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2-(4-Methoxystyryl)-1-methylpyridinium 4-chlorobenzenesulfonate

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There are two crystallographically independent ion pairs in the asymmetric unit of the title compound, $C_{15}H_{16}NO^+\cdot C_6H_4ClO_3S^-$. Both cations adopt an *E* configuration with respect to the C═C bond. The dihedral angle between the pyridinium and benzene rings of the two cations are 6.0 (3) and 2.6 (2)°. In the crystal structure, independent cations and anions are individually linked into alternate layers parallel to the *ab* plane *via* weak C—H···O interactions; these layers are interconnected through weak intra- and intermolecular C—H···O interactions, forming a three-dimensional network. C—H···π interactions involving the benzene and pyridinium rings also help to stabilize the crystal structure.

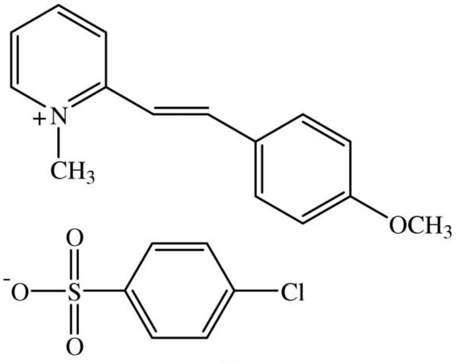
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.069
wR factor = 0.200
Data-to-parameter ratio = 13.4

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

Comment

Much interest has been focussed on organic non-linear optical (NLO) materials due to their promising applications in telecommunications, optical computing and laser technology (Chemla *et al.*, 1987). A prerequisite for materials to exhibit NLO properties is that they crystallize in a non-centrosymmetric space group (Williams, 1984). The title compound, (I), was synthesized as part of our ongoing studies of NLO materials (Jindawong *et al.*, 2005; Chantrapromma *et al.*, 2005; Chantrapromma, Ruanwas, Fun *et al.*, 2006; Chantrapromma, Jindawong *et al.*, 2006; Chantrapromma, Ruanwas, Jindawong *et al.*, 2006; Fun *et al.*, 2006). The X-ray crystal structure determination of (I) was carried out in order to acquire detailed information on the molecular packing. Crystallization of (I) in a centrosymmetric space group precludes the presence of second-order NLO properties.



(I)

The asymmetric unit of (I) contains two crystallographically independent ion pairs (*A* and *B*) (Fig. 1) in which the bond lengths and angles are the same within experimental error.

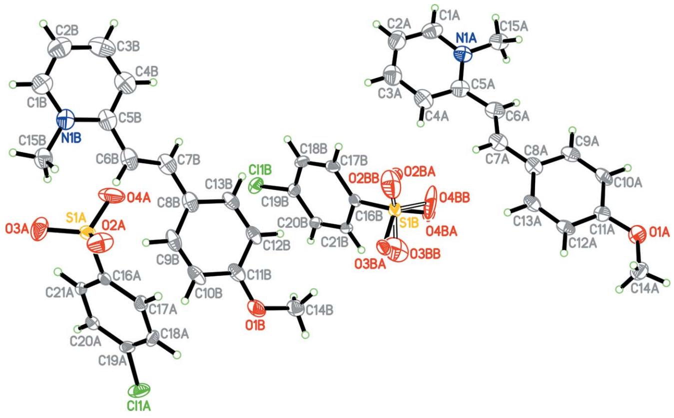


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The minor disorder component is shown with open bonds.

