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2-(4-Hydroxystyryl)-1-methylpyridinium 4-methoxybenzenesulfonate

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.055
wR factor = 0.165
Data-to-parameter ratio = 27.5

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

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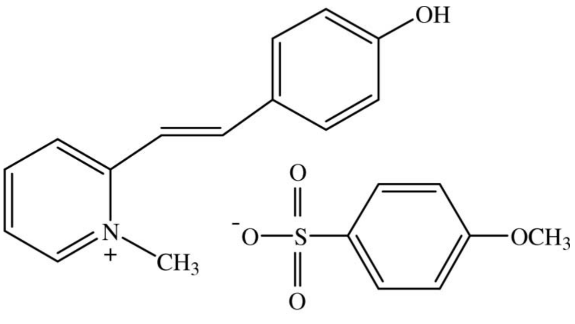
In the title compound, $C_{14}H_{14}NO^+\cdot C_7H_7SO_4^-$, the cation is almost planar and adopts an E configuration. The pyridinium and benzene rings of the cation make dihedral angles of 88.01 (8) and 87.37 (8)°, respectively, with the benzene ring of the anion. In the crystal structure, the cations and anions are arranged in layers parallel to the (011) plane. The cations and anions are linked through O—H···O and C—H···O hydrogen bonds, and C—H···π interactions.

Comment

The most important requirement for non-linear optical (NLO) materials to exhibit second-order NLO properties is for the molecules to be oriented in a non-centrosymmetric environment (Williams 1984). The X-ray crystal structure determination of the title compound, (I), was carried out in order to obtain detailed information of the molecular packing of (I), and to gain more information on the effect of the counter-anion on the crystal packing and the NLO properties of similar compounds (Chantrapromma, Ruanwas, Jindawong *et al.*, 2006; Chantrapromma, Ruanwas, Fun & Patil, 2006). However, compound (I) crystallizes in the centrosymmetric space group $P2_1/c$ and does not exhibit second-order NLO properties.



(I)

The asymmetric unit of (I) contains a $C_{14}H_{14}NO^+$ cation and a $C_7H_7SO_4^-$ anion (Fig. 1). The bond distances and angles in both cation and anion have normal values (Allen *et al.*, 1987).

The sulfonate O atoms of the anion are disordered over two positions. The methoxy group at C18 is coplanar with the attached benzene ring [torsion angle C21—O2—C18—C19 = −179.07 (17)°].

The cation is almost planar and exists in an E configuration with respect to the C6═C7 double bond [1.322 (2) Å]. The dihedral angle between the pyridinium and benzene rings is 4.50 (8)°; this compares with 3.46 (8)° in 2-(4-hydroxystyryl)-1-methylpyridinium p-toluenesulfonate, (II) (Chan-

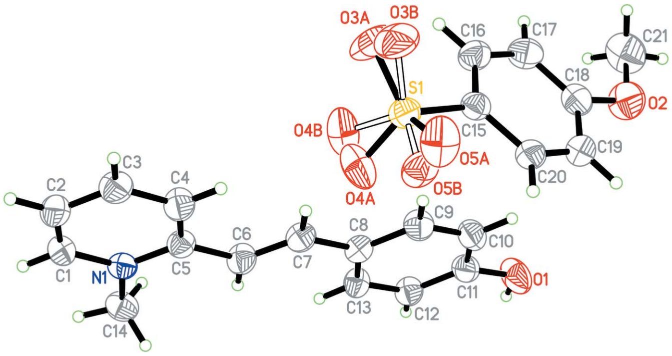


Figure 1
The asymmetric unit of (I), showing 40% probability displacement ellipsoids and the atom-numbering scheme. The sulfonate O atoms are disordered over two positions and both are shown.

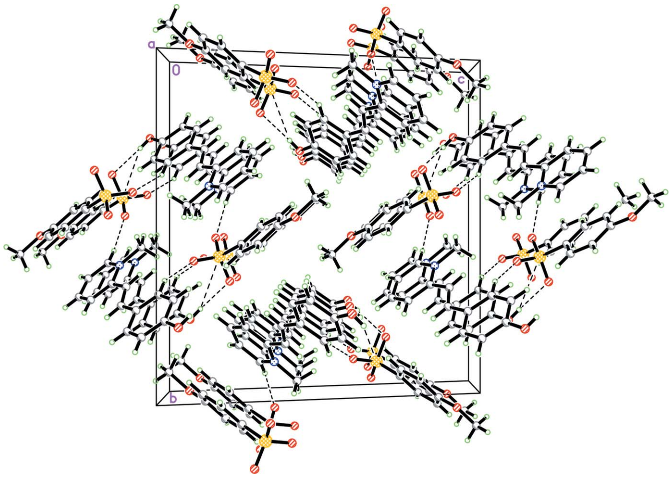


Figure 2
A packing diagram for (I), viewed approximately down the *a* axis. Hydrogen bonds are shown as dashed lines.

