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The 1:1 proton-transfer compound of 5-sulfosalicylic acid with 4-aminobenzoic acid

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.117
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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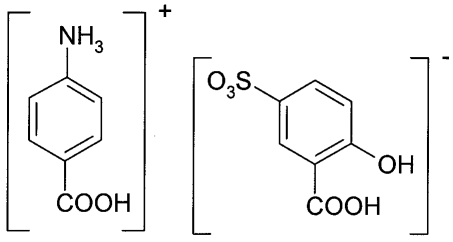
The crystal structure of the anhydrous 1:1 proton-transfer compound of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with 4-aminobenzoic acid, *viz*. 4-carboxyanilinium 3-carboxy-4-hydroxybenzenesulfonate, $C_7H_8NO_2^+\cdot C_7H_5O_6S^-$, displays a hydrogen-bonded polymeric network structure involving primarily all aminium H-atom donors and sulfonate O-atom acceptors, and is propagated through homomolecular cyclic tail-to-tail interactions between the carboxylic acid substituent groups of both cation and anion species. In addition, there are some cation–anion π–π stacking associations.

Comment

The aromatic sulfonic acid 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) has proved a particularly good acid for the protonation of Lewis bases and the promotion of molecular assembly through hydrogen-bonding associations involving all O-atom acceptors of the sulfonate group, together with the carboxylic acid and phenolic H-atom donor groups. In addition, these compounds often incorporate water molecules of solvation which, when present, are usually involved in direct $N^+—H\cdots O$(water) rather than $N^+—H\cdots O$(sulfonate) associations. Known 5-SSA compounds of this type are with aniline (1:1 anhydrate; Bakasova *et al.*, 1991), theophylline (1:1 monohydrate; Madarasz *et al.*, 2002), trimethoprim (1:1 dihydrate; Raj *et al.*, 2003), 4,4′-bipyridine (1:2 dihydrate; Muthiah *et al.*, 2003), guanidine [1:1 anhydrate (Zhang *et al.*, 2004) and 1:2 monohydrate (Smith, Wermuth & Healy, 2004*a*)], and a series of bicyclo heteroaromatic Lewis bases (Smith, Wermuth & White, 2004), including quinoline (1:1 trihydrate), 8-hydroxyquinoline (1:1 monohydrate), 8-aminoquinoline (1:1 dihydrate) and quinaldic acid (an anhydrous 1:1:1 quinaldic acid adduct). Also reported are the structures of a series of 1:1 compounds with the 4-halo-substituted anilines [4-fluoroaniline and 4-bromoaniline (both monohydrates), and 4-chloroaniline (a hemihydrate) (Smith *et al.*, 2005)]. We have also determined the structures of the 1:1 compounds with 1,4-phenylenediamine (an anhydrate in which the dianionic 5-SSA anion is found) and with brucine (a monohydrate) (Smith, Wermuth & Healy, 2004*b*).

4-Aminobenzoic acid (PABA), as well as being an essential biological molecule, acting as a bacterial cofactor involved in the synthesis of folic acid, has proved a particularly versatile reagent for structure extension through linear hydrogen-bonding associations, through both the carboxylic acid and amine functional groups. This property was recognized by Etter & Frankenbach (1989) as a possible tool for promoting co-crystallization, with the aim of designing noncentrosym-

metric organic materials. However, among the many reported co-crystals of PABA, only one, the 1:1 proton-transfer compound with 3,5-dinitrobenzoic acid (Etter & Frankenbach, 1989), has been found to crystallize in a noncentrosymmetric space group. Other reported compounds with PABA include neutral adducts with compounds such as 4-nitropyridine-*N*-oxide (1:1; Lechat, 1984), 1,3,5-trinitrobenzene (1:1; Lynch, Smith, Byriel & Kennard, 1994), urea (2:1; Smith, Baldry *et al.*, 1997), 4-(4-nitrobenzyl)pyridine (1:1; Smith, Lynch *et al.*, 1997) and 4-aminobenzonitrile (1:1; Smith *et al.*, 2000), as well as a number of proton-transfer compounds. In a small number of these, the carboxylic acid group of PABA (pK_{a1} = 2.38) protonates the amino group of the Lewis base, *e.g.* diethylamine (1:1; Smith *et al.*, 1999) or 2-aminopyrimidine (2:1; Lynch, Smith, Freney *et al.*, 1994). However, in the majority of examples, the amino group of PABA is protonated [3,5-dinitrosalicylic acid (2:1; Smith *et al.*, 1995), 2,4,6-trinitrobenzoic acid (1:1; Lynch *et al.*, 1992*a*), 2,4-dichloroacetic acid (1:1; Lynch *et al.*, 1992*b*) and (2-carboxyphenoxy)acetic acid (1:1; Byriel *et al.*, 1991)]. An unusual 3:1:1 PABA:2,4,6-trinitrobenzoic acid:1,3,5-trinitrobenzene co-crystal is also known (Lynch *et al.*, 1992*c*).



