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4-(4′-Hydroxy-3′-methoxystyryl)-1-methylpyridinium 4-chlorobenzenesulfonate

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Key indicators

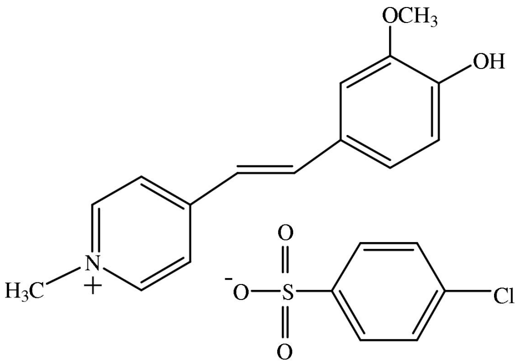
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.126
Data-to-parameter ratio = 13.3

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

The title compound, $C_{15}H_{16}NO_2^+\cdot C_6H_4ClO_3S^-$, is isomorphous with the 4-bromobenzenesulfonate derivative. The cation is almost planar and the benzene ring of the anion makes dihedral angles of 82.79 (1) and 76.39 (1)° with the mean planes through the benzene ring of the cation and the pyridinium ring, respectively. The cations and anions are packed as alternate layers parallel to the *ac* plane. These layers are interconnected through O—H···O, C—H···O and C—H···π interactions to form a three-dimensional network.

Comment

In recent years, much effort has been focused on the development of new materials with nonlinear optical (NLO) properties (Marder *et al.*, 1991; Usman *et al.*, 2000; Nogi *et al.*, 2000; Umezawa *et al.*, 2002; Feng *et al.*, 2005; Ye *et al.*, 2005). Organic molecules that exhibit second-order NLO properties usually consist of a frame with a delocalized π system, end-capped with either a donor or an acceptor substituent or both. Several organic compounds, such as single crystals of stilbazolium *p*-toluenesulfonate derivatives, show second-order NLO properties. Oudar & LePerson (1975) reported the effect on conjugation length of using stilbene instead of a benzene π system. In our continuing research on NLO materials (Rahman *et al.*, 2003; Jindawong *et al.*, 2005), the title compound, (I), was synthesized and its crystal structure is reported here. Compound (I) is isomorphous with the 4-bromobenzensulfonate derivative, $C_{15}H_{16}NO_2^+\cdot C_6H_4BrO_3S^-$, (II) (Jindawong *et al.*, 2005).



(I)

The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The asymmetric unit of (I) contains a $C_{15}H_{16}NO_2^+$ cation and a $C_6H_4ClO_3S^-$ anion. The cation exists in an *E* configuration with respect to the C13=C14 double bond. The bond lengths and angles in both cation and anion are normal (Allen *et al.*,

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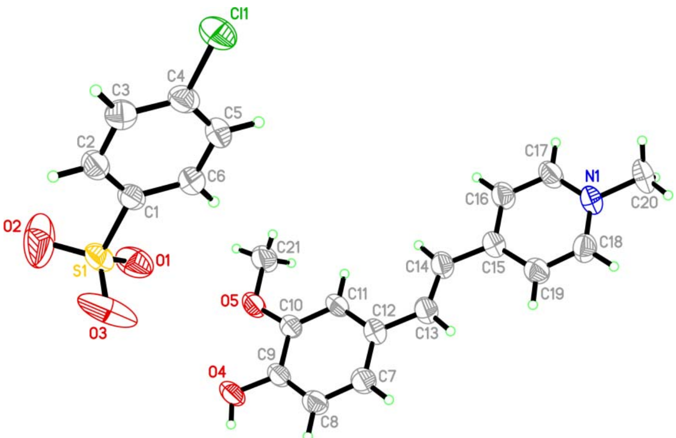

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

1987). In the cation, the dihedral angle between the styryl and pyridinium rings is 6.48 (1)°, compared with 7.1 (2)° in (II). The methoxy substituent is almost coplanar with the styryl ring, with a C21—O5—C10—C11 torsion angle of 2.9 (4)° [2.8 (4)° in (II)]. The benzene ring in the 4-chlorobenzenesulfonate anion makes a dihedral angle of 82.79 (1)° [82.00 (8)° in (II)] with the benzene ring of the cation and 76.39° [74.96 (8)° in (II)] with the pyridinium ring.

In the solid state, the cations and anions are packed in a manner similar to that in (II) (Table 2 and Fig. 2). The crystal structure is stabilized by C—H⋯π interactions involving the benzene ring (centroid *Cg*1) of the anions (Table 2).

