

Different supramolecular assemblies in two 1:1 proton-transfer compounds of sulfobenzoic acids with aromatic amines

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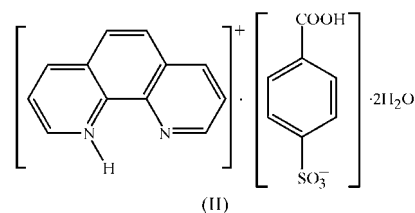
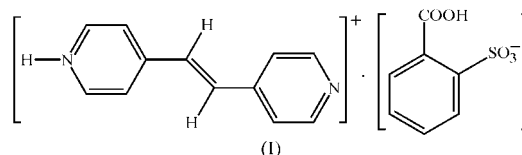
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Two 1:1 proton-transfer complexes of sulfobenzoic acids with aromatic amines, namely 4-[2-(4-pyridyl)ethenyl]pyridinium 2-carboxybenzenesulfonate, $C_{12}H_{11}N_2^+ \cdot C_7H_5O_5S^-$, (I), and 1,10-phenanthroline-1-ium 4-carboxybenzenesulfonate dihydrate, $C_{12}H_9N_2^+ \cdot C_7H_5O_5S^- \cdot 2H_2O$, (II), have very different hydrogen-bonding patterns compared with reported organic sulfobenzoic acid complexes. In (I), two cations and two anions form a four-molecule loop, in which π - π interactions occur. In (II), the anions and water molecules form a three-dimensional hydrogen-bonding network, while the cations only act as pendant components. The water molecules play a central role in the formation of the abundant hydrogen-bonding architecture in (II). The relative poorness and richness of hydrogen bonds in (I) and (II), respectively, give rise to novel hydrogen-bonding patterns.

Comment

Intermolecular interactions such as hydrogen bonds and π - π stacking play an essential role in the formation of supramolecular organic complexes (Lehn, 2007; Egli & Sarkhel, 2007). In the supramolecular systems constructed by organic synthons, carboxylic acids and protonated amines are commonly used as donors or acceptors for hydrogen bonds (Raj *et al.*, 2003). Recently, 5-sulfosalicylic acid supramolecular systems containing both sulfonate and carboxylate groups have been extensively explored (Smith, 2005; Smith *et al.*, 2005, 2006*a,b,c*; Fan *et al.*, 2005), while investigations of sulfobenzoic acid organic complexes are sparse. A search of the Cambridge Structural Database (CSD; January 2007 update; Allen, 2002) gave only six sulfobenzoic organic complexes, *viz.* two guanidinium complexes (guanidinium 4-carboxybenzenesulfonate and guanidinium 3-carboxybenzenesulfonate; Videnova-Adrabsinska *et al.*, 2001), 4,4'-bipyridinium bis(2-carboxybenzenesulfonate) dihydrate (Li *et al.*, 2004), bis{4-[(4-pyridyl)ethenyl]pyridinium} 4-sulfonato-

benzoate trihydrate (Zhang & Zhu, 2006), tetraphenylphosphonium 2-sulfobenzoic acid (Ferrer *et al.*, 2002) and dicyclohexylammonium 2-carboxybenzenesulfonate dihydrate (Ng, 1995). Sulfobenzoic acid has five potential sites for hydrogen bonds: (i) two carboxyl O atoms and (ii) three sulfonate O atoms. Therefore, further exploration of the sulfobenzoic acid organic systems will provide abundant supramolecular architectures. We report here two novel sulfobenzoic acid organic complexes, (I) and (II), which are, respectively, poor and rich in hydrogen bonds.



Both (I) and (II) are 1:1 proton-transfer organic complexes and each contains one protonated amine cation and one deprotonated acid anion. Complex (I) is an anhydrous species, while complex (II) contains two water molecules. As expected, the sulfonic acid H atoms from 2-sulfobenzoic acid or 4-sulfobenzoic acid are transferred to the protonation sites on the N atoms of 1,2-di-4-pyridylethylene or 1,10-phenanthroline in (I) and (II), respectively (Figs. 1 and 2). The protonations at the N atoms in both structures are further confirmed by the C—N bond distances and C—N—C bond angles in the amine cations. According to an investigation of the CSD by Athimoolam & Natarajan (2007), the protonation of the amine N atom generally results in a slight deformation of the ring and consequently a slightly larger C—N—C bond angle ($>120^\circ$); this phenomenon can also be observed in the title structures, in that both the C17—N2—C19 angle in (I) and the C8—N1—C18 angle in (II) are larger than 120° (Tables 1 and 3). The carboxyl group in (I) forms an interplanar angle of $74.0(1)^\circ$ with its attached benzene ring owing to the neighboring steric effect of the sulfonate group, while in (II), the carboxyl group is nearly coplanar with the benzene ring [$3.8(1)^\circ$].

