom-numbering scheme for the 2-carboxyquinolinium cation, the 2-carboxy-4,5-dichlorobenzoate anion, the quinolinium-2-carboxylate adduct molecule and the water molecule of solvation in (III). Dashed lines indicate the interspecies hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

H$\cdots$O hydrogen bonds form a primary cyclic $R_2^2(9)$ association which encloses an intramolecular $N^+{-}H\cdots N_{amine}$ contact [N1A—H$\cdots$N8A = 2.829 (2) Å]. Propagation down a 2_1 screw axis in the unit cell [as is also found in (I)] is through a three-centre aminium $N^+{-}H\cdots O,O'_{carboxyl}$ association. Again, this is analogous to the mode of propagation found in a number of other proton-transfer compounds of 8-aminoquinoline with aromatic carboxylic acids (Smith, Wermuth, Bott *et al.*, 2001).

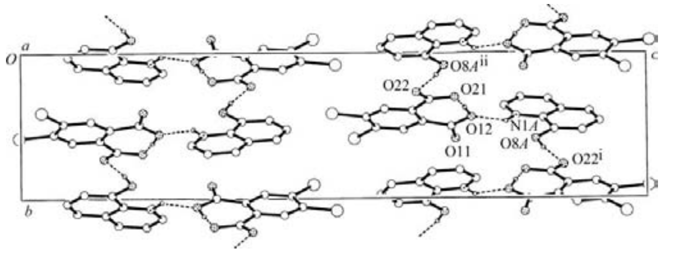

Figure 4
The hydrogen-bonded cation–anion chain structure in (I), viewed down the *a*-axis direction. Hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted. [Symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$.]

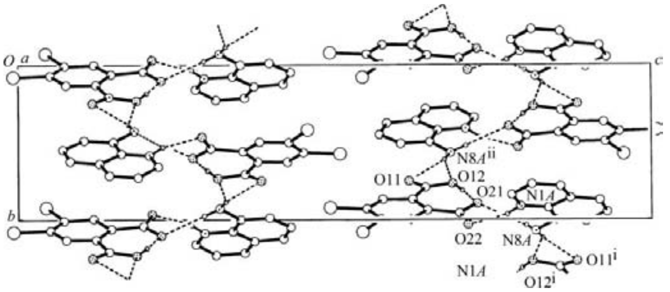

Figure 5
A view of the chain extension in the one-dimensional hydrogen-bonded chain structure of (II), viewed down the *a*-axis direction. Hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted. See Fig. 4 for symmetry codes.

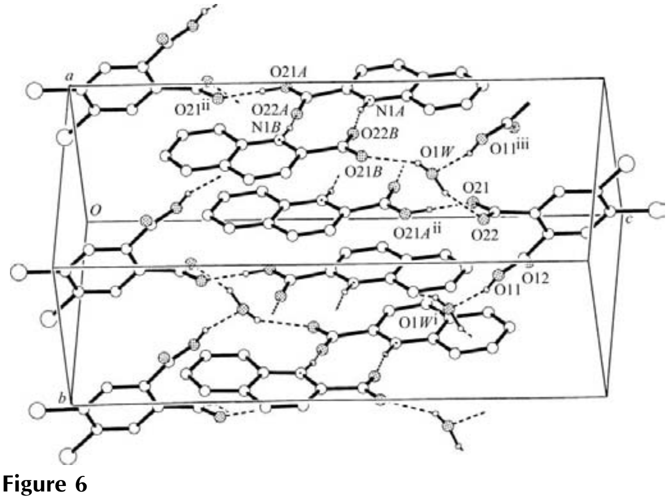

Figure 6
A perspective view of the chain extension in the one-dimensional hydrogen-bonded structure of (III). Hydrogen bonds are shown as dashed lines. H atoms not involved in these interactions have been omitted. See Table 3 for symmetry codes.

With the adduct hydrate, (III), the basic hydrogen-bonding pattern is quite different. The asymmetric unit comprises the protonated quinaldic acid cation, the hydrogen 4,5-dichlorophthalate anion, a zwitterionic quinaldic acid adduct molecule and a water molecule of solvation (Fig. 3). The two quinaldic acid species form a hydrogen-bonded cyclic pseudo-dimer through $N^+{-}H\cdots O_{carboxyl}$ interactions [graph set $R_2^2(10)$].

These units are similar to those found in the structures of the quinolinium-2-carboxylate adducts of the 1:1 proton-transfer salts of quinaldic acid with both 5-sulfosalicylic acid (Smith, Wermuth & White, 2004) and 2,4,6-trinitrobenzenesulfonic acid (Smith, Wermuth & White, 2008*a*). The quinaldic acid adduct species is also found to be zwitterionic in both the parent acid structure (Dobrzyńska & Jerzykiewicz, 2004) and in the non-transfer adduct compound L-tartaric acid–quinaldic acid (1/2) (Smith *et al.*, 2006). However, they are absent in the 1:1 proton-transfer compound 2-carboxyquinolinium 3,5-dinitrosalicylate (Smith, Wermuth, Healy & White, 2007).

With both (I) and (II), there are additional π–π interactions due to partial aromatic ring overlap of the anion (C1–C6) with C5*A*–C10*A* of the cation [ring centroid separation = 3.6642 (13) Å and dihedral angle = 1.29 (1)° in (I), compared with values of 3.6715 (9) Å and 2.16 (1)° in (II)].

