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

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Key indicators

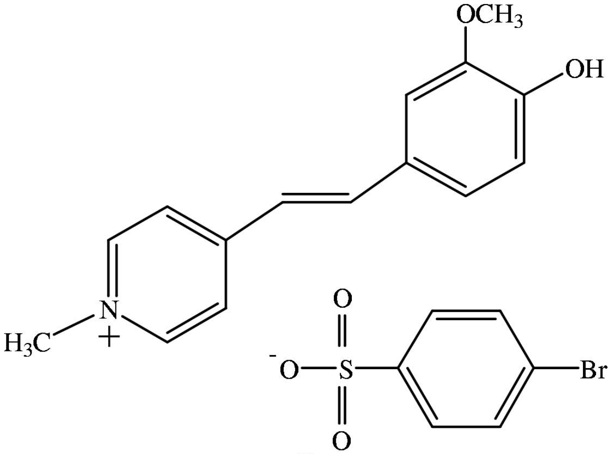
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.092
Data-to-parameter ratio = 15.6

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

In the title compound, $C_{15}H_{16}NO_2^+\cdot C_6H_4BrSO_3^-$, the cation is almost planar. The benzene ring of the anion makes dihedral angles of 82.00 (8) and 74.96 (8)° with the mean planes through the benzene ring of the cation and the pyridinium ring, respectively. In the solid state, 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

Several organic compounds such as single crystals of stilbazolium *p*-toluenesulfonate derivatives show second-order non-linear optical (NLO) properties and are useful materials for applications in optical switching, telecommunications, data storage and photonics through the frequency doubling effect (Marder *et al.*, 1991; Jones, 1997; Umezawa *et al.*, 2002). The second-order non-linear effect requires a non-centrosymmetric structure of the bulk materials. Benzenesulfonate is most frequently used to co-crystallize with cations to form compounds which are expected to have non-linear optical properties (Usman *et al.*, 2000; Nogi *et al.*, 2000; Umezawa *et al.*, 2002). Oudar & LePerson (1975) reported the effect of conjugation length by using stilbene instead of a benzene π-system.



(I)

As part of our research on non-linear optical materials (Rahman *et al.*, 2003), the title compound, (I), was synthesized using methoxystyryl-1-methylpyridinium as an NLO-chromophore and its crystal structure is reported here. The non-linearity associated with a chromophore in organic materials leads to observable bulk non-linearity, but only if the chromophores are oriented in a non-centrosymmetric environment

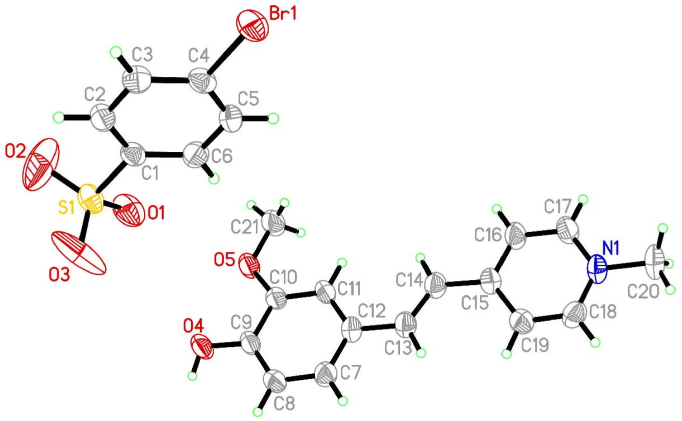


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

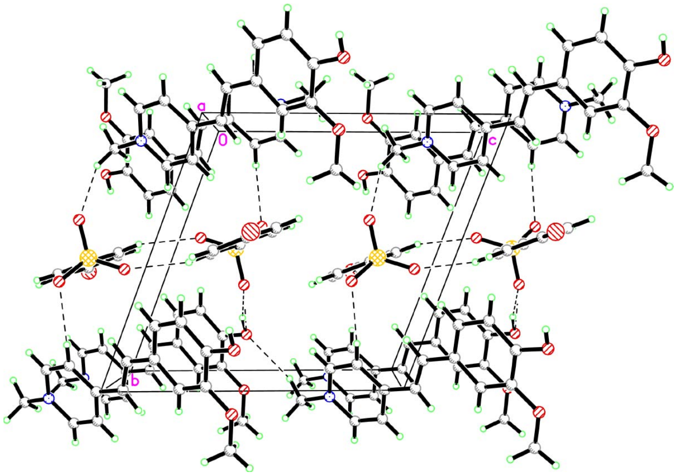


Figure 2
The packing diagram of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

(Williams, 1984). Unfortunately, the title compound crystallized in space group $P\overline{1}$ and does not exhibit second-order non-linear optical properties.

The asymmetric unit of (I) (Fig. 1) contains a $C_{15}H_{16}NO_2^+$ cation and a $C_6H_4BrSO_3^-$ anion. The cation exists in an *E* configuration with respect to the C13═C14 double bond. In the cation, the dihedral angle between the styryl and pyridinium rings is 7.1 (2)°. The methoxy substituent is almost coplanar with the styryl ring, with a C21—O5—C10—C11 torsion angle of 2.8 (4)°. The benzene ring in the 4-bromobenzenesulfonate anion makes a dihedral angle of 82.00 (8)° with with the benzene ring of the cation and 74.96 (8)° with the pyridinium ring. The bond lengths and angles (Table 1) in both cation and anion have normal values (Allen *et al.*, 1987) and are comparable to those reported for closely related structures (Rahman *et al.*, 2003; Zhang *et al.*, 1997).