The minor differences in the molecular and crystal structures of (I) and (II) can be related to the difference in the atomic sizes of the Cl and Br atoms.

Experimental

The title compound, (I), was synthesized following the same procedure as for compound (II) (Jindawong *et al.*, 2005). The solid that formed was filtered, washed with diethyl ether and recrystallized from methanol to give red crystals (3.52 g, 75%, m.p. 540–541 K).

Crystal data

$C_{15}H_{16}NO_2^+ \cdot C_6H_4ClO_3S^-$
$M_r = 433.89$
Triclinic, $P\overline{1}$
$a = 9.8153\ (16)$ Å
$b = 10.4218\ (17)$ Å
$c = 10.5894\ (17)$ Å
$\alpha = 110.538\ (2)°$
$\beta = 93.864\ (2)°$
$\gamma = 97.819\ (2)°$
$V = 997.2\ (3)$ Å^3
$Z = 2$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9566 reflections
$\theta = 2.1–25.0°$
$\mu = 0.33$ mm^{-1}
$T = 293\ (2)$ K
Block, red
0.50 × 0.27 × 0.19 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.899$, $T_{max} = 0.939$
9566 measured reflections
3517 independent reflections
3150 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

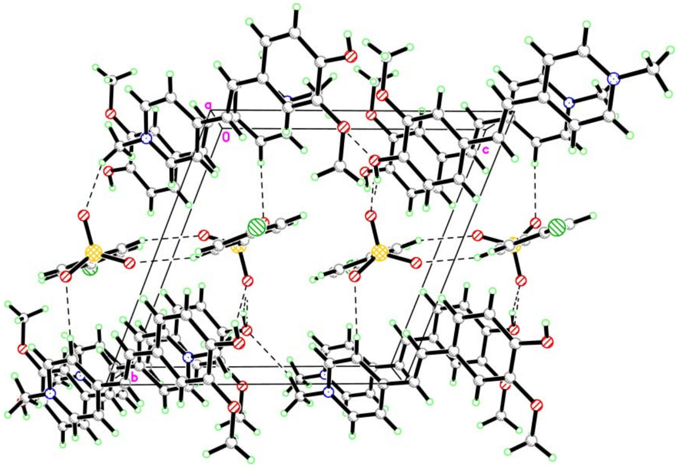

Figure 2
A crystal packing diagram of (I) viewed along the *a* axis. The C—H⋯O hydrogen bonds are shown as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.126$
$S = 1.04$
3517 reflections
265 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2 + 0.5159P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C4	1.738 (2)	O5—C10	1.361 (3)
S1—O1	1.413 (2)	O5—C21	1.424 (3)
S1—O3	1.4334 (19)	N1—C17	1.337 (3)
S1—O2	1.440 (2)	N1—C18	1.344 (3)
S1—C1	1.780 (2)	N1—C20	1.479 (3)
O4—C9	1.358 (2)	C13—C14	1.328 (3)
C21—O5—C10—C11	−2.9 (4)	C11—C12—C13—C14	−1.7 (4)
C21—O5—C10—C9	176.5 (2)	C12—C13—C14—C15	178.6 (2)
C7—C12—C13—C14	179.6 (2)	C13—C14—C15—C16	175.6 (2)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the anion ring C1–C6.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O4—H4*A*⋯O2^{i}	0.82	1.79	2.577 (4)	161
C2—H2*B*⋯O1^{ii}	0.93	2.38	3.180 (3)	144
C6—H6*A*⋯O3^{i}	0.93	2.59	2.934 (3)	103
C19—H19*A*⋯O3^{iii}	0.93	2.36	3.257 (3)	163
C20—H20*B*⋯O4^{iv}	0.96	2.43	3.367 (4)	165
C20—H20*C*⋯O2^{v}	0.96	2.55	3.420 (4)	151
C16—H16*A*⋯*Cg*1^{vi}	0.93	2.58	3.476 (2)	162
C21—H21*A*⋯*Cg*1^{vii}	0.96	2.84	3.626 (3)	140

Symmetry codes: (i) x, y, z; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y+2, -z+1$; (iv) $x-1, y, z-1$; (v) $-x, -y+3, -z+1$; (vi) $x-1, y+1, z$; (vii) $-x+1, -y+3, -z+2$.

H atoms were placed in calculated positions and treated as riding atoms, with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The U_{iso}(H) values were constrained to be 1.5U_{eq} of the carrier atom for hydroxy and methyl H atoms and 1.2U_{eq} for the remaining H atoms. A rotating-group model was used for the methyl groups.

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Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); 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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