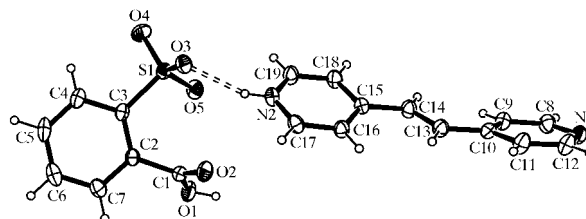


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are shown as dashed lines.

Three anhydrous 1:1 sulfonatobenzoic acid complexes have been reported, and their structures are zero-dimensional species without extended hydrogen bonding (Ferrer *et al.*, 2002) or three-dimensional networks (Videnova-Adrabinska *et al.*, 2001). Complex (I) forms a four-molecule loop (Fig. 3) via $N\cdots H-O$ and $O-H\cdots N$ hydrogen bonds (Table 2). Only one sulfonate O atom and one carboxyl O atom are involved in the hydrogen bonds. In this loop, there is a $\pi-\pi$ stacking effect between two protonated 1,2-di-4-pyridylethylene molecules, with a $Cg1\cdots Cg2(1-x, -y, 1-z)$ separation of 3.9739 (15) Å and a dihedral angle of 23.8 (1)° (where Cg1 and Cg2 are the centroids of the N1/C8–C12 and N2/C15–C19 rings). Moreover, significant $\pi-\pi$ interactions exist between loops [$Cg1\cdots Cg1(2-x, -y, 1-z) = 3.6914$ (16) Å]. This hydrogen-bonding loop is the first such unit reported in sulfobenzoic organic systems.

The hydrogen-bonding pattern in complex (II) is also novel and very different from those of reported sulfobenzoic acid organic complexes, in which hydrogen-bonding networks are formed by both cations and anions. In (II), the anions and water molecules form a three-dimensional hydrogen-bonding network with large cavities (Fig. 4 and Table 4), in which the cations are hydrogen bonded as pendant components and occupy the cavities of the networks. Compared with the more limited hydrogen-bonding characteristic in complex (I), abundant hydrogen bonding is observed in complex (II). All five O atoms of the 4-sulfobenzoic acid unit are involved in the formation of hydrogen bonds. It is obvious that water molecules also play a crucial role in the formation of the three-dimensional hydrogen-bonded network. Each of the two

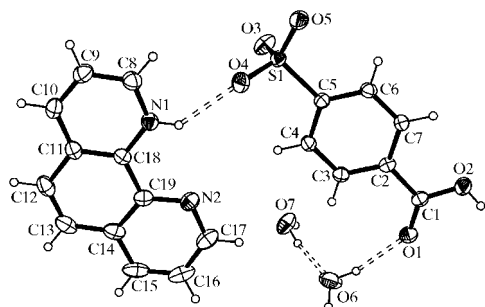


Figure 2

The molecular structure of (II), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and hydrogen bonds are shown as dashed lines.

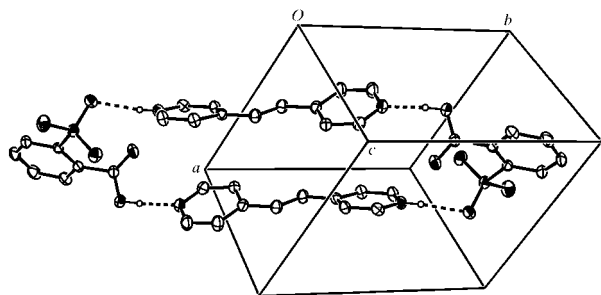


Figure 3

The hydrogen-bonding loop of (I). Hydrogen bonds are shown as dashed lines.

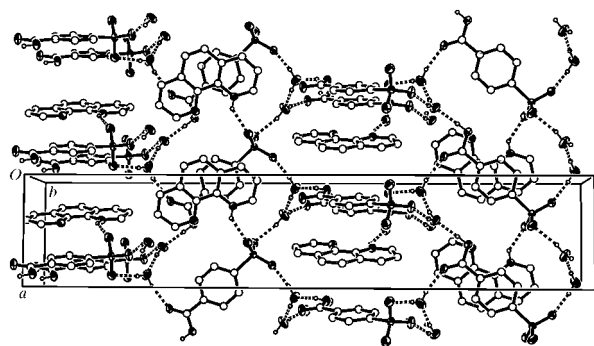


Figure 4

The three-dimensional hydrogen-bonding network of (II). Hydrogen bonds are shown as dashed lines. Bonds of the cations are shown as open bonds and the N, O and S atoms are shown with octant shading.

water molecules forms three hydrogen bonds with carboxyl and sulfonate groups and another water molecule, resulting in the hydrogen bonding extending in three directions. There are also strong $\pi-\pi$ stacking interactions involving protonated 1,10-phenanthroline and 4-sulfonatobenzoic acid units. The centroid-to-centroid distances are 3.7109 (13), 3.6668 (13) and 3.7976 (13) Å for $Cg1\cdots Cg2(x, 1+y, z)$, $Cg2\cdots Cg3(x, -1+y, z)$ and $Cg2\cdots Cg3(1+x, -1+y, z)$, respectively (Cg1, Cg2 and Cg3 are the centroids of the N1/C8–C11/C18, C2–C7 and C11–C14/C18/C19 rings).

