Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen bonding in proton-transfer compounds of 5-sulfosalicylic acid with bicyclic heteroaromatic Lewis bases

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Received 7 April 2004
Accepted 15 June 2004
Online 21 July 2004

The crystal structures of quinolinium 3-carboxy-4-hydroxybenzenesulfonate trihydrate, $C_9H_8N^+\cdot C_7H_5O_6S^-\cdot 3H_2O$, (I), 8-hydroxyquinolinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, $C_9H_8NO^+\cdot C_7H_5O_6S^-\cdot H_2O$, (II), 8-aminoquinolinium 3-carboxy-4-hydroxybenzenesulfonate dihydrate, $C_9H_9N_2^+\cdot C_7H_5O_6S^-\cdot 2H_2O$, (III), and 2-carboxyquinolinium 3-carboxy-4-hydroxybenzenesulfonate quinolinium-2-carboxylate, $C_{10}H_8NO_2^+\cdot C_7H_5O_6S^-\cdot C_{10}H_7NO_2$, (IV), four proton-transfer compounds of 5-sulfosalicylic acid with bicyclic heteroaromatic Lewis bases, reveal in each the presence of variously hydrogen-bonded polymers. In only one of these compounds, *viz*. (II), is the protonated quinolinium group involved in a direct primary $N^+—H\cdots O$(sulfonate) hydrogen-bonding interaction, while in the other hydrates, *viz*. (I) and (III), the water molecules participate in the primary intermediate interaction. The quinaldic acid (quinoline-2-carboxylic acid) adduct, (IV), exhibits cation–cation and anion–adduct hydrogen bonding but no direct formal heteromolecular interaction other than a number of weak cation–anion and cation–adduct π–π stacking associations. In all other compounds, secondary interactions give rise to network polymer structures.

Comment

We have previously reported the crystal structures of a number of proton-transfer compounds of 3,5-dinitrosalicylic acid (DNSA) with both monocyclic and polycyclic heteroaromatic Lewis bases (Smith *et al*., 1995, 1996; Smith, Wermuth & Healy, 2003; Smith, Wermuth, Healy & White, 2003, 2004). In all of these compounds, the resulting aminium cations subsequently form direct primary hydrogen-bonding interactions with the carboxylate groups of the DNSA anions; these interactions, together with secondary hydrogen bonding, lead to the formation of both network and framework polymer structures. The secondary interactions can be either strong [$O—H\cdots O$ or $N—H\cdots O$, depending on the nature of the substituent group on the heterocyclic ring, *e.g.* with 8-aminoquinoline (Smith, Wermuth Bott *et al*., 2001), 8-hydroxyquinoline (Smith, Wermuth & White, 2001) and quinaldic acid (Smith, Wermuth, Healy & White, 2004)] or weak but extensive [$C—H\cdots O$, *e.g.* with quinoline, 1,10-phenanthroline and 2,2′-bipyridine (Smith, Wermuth, Healy & White, 2004)]. Cation–anion π–π stacking is rare and is almost exclusive to the polycyclic aromatic Lewis bases, quinoline and 1,10-phenanthroline (Smith, Wermuth, Healy & White, 2004).

With aromatic sulfonic acids, the acid strength is even greater than that of DNSA ($pK_a = 2.2$), so proton transfer will occur on reaction of these acids with most Lewis bases. Furthermore, with deprotonation of the sulfonate group, the three O atoms provide an additional set of proton-accepting centres for hydrogen-bonding associations, enhancing the potential for self-assembly. The guanidinium salts of aromatic sulfonates have been investigated as potentially useful optical materials, generated because of the compatibility of their adjacent NH donors with two of the sulfonate O-atom acceptors, giving rise to a primary cyclic $R_2^2(8)$ interaction. This interaction results in the assembly of hydrogen-bonded sheet structures, which may have interlayer linkages through the third sulfonate O atom, giving network polymer structures, hopefully with induced asymmetry (Russell *et al*., 1994*a*,*b*).

