

4-Fluoro-2-(phosphonomethyl)-  
benzenesulfonic acid monohydrateFabrizio Adani,<sup>a</sup> Enzo Montoneri<sup>b</sup> and Philip J.  
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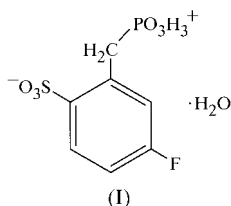
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The title compound,  $C_7H_8FO_6PS \cdot H_2O$ , contains both phosphonic and sulfonic acid functionalities. An extensive network of  $O-H \cdots O$  hydrogen bonds is present in the crystal structure. The three acidic protons are associated with the phosphonate group. Two protons experience typical hydrogen-bond contacts with the sulfonate-O atoms, while the third has a longer covalent bond of 1.05 (3) Å to the phosphonate-O atom and a short hydrogen-bond contact of 1.38 (3) Å to the water O atom (all  $O-H \cdots O$  angles are in the range 162–175°). The sulfonate group is positioned so that one S–O bond is nearly coplanar with the phenyl ring [torsion angle  $O-S-C-C$  –8.6 (2)°]. The phosphonate group is oriented approximately perpendicular to the ring [torsion angle  $P-C-C-C$  99.2 (2)°] with one P–O bond *anti* to the benzyl C–C bond. The molecules pack in layers in the *b*–*c* plane with the water molecules in between adjacent pairs of inverted layers.

## Comment

The title compound, (I), was prepared as part of a study of fluorinated arylphosphonic acids and aryl sulfophosphonic acids (Montoneri, Savarino *et al.*, 1994; Montoneri, Viscardi *et al.*, 1994) and their metal salts (Langley *et al.*, 1996; Benedetto *et al.*, 1997). Compounds of this type are of interest, in part, for their ion exchange and proton-conducting potential (Alberti, Casciola *et al.*, 1992; Alberti, Casciola, Palombari & Peraio, 1992).



The central portion of the molecule (Fig. 1) is flat with the atoms of the ring showing an average deviation of 0.006 (2) Å

from the least-squares plane and appended atoms all within 0.11 Å of the plane. The C1–C7 bond is rotated so that the phosphonic acid group is pointing away from the ring [torsion angle  $P-C7-C1-C6$  –76.9 (3)°] and one P–O bond is *anti* to the C1–C7 bond while the other two are *gauche* [torsion angle  $O4-P-C7-C1$  –59.9 (2)°]. The sulfonate group has one S–O bond almost eclipsing the ring, while the other two are in *gauche* positions [torsion angle  $O2-S-C2-C1$  –66.5 (2)°] and the methylene carbon is bent away from the sulfonate group by approximately 4°, as is the methyl group in *o*-toluenesulfonic acid (Taga & Kobayashi, 1990). The three acidic protons are distributed in a manner which is consistent with the acid strengths of the functional groups. The phosphonate group retains two acidic protons, H4 and H5, with covalent O–H bonds of approximately 0.85 Å. The third acidic proton (H6) is located between one of the phosphonate O atoms and the water molecule,  $O-H$  1.05 (3),  $H \cdots O$  1.38 (3) Å. This arrangement fits on the continuum of  $O-H \cdots O$  distances obtained in a recent study of such interactions (Steiner & Saenger, 1994). The lengths of the P–O bonds (Table 1) suggest that the  $O4-H4$  and  $O5-H5$  bonds are stronger than the  $O6-H6$  bond. These data, together with the nearly equivalent S–O distances, suggest a complete proton transfer from the stronger sulfonic acid to the weaker phosphonic acid and a partial proton transfer from the latter function to the water molecule. Thus, the molecule actually exists in the solid state as a zwitterion that is intermediate between the two extremes  $^-O_3SC_6H_3FCH_2PO_3H_3^+ \cdot H_2O$  and  $^-O_3SC_6H_3FCH_2PO_3H_2 \cdot H_3O^+$ . This arrangement is consistent with the structure of *o*-toluenesulfonic acid dihydrate (Taga & Kobayashi, 1990) in which the acidic proton is fully transferred from the  $SO_3^-$  group to one of the water molecules to produce  $H_3O^+$ . In the presence of the more basic phosphonate group in (I), the proton transfer is not complete and a symmetrical hydronium ion is not formed.

