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A dianionic 5-sulfonatosalicylate species in the proton-transfer compound bis(benzylaminium) 3-carboxylato-4-hydroxybenzenesulfonate

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The crystal structure of anhydrous bis(benzylaminium) 5-sulfonatosalicylate, $2C_7H_{10}N^+ \cdot C_7H_4O_6S^{2-}$, from the reaction of benzylamine with 5-sulfosalicylic acid, shows the presence of a dianionic 5-sulfonatosalicylate species, uncommon among proton-transfer compounds of this acid with organic Lewis bases. Hydrogen-bonding interactions between both aminium $N^+ - H$ groups of the two cations and both the sulfonate and carboxylate O-atom acceptors of the anions give a layered two-dimensional network structure.

Key indicators

Single-crystal X-ray study

$T = 297\text{ K}$

Mean $\sigma(C-C) = 0.005\text{ \AA}$

R factor = 0.047

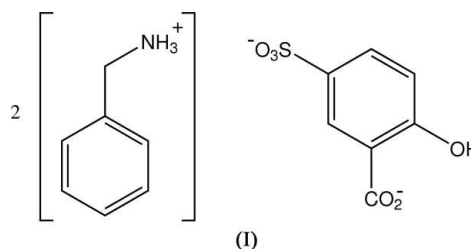
wR factor = 0.172

Data-to-parameter ratio = 15.9

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

Comment

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, *viz.* with aniline (Bakasova *et al.*, 1991), the 4-*X*-substituted anilines ($X = F, Cl, Br$) (Smith *et al.*, 2005a), 3-aminobenzoic acid (Smith *et al.*, 2005) and 4-aminobenzoic acid (Smith *et al.*, 2005b). In only one compound with bifunctional 1,4-phenylenediamine is the dianionic 5-SSA species found (Smith *et al.*, 2005). The 1:1 stoichiometric reaction of 5-SSA with the moderately strong monofunctional aromatic-aliphatic Lewis base benzylamine (BZA) ($pK_a = 9.35$) was expected to give a 1:1 proton-transfer compound with 5-SSA, such as was found in the structure of its compound with the analogous 3,5-dinitrosalicylic acid (Smith *et al.*, 2002). However, the structure of the anhydrous compound formed from the reaction of 5-SSA with BZA in 95% ethanol, benzylaminium 5-sulfosalicylate, (I), reported here, shows the presence of a dianionic 5-SSA species.



In (I), the BZA cation species (*A* and *B*) and the 5-SSA dianion (Fig. 1) form a two-dimensional hydrogen-bonded network structure which extends in the unit cell across the *ac* plane (Fig. 2). Similar hydrogen-bonded layered structures have been found in other 5-SSA proton-transfer compounds, *e.g.* with 2,6-diaminopyridine and 1,4-phenylenediamine (Smith *et al.*, 2005). The H-atom donors of the *A*-cation aminium group are involved in three interactions with separate carboxylate O-atom acceptors, while the *B*-cation interacts with only sulfonate O-atom acceptors [five in total, to four

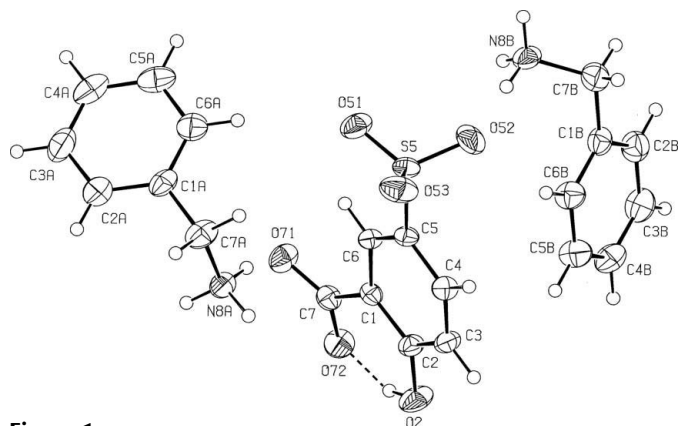


Figure 1
The molecular configuration and atom-numbering scheme for the two BZA cations (*A* and *B*) and the 5-SSA dianion in (*I*). Displacement ellipsoids are drawn at the 40% probability level. The dashed line indicates a hydrogen bond.