In the solid state, the cations and anions are packed as alternate layers parallel to the *ac* plane (Fig. 2). In addition to the electrostatic interactions, the cationic and anionic layers are interconnected through O4—H4···O3($-x$, $1-y$, $1-z$) hydrogen bonds and a number of C—H···O interactions (Table 2) to form a three-dimensional network. The crystal structure is further stabilized by C—H···π interactions involving the benzene ring (centroid *Cg*1) of the anion (Table 2).

Experimental

Silver(I) 4-bromobenzenesulfonate (compound *A*) was synthesized by mixing a solution (1:1 molar ratio) of 4-bromobenzenesulfonyl chloride (3.01 g, 11.76 mmol) in hot methanol and sodium hydroxide (0.48 g, 11.51 mmol) in hot methanol. The resulting colourless solution containing a white solid of sodium chloride was evaporated, dissolved in water and mixed with dichloromethane. The dichloromethane part was then evaporated and the remainder was dissolved in hot methanol, followed by the addition of a solution of sodium hydroxide (0.48 g, 11.51 mmol) and silver nitrate (2.00 g, 11.73 mmol) in hot methanol. The solid nitrate in the resulting solution was then filtered off and discarded. Compound *A* was obtained after allowing the resulting filtrate to stand in air for a few days (2.77 g, 68%).

4(4′-Hydroxy-3′-methoxystyryl)-1-methylpyridinium iodide (compound *B*) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,4-dimethylpyridinium iodide (2.00 g, 8.51 mmol), vanillin (1.30 g, 8.50 mmol) and piperidine (0.85 g, 8.60 mmol). The resulting solution was refluxed for 2 h under a nitrogen atmosphere. The solid which formed was filtered, washed with diethyl ether and recrystallized from methanol, to give brown crystals of compound *B* (1.98 g, 63%, m.p. 540–541 K).

The title compound was synthesized by mixing compound *A* (0.20 g, 0.59 mmol) in hot methanol (50 ml) and a solution of compound *B* (0.22 g, 0.59 mmol) in hot methanol (40 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 red solution was evaporated to yield a red solid. The red solid was dissolved in methanol and ethanol (1:1) to give red single crystals of (I), after allowing the resulting solution to stand in ambient temperature for several days (m.p. 515–516 K).

Crystal data

$C_{15}H_{16}NO_2^+\cdot C_6H_4BrO_3S^-$
$M_r = 478.35$
Triclinic, $P\overline{1}$
$a = 9.9319$ (7) Å
$b = 10.3666$ (8) Å
$c = 10.5606$ (8) Å
$\alpha = 109.71$ (1)°
$\beta = 94.138$ (1)°
$\gamma = 98.458$ (1)°
$V = 1003.79$ (15) Å^3
$Z = 2$
$D_x = 1.583$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4970 reflections
$\theta = 2.1$–28.3°
$\mu = 2.19$ mm^{-1}
$T = 293$ (2) K
Block, pale yellow
0.47 × 0.24 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.543$, $T_{\max} = 0.638$
6754 measured reflections
4418 independent reflections
3596 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 28.3°$
$h = -12 \rightarrow 13$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.092$
$S = 1.04$
4118 reflections
264 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.892 (2)	O5—C10	1.363 (3)
S1—O2	1.420 (3)	O5—C21	1.422 (3)
S1—O1	1.429 (2)	N1—C17	1.341 (3)
S1—O3	1.438 (3)	N1—C18	1.343 (4)
S1—C1	1.774 (2)	N1—C20	1.474 (3)
O4—C9	1.354 (3)	C13—C14	1.322 (4)
C11—C12—C13—C14	1.8 (5)	C13—C14—C15—C16	−174.7 (3)
C12—C13—C14—C15	−178.9 (3)	C13—C14—C15—C19	5.5 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{i}	0.82	1.78	2.578 (4)	165
C2—H2···O2^{ii}	0.93	2.38	3.160 (4)	141
C6—H6···O1	0.93	2.57	2.919 (4)	103
C19—H19···O1^{iii}	0.93	2.38	3.269 (4)	160
C20—H20*B*···O3^{iv}	0.96	2.53	3.394 (5)	150
C20—H20*C*···O4^{v}	0.96	2.45	3.383 (4)	164
C16—H16···*Cg*1^{vi}	0.93	2.58	3.465 (3)	160
C21—H21*D*···*Cg*1^{vii}	0.96	2.84	3.627 (3)	140

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, 1+z$; (iv) $x, y-1, 1+z$; (v) $1+x, y, 1+z$; (vi) $1-x, -y, 1-z$; (vii) $x-1, y-1, z$. *Cg*1 is the benzene ring centroid.

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 $U_{\rm iso}$ values were constrained to be $1.5U_{\rm eq}$ of the carrier atom for hydroxyl and methyl H atoms and $1.2U_{\rm eq}$ for the remaining H atoms. A rotating-group model was used for the methyl groups.

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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