The anion species in (I) and (II) are conformationally similar but differ significantly from that found in (III). Both (I) and (II) have a short intramolecular carboxylic acid O—H···O$_{\text{carboxylate}}$ hydrogen bond, resulting in the anions being essentially planar, with a C2—C1—C21—O22 torsion angle of 171.3 (2)° in (I) and 174.38 (15)° in (II), and a C1—C2—C21—O22 torsion angle of −176.6 (2)° in (I) and −175.88 (15)° in (II). With (III), the two carboxyl groups of the anion are rotated out of the plane of the benzene ring, with corresponding torsion angles of −38.2 (3) and 125.4 (2)°. In (III), the carboxylic acid groups of both quinaldic acid species (*A* and *B*) are essentially planar, with N1—C2—C21—O21 torsion angles of −177.7 (2) and 173.8 (2)°, respectively. In addition, there are solvent-accessible voids of 171 Å^3 in the structure of (III).

Experimental

Compounds (I)–(III) were synthesized by heating together for 10 min under reflux 1 mmol quantities of 4,5-dichlorophthalic acid and, respectively, 8-hydroxyquinoline (quinolin-8-ol), 8-aminoquinoline and quinoline-2-carboxylic acid (quinaldic acid) in ethanol–water (8:2 *v*/*v*, 50 ml) for (I) and (III) or in ethanol (95%, 50 ml) for (II). Compound (I) was obtained as pale-yellow flat prismatic crystals (m.p. 499 K), (II) as pale-brown flat prisms (m.p. 471 K) and (III) as colourless prisms (m.p. 453–455 K) after partial room-temperature evaporation of the solvent.

Compound (I)

Crystal data

$C_9H_8NO^+\cdot C_8H_3Cl_2O_4^-$
M_r = 380.17
Orthorhombic, $P2_12_12_1$
a = 6.8915 (3) Å
b = 7.2887 (2) Å
c = 30.8009 (8) Å
V = 1547.13 (9) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 4.06 mm^{-1}
T = 130 (2) K
0.61 × 0.56 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur KM-4 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.112, $T_{\max}$ = 0.443
4879 measured reflections
2506 independent reflections
2437 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1*A*—H1*A*···O12	0.95 (3)	2.01 (3)	2.830 (3)	145 (3)
O8*A*—H8*A*···O22$^{\text{i}}$	0.84 (4)	1.78 (4)	2.607 (2)	171 (4)
O12—H12···O21	0.96 (4)	1.44 (4)	2.389 (2)	173 (4)

Symmetry code: (i) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O21—H12···O12	1.01 (3)	1.39 (3)	2.3922 (18)	174 (3)
N1*A*—H1*A*···O11	0.87 (2)	1.91 (2)	2.7002 (19)	152 (2)
N8*A*—H81*A*···O12	0.80 (2)	2.21 (2)	3.0116 (19)	176 (3)
N8*A*—H82*A*···O21$^{\text{i}}$	0.86 (2)	2.53 (2)	3.314 (2)	152.2 (18)
N8*A*—H82*A*···O22$^{\text{i}}$	0.86 (2)	2.40 (2)	3.189 (2)	153.8 (18)

Symmetry code: (i) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.06
2506 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.40 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), with 662 Friedel pairs
Flack parameter: 0.035 (15)

Compound (II)

Crystal data

$C_9H_9N_2^+\cdot C_8H_3Cl_2O_4^-$
M_r = 379.19
Orthorhombic, $P2_12_12_1$
a = 7.2003 (6) Å
b = 7.3039 (6) Å
c = 29.438 (3) Å
V = 1548.2 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 130 (2) K
0.45 × 0.40 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.842, $T_{\max}$ = 0.956
9645 measured reflections
3529 independent reflections
3425 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.073
S = 1.07
3529 reflections
242 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), with 1427 Friedel pairs
Flack parameter: 0.04 (5)

Compound (III)

Crystal data

$C_{10}H_8NO_2^+\cdot C_8H_3Cl_2O_4^-\cdot C_{10}H_7NO_2\cdot H_2O$
M_r = 599.36
Triclinic, $P\overline{1}$
a = 7.1893 (9) Å
b = 10.1172 (13) Å
c = 19.520 (3) Å
α = 87.558 (2)°
β = 88.577 (2)°
γ = 83.996 (2)°
V = 1410.4 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 130 (2) K
0.40 × 0.30 × 0.25 mm

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O11—H11⋯O1W^{i}	0.85 (4)	1.70 (4)	2.510 (3)	159 (4)
O21A—H21A⋯O21^{ii}	0.90 (4)	1.64 (4)	2.531 (2)	179 (5)
N1A—H1A⋯O22B	0.96 (4)	1.84 (4)	2.788 (3)	168 (3)
N1B—H1B⋯O22A	0.99 (3)	1.80 (3)	2.756 (3)	163 (3)
O1W—H1W⋯O22	0.98 (4)	1.92 (4)	2.771 (3)	143 (4)
O1W—H2W⋯O21B	0.92 (4)	1.71 (4)	2.625 (3)	169 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z+1$.

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.865$, $T_{\max} = 0.931$
6939 measured reflections
4878 independent reflections
3980 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.094$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.160$
$S = 1.03$
4878 reflections
390 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

In all three compounds, H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined, giving distance ranges N—H = 0.80 (2)–0.97 (3) Å and O—H = 0.84 (4)–1.01 (3) Å. All other H atoms were included at calculated positions, with C—H = 0.93–0.95 Å, and treated as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007) for (I); *SMART* (Bruker, 2000) for (II) and (III). Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007) for (I); *SMART* for (II) and (III). Data reduction: *CrysAlis RED* for (I); *SAINT* (Bruker, 1999) for (II) and (III). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3186). Services for accessing these data are described at the back of the journal.

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