(I)

The crystal structure of the title compound, (I), reported here, is the product of the reaction of 5-sulfosalicylic acid with 4-aminobenzoic acid in 50% aqueous ethanol, [(PABA)$^+$-(5-SSA)$^-$] (Fig. 1), in which, as expected, the sulfonic acid group of 5-SSA has protonated the amine N atom of PABA. The three H atoms of this anilinium group are subsequently involved in extensive N$^+$—H···O$^-$ hydrogen-bonding interactions with O-atom acceptors of four different 5-SSA sulfonate groups [N···O 2.719–2.872 (2) Å] (Table 1). In addition, there are secondary structure extensions involving the carboxylic acid groups of both the PABA cations and the 5-SSA anions in tail-to-tail homomolecular $R_2^2(8)$ cyclic hydrogen bonds. With 5-SSA, the association is centrosymmetric [O72—H72···O71^{iv} 2.6923 (17) Å], while with PABA, the pairs are glide-related [O721—H721···O711^{v} 2.6303 (19) Å] [symmetry codes: (iv) $1-x, 2-y, 1-z$; (v) $1-x, y, \frac{3}{2}-z$]. Although the planar $R_2^2(8)$ association is very common among carboxylic acids, and is also found as the structure extender in the 5-SSA compounds with 4-chloro- and 4-bromoaniline (Smith *et al.*, 2005), the distorted glide-related association in (I) (Fig. 2) is unusual.

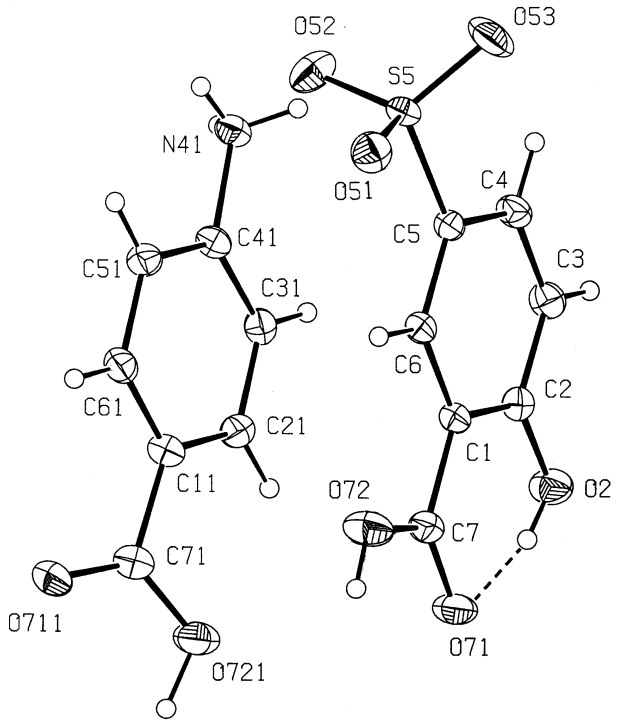


Figure 1
The molecular configuration and atom-numbering scheme for the PABA cation and 5-SSA anion in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line represents a hydrogen bond.

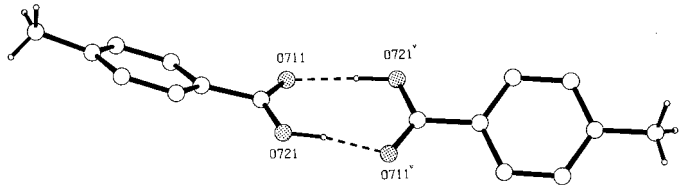


Figure 2
The glide-related homomolecular PABA carboxylic acid pairs involved in the hydrogen-bonding extending interactions, showing the distortion of the cyclic dimer. For symmetry code, see Table 1. Dashed lines represent hydrogen bonds.

