2-[(E)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate

Boonwasana Jindawong,[a]
Suchada Chantrapromma,[a]*
Hoong-Kun Fun[b]* **and**
Chatchanok Karalai[a]

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Correspondence e-mail: suchada.c@psu.ac.th, hkfun@usm.my

In the title compound, $C_{19}H_{18}NO_2^+ \cdot C_7H_7SO_3^-$, the cation is almost planar and the benzene ring of the anion makes dihedral angles of 59.17 (9) and 60.59 (10)° with the mean planes through the quinolinium and benzene ring of the cation, respectively. The cations and anions are packed as alternate layers along the b axis. These layers are interconnected through O—H···O and C—H···O interactions to form a three-dimensional network. The structure is stabilized by these interactions and C—H···π interactions.

Comment

The search for new organic materials that exhibit large molecular second-order optical nonlinearities is of considerable interest because of their wide range of potential applications, such as in the frequency doubling of lasers and optical data storage applications (Chemla & Zyss, 1987; Marder et al., 1991; Usman et al., 2000; Umezawa et al., 2002; Feng et al., 2005; Ye et al., 2005). Most organic crystals are colorless in the visible region, which are better for usage as non-linear optical (NLO) materials when compared with most inorganic crystals which are generally colored (Chemla & Zyss, 1987; Chia et al., 1995; Zhengdong et al., 1997). An organic crystal with delocalized π-electrons usually displays a large NLO response (Prasad & William, 1991). Most of these crystals are composed of aromatic molecules that are substituted with π-electron donors and acceptors, which exhibit intramolecular charge transfer.

(I)
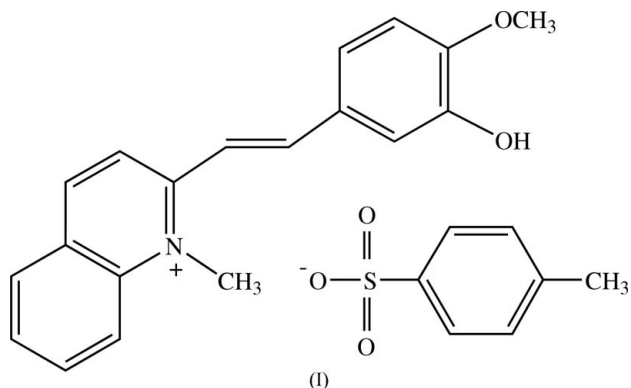
One generally successful and popular approach to obtaining NLO materials is to find a substance that crystallizes in a non-centrosymmetric space group. Oudar & LePerson (1975) have also reported the effect of conjugation length, using stilbene instead of a benzene π-system. In our continuing research on NLO materials (Rahman et al., 2003; Jindawong et al., 2005; Chantrapromma et al., 2005), we expected that the two rings of quinoline, with the ethylenic C=C lying in the same molecular
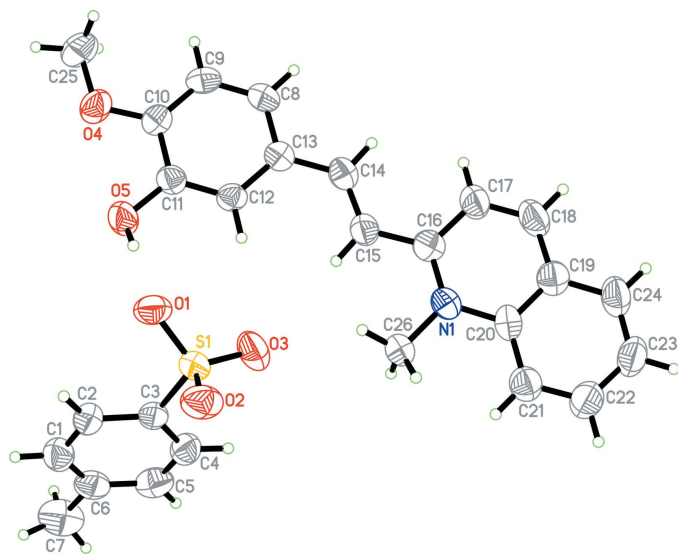
Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

plane, would change the molecular packing from centrosymmetric, as in our previous report (Rahman *et al.*, 2003), to non-centrosymmetric. For this reason, the title compound, (I), was designed and synthesized. The X-ray study of (I) was carried out in order to obtain detailed information on its crystal structure.

