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4-Carboxyanilinium hydrogensulfate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.048
wR factor = 0.123
Data-to-parameter ratio = 19.4

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

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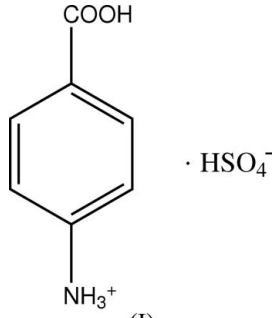
The cohesion in the title structure (*p*-CPABS), $C_7H_8NO_2^+\cdot HSO_4^-$, is assured by an intricate three-dimensional hydrogen-bonded network of types N—H···O and O—H···O involving anions, carboxyl and amino groups in addition to the ionic interactions.

Comment

The electrical, magnetic and optical properties (Kagan *et al.*, 1999; Hill, 1998) of hybrid compounds (Mazeaud *et al.*, 2000; Soghomonian *et al.*, 1995; Mayer *et al.*, 1999; Bagieu-Beucher, 1990; Ravikumar *et al.*, 2002) make them very interesting materials because of their structural topologies and potential applications in the field of new materials science (Siegel *et al.*, 1998; Baker *et al.*, 1992).



(I)

p-Carboxyaniline (4-aminobenzoic acid, PABA) is an important biological molecule, acting as an antagonist to the action of the drug sulfonilamide in competition for essential growth metabolites (Pauling & Hayward, 1964), as well as being an essential bacterial cofactor involved in the synthesis of folic acid (Robinson, 1966) and proving a particularly versatile reagent for structure extension through linear

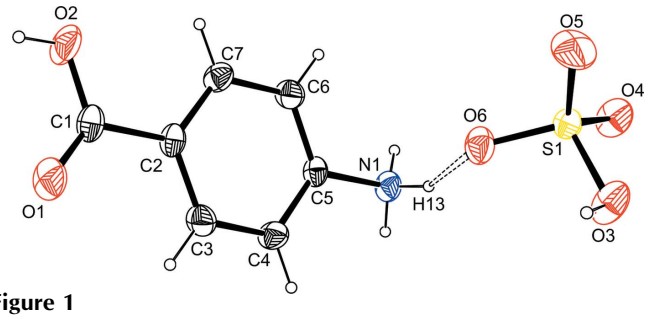


Figure 1
The asymmetric unit o *p*-CPABS, with the atom-labelling scheme. Displacement ellipsoids are drawn at the the 50% probability level and H atoms are shown as small spheres of arbitrary radius. The hydrogen bond is shown as a double dashed line.

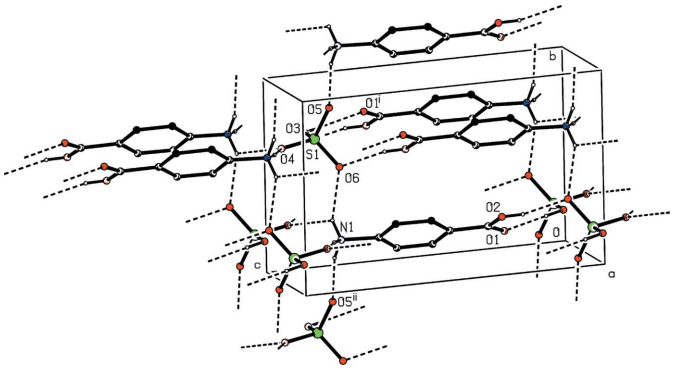


Figure 2
A partial packing view of (I), showing the hydrogen-bonding network. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (i) x, $y-1$, z; (ii) $1-x$, $1-y$, $1-z$.]

hydrogen-bonding associations, through both the carboxylic acid and amine functional groups. This property was recognized as a possible tool for promoting co-crystallization, with the aim of designing noncentrosymmetric organic materials (Etter & Frankenbach, 1989).

In our systematic investigation of organic–inorganic hybrid materials, including sulfuric acid and various nucleic acids or amino acids, three structures have been already reported, namely diglycinium sulfate (Cherouana *et al.*, 2002), guanidinium sulfate monohydrate (Cherouana, Benali-Cherif *et al.*, 2003) and *m*-carboxyphenylammonium bisulfate (Cherouana, Bendjeddou *et al.*, 2003). We report here the fourth such compound, the title compound, (I).

The asymmetric unit of (I) (*p*-CPABS) contains one *p*-carboxyphenylammonium cation and one bisulfate anion (Fig. 1). The average of the terminal S—O bond lengths [1.4445 (14) Å] is shorter than the S—OH bond length [1.5609 (14) Å], which confirms the presence of the H atom in the bisulfate anion, supported also by its involvement in a hydrogen bond (see below). The O—S—O bond angles of the HSO_4^- anions are in the range 102.63 (8)–115.35 (10)°, confirming a tetrahedral configuration, and are similar to those in other reported sulfates. The geometry of the organic cation is normal and in good agreement with that observed in *p*-carboxyphenylammonium dihydrogenmonophosphate monohydrate (Benali-Cherif *et al.*, 2002).

The three H atoms of the phenylammonium group are involved in extensive N—H···O hydrogen-bonding interactions with the O-atom acceptors of four different bisulfate anions (Table 1). In addition, there are secondary structure extensions involving the carboxylic acid group of the cations and the bisulfate anions (Table 1). Such an intricate three-dimensional hydrogen-bonding framework ensures the cohesion of the crystal structure (Fig. 2).

Experimental

Colourless prismatic single crystals of *p*-CPABS were obtained by slow evaporation, at room temperature, of an equimolar solution of 4-aminobenzoic acid (PABA) and sulfuric acid.

Crystal data

$C_7H_8NO_2^+\cdot HO_4S^-$
M_r = 235.21
Triclinic, $P\overline{1}$
a = 5.2058 (6) Å
b = 7.5770 (7) Å
c = 11.837 (2) Å
α = 93.356 (7)°
β = 95.187 (7)°
γ = 92.785 (6)°
V = 463.51 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.36 mm^{-1}
T = 293 K
0.25 × 0.1 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
7756 measured reflections
2693 independent reflections
2205 reflections with $I > 2\sigma(I)$
R_{int} = 0.091

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.123
S = 1.08
2693 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H13···O6	0.89	2.13	2.918 (2)	147
N1—H12···O5^{i}	0.89	1.89	2.748 (2)	163
N1—H13···O4^{ii}	0.89	2.53	3.056 (2)	119
N1—H11···O4^{iii}	0.89	1.92	2.802 (2)	170
O2—H2···O6^{iv}	0.82	1.85	2.647 (2)	164
O3—H3···O1^{v}	0.82	1.87	2.688 (2)	173

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

The OH and NH_3 H atoms of the anion and cations could be located in difference Fourier syntheses, but they were introduced in calculated positions and treated as riding on their parent atoms, with N—H = 0.89 Å and O—H = 0.82 Å, and with U_{iso}(H) = 1.5U_{eq}(N,O). Aromatic H atoms were located in difference Fourier syntheses but were treated as riding on their parent C atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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