The molecules of (I) can be viewed as forming layers (Fig. 2) in the *b*–*c* plane which then stack in the *a* direction. The sulfonate and phosphonic acid groups are directed to opposite faces of the layer and the water molecules are located between

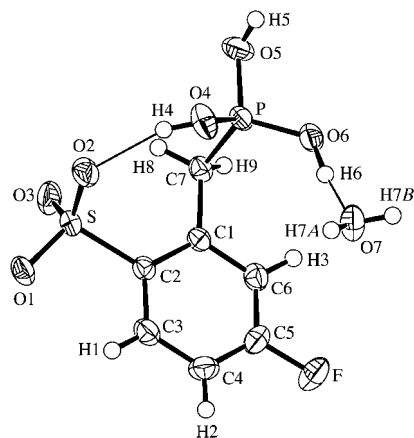
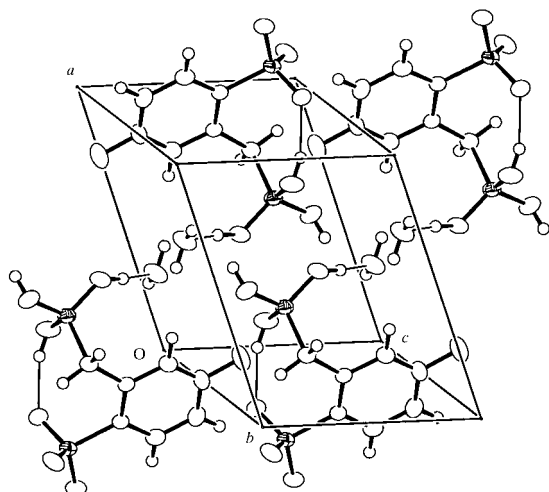


Figure 1

An ORTEP diagram (Johnson, 1976) showing the molecular structure and atom-labeling scheme of (I). Hydrogen bonds are shown by narrow lines. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

every other pair of layers, closely associated with the phosphonic acid functionality. This packing scheme is somewhat different from what is observed for the isomeric 4-fluoro-3-sulfonatobenzylphosphonic acid hydrate (Benedetto *et al.*, 1997). That structure also contains layers with the acidic groups on opposite faces, however, the water molecules are associated with the sulfonate groups in between every pair of layers.



**Figure 2**  
An ORTEPII diagram (Johnson, 1976) showing the crystal packing of (I). Figure details are as for Fig. 1.

## Experimental

The procedure for the synthesis of (I) has been reported (Montoneri, Savarino *et al.*, 1994).

### Crystal data

$C_7H_8FO_6PS \cdot H_2O$   
 $M_r = 288.18$   
 Triclinic,  $P\bar{1}$   
 $a = 8.486$  (1) Å  
 $b = 9.247$  (3) Å  
 $c = 7.917$  (2) Å  
 $\alpha = 104.84$  (2)°  
 $\beta = 110.00$  (1)°  
 $\gamma = 97.37$  (2)°  
 $V = 548.1$  (2) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.746$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 21 reflections  
 $\theta = 19.7$ – $22.6$ °  
 $\mu = 0.460$  mm<sup>-1</sup>  
 $T = 296$  K  
 Slab, colorless  
 $0.30 \times 0.30 \times 0.10$  mm

### Data collection

Rigaku AFC-6S diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{min} = 0.908$ ,  $T_{max} = 0.955$   
 2051 measured reflections  
 1909 independent reflections  
 1907 reflections with  $I > 0$

$R_{int} = 0.021$   
 $\theta_{max} = 25$ °  
 $h = 0 \rightarrow 10$   
 $k = -10 \rightarrow 10$   
 $l = -9 \rightarrow 8$   
 3 standard reflections every 150 reflections  
 intensity decay: 0.90%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.044$   
 $wR(F^2) = 0.064$   
 $S = 1.98$   
 1907 reflections  
 173 parameters  
 Only coordinates of H atoms refined

