organic compounds

Layered structures in proton-transfer compounds of 5-sulfosalicylic acid with the aromatic polyamines 2,6-diaminopyridine and 1,4-phenylenediamine

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The crystal structures of two proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) with the aromatic polyamines 2,6-diaminopyridine [namely 2,6-diaminopyridinium 3-carboxy-4-hydroxybenzene-sulfonate monohydrate, $C_5H_8N_3{}^+ \cdot C_7H_5O_6S^- \cdot H_2O$, (I)] and 1,4-phenylenediamine [namely 1,4-phenylenediaminium 3-carboxylato-4-hydroxybenzenesulfonate, $C_6H_{10}N_2{}^{2+} \cdot C_7H_4O_6S^{2-}$, (II)] have been determined. Both compounds feature extensively hydrogen-bonded three-dimensional layered polymer structures having significant interlayer π–π inter-actions between the cation and anion species. In (I), the pyridine N atom of the Lewis base is protonated and forms a direct hydrogen-bonding interaction with the water molecule, which together with the two amine groups of the cation and the carboxylic acid group of the anion also give additional interactions with O-atom acceptors of the sulfonate group. In (II), a dianionic species results from deprotonation of both the sulfonic and the carboxylic acid groups, and all available O-atom acceptors interact with all dication donors, which lie about inversion centres.

Comment

The systematics of the solid-state structures of the proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) with Lewis bases have been widely studied because of the good crystallinity of many of the compounds. This feature is a result of the presence of sulfon-ate and potential carboxyl O-atom acceptors available for hydrogen-bonding interactions and has been useful for the study of certain difficult-to-crystallize bases, *e.g.* theophylline (a monohydrate; Madarasz *et al.*, 2002), trimethoprim (a dihydrate; Raj *et al.*, 2003) and pyrimethamine (a mono-hydrate; Hemamalini *et al.*, 2005). However, examples of the

dianionic 5-SSA species are rare, being found only in bis-(guanidinium) 5-sulfosalicylate monohydrate (Smith, Wermuth & Healy, 2004). Although anhydrous compounds of 5-SSA are known, for example the 1:1 compounds with
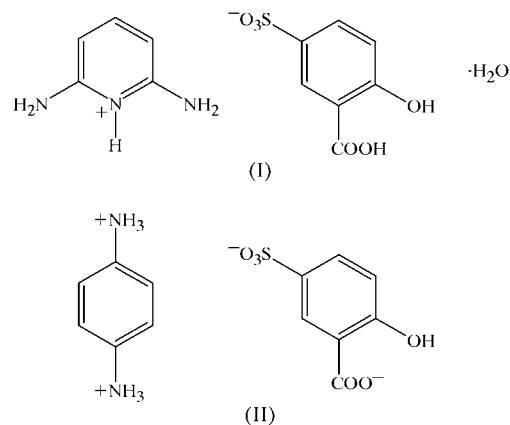
guanidine (Zhang *et al.*, 2004) and 1,10-phenanthroline (Fan *et al.*, 2005), the structures usually incorporate at least one water solvent molecule, which acts in a donor/acceptor capacity, usually involving the aminium group in a direct hydrogen-bonding interaction. This, with additional interactions, results in mostly three-dimensional polymer structures, which in only a small number of cases (those compounds with polycyclic heteroaromatic amines) involve π–π stacking effects (Smith, Wermuth & White, 2004).

Aniline-type proton-transfer compounds lend themselves to structure building since the protonated primary amine group will often give up to six interactions with available acceptor atoms. The structures of the 1:1 compounds of 5-SSA with aniline (Bakasova *et al.*, 1991), the 4-X-substituted anilines (X = F, Cl and Br; Smith *et al.*, 2005a) and 4-amino-benzoic acid (Smith *et al.*, 2005b) have been reported. However, apart from the structures of two 5-SSA compounds with diamines, namely ethylenediaminium bis(5-sulfosalicy-
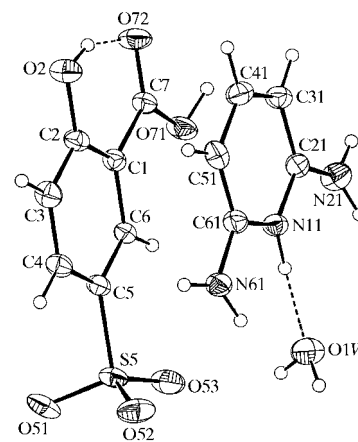

Figure 1
The configurations and atom-numbering scheme for the DAP$^+$ cation, the 5-SSA$^-$ anion and the water molecule in (I). Non-H atoms are shown as 30% probability displacement ellipsoids and hydrogen bonds are shown as dashed lines.

