

2-(4-Hydroxystyryl)-1-methylpyridinium
p-toluenesulfonateSuchada Chantrapromma,^{a,‡}
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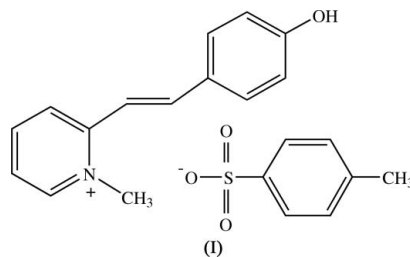
Key indicators

Single-crystal X-ray study
T = 297 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
Disorder in main residue
R factor = 0.046
wR factor = 0.145
Data-to-parameter ratio = 20.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{14}\text{H}_{14}\text{NO}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^-$, the cation is almost planar and adopts an *E* configuration. In the crystal structure, the cations and anions are packed as alternate layers parallel to the *ac* plane. These layers are interconnected through $\text{O}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions, forming a three-dimensional supramolecular network.

Comment

Much interest has been devoted to organic compounds which show non-linear optical (NLO) properties as these NLO materials are useful for applications in optical switching, data storage and optical communications (Crasta *et al.*, 2004; Feng *et al.*, 2005; Hong *et al.*, 2005; Marder *et al.*, 1991; Usman *et al.*, 2000; Umezawa *et al.*, 2002; Ye *et al.*, 2005). Organic molecules that exhibit second-order non-linear optical properties usually consist of a frame with a delocalized π system, end-capped with either a donor or an acceptor substituent or both. The most important requirement for these materials to exhibit second-order NLO properties is for the molecules to be oriented in a non-centrosymmetric environment (Williams, 1984). Benzenesulfonate is frequently used to co-crystallize with cations to form compounds which are expected to have NLO properties (Lakshmana Perumal *et al.*, 2002; 2004; Jindawong *et al.*, 2005). Our continuing research on non-linear optical materials (Rahman *et al.*, 2003; Jindawong *et al.*, 2005; Chantrapromma *et al.*, 2005) has led us to synthesize the title compound, (I), and its crystal structure is reported here. However, compound (I) crystallized in the centrosymmetric space group $P2_1/c$ and does not exhibit second-order NLO properties.



Selected bond distances and angles are listed in Table 1. The bond distances and angles in both cation and anion have normal values (Allen *et al.*, 1987). The cation is almost planar and exists in an *E* configuration with respect to the $\text{C}_6=\text{C}_7$ double bond [1.323 (3) Å]; the dihedral angle between the benzene and pyridinium rings is 3.46 (8)°.

In the crystal packing, the cations and anions are packed as alternate layers parallel to the *ac* plane (Fig. 2). The cationic

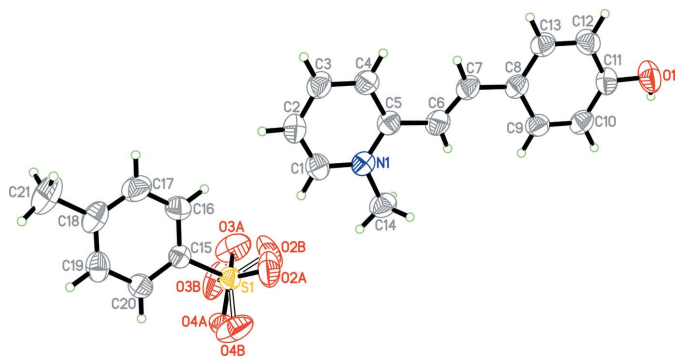


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Both disorder components are shown.

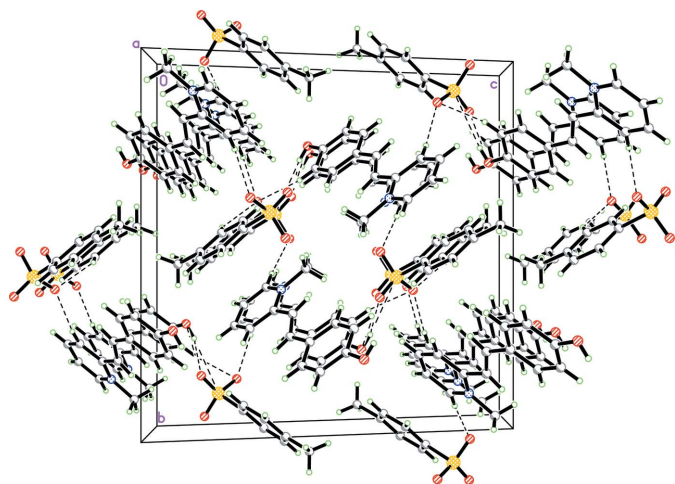


Figure 2
The packing diagram of (I), viewed approximately down the *a* axis. Hydrogen bonds are shown as dashed lines.