$w = 4F_o^2/\sigma^2(F_o^2)$   
 $(\Delta/\sigma)_{max} = 0.016$   
 $\Delta\rho_{max} = 0.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.36$  e Å<sup>-3</sup>  
 Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic  
 Extinction coefficient:  $7.2$  (2)  $\times 10^{-7}$

**Table 1**  
Selected geometric parameters (Å, °).

S—O1	1.471 (2)	P—O5	1.546 (2)
S—O2	1.447 (2)	P—O6	1.498 (2)
S—O3	1.451 (2)	P—C7	1.784 (3)
S—C2	1.776 (2)	F—C5	1.359 (3)
P—O4	1.547 (2)		
O1—S—O2	111.7 (1)	O5—P—O6	110.0 (1)
O1—S—O3	110.5 (1)	O5—P—C7	104.7 (1)
O1—S—C2	105.9 (1)	O6—P—C7	112.8 (1)
O2—S—O3	113.4 (1)	C2—C1—C7	123.6 (2)
O2—S—C2	107.1 (1)	C6—C1—C7	118.8 (2)
O3—S—C2	107.9 (1)	S—C2—C1	121.4 (2)
O4—P—O5	111.0 (1)	S—C2—C3	118.0 (2)
O4—P—O6	109.0 (1)	P—C7—C1	110.6 (2)
O4—P—C7	109.2 (1)		

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 <sup>i</sup> ···O2	0.84	1.83	2.645 (2)	163
O5—H5 <sup>i</sup> ···O1 <sup>i</sup>	0.85	1.83	2.678 (3)	175
O6—H6 <sup>i</sup> ···O7	1.05 (3)	1.38 (3)	2.418 (2)	171 (2)
O7—H7A <sup>ii</sup> ···O1 <sup>ii</sup>	0.85	1.85	2.695 (3)	174
O7—H7B <sup>iii</sup> ···O3 <sup>iii</sup>	0.85	1.84	2.682 (2)	173

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

The H atoms were located on difference electron-density maps and their positions refined with isotropic displacement parameters set at 1.2 times that of the attached atom at the time of their inclusion; C—H range 0.90 (2)–0.99 (2) Å. Several of the O—H bond lengths refined to unrealistically short values (*i.e.* less than 0.8 Å) and were subsequently placed in fixed positions along the same O—H vector.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structure: *MITHRIL* (Gilmore, 1983); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1237). Services for accessing these data are described at the back of the journal.

## References

- Alberti, G., Casciola, M., Costantino, U., Peraio, A. & Montoneri, E. (1992). *Solid State Ionics*, **50**, 315–322.  
 Alberti, G., Casciola, M., Palombari, R. & Peraio, A. (1992). *Solid State Ionics*, **58**, 339–344.  
 Benedetto, A. F., Squattrito, P. J., Adani, F. & Montoneri, E. (1997). *Inorg. Chim. Acta*, **260**, 207–216.  
 Gilmore, C. J. (1983). *MITHRIL*. University of Glasgow, Scotland.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Langley, K. J., Squattrito, P. J., Adani, F. & Montoneri, E. (1996). *Inorg. Chim. Acta*, **253**, 77–85.  
 Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.  
 Molecular Structure Corporation (1991). *TEXSAN*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.  
 Montoneri, E., Savarino, P., Viscardi, G. & Gallazzi, M. C. (1994). *Phosphorus Sulfur Silicon Relat. Elem.* **86**, 145–155.  
 Montoneri, E., Viscardi, G., Ricca, G. & Gallazzi, M. C. (1994). *Phosphorus Sulfur Silicon Relat. Elem.* **86**, 123–128.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Steiner, T. & Saenger, W. (1994). *Acta Cryst.* **B50**, 348–357.  
 Taga, T. & Kobayashi, T. (1990). *Acta Cryst.* **C46**, 2243–2245.  
 Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.