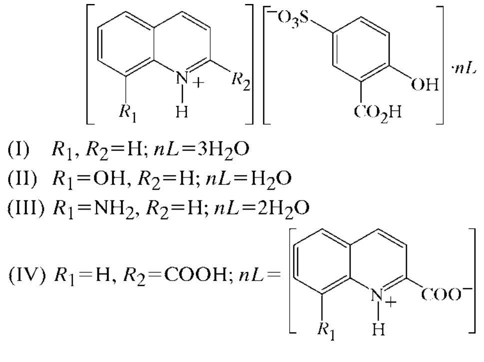
For this initial structural study, we therefore chose 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA), which has structural features similar to DNSA and to the closer analogue 5-nitrosalicylic acid (5-NSA). These acids have additional interactive substituent carboxylic acid and phenol functional groups that lend themselves to secondary *n*-dimensional hydrogen-bonding extension. Not only is 5-SSA structurally similar to 5-NSA, but also the acid strength of 5-SSA makes it capable of protonating water, and several hydrated structures of the acid are known, *viz*. the dihydrate (Attig & Mootz, 1977; Aliev *et al*., 1995), the dideuterate (Attig & Williams, 1977), the trihydrate (Attig & Mootz, 1977) and the pentahydrate (Merschenz-Quack & Mootz, 1990). With many of these, protonated polyaqua species have been identified, for example, the $H_7O_3^+$ cation of the trihydrate (Mootz & Fayos, 1970). This feature is considered to be responsible for the unusual conductivity properties of the acid and many of its compounds, for example, with the lanthanum, praseodymium and samarium sulfosalicylate nonahydrates (Aliev, Atovmyan, Baranova & Pirkes, 1991; Aliev, Baranova, Atovmyan, Pirkes *et al*., 1991). The structures of the 5-SSA proton-transfer compounds with the Lewis bases aniline (1:1; Bakasova *et al*., 1991), theophylline (a 1:1 monohydrate; Madarasz *et al*., 2002), trimethoprim (a 1:1 dihydrate; Raj *et al*., 2003) and 4,4′-bipyridine (a 1:2 dihydrate; Muthiah *et al*., 2003) are also known, while the structures of two different guanidinium (GU) salts have also been reported recently; the first is that of anhydrous $(GU)^+\cdot(5\text{-SSA})^-$ (Zhang *et al*., 2004), while the second is the hydrate $2(GU)^+\cdot(5\text{-SSA})^{2-}\cdot H_2O$ (Smith, Wermuth & Healy, 2004). As well as the chemical difference due to deprotonation of both the

DOI: 10.1107/S010827010401457X

sulfonic and carboxylic acid groups of 5-SSA in the hydrate, the expected cyclic $R_2^2(8)$ $\mathrm{N-H\cdots O}$ guanidinium–sulfonate interactions (Russell *et al.*, 1994*a*,*b*) are absent in the hydrate but present in the anhydrate (Zhang *et al.*, 2004).

The choice of Lewis bases for this study was influenced by experience with DNSA; the polycyclic aromatic analogues were found to be particularly efficient in structure building through both hydrogen bonding and, to a lesser extent, cation–anion π–π associations. The nitrogen bases selected were the parent bicyclic heteroaromatic quinoline (QUIN), the common 8-subsituted quinolines 8-hydroxyquinoline (oxine, 8-HQ) and 8-aminoquinoline (8-AQ), and quinoline-2-carboxylic acid (quinaldic acid, QA). Of these, oxine has proved most useful as a molecule with good structure-extending ability, achieved through secondary hydrogen bonding, forming both neutral and proton-transfer structures as well as molecular adducts. With a number of these structures, the reactions occur readily in the solid state (Rastogi *et al.*, 1977; Singh *et al.*, 1994, 1999, 2000). The crystal structures of both the 1:1 and the 1:2 compound with salicylic acid (SA), *viz*. $(8\text{-HQ})^+\cdot(\mathrm{SA}^-)$ (Singh *et al.*, 2000; Smith, Wermuth & White, 2003) and $(8\text{-HQ})^+\cdot(\mathrm{SA})^-\cdot(\mathrm{SA})$ (Jebamony & Muthiah, 1998), are known and both formation reactions proceed in the solid state. Kemp's triacid (*cis*-*cis*-1,3,5-trimethylhexane-1,3,5-tricarboxylic acid) exhibits proton transfer as well as the retention of a partial oxine molecule in the crystal structure (Smith *et al.*, 2000), while a series of six 1:1 compounds with the nitrobenzoic acids, including DNSA and 5-NSA (Smith, Wermuth & White, 2001), contains two hydrates. We have also reported the structure of the guanidinium monohydrate salt of the analogous substituted oxine, 7-iodo-8-hydroxyquinolinesulfonic acid (ferron; Smith, Wermuth & Healy, 2003), in which the hydrogen bonding is extensive. Examples of neutral adducts are less common but are found in the 1:1 complexes with chloranil (Prout & Wheeler, 1967) and 1,3,5-trinitrobenzene (Castellano & Prout, 1971), while the compound with 1,2,3-trihydroxybenzene (THB; Singh *et al.*, 1994) is a 2:1 proton-transfer adduct $[(8\text{-HQ})^+\cdot(\mathrm{THB})^-\cdot(8\text{-HQ})]$. Few structures of proton-transfer compounds of the other quinoline analogues used here have been reported; for 8-AQ, they are limited to a series of compounds with nitro-substituted carboxylic acids (Smith, Wermuth, Bott *et al.*, 2001), although the structure of the non-transfer compound with Kemp's triacid is known (Smith *et al.*, 2000). For quinoline and quinaldic acid, the only known examples are the 1:1 proton-transfer compounds with DNSA, and in the quinoline structure, there is evidence of π–π interaction (Smith, Wermuth, Healy & White, 2004).