trapromma, Ruanwas, Jindawong *et al.*, 2006) and 4.52 (8)° in 2-(4-hydroxystyryl)-1-methylpyridinium 4-bromobenzenesulfonate, (III) (Chantrapromma, Ruanwas, Fun & Patil, 2006).

In the asymmetric unit of (I), the cation and anion are almost perpendicular to each other; the benzene ring of the anion makes dihedral angles of 88.01 (8) and 87.37 (8)°, respectively, with the pyridinium and benzene rings of the cation [12.45 (8) and 15.49 (9)° in (II), and 67.06 (8) and 71.56 (8)° in (III)].

In the crystal packing of (I), the cations and anions are arranged in layers approximately parallel to the (011) plane (Fig. 2). The cations and anions are linked through O—H···O and C—H···O hydrogen bonds, and C—H···π interactions involving the C8–C13 benzene ring (Table 1).

Experimental

2-(4-Hydroxystyryl)-1-methylpyridinium iodide (compound *A*) was synthesized according to our previously reported procedure (Chantrapromma, Ruanwas, Jindawong *et al.*, 2006). Silver(I) 4-methoxybenzenesulfonate (compound *B*) was synthesized from a solution (1:2:1 molar ratio) of 4-methoxybenzenesulfonyl chloride (2.07 g, 10 mmol), sodium hydroxide (0.81 g, 20 mmol) and silver nitrate (1.71 g, 10 mmol) in hot methanol (50 ml). The mixture was stirred for 10 min and then filtered. The resulting colourless solution was evaporated to yield white compound *B* (m.p. 516–518 K). The title compound was synthesized by mixing solutions of *A* (0.17 g, 0.5 mmol) and *B* (0.14 g, 0.5 mmol), each in hot methanol (50 ml), which gave a yellow mass of silver iodide immediately. After stirring the mixture for 30 min, the silver iodide was filtered off and the resulting yellow solution was evaporated to yield a yellow solid. Single crystals of (I) suitable for X-ray analysis were obtained by recrystallization from a solution in methanol at ambient temperature over several days (m.p. 524–526 K).

Crystal data

$C_{14}H_{14}NO^+\cdot C_7H_7O_4S^-$
$M_r = 399.46$
Monoclinic, $P2_1/c$
$a = 6.8786$ (1) Å
$b = 17.2639$ (2) Å
$c = 17.2828$ (3) Å
$\beta = 110.231$ (1)°
$V = 1925.74$ (5) Å^3
$Z = 4$
$D_x = 1.378$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.20$ mm^{-1}
$T = 297$ (2) K
Block, yellow
0.54 × 0.40 × 0.31 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.899$, $T_{max} = 0.940$
33183 measured reflections
7859 independent reflections
4860 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 34.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.165$
$S = 1.03$
7859 reflections
286 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 0.3021P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O4A^{i}	0.75 (3)	2.07 (3)	2.821 (4)	178 (4)
C1—H1*B*···O3A^{ii}	0.93	2.16	3.064 (9)	164
C7—H7*A*···O4*A*	0.93	2.59	3.473 (3)	158
C12—H12*A*···O4A^{i}	0.93	2.59	3.295 (4)	133
C13—H13*A*···O5A^{iii}	0.93	2.46	3.322 (5)	154
C14—H14*B*···O5A^{iv}	0.96	2.59	3.475 (4)	153
C21—H21*A*···$Cg1^{v}$	0.96	2.92	3.610 (3)	130

Symmetry codes: (i) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+2, -y+1, -z+1$. *Cg*1 is the centroid of the C8–C13 ring.

In the anion, the O atoms of the sulfonate group are disordered over two positions. The corresponding occupancies were initially refined and later fixed at 0.56 and 0.44. The hydroxyl H atom was located in a difference map and refined isotropically. The remaining H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.96 Å. The U_{iso}(H) values were set equal to $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms, and $1.2U_{eq}$ for the

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remaining H atoms. A rotating-group model was used for the methyl groups.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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