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## Key indicators

Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å  
 $R$  factor = 0.045  
 $wR$  factor = 0.158  
Data-to-parameter ratio = 10.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## 3-Carboxyanilinium 3-carboxy-4-hydroxybenzenesulfonate: the 1:1 proton-transfer compound of 5-sulfosalicylic acid with 3-aminobenzoic acid

The crystal structure of the anhydrous 1:1 proton-transfer compound of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with 3-aminobenzoic acid,  $\text{C}_7\text{H}_8\text{NO}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_6\text{S}^-$ , shows heteromeric cyclic  $R_2^2(8)$  carboxylic acid dimers formed through hydrogen-bonding interactions between the cation and anion species. Aminium-sulfonate  $\text{N}-\text{H} \cdots \text{O}$  interactions link these dimers into zigzag chains and also give interchain associations. Cation-anion  $\pi-\pi$  ring interactions are also present, resulting in a three-dimensional layered polymer structure.

## Comment

The structures of a number of 1:1 proton-transfer compounds of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) with aniline-type Lewis bases have been reported. These include compounds with aniline (Bakasova *et al.*, 1991), the 4-*X*-substituted anilines ( $X = \text{F}, \text{Cl}, \text{Br}$ ) (Smith *et al.*, 2005a), 4-aminobenzoic acid (PABA) (Smith *et al.*, 2005b) and 1,4-phenylenediamine (in which 5-SSA is dianionic) (Smith *et al.*, 2005). Although the isomeric aminobenzoic acids are quite strong for organic acids ( $\text{pK}_{\text{a}1}$  range 2.1–3.1), in the presence of stronger acids such as the nitrobenzoic acids or sulfonic acids, *e.g.* 5-SSA, protonation of the amine substituent will occur (for 3-aminobenzoic acid,  $\text{pK}_{\text{a}2} = 4.7$ ). The resultant aminium group is particularly effective in giving up to six hydrogen-bonding interactions usually with available O-atom acceptors, resulting in the formation of highly crystalline materials. In these crystals, it is unusual that water molecules of solvation are incorporated, contrasting with those compounds of 5-SSA with heteroaromatic Lewis bases where water is often found, acting in a proton donor-acceptor capacity. Furthermore, with these hydrates, direct  $\text{N}^+ - \text{H} \cdots \text{O}(\text{water})$  rather than  $\text{N}^+ - \text{H} \cdots \text{O}(\text{sulfonate})$  associations are more commonly found (Haynes *et al.*, 2004). 3-Aminobenzoic acid (MABA) is less effective than PABA for the promotion of linear hydrogen-bonding extensions so that the structures of the proton-transfer compounds of MABA with organic acids are fewer. They include 1:1 compounds with 3,5-dinitrobenzoic acid (Lynch *et al.*, 1994), 3,5-dinitrosalicylic acid (Smith *et al.*, 1995a) and pyrazine-2,3-dicarboxylic acid (a dihydrate) (Smith *et al.*, 1995b). Compounds in which MABA does not give proton transfer are the adducts with 2-aminopyrimidine (Smith *et al.*, 1995) and 2-aminobenzothiazole (Lynch *et al.*, 1998).

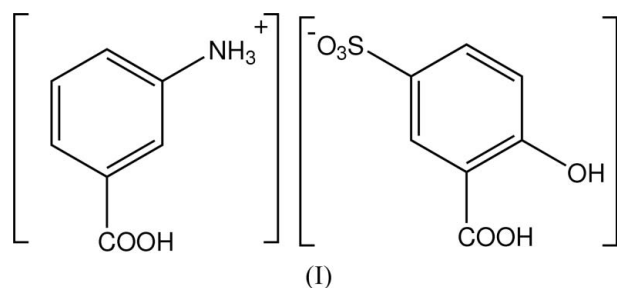
The structure of the anhydrous 1:1 proton-transfer compound formed from the reaction of 5-SSA with MABA in 50% aqueous ethanol, *viz.* 3-carboxyanilinium 5-sulfonato-salicylate, (I) (Fig. 1), has been determined and is reported here. In (I), the MABA cation and 5-SSA anion species form