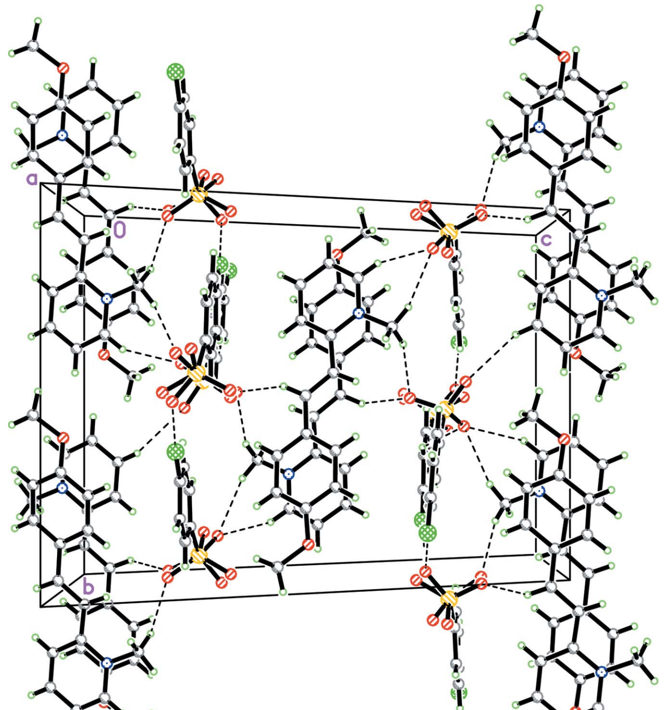


Figure 2
The packing of (I), viewed approximately down the *a* axis. Weak C—H⋯O interactions are shown as dashed lines.

Both cations adopt an *E* configuration with respect to the C6═C7 double bond. The torsion angle C5/C6/C7/C8 = 179.7 (4)° in cation *A* and 179.3 (4)° in cation *B*. The dihedral angle between the pyridinium and benzene rings in cation *A* is 6.0 (3)° and 2.6 (2)° in cation *B*. The sulfonate group in anion *B* is disordered over two sites (see *Experimental*). In each independent cation the methoxy group is twisted from the plane of the benzene ring, as indicated by the torsion angles [C14/O1/C11/C12 = −10.1 (5)° in *A* and −6.6 (5)° in *B*]. The bond distances and angles in both cations and both anions have normal values (Allen *et al.*, 1987) and are comparable with those in closely related compounds (Jindawong *et al.*, 2005; Chantrapromma *et al.*, 2005; Chantrapromma, Ruanwas, Fun & Patil, 2006; Chantrapromma, Ruanwas, Jindawong *et al.*, 2006).

In the crystal structure, independent cations and anions are individually packed in alternate layers parallel to the *ab* plane (Fig. 2). The cationic and anionic layers are interconnected through weak intra- and intermolecular C—H⋯O interactions (Table 1), forming a three-dimensional network. The crystal structure is further stabilized by C—H⋯π interactions involving the pyridinium and benzene rings (Table 1).

Experimental

Silver(I) 4-chlorobenzenesulfonate (compound *A*) was synthesized according to our previously reported procedure (Chantrapromma, Jindawong *et al.*, 2006; Chantrapromma, Ruanwas, Fun & Patil, 2006; Chantrapromma, Ruanwas, Jindawong *et al.*, 2006). 2-[(4-Methoxyphenyl)ethenyl]-1-methylpyridinium iodide (compound *B*) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylpyridinium iodide (2.00 g, 8.51 mmol), 4-methoxybenzaldehyde (1.03 ml, 8.51 mmol) and piperidine (0.84 ml, 8.51 mmol). The resulting solution was refluxed for 3 h under a nitrogen atmosphere. The resulting solid was filtered, washed with chloroform and recrystallized from methanol, giving a yellow solid of compound *B* (yield 2.00 g, 66%; m.p. 498–499 K). The title compound, (I), was synthesized by mixing solutions of compound *A* (0.20 g, 0.66 mmol) in hot methanol (50 ml) and compound *B* (0.23 g, 0.66 mmol) in hot methanol (40 ml). The mixture immediately yielded a yellow solid of silver iodide which was filtered off after stirring the mixture for 30 min. The resulting yellow solution was evaporated, yielding a yellow solid. Yellow needle-shaped single crystals of (I) were obtained by recrystallization from methanol/ethanol solution (1:1 *v*/*v*) after several days (m.p. 470–471 K).