late) tetrahydrate (Gao *et al.*, 2004) and 4,4′-bipyridinium bis(5-sulfosalicylate) dihydrate (Muthiah *et al.*, 2003), no polyfunctional aniline-type compounds are known. We therefore attempted to obtain crystalline compounds of 5-SSA with aromatic polyamines with the aim of maximizing structure enhancement through both hydrogen bonding and possibly π–π interactive effects. The work has yielded limited success to date, but the two compounds whose crystal structures are reported here represent exceptions where good crystalline products were obtained. These compounds resulted from the reaction of 5-SSA with the aromatic polyamines 2,6-diaminopyridine (DAP) and 1,4-phenylenediamine (PDA), *viz.* 2,6-diaminopyridinium 5-sulfosalicylate monohydrate, (I), and 1,4-phenylenediaminium 5-sulfosalicylate, (II). Figs. 1 and 2 show the atom-numbering schemes used for the 5-sulfosalicylate anion and aminium cations in (I) and (II); these numbering schemes are consistent with those previously employed in 5-SSA structures reported by this group (Smith, Wermuth & Healy, 2004; Smith, Wermuth & White, 2004; Smith *et al.*, 2005*a*,*b*). Both (I) and (II) involve proton transfer with subsequent extensive hydrogen bonding involving available H-atom donor and acceptor atoms of both cation and anion species, giving in both compounds three-dimensional layered polymer structures (Tables 1 and 2).

In (I) (Fig. 3), single proton transfer to only the pyridine hetero N atom occurs, and this group subsequently participates in a single hydrogen-bonding interaction with the water molecule [N···O = 2.775 (5) Å]. The water molecule also provides hydrogen-bonding links between sulfonate O-atom acceptors extending along the *c* direction [O1W···O53 = 2.897 (5) Å and O1W···O51^i = 2.789 (5) Å; symmetry code: (i) *x*, *y*, *z* + 1], giving a total of five interactions for the sulfonate groups, including one with the carboxylic acid group of the 5-SSA anion [O71—H71···O51^{iii} = 2.621 (4) Å;
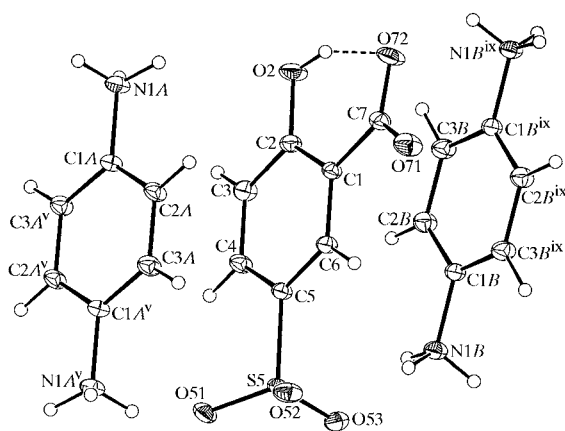
symmetry code: (iii) *x* − 1, *y*, *z*]. The result is the formation of an undulating layer structure in which the alternating DAP$^+$ cations and 5-SSA$^-$ anions partially superimpose down the *c* axial direction, with significant π–π ring interactions [ring centroid separation Cg···Cg = 3.54 (1) (intra) and 3.56 (1) Å (inter)]. The overall result is a three-dimensional polymer structure. There is no occurrence of the $R_2^2(8)$ dimer interaction found in the small number of reported co-crystals of DAP [1:1 proton-transfer compounds with 2-nitrobenzoic acid (Smith *et al.*, 1999) and 2,4,6-trinitrobenzoic acid (Smith *et al.*, 2000)]. However, this interaction is probably absent because of the interjection in (I) of the water molecule into the hydrogen-bonding pattern.

The structure of (II), except for the layering, differs markedly from that of (I) and those of the majority of the proton-transfer compounds of 5-SSA. The most unusual feature is the presence of dianionic 5-SSA species, despite the use of 1:1 stoichiometric reactant ratios in the preparation. Both amine groups of the PDA molecule are protonated, which is also unusual considering that the second amine group is relatively acidic (p$K_{a1,2}$ = 2.67 and 6.60). The crystallographic repeat unit comprises the 5-SSA^{2-} anion and two centrosymmetric PDA^{2+} half-cations (*A* and *B*; Fig. 2). The A^v and B^{ix} molecular portions represent the inversion-generated halves of the two molecules [symmetry codes: (v) −*x*, −*y*, −*z* + 1; (ix) −*x* + 1, −*y* + 1, −*z*]. The cations and anions form two-dimensional sheet structures through a number of hydrogen-bonding interactions involving all potential donor and acceptor atoms of both molecular species [range 2.725 (3)–3.114 (2) Å]. These sheets are interlinked by N$^+$—H···O hydrogen-bonding interactions (Fig. 4) and stack down the *c* cell direction, the alternating cation *A*–anion–cation *B* separation indicating significant π–π interaction [the inter-ring centroid distances are cation *A*–anion = 3.73 (1) Å and cation *B*–anion = 3.75 (1) Å]. The overall result is a three-dimensional polymer structure.