and anionic layers are interconnected through O—H...O hydrogen bonds and C—H...O weak interactions (Table 2). The crystal structure is further stabilized by C—H... π interactions involving the benzene ring of the anion (Table 2).

Experimental

2-(4-Hydroxystyryl)-1-methylpyridinium iodide (compound *A*) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylpyridinium iodide (2.00 g, 8.5 mmol), 4-hydroxybenzaldehyde (1.04 g, 8.5 mmol) and piperidine (0.72 g, 8.5 mmol). The resulting solution was refluxed for 3 h under a nitrogen atmosphere. The resultant solid was filtered off, washed with diethyl ether and recrystallized from methanol, to give orange crystals of compound *A* (1.78 g, 62%; m.p. 534–536 K). Silver(I) *p*-toluenesulfonate (compound *B*) was synthesized from a solution (1:1:1 molar ratio) of *p*-toluenesulfonic acid (1.90 g, 10.0 mmol), sodium hydroxide (0.40 g, 10.0 mmol) and silver nitrate (1.70 g, 10.0 mmol) in hot methanol (Okada *et al.*, 1990). The mixture was stirred for *ca* 5 min and the white compound *B* was precipitated during stirring (1.95 g, 70%). The title compound was synthesized by mixing compound *A* (0.24 g, 0.7 mmol) in hot methanol (25 ml) and a solution of compound *B* (0.20 g, 0.7 mmol) in hot methanol (50 ml). The mixture yielded a yellow solid of silver iodide immediately. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting orange solution

was evaporated to yield an orange solid. The orange solid was then dissolved in methanol. After allowing the resulting solution to stand at ambient temperature for several days, orange single crystals of (I) suitable for X-ray diffraction studies were obtained (m.p. 526–527 K).

Crystal data

$C_{14}H_{14}NO^+ \cdot C_7H_7O_3S^-$
 $M_r = 383.46$
Monoclinic, $P2_1/c$
 $a = 6.8104$ (1) Å
 $b = 16.8958$ (2) Å
 $c = 17.4608$ (2) Å
 $\beta = 108.828$ (1)°
 $V = 1901.66$ (4) Å³
 $Z = 4$

$D_x = 1.339$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5556 reflections
 $\theta = 1.7$ – 30.0°
 $\mu = 0.20$ mm⁻¹
 $T = 297$ (2) K
Block, orange
 $0.53 \times 0.51 \times 0.43$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.901$, $T_{\max} = 0.919$
35885 measured reflections

5555 independent reflections
4366 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -23 \rightarrow 23$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.145$
 $S = 1.07$
5555 reflections
274 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.5805P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C11	1.359 (2)	N1—C5	1.361 (2)
N1—C1	1.354 (2)	N1—C14	1.481 (2)
N1—C5—C6—C7	−170.20 (16)	C6—C7—C8—C13	171.82 (18)
C5—C6—C7—C8	178.08 (16)	C6—C7—C8—C9	−6.7 (3)

Table 2

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>
O1—H1O <i>A</i> ...O4A ⁱ	0.79	1.98	2.725 (3)	157
C1—H1...O2A	0.93	2.32	3.243 (5)	173
C4—H4...O3A ⁱⁱ	0.93	2.55	3.472 (4)	169
C10—H10...O3A ⁱ	0.93	2.52	3.404 (4)	158
C19—H19...O3A ⁱⁱⁱ	0.93	2.57	3.295 (4)	135
C20—H20...O4A	0.93	2.58	2.932 (3)	103
C13—H13...Cg1 ⁱⁱ	0.93	2.89	3.666 (2)	142

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x - 1, y, z$. Cg1 is the centroid of the benzene ring of the anion.

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 0.58 and 0.42. H atoms were placed in calculated positions with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The $U_{\text{iso}}(\text{H})$ values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for hydroxyl and methyl

H atoms and $1.2U_{eq}$ for the 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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