The crystal structures reported here are those of the 5-sulfosalicylates with QUIN [quinolinium 5-sulfosalicylate trihydrate, $(\mathrm{QUIN})^+\cdot(5\text{-SSA})^-\cdot3\mathrm{H_2O}$, (I)], 8-HQ [8-hydroxyquinolinium 5-sulfosalicylate monohydrate, $(8\text{-HQ})^+\cdot(5\text{-SSA})^-\cdot\mathrm{H_2O}$, (II)] and 8-AQ [8-aminoquinolinium 5-sulfosalicylate dihydrate, $(8\text{-AQ})^+\cdot(5\text{-SSA})^-\cdot2\mathrm{H_2O}$, (III)], and the adduct structure with QA [quinolinium-2-carboxylic acid 5-sulfosalicylate quinoline-2-carboxylic acid (1/1), $(\mathrm{QA})^+\cdot(5\text{-SSA})^-\cdot(\mathrm{QA})$, (IV)]. Fig. 1 shows the atom-numbering scheme used for each of the four structures. All of these examples involve proton transfer, but in only one compound, *viz*. (II), is primary direct $\mathrm{N^+-H\cdots O}$(sulfonate) hydrogen bonding found; this situation contrasts with that reported for the analogous series of compounds with DNSA (Smith, Wermuth, Healy & White, 2004). There is no occurrence of the $R_2^2(8)$ dimer interaction found in the anhydrous guanidinium sulfonates (Russell *et al.*, 1994*a*,*b*; Zhang *et al.*, 2004) but absent in the bis(guanidinium) 5-sulfosalicylate hydrate structure (Smith, Wermuth & Healy, 2004). The presence of water of solvation in this last structure and in compounds (I)–(III) of the current series (a feature that is rare among the DNSA analogues) appears to be the main contributing factor, resulting from a deficiency of proton-donor groups able to satisfy the additional acceptor requirements of sulfonate O atoms. In the case of (IV) (in which, in addition, there are 42 Å^3 solvent-free voids in the lattice, capable of accommodating water molecules), the QA adduct molecule also acts as both a donor and an acceptor, providing a structure in which there is no direct formal heteromolecular interaction. However, (IV) exhibits significant cation–anion and cation–adduct π–π stacking interactions, while in (I), there is π–π stacking but it is homomolecular, involving both cation–cation and anion–anion stacking interactions. All other structures exhibit extensive secondary hydrogen bonding, utilizing the sulfonate acceptor O atoms, which results in framework polymer structures. Tables 1–4 list the hydrogen-bonding geometries for (I)–(IV) and the symmetry codes used in the following discussion.