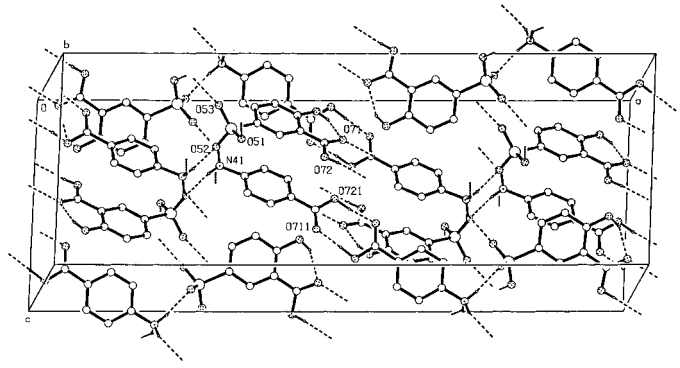


Figure 3
A perspective view of the packing of (I) in the unit cell, viewed approximately down the *b* direction, showing hydrogen-bonding associations as dashed lines. Non-interactive H atoms have been omitted for clarity.

No intermolecular associations involving the phenolic O atom of the 5-SSA anion are present, but there are some cation–anion π–π ring-stacking interactions [ring centroid separation $C_g\cdots C_g$ 3.79 (1) Å and interplanar dihedral angle 6.4 (1)°]. The result in (I) is a three-dimensional framework polymeric structure (Fig. 3).

The structural features of the 5-SSA anions of (I) are similar to those in previously reported compounds. These include the intramolecular OH(phenol)···O(carboxyl) hydrogen bond [2.609 (2) Å], which maintains coplanarity of the carboxyl group and the benzene ring [torsion angle C2—C1—C7—O72 −179.6 (1)°], and the presence of a significant ring-H···O(sulfonate) interaction [C6—H6···O51 2.893 (2) Å], giving a C6—C5—S5—O51 torsion angle of −162.6 (1)°. Similarly, PABA cations show a slightly greater than usual deviation from the planarity which is almost a standard feature of this acid and its compounds [torsion angle C21—C11—C71—O711 − 161.1 (2)°]. It is of interest that the cyclic carboxylic acid association is present in the structure of the β-polymorph of the parent PABA (Lai & Marsh, 1967) but not in the α-polymorph (Alleaume *et al.*, 1966), where only intermolecular carboxylic acid–amine interactions are found.

Experimental

The title compound was synthesized by heating equimolar quantities (1 mmol) of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) and 4-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 crystal plates of (I) [m.p. 520.2–522.0 K (decomposition)].

Crystal data

$C_7H_8NO_2^+\cdot C_7H_5O_6S^-$
M_r = 355.31
Monoclinic, $C2/c$
a = 32.264 (3) Å
b = 7.6517 (7) Å
c = 12.0672 (11) Å
β = 95.242 (2)°
V = 2966.6 (5) Å^3
Z = 8
D_x = 1.591 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5543 reflections
θ = 2.2–27.5°
μ = 0.26 mm^{-1}
T = 295 (2) K
Cut block, pale brown
0.40 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
8997 measured reflections
3361 independent reflections
3011 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 27.5°
$h = -32 \rightarrow 41$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.117
S = 1.05
3361 reflections
241 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 1.1096P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O71	0.78 (2)	1.91 (2)	2.6089 (18)	149 (2)
N41—H41A···O52^{i}	0.84 (2)	1.93 (2)	2.7589 (19)	170 (2)
N41—H41B···O53^{ii}	0.86 (3)	2.06 (2)	2.7959 (19)	142 (2)
N41—H41B···O52	0.86 (3)	2.53 (3)	2.8721 (19)	104 (2)
N41—H41C···O51^{iii}	0.93 (2)	1.84 (2)	2.7192 (19)	156 (2)
O72—H72···O71^{iv}	0.77 (3)	1.92 (3)	2.6923 (17)	175 (3)
O721—H721···O711^{v}	0.98 (4)	1.66 (4)	2.6303 (19)	172 (3)
C6—H6···O51	0.93	2.52	2.8932 (19)	105

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $-x+\frac{1}{2}, +y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, y-1, z$; (iv) $-x+1, -y+2, -z+1$; (v) $-x+1, y, -z+\frac{3}{2}$.

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 = 0.93 Å) using the riding-model approximation, with U_{eq}(H) fixed at 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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