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hydrogen-bonded heterodimers through symmetric cyclic  $R_2^2(8)$  carboxylic acid interactions [ $O\cdots O = 2.677(4)$  and  $2.679(4)$  Å]. This is in contrast with the structure of the isomeric compound with PABA (Smith *et al.*, 2005*b*), where both the PABA cations and the 5-SSA anions are involved in homomolecular  $R_2^2(8)$  associations. In (I), the ion pairs form zigzag chains through head-to-tail  $N^+ - H \cdots O$  (sulfonate) interactions [ $N31 \cdots O53^{iv} = 2.921(5)$  Å; symmetry code: (iv)  $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ], which run along the  $b$  axial direction (Figs. 2 and 3). The chains so formed are linked along the other two axial directions by similar  $N - H \cdots O$  interactions (Table 1), giving a three-dimensional layered structure. In addition, there are some cation–anion  $\pi$ – $\pi$  ring stacking interactions between the stacks which form down the  $a$  axial direction [ring centroid separation =  $3.73(1)$  Å and interplanar dihedral angle =  $2.4(1)^\circ$ ].



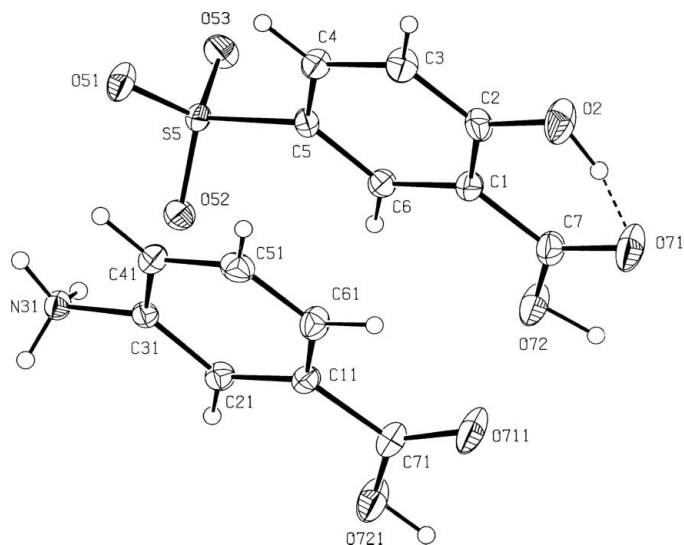
Structurally, the 5-SSA anions are similar to those in previously reported compounds. The carboxylic acid group is essentially coplanar with the benzene ring [ $C2-C1-C7-O72 = 177.7(4)^\circ$ ] because of the intramolecular  $O-H(\text{phenol}) \cdots O(\text{carboxyl})$  hydrogen bond [ $O \cdots O = 2.598(5)$  Å]. The carboxylic acid group of the MABA cation shows significant deviation from coplanarity with the benzene ring [ $C21-C11-C71-O711 = 167.1(4)^\circ$ ] as is observed in the compound with 3,5-dinitrosalicylic acid ( $-153^\circ$ ; Smith *et al.*, 1995*a*) but different from the equivalent angle in the planar parent acid ( $-178^\circ$ ; Voogd *et al.*, 1980).

## Experimental

The title compound was synthesized by heating 1 mmol quantities of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) and 3-aminobenzoic acid 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 solution gave pale-brown prismatic crystals of (I) (m.p. 541 K).