(I) $R_1, R_2=\mathrm{H}$; $nL=3\mathrm{H_2O}$

(II) $R_1=\mathrm{OH}$, $R_2=\mathrm{H}$; $nL=\mathrm{H_2O}$

(III) $R_1=\mathrm{NH_2}$, $R_2=\mathrm{H}$; $nL=2\mathrm{H_2O}$

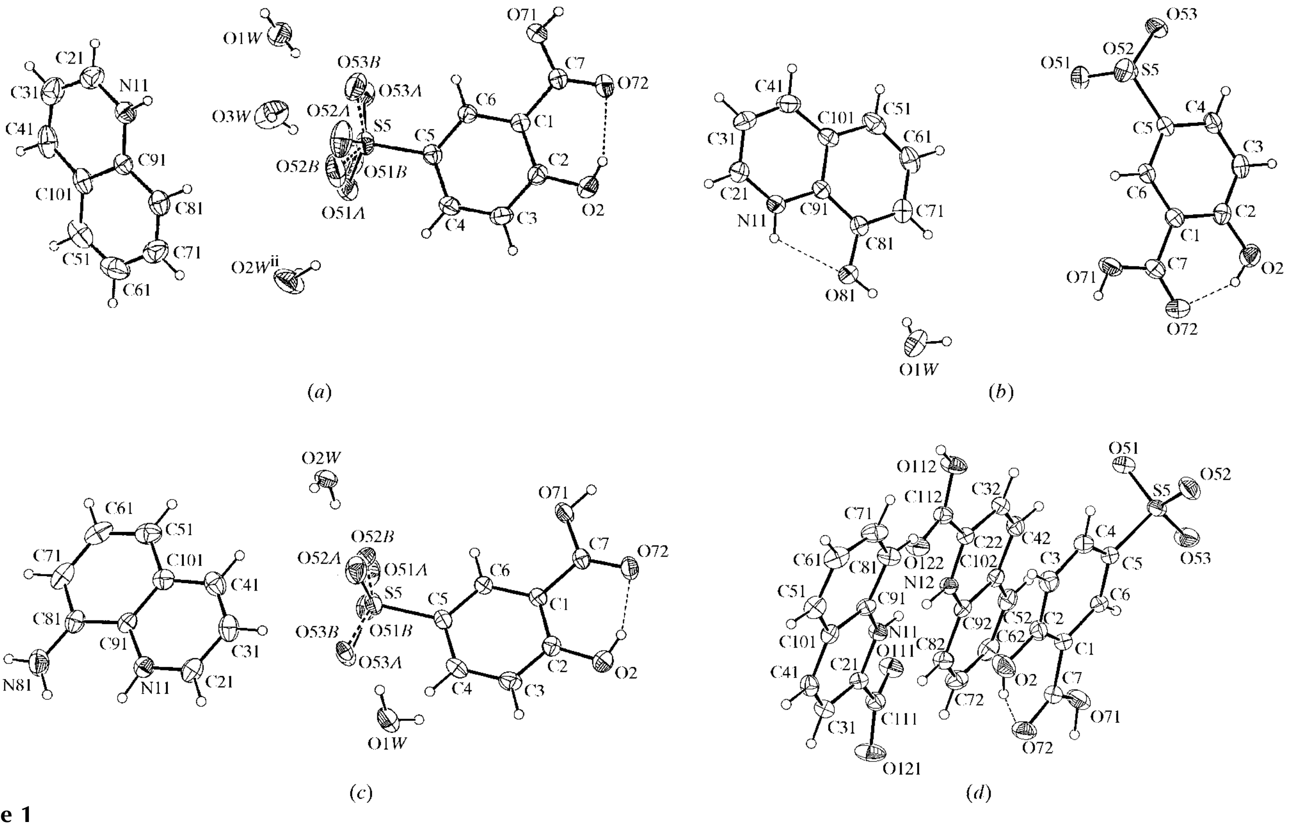
(IV) $R_1=\mathrm{H}$, $R_2=\mathrm{COOH}$; $nL=$

Compound (I) with quinoline, $(\mathrm{QUIN})^+\cdot(5\text{-SSA})^-\cdot3\mathrm{H_2O}$, contains a 5-SSA anion with a rotationally disordered sulfonate group [O51*A*–O53*A* and O51*B* –O53*B*, with occupancies 0.74 (1):0.26 (1); Fig. 1*a*]. Only the three primary (*A*) sites are considered in the discussion. These sites are involved in three hydrogen-bonding interactions. Although none of these is a direct $\mathrm{N^+-H\cdots O}$(sulfonate) link, there is a primary interaction between the quinolinium H atom and a water molecule ($\mathrm{N11\cdots O1}W^{\mathrm{iv}}$; Fig. 2). The H atoms of this water molecule allow propagation of the structure through interactions with sulfonate atom O53 and a second glide-related water molecule (O3W^{i}). There is further extension *via* atom O3*W* through both of its H atoms to different sulfonate O-atom acceptors (O52*A* and O53A^{iv}). The third water molecule (O2*W*) links sulfonate atom O51A^{ii} of a 5-SSA anion with carboxylic acid atom O72$^{\mathrm{iii}}$ and serves as an acceptor for another 5-SSA carboxyl H atom (O71—H7$\cdots$O2$W^{\rm v}$). Both the 5-SSA anions and the QUIN cations form homomolecular stacks along the *b* direction, with a separation of *b*/2 (3.613 Å), a distance indicative of significant π–π interactions. The result is a three-dimensional framework polymer.

In the 8-HQ compound [(8-HQ)$^+\cdot$(5-SSA)$^-\cdot$H$_2$O], (II) (Fig. 1*b*), there is a direct N$^+$—H$\cdots$O(sulfonate) interaction (N11$\cdots$O53$^{\rm viii}$). The 8-hydroxy substituent group of the 8-HQ cation is associated intermolecularly with only the solvent water molecule (O1*W*) but has an usual intramolecular association with quinolinium atom H11. The water H atoms extend the structure *via* different sulfonate groups (O1*W*$\cdots$O51$^{\rm vi}$ and O1*W*$\cdots$O52$^{\rm vii}$), while the fourth formal hydrogen bond to the sulfonate group is one involving the carboxylic acid H atom (O71—H7$\cdots$O51$^{\rm vii}$). The result is a three-dimensional network structure (Fig. 3) with no significant π–π interactions.