In conclusion, these two organic complexes have hydrogen-bonding, $\pi-\pi$ stacking and charge-transfer interactions, assembling the molecular structures into supramolecular architectures, and both hydrogen-bonding patterns in (I) and (II) are novel and very different from those reported for sulfobenzoic organic systems.

Experimental

A mixture of 2-sulfobenzoic acid (0.051 g, 0.25 mmol), 1,2-di-4-pyridylethylene (0.046 g, 0.29 mmol) and water (10 ml) was refluxed for 5 h. After cooling to room temperature, pale-yellow brick-shaped crystals of (I) were obtained by filtration. A mixture of $SnSO_4$ (0.086 g, 0.40 mmol), potassium hydrogen 4-sulfobenzoate (0.096 g, 0.40 mmol), 1,10-phenanthroline monohydrate (0.079 g, 0.40 mmol), 12 M HNO_3 (0.1 ml) and water (15 ml) was sealed in a 30 ml Teflon-lined stainless steel autoclave and heated at 433 K for 72 h. After cooling to room temperature, the colorless solid was filtered off and washed with water. Crystals were obtained by recrystallization from water. The synthetic procedure without $SnSO_4$ did not lead to the formation of complex (II). Thermogravimetric analysis revealed that a weight loss in the temperature range 298–375 K corresponds to the release of two water molecules (calculated 8.61%, found 8.80%).

Compound (I)

Crystal data

$C_{12}H_{11}N_2^+ \cdot C_7H_5O_5S^-$

$M_r = 384.40$

Triclinic, $P\bar{1}$

$a = 8.7451$ (11) Å

$b = 10.0346$ (13) Å

$c = 10.7877$ (14) Å

$\alpha = 95.377$ (1)°

$\beta = 104.954$ (1)°

$\gamma = 104.047$ (2)°

$V = 874.82$ (19) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.22$ mm⁻¹

$T = 295$ (2) K

$0.31 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.935$, $T_{\max} = 0.953$
4632 measured reflections
3095 independent reflections
2534 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.111$
 $S = 0.86$
3095 reflections
250 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

N1—C12	1.328 (3)	N2—C17	1.331 (3)
N1—C8	1.329 (3)	N2—C19	1.335 (3)
C12—N1—C8	117.2 (2)	C17—N2—C19	121.94 (18)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O3	0.83 (3)	2.004 (14)	2.798 (2)	160 (3)
O1—H1A \cdots N1 ⁱ	0.86 (3)	1.76 (3)	2.617 (2)	175 (3)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Compound (II)

Crystal data

$\text{C}_{12}\text{H}_9\text{N}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_5\text{S}^- \cdot 2\text{H}_2\text{O}$
 $M_r = 418.41$
Tetragonal, $P4_1$
 $a = 7.1807$ (6) \AA
 $c = 36.171$ (3) \AA
 $V = 1865.1$ (3) \AA^3
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.22 \text{ mm}^{-1}$
 $T = 295$ (2) K
 $0.33 \times 0.31 \times 0.25 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.931$, $T_{\max} = 0.947$
11629 measured reflections
4269 independent reflections
3975 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.099$
 $S = 0.80$
4269 reflections
280 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
Absolute structure: Flack (1983), 1882 Friedel pair
Flack parameter: 0.04 (6)

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

N1—C8	1.332 (3)	N2—C17	1.319 (3)
N1—C18	1.356 (3)	N2—C19	1.345 (3)
C8—N1—C18	122.93 (19)	C17—N2—C19	117.0 (2)

Table 4

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H6B \cdots O1	0.844 (10)	1.956 (12)	2.783 (3)	166 (3)
O6—H6A \cdots O3 ⁱ	0.851 (10)	1.957 (12)	2.786 (3)	164 (3)
O7—H7B \cdots O6	0.85 (3)	1.83 (3)	2.674 (3)	170 (4)
O7—H7A \cdots O5 ⁱⁱ	0.848 (10)	1.915 (15)	2.731 (3)	161 (3)
N1—H1A \cdots O4	0.825 (10)	2.13 (2)	2.805 (2)	139 (3)
O2—H2A \cdots O7 ⁱⁱⁱ	0.86 (3)	1.737 (11)	2.588 (2)	171 (3)

Symmetry codes: (i) $y, -x + 1, z - \frac{1}{4}$; (ii) $y, -x + 2, z - \frac{1}{4}$; (iii) $x + 1, y, z$.

H atoms on C atoms were placed in idealized positions and refined as riding atoms [$\text{C—H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. H atoms involved in hydrogen-bonding interactions (pyridinium, carboxyl and water) were located from difference Fourier maps and refined with distance restraints [$\text{O—H} = 0.85$ (1) \AA and $\text{N—H} = 0.82$ (1) \AA] and fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$].

For both compounds, data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3086). Services for accessing these data are described at the back of the journal.

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