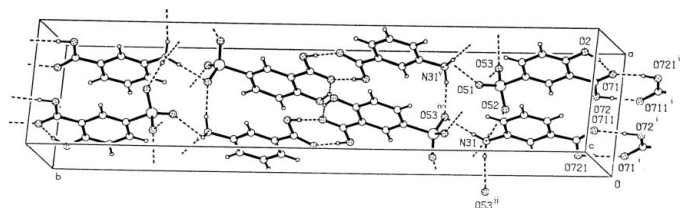
### Crystal data

$C_7H_8NO_2^+ \cdot C_7H_5O_6S^-$	$D_x = 1.620 \text{ Mg m}^{-3}$
$M_r = 355.31$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 7.3325(14)$ Å	reflections
$b = 31.430(5)$ Å	$\theta = 10.3\text{--}17.5^\circ$
$c = 6.3749(18)$ Å	$\mu = 0.27 \text{ mm}^{-1}$
$\beta = 97.35(2)^\circ$	$T = 297(2)$ K
$V = 1457.1(6)$ Å <sup>3</sup>	Prism, pale brown
$Z = 4$	$0.25 \times 0.10 \times 0.07$ mm



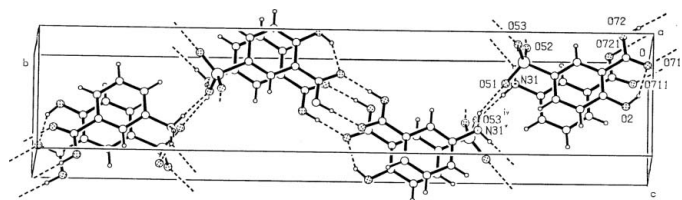
**Figure 1**

The molecular configuration and atom-numbering scheme for the MABA cation and 5-SSA anion in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates a hydrogen bond.



**Figure 2**

Perspective view of the packing of (I) in the unit cell, viewed approximately down the  $c$ -axis direction, showing hydrogen-bonding associations as dashed lines. [Symmetry code: (v)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; for other codes, see Table 1].



**Figure 3**

Perspective view of the packing of (I) in the unit cell, viewed approximately down the  $a$ -axis direction, showing the zigzag chain-polymer extensions. Dashed lines indicate hydrogen bonds.

### Data collection

Rigaku AFC-7R diffractometer	1655 reflections with $I > 2\sigma(I)$
$\omega$ – $2\theta$ scans	$R_{\text{int}} = 0.040$
Absorption correction: $\psi$ scan	$\theta_{\text{max}} = 25.0^\circ$
(TEXSAN for Windows;	$h = -8 \rightarrow 4$
Molecular Structure	$k = 0 \rightarrow 37$
Corporation, 1999)	$l = -7 \rightarrow 7$
$T_{\text{min}} = 0.936, T_{\text{max}} = 0.981$	3 standard reflections
3013 measured reflections	frequency: 150 min
2573 independent reflections	intensity decay: 15.8%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.158$   
 $S = 0.90$   
 2573 reflections  
 241 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 5.4071P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.008$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

to solve structure: *SIR92* (Altomare, 1994); 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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**Table 1**  
 Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O71$	0.92 (6)	1.77 (6)	2.598 (5)	149 (5)
$O72-H72\cdots O711^i$	0.90 (5)	1.78 (5)	2.677 (4)	180 (6)
$O721-H721\cdots O71^i$	0.90 (5)	1.78 (5)	2.679 (4)	180 (6)
$N31-H31A\cdots O53^{ii}$	0.88 (4)	1.95 (4)	2.825 (5)	171 (4)
$N31-H31B\cdots O52$	0.95 (5)	2.02 (5)	2.837 (5)	143 (4)
$N31-H31B\cdots O51^{iii}$	0.95 (5)	2.34 (5)	2.889 (5)	116 (4)
$N31-H31C\cdots O53^{iv}$	0.89 (6)	2.03 (6)	2.921 (5)	177 (5)

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

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions ( $C-H = 0.96 \text{ \AA}$ ) using a riding-model approximation, with  $U_{eq}$  values fixed at  $1.2U_{eq}(C)$ . A 15.8% decay in the diffraction intensities during data collection was allowed for using a linear correction.

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

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