Compound (III) with 8-AQ [(8-AQ)$^+\cdot$(5-SSA)$^-\cdot$2H$_2$O] has a rotationally disordered sulfonate group similar to that in (I) [O51*A*–O53*A* and O51*B*–O53*B*, with occupancies 0.74 (2):0.26 (2); Fig. 1*c*], with all three O atoms of the primary group acting as H-atom acceptors in four hydrogen-bonding interactions. Three of these are with water molecules (O1*W*$\cdots$O53*A*, O2*W*$\cdots$O52*A* and O2*W*$\cdots$O51*A*$^{\rm x}$) and the fourth is a much weaker bond to the 8-amine group of an inversion-related 8-AQ cation (N81$\cdots$O51*A*$^{\rm xii}$). This last interaction is the only direct 5-SSA$\cdots$8-AQ contact. The sulfonate–water interactions extend the structure along the *a* direction (Fig. 4), while one of the water molecules also extends the structure in the *b* direction through both O atoms of the carboxylic acid group of the 5-SSA anion (O71$\cdots$O1*W*$^{\rm xi}$ and O1*W*$\cdots$O72$^{\rm ix}$). The second water molecule similarly extends the structure along the *b* axis through the amine and quinolinium groups [2.768 (3) and 3.026 (3) Å]. There are no π–π cation–cation or cation–anion interactions with the two-dimensional sheet structure, which is only weakly linked in the third dimension *via* a hydrogen bond between the single 8-amine N atom (N81) and sulfonate atom O51.

The structure of the compound of 5-SSA with quinaldic acid [(QA)$^+\cdot$(5-SSA)$^-\cdot$(QA)], (IV) (Fig. 1*d*), is unusual in many respects when compared with (I)–(III). Not only is (IV) anhydrous (although it has the previously mentioned 42 Å^3 solvent-free voids in the crystal structure), with an adduct QA molecule in the structure, but also there are no formal heteromolecular hydrogen-bonding linkages between the 5-SSA anion and either the cationic or the neutral QA species. While both QA species have protonated hetero N atoms, one (N12$^+$—H12) is derived from the 5-SSA sulfonic acid group and the other (N11$^+$—H11) comes from a zwitterionic transfer from the adjacent carboxylic acid group. The two carboxyl groups are linked linearly by a single short hydrogen bond [O112$\cdots$O121$^{\rm viii}$ = 2.478 (2) Å; Fig. 5]. The two QA species are laterally associated to form a homomeric pseudocentrosymmetric cyclic $R_2^2(10)$ dimer through their N$^+$H and carboxyl O atoms [N$\cdots$O = 2.803 (2) and 2.855 (2) Å]. These groups also participate in the usual intramolecular N—H$\cdots$O associations [2.704 (2) and 2.719 (2) Å]. The 5-SSA anions are



(*a*) (*b*)

(*c*) (*d*)

Figure 1

The molecular configurations and atom-numbering schemes for (*a*) (I), (*b*) (II), (*c*) (III) and (*d*) (IV). Non-H atoms are shown as 30% probability displacement ellipsoids. [Symmetry code: (ii) $x,\ 2-y,\ z-\frac{1}{2}$.]

similarly propagated linearly along the *a* direction *via* strong head-to-tail O(carboxyl)$\cdots$O(sulfonate) hydrogen bonds [O71$\cdots$O51^{x} = 2.5758 (19) Å], the only heteromolecular contact being a weak C—H$\cdots$O association [C62$\cdots$O53-($\frac{3}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) = 3.333 (3) Å]. The QA cation and the 5-SSA anion (molecule 1) ring systems superimpose down the *b* direction, with significant π–π interaction [$Cg_m\cdots Cg_n$ and $\alpha_{m,n}$ of 3.827 (3) Å and 1.5 (1)°, 3.787 (3) Å and 3.4 (1)°, 3.678 (3) Å and 4.8 (1)°, and 3.661 (3) Å and 2.2 (1)° for (m,n) = (1,2), (1,3), (2,3) and (3,4), respectively; numbers refer to the six-membered rings N11–C9 (1), N12–C92 (2), C1–C6 (3) and C51–C101 (4); Cg_m is the centroid of ring *m*, and $\alpha_{m,n}$ is the angle between the planes of rings *m* and *n*]. The result is a sheet structure, which is linked only by these π–π interactions along *b* (Fig. 5).

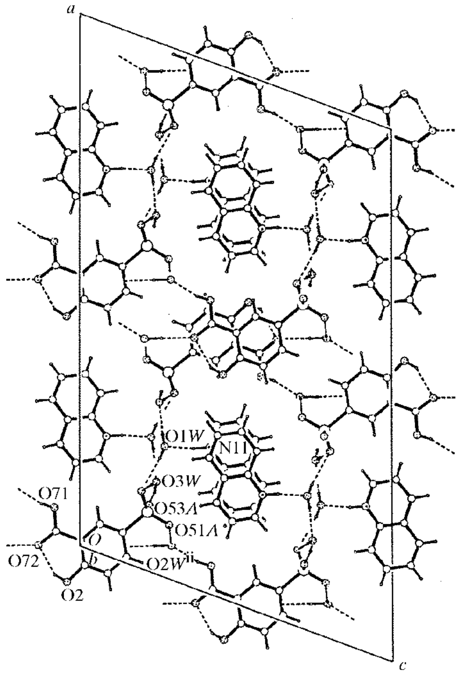


Figure 2
Homomolecular stacks of QUIN cations and 5-SSA anions in (I), viewed in the unit cell along the *b* axis, showing interstack hydrogen-bonding associations (broken lines) involving the water molecules. [Symmetry code: (ii) x, $2-y$, $z-\frac{1}{2}$.]