Crystal data

$C_{15}H_{16}NO^+\cdot C_6H_4ClO_3S^-$
$M_r = 417.91$
Monoclinic, $P2_1/c$
$a = 15.2016\ (5)$ Å
$b = 13.7923\ (4)$ Å
$c = 22.0003\ (7)$ Å
$\beta = 123.274\ (2)°$
$V = 3856.5\ (2)$ Å^3
$Z = 8$
$D_x = 1.440$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 100.0\ (1)$ K
Needle, yellow
0.56 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min} = 0.836$, $T_{\max} = 0.947$
47660 measured reflections
7521 independent reflections
5951 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.200$
$S = 1.05$
7521 reflections
563 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 9.2696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.75$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1*A*—H1*A*···O2*A*$^{\rm i}$	0.93	2.34	3.203 (5)	155
C3*A*—H3*A*···O3*A*$^{\rm ii}$	0.93	2.56	3.420 (6)	154
C6*A*—H6*A*···O4*BA*$^{\rm iii}$	0.93	2.59	3.343 (12)	139
C7*B*—H7*B*···O4*A*$^{\rm ii}$	0.93	2.44	3.244 (6)	145
C15*A*—H15*B*···O2*A*$^{\rm i}$	0.96	2.47	3.368 (5)	155
C15*A*—H15*C*···O4*BA*$^{\rm iii}$	0.96	2.29	3.194 (13)	156
C15*B*—H15*E*···O4*A*	0.96	2.54	3.456 (6)	159
C17*B*—H17*B*···O2*BA*	0.93	2.48	2.850 (15)	104
C20*A*—H20*A*···O2*BA*$^{\rm iv}$	0.93	2.33	3.207 (17)	158
C20*B*—H20*B*···O2*A*$^{\rm v}$	0.93	2.53	3.282 (6)	138
C9*A*—H9*A*···*Cg*5$^{\rm iii}$	0.93	3.36	3.857 (4)	116
C9*B*—H9*B*···*Cg*4	0.93	3.15	3.706 (4)	120
C10*A*—H10*A*···*Cg*5$^{\rm iii}$	0.93	2.97	3.652 (4)	131
C10*B*—H10*B*···*Cg*1$^{\rm iv}$	0.93	3.32	3.628 (6)	102
C10*B*—H10*B*···*Cg*4	0.93	3.14	3.695 (4)	121
C12*A*—H12*A*···*Cg*4$^{\rm vi}$	0.93	2.68	3.475 (4)	144
C12*B*—H12*B*···*Cg*5	0.93	2.69	3.470 (4)	142
C15*A*—H15*A*···*Cg*3$^{\rm vii}$	0.96	2.67	3.449 (5)	138
C15*B*—H15*F*···*Cg*2$^{\rm iv}$	0.96	2.78	3.532 (5)	136

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+2, -z$; (iv) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (vi) $-x+1, -y+2, -z+1$; (vii) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$. *Cg*1 is the centroid of pyridinium ring C1*A*–C5*A*/N1*A*; *Cg*2, *Cg*3, *Cg*4, *Cg*5 are the centroids of benzene rings C8*A*–C13*A*, C8*B*–C13*B*, C16*A*–C21*A* and C16*B*–C21*B*, respectively.

The O atoms of the sulfonate group in anion *B* are disordered over two sites. The site occupancies for the major and minor components were initially refined but subsequently fixed at 0.65 and 0.35. The corresponding O atoms in cation *A* may be disordered to a lesser extent, but no disorder model could be refined. The highest electron density peak is located 0.84 Å from atom Cl1*B*. All H atoms were placed in calculated positions, with C—H distances of 0.93 Å for aromatic and 0.96 Å for CH and CH_3 H atoms. $U_{\rm iso}$(H) values were refined independently, except for atoms H1*A*–H9*A* and H1*B*–H9*B*, for which $U_{\rm iso}$(H) was set to $1.2U_{\rm eq}$(C). 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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