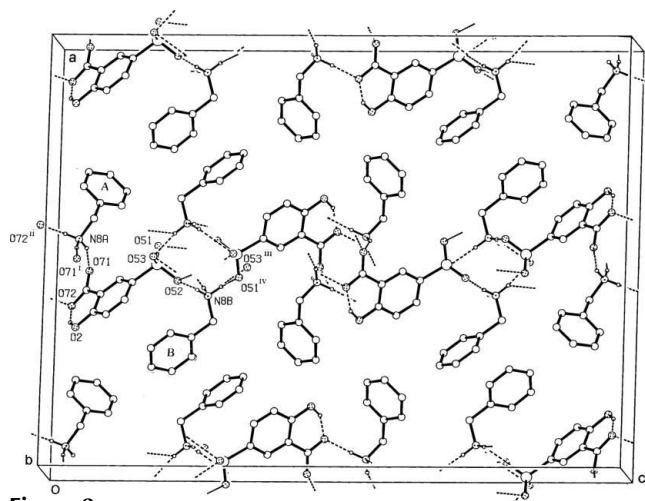


Figure 2
A perspective view of the packing of (*I*) in the unit cell, viewed approximately down the *b* axis, showing hydrogen-bonding associations as dashed lines. For symmetry codes, see Table 1. H atoms not involved in hydrogen bonding have been omitted.

separate groups, with one a symmetrical cyclic $R_2^2(4)$ interaction] (Table 1). There are no bidentate $R_2^2(8)$ N—H...O interactions which have the highest incidence among organic sulfonate structures (Haynes *et al.*, 2004).

The 5-SSA anions have the usual intramolecular O(phenol)—H...O(carboxyl) hydrogen bond [2.553 (4) Å], with the carboxylate group lying slightly out of the plane of the benzene ring [torsion angle C2—C1—C7—O71 = 163.8 (3)°]. The two benzylammonium cations are conformationally different [C2—C1—C7—N8 torsion angle = 83.7 (4)° in *A* and 126.2 (4)° in *B*].

Experimental

The title compound was synthesized by heating 1 mmol quantities of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) and benzylamine in 95% ethanol/water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, total room-temperature evaporation

of the hot-filtered solution gave colourless prisms of (*I*) (m.p. 303.6–305.6 K).

Crystal data

$2C_7H_{10}N^+ \cdot C_7H_4O_6S^{2-}$
 $M_r = 432.48$
 Monoclinic, $C2/c$
 $a = 24.686$ (5) Å
 $b = 5.144$ (2) Å
 $c = 32.705$ (6) Å
 $\beta = 90.111$ (14)°
 $V = 4153$ (2) Å³

$Z = 8$
 $D_x = 1.383$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.20$ mm⁻¹
 $T = 297$ (2) K
 Prism, colourless
 $0.35 \times 0.27 \times 0.18$ mm

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (TEXSAN; Molecular Structure Corporation, 1999)
 $T_{\min} = 0.934$, $T_{\max} = 0.965$
 5249 measured reflections

4768 independent reflections
 2396 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 27.5^\circ$
 3 standard reflections
 frequency: 150 min
 intensity decay: 2.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.172$
 $S = 0.87$
 4768 reflections
 299 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O72	0.93 (4)	1.69 (4)	2.553 (4)	153 (4)
N8A—H81A...O71 ⁱ	0.95 (4)	1.87 (4)	2.786 (4)	163 (3)
N8A—H82A...O72 ⁱⁱ	0.92 (4)	1.81 (4)	2.697 (4)	161 (3)
N8A—H83A...O71	0.92 (4)	2.20 (5)	3.063 (4)	157 (3)
N8B—H81B...O52 ⁱⁱⁱ	0.90 (4)	2.21 (4)	3.074 (5)	160 (4)
N8B—H81B...O53 ⁱⁱⁱ	0.90 (4)	2.38 (4)	3.094 (5)	137 (3)
N8B—H82B...O51 ^{iv}	0.91 (5)	2.49 (4)	2.961 (5)	113 (3)
N8B—H82B...O53 ^v	0.91 (5)	1.95 (4)	2.814 (5)	159 (4)
N8B—H83B...O52	0.97 (6)	1.85 (6)	2.818 (5)	176 (6)

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

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 = 0.95 Å) using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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: *SIR92* (Altomare *et al.*, 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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