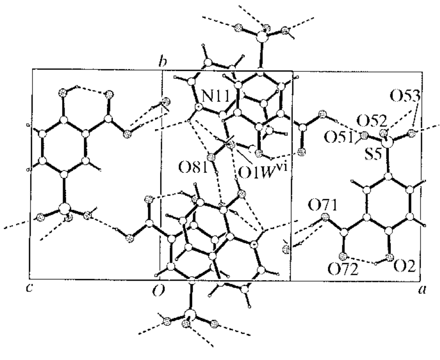


Figure 3
The hydrogen-bonding associations between 8-HQ cations, 5-SSA anions and the water molecule in (II), in a perspective view of the packing in the unit cell viewed perpendicular to *b*. [Symmetry code: (vi) $1-x$, $1-y$, $-z$.]

An usual intramolecular hydrogen bond is found, as expected, between the phenol OH group and a carboxylate group in the 5-SSA anion in each structure [O2—H2$\cdots$O72 = 2.613 (2), 2.602 (3), 2.606 (2) and 2.605 (2) Å for (I), (II), (III) and (IV), respectively]. This hydrogen bond maintains coplanarity of the carboxylic acid group with the benzene ring [C2—C1—C7—O71 = −178.9 (2), 179.3 (2), 178.0 (2) and 178.8 (2)°, respectively] and is similar to but significantly shorter than that found in the structure of the parent salicylic acid (O$\cdots$O = 2.640 Å; Sundaralingam & Jensen, 1965) and in substituted salicylic acids generally. The carboxylic acid groups in all structures are involved in strong hydrogen-bonding interactions with either sulfonate or water O-atom acceptors [O$\cdots$O = 2.530 (2)–2.607 (3) Å]. In (I) and (III), the second (carbonyl) O atom is also involved in an interaction with a water O atom, while in none of the structures is there any intermolecular phenol O-atom participation. The rotational disorder in the sulfonate group, which is present to almost an identical degree in both (I) and (III), has not been reported previously for 5-SSA compounds but is not an unexpected phenomenon. However, it appears unusual in these types of structures, where self-assembly through strong hydrogen-bonding interactions involving the sulfonate group is a feature. Furthermore, all four structures exhibit significant intramol-

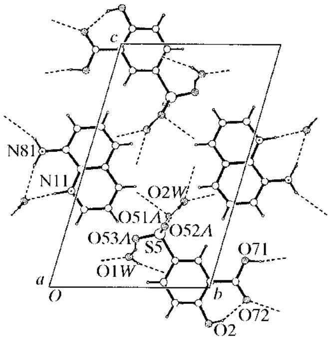


Figure 4
The hydrogen-bonding associations between 8-AQ cations, 5-SSA anions and water molecules in (III), in a partial section of the unit cell viewed along *b*.

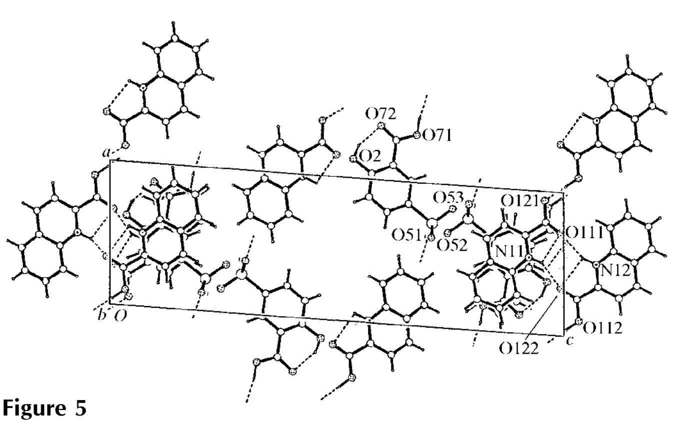


Figure 5
A view of the partial packing of the QA cations, 5-SSA anions and QA adduct molecules in (IV), in the unit cell viewed down *b*, showing the heteromolecular stacks and inter-species hydrogen-bonding associations. The molecule labelled is related by ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$) to the molecule of the asymmetric unit.

ecular aromatic C—H···O(sulfonate) hydrogen-bonding interactions, which maintain near coplanarity of the plane of the aromatic ring and one of the S5—O53 bond vectors. This configuration is reflected in the C6···O53 contacts [ranging from 2.733 (3) Å in (II) to 2.928 (8) Å in (III)] and in the corresponding C6—C5—S5—O53 torsion angles [1.6 (2)° in (II) to −28.6 (4)° in (III)]. The maximum deviation from coplanarity occurs for the two disordered compounds [*viz*. (I) and (III)].