In the 5-SSA anion species in (I) and (II), similar structural and conformational features to those previously observed (Smith, Wermuth & Healy, 2004; Smith, Wermuth & White,

Figure 2
The atom-numbering scheme for the two centrosymmetric half-PDA^{2+} cations (*A* and *B*) and the 5-SSA^{2-} anion in (II) (30% probability displacement ellipsoids). The intramolecular hydrogen bond is shown as a dashed line. [Symmetry codes: (v) −*x*, −*y*, −*z* + 1; (ix) −*x* + 1, −*y* + 1, −*z*.]
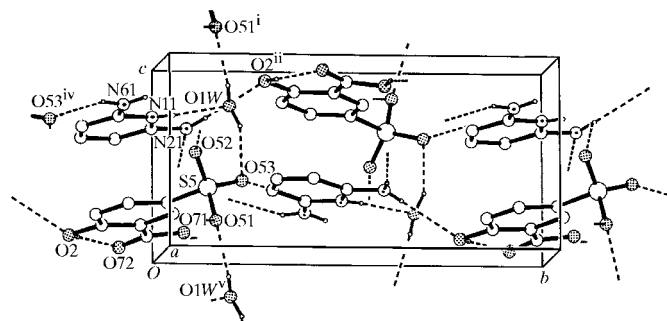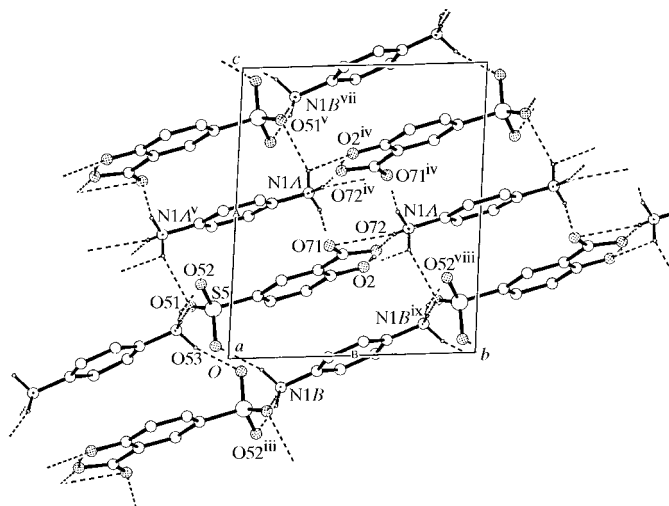

Figure 3
Structure extension through hydrogen-bonding interactions (shown as broken lines) in (I), viewed along the *a* cell direction. Hydrogen bonds are shown as dashed lines. [Symmetry code: (v) *x*, *y*, *z* − 1; for other symmetry codes, see Table 1.]

Figure 4
A perspective view of the hydrogen-bonding associations in the layered structure of (II), viewed along the *a* cell direction. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (vii) $x, y, z + 1$; (viii) $x, y + 1, z$; (ix) $-x + 1, -y + 1, -z$; for other symmetry codes, see Table 2.]

2004; Smith *et al.*, 2005a,b) are found. The usual intramolecular hydrogen bond is found between the phenol OH group and a carboxyl O atom [O2—H2···O72: 2.605 (4) Å for (I), contracting as expected in (II) to 2.558 (2) Å, where the carboxylic acid group is deprotonated]. This deprotonation also results in a greater deviation from coplanarity of the overall group with the benzene ring [C2—C1—C7—O71 = 171.1 (2)° for (II), *cf.* 176.3 (3)° for (I)]. There is no occurrence of the strong intermolecular $R_2^2(8)$ cyclic carboxylic acid interaction that is found in the 4-chloro- and 4-bromo-anilinium compounds with 5-SSA (Smith *et al.*, 2005a), nor of the anilinium–sulfonate $R_2^2(8)$ dimer interaction commonly found in the anhydrous guanidinium sulfonates (Russell *et al.*, 1994; Zhang *et al.*, 2004; Haynes *et al.*, 2004).

Experimental

The title compounds were synthesized by heating 1 mmol quantities of 5-SSA and, respectively, DAP or PDA in 50% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave pale-brown crystals of both (I) (m.p. 524–526 K) and (II) (m.p. >555 K).