Experimental

Compounds (I)–(IV) were synthesized by heating, under reflux, 1 mmol quantities of 5-SSA and, respectively, QUIN, 8-HQ, 8-AQ and QA in 50% ethanol/water (50 ml) for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave pale-pink prisms of (I) (m.p. 501.7–503.3 K), large yellow prisms of (II) (m.p. 505.2–506.9 K), brown prisms of (III) (m.p. 504.8–507.4 K) and yellow plates of (IV) (m.p. 484.5–488.1 K).

Compound (I)

Crystal data

$C_9H_8N^+\cdot C_7H_5O_6S^-\cdot 3H_2O$
$M_r = 401.38$
Monoclinic, $C2/c$
$a = 29.194$ (2) Å
$b = 7.2253$ (5) Å
$c = 18.2715$ (13) Å
$\beta = 110.524$ (1)°
$V = 3609.5$ (4) Å^3
$Z = 8$

$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3896 reflections
$\theta = 2.2$–26.9°
$\mu = 0.23$ mm^{-1}
$T = 295$ (2) K
Block, pink
0.50 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.889$, $T_{\max} = 0.933$
9200 measured reflections

3180 independent reflections
2770 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 25.0°$
$h = -30 \rightarrow 34$
$k = -5 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.118$
$S = 1.03$
3180 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 2.2682P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O72	0.75 (3)	1.93 (4)	2.613 (2)	150 (4)
O1*W*—H1*A*···O53*A*	0.80 (4)	2.07 (4)	2.761 (4)	145 (3)
O1*W*—H1*B*···O3*W*$^{\rm i}$	0.82 (3)	1.92 (3)	2.708 (4)	162 (3)
O2*W*—H2*A*···O51*A*$^{\rm ii}$	0.87 (2)	1.99 (2)	2.811 (7)	156 (2)
O2*W*—H2*B*···O72$^{\rm iii}$	0.95 (3)	1.86 (3)	2.817 (3)	180 (4)
O3*W*—H3*A*···O53*A*$^{\rm iv}$	0.94 (2)	1.92 (2)	2.864 (8)	179 (2)
O3*W*—H3*B*···O52*A*	0.82 (5)	1.95 (5)	2.721 (6)	157 (5)
O71—H7···O2*W*$^{\rm v}$	0.79 (3)	1.76 (3)	2.535 (3)	166 (3)
N11—H11···O1*W*$^{\rm iv}$	0.93 (3)	1.75 (3)	2.670 (3)	173 (3)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x, 2 - y, \frac{1}{2} + z$; (iii) $-x, y, \frac{1}{2} - z$; (iv) $x, y - 1, z$; (v) $x, y, z - 1$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O72	0.83 (6)	1.88 (6)	2.602 (3)	146 (2)
O81—H81···O1*W*	0.82 (3)	1.77 (4)	2.585 (3)	169 (3)
O1*W*—H1*A*···O51$^{\rm vi}$	0.89 (4)	1.86 (4)	2.748 (3)	179 (4)
O1*W*—H1*B*···O52$^{\rm vii}$	0.83 (4)	2.02 (4)	2.832 (3)	166 (3)
O71—H7···O51$^{\rm vii}$	0.83 (4)	1.79 (4)	2.607 (3)	169 (3)
N11—H11···O81	0.90 (2)	2.21 (2)	2.658 (3)	110 (2)
N11—H11···O53$^{\rm viii}$	0.90 (2)	1.99 (3)	2.733 (3)	140 (2)

Symmetry codes: (vi) $1 - x, 1 - y, -z$; (vii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $x - 1, y, z$.

Compound (II)

Crystal data

$C_9H_8NO^+\cdot C_7H_5O_6S^-\cdot H_2O$
$M_r = 381.35$
Monoclinic, $P2_1/n$
$a = 13.236$ (2) Å
$b = 10.6515$ (18) Å
$c = 13.549$ (2) Å
$\beta = 119.135$ (3)°
$V = 1668.4$ (5) Å^3
$Z = 4$
$D_x = 1.518$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2706 reflections
$\theta = 2.6$–25.5°
$\mu = 0.24$ mm^{-1}
$T = 295$ (2) K
Block, yellow
0.45 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SABABS*; Bruker, 1999)
$T_{\min} = 0.917$, $T_{\max} = 0.953$
8547 measured reflections

2934 independent reflections
2255 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.063$
$\theta_{\max} = 25.0°$
$h = -14 \rightarrow 15$
$k = -10 \rightarrow 12$
$l = -16 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 1.01$
2934 reflections
257 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.033$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Compound (III)

Crystal data

$C_9H_9N_2^+\cdot C_7H_5O_6S^-\cdot 2H_2O$
$M_r = 398.39$
Triclinic, $P\overline{1}$
$a = 6.9047$ (9) Å
$b = 9.2914$ (12) Å
$c = 14.5106$ (19) Å
$\alpha = 73.240$ (2)°
$\beta = 84.138$ (3)°
$\gamma = 79.889$ (2)°
$V = 876.2$ (2) Å^3
$Z = 2$
$D_x = 1.510$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1719 reflections
$\theta = 2.3$–26.2°
$\mu = 0.23$ mm^{-1}
$T = 295$ (2) K
Block, brown
0.45 × 0.40 × 0.35 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.900$, $T_{\max} = 0.921$
4662 measured reflections

3050 independent reflections
2364 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 7$
$k = -10 \rightarrow 11$
$l = -9 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.098$
$S = 0.96$
3050 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O72	0.81 (3)	1.86 (3)	2.606 (2)	151 (3)
O1*W*—H1*A*···O53*A*	0.95 (5)	1.95 (5)	2.844 (9)	156 (4)
O1*W*—H1*B*···O72^{ix}	0.85 (4)	2.08 (4)	2.819 (3)	145 (3)
O2*W*—H2*A*···O52*A*	0.85 (3)	1.95 (3)	2.791 (8)	172 (3)
O2*W*—H2*B*···O51*A*^{x}	0.81 (4)	1.93 (4)	2.735 (6)	168 (4)
N11—H11···O2*W*^{iv}	0.93 (3)	1.84 (3)	2.768 (3)	173 (2)
O71—H71···O1*W*^{xi}	0.88 (3)	1.67 (3)	2.530 (2)	164 (2)
N81—H81*A*···O2*W*^{iv}	0.90 (3)	2.15 (3)	3.026 (3)	167 (3)
N81—H81*B*···O51*A*^{xii}	0.86 (3)	2.42 (3)	3.234 (7)	158 (3)

Symmetry codes: (iv) $x, y-1, z$; (ix) $-x, 2-y, -z$; (x) $1+x, y, z$; (xi) $x, 1+y, z$; (xii) $1-x, -y, 1-z$.

Compound (IV)

Crystal data

$C_{10}H_8NO_2^+\cdot C_7H_5O_6S^-\cdot C_{10}H_7NO_2$
$M_r = 564.52$
Monoclinic, $P2_1/n$
$a = 8.3173$ (10) Å
$b = 11.2674$ (14) Å
$c = 26.245$ (3) Å
$\beta = 94.284$ (2)°
$V = 2452.6$ (5) Å^3
$Z = 4$
$D_x = 1.529$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4705 reflections
$\theta = 2.4$–27.4°
$\mu = 0.20$ mm^{-1}
$T = 295$ (2) K
Block, yellow
0.45 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
12 592 measured reflections
4316 independent reflections
3671 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 13$
$l = -26 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.06$
4316 reflections
381 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.819P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 4
Hydrogen-bonding geometry (Å, °) for (IV).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O72	0.85 (2)	1.82 (2)	2.605 (2)	153 (2)
N11—H11···O111	0.85 (2)	2.37 (2)	2.719 (2)	105.4 (19)
N11—H11···O122	0.85 (2)	2.05 (2)	2.803 (2)	148 (2)
N12—H12···O111	0.90 (2)	2.00 (2)	2.855 (2)	159 (2)
N12—H12···O122	0.90 (2)	2.34 (2)	2.704 (2)	104.2 (18)
O71—H7···O51^{x}	0.94 (3)	1.64 (3)	2.5758 (19)	172 (3)
O112—H112···O121^{viii}	0.95 (3)	1.52 (3)	2.478 (2)	179 (2)

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

The sulfonate groups of both (I) and (III) were found to be rotationally disordered, so the O atoms of these groups were modelled over six sites (O51*A*–O53*A* and O51*B*–O53*B*), with site occupancies [0.76 (1):0.24 (1) for (I) and 0.74 (2):0.26 (2) for (III)] determined by least-squares refinement. H atoms involved in hydrogen-bonding interactions were located from a difference map, and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinements at calculated positions (C—H = 0.95 Å) and treated as riding, with $U_{\rm iso}$(H) values fixed at $1.2U_{\rm eq}$(parent atom). For refined water H atoms, the mean O—H distances are 0.81 (5) Å for (I), 0.85 (5) Å for (II) and 0.86 (5) Å for (III).

For all compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

The authors acknowledge financial support from The School of Physical and Chemical Sciences of Queensland University of Technology and The University of Melbourne.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1450). Services for accessing these data are described at the back of the journal.

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