Compound (I)

Crystal data

$C_5H_8N_3^+ \cdot C_7H_5O_6S^- \cdot H_2O$	$D_x = 1.584$ Mg m^{-3}
$M_r = 345.34$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
$a = 8.4778$ (15) Å	reflections
$b = 13.085$ (2) Å	$\theta = 12.6–15.8°$
$c = 6.7562$ (11) Å	$\mu = 0.27$ mm^{-1}
$\beta = 105.001$ (14)°	$T = 297$ (2) K
$V = 723.9$ (2) Å^3	Prism, pale brown
$Z = 2$	$0.40 \times 0.30 \times 0.30$ mm

Data collection

Rigaku AFC-7R diffractometer	$h = -4 \rightarrow 11$
ω–2θ scans	$k = 0 \rightarrow 17$
1965 measured reflections	$l = -8 \rightarrow 8$
1726 independent reflections	3 standard reflections
1406 reflections with $F^2 > 2\sigma(F^2)$	frequency: 150 min
$R_{int} = 0.014$	intensity decay: 0.5%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.034$	independent and constrained
$wR(F^2) = 0.112$	refinement
$S = 0.89$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.0953P]$
1726 reflections	where $P = (F_o^2 + 2F_c^2)/3$
243 parameters	$(\Delta/\sigma)_{max} = 0.002$
	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O72	0.77 (8)	1.89 (8)	2.605 (4)	154 (8)
O1W—H1A···O51^i	0.79 (6)	2.02 (5)	2.789 (5)	163 (6)
O1W—H1B···O53	0.85 (6)	2.10 (5)	2.897 (5)	157 (6)
N11—H11···O1W	0.78 (4)	2.00 (4)	2.775 (5)	173 (6)
N21—H21A···O2^{ii}	0.76 (6)	2.35 (6)	3.054 (5)	154 (6)
N21—H21B···O52^{iii}	0.94 (5)	2.04 (5)	2.936 (6)	161 (4)
N61—H61B···O53^{iv}	0.81 (6)	2.49 (6)	3.252 (6)	158 (5)
O71—H71···O51^{iii}	0.93 (6)	1.71 (6)	2.621 (4)	166 (6)

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

Compound (II)

Crystal data

$C_6H_{10}N_2^{2+} \cdot C_7H_4O_6S^{2-}$	Mo $K\alpha$ radiation
$M_r = 326.32$	Cell parameters from 25
Triclinic, $P\bar{1}$	reflections
$a = 6.9800$ (14) Å	$\theta = 12.7–17.2°$
$b = 9.1573$ (15) Å	$\mu = 0.28$ mm^{-1}
$c = 10.849$ (2) Å	$T = 297$ (2) K
$\alpha = 84.618$ (14)°	Prism, pale brown
$\beta = 97.698$ (16)°	$0.40 \times 0.30 \times 0.25$ mm
$\gamma = 102.879$ (14)°	
$V = 668.4$ (2) Å^3	
$Z = 2$	
$D_x = 1.621$ Mg m^{-3}	

Data collection

Rigaku AFC-7R diffractometer	$h = -3 \rightarrow 9$
ω–2θ scans	$k = -11 \rightarrow 11$
3477 measured reflections	$l = -14 \rightarrow 13$
3067 independent reflections	3 standard reflections
2678 reflections with $F^2 > 2\sigma(F^2)$	frequency: 150 min
$R_{int} = 0.034$	intensity decay: 0.8%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 2.7752P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.83$	$(\Delta/\sigma)_{max} = 0.002$
3067 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
227 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

organic compounds

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O72	0.88 (4)	1.74 (4)	2.558 (2)	152 (4)
N1A—H11$A\cdots$O71^{i}	0.99 (4)	2.41 (4)	3.114 (2)	128 (3)
N1A—H11$A\cdots$O72^{i}	0.99 (4)	1.84 (4)	2.808 (3)	168 (3)
N1B—H11$B\cdots$O53	0.96 (3)	1.90 (3)	2.812 (2)	157 (3)
N1A—H12$A\cdots$O71^{ii}	0.91 (3)	1.83 (3)	2.725 (3)	166 (3)
N1B—H12$B\cdots$O52^{iii}	0.89 (3)	2.01 (4)	2.868 (3)	161 (3)
N1A—H13$A\cdots$O2^{iv}	0.90 (3)	2.43 (3)	3.015 (3)	123 (2)
N1A—H13$A\cdots$O51^{v}	0.90 (3)	2.14 (3)	2.905 (3)	143 (3)
N1B—H13$B\cdots$O51^{vi}	0.84 (3)	1.95 (3)	2.794 (3)	177 (3)

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

H atoms involved in hydrogen-bonding interactions (pyridinium, anilinium, carboxyl, phenol and water) were located by difference methods, and their positional and isotropic displacement parameters were refined. Other H atoms were included in the respective refinements at calculated positions (C—H = 0.95 Å) as riding atoms, with U_{eq} values fixed at $1.2U_{eq}$(C).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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