Compound (I) is found to crystallize in the centrosymmetric space group $P2_1/n$ and, therefore, has no second-order nonlinear optical properties. 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) consists of a $C_{19}H_{18}NO_2^+$ cation and a $C_7H_7SO_3^-$ anion. The quinolinium ring system (C16–C24/N1) is essentially planar, with a maximum deviation of 0.029 (2) Å for atom N1. The H atoms attached to C14 and C15 are *trans* to each other; thus the cation exists in an *E* configuration [the C13—C14—C15—C16 torsion angle is −178.1 (2)°]. The bond distances and angles (Table 1) in both the cation and the anion have normal values (Allen *et al.*, 1987) and are comparable to those in a related structure (Rahman *et al.*, 2003). The cation is almost planar, the dihedral angle between the benzene and quinolinium rings being 2.59 (9)°. The methoxy substituent deviates slightly from the plane of the benzene ring, with torsion angles of 7.5 (3)° for C25—O4—C10—C9 and 177.0 (2)° for C8—C9—C10—O4. The benzene ring in the 4-methylbenzenesulfonate anion makes dihedral angles of 60.59 (10)° with the benzene ring of the cation and 59.17 (9)° with the quinolinium ring system.

In the crystal structure, atoms O2 and O3 of the anion are involved in weak C—H⋯O interactions, while atom O1 is involved in O—H⋯O hydrogen bonds (Table 2). The molecules form alternate layers of cations and anions along the *b* axis. These layers are interconnected through O—H⋯O hydrogen bonds and weak C—H⋯O interactions to form a three-dimensional network (Fig. 2 and Table 2). The crystal
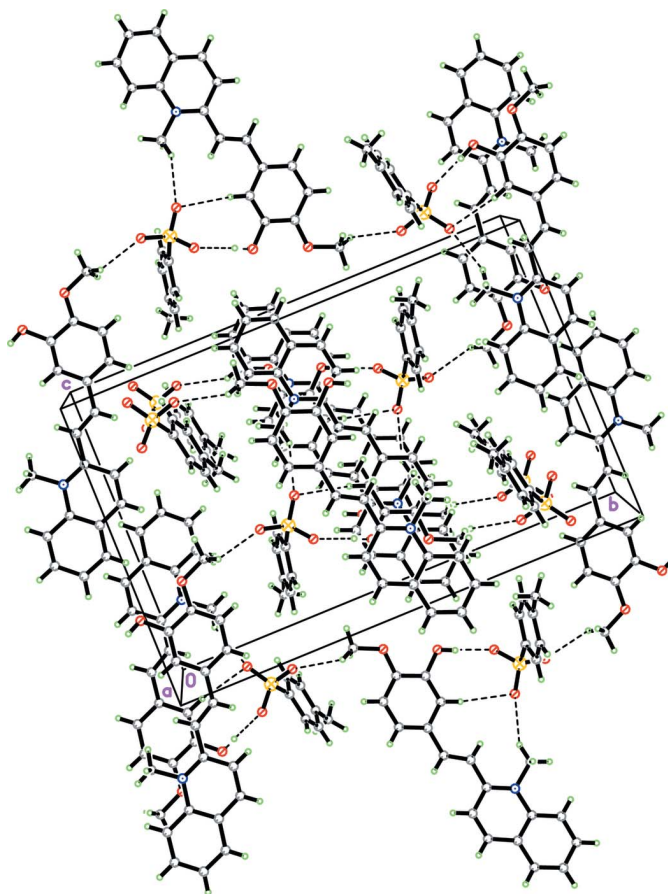

Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

structure is further stabilized by C—H⋯π interactions involving the centroid, *Cg*1, of the benzene ring (C8–C13) of the cation (Table 2).

Experimental

2-[(4-Methoxy-3-hydroxyphenyl)ethenyl]-*N*-methylquinolinium iodide (compound *A*) was synthesized from a mixture (1:1:1 molar ratio) of *N*-2-dimethylquinolinium iodide (1.98 g, 6.94 mmol), isovanillin (1.06 g, 6.94 mmol) and piperidine (0.60 g, 7.09 mmol) in methanol under reflux for 2 h in a nitrogen atmosphere. The solid that formed was filtered, washed with diethyl ether and recrystallized from methanol to give red–brown crystals of compound *A* (2.00 g, 68%, m.p. 491–493 K). The title compound was synthesized by mixing compound *A* (0.30 g, 0.72 mmol) in hot methanol (50 ml) and a solution of silver(I) *p*-toluenesulfonate (compound *B*) (0.20 g, 0.72 mmol) in hot methanol (30 ml), in a manner similar to that previously reported (Rahman *et al.*, 2003). The mixing immediately yielded yellow solid silver iodide. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated to yield an orange solid. Colorless single crystals of (I) suitable for X-ray data collection were obtained by recrystallization from methanol and dichloromethane (1:1) after several days at ambient temperature (m.p. 526–528 K).

Crystal data

$C_{19}H_{18}NO_2{}^+ \cdot C_7H_7O_3S^-$	$D_x = 1.386$ Mg m^{-3}
$M_r = 463.54$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3913
$a = 7.3382\ (3)$ Å	reflections
$b = 21.8714\ (7)$ Å	$\theta = 1.7$–$25.0°$
$c = 14.0755\ (4)$ Å	$\mu = 0.19$ mm^{-1}
$\beta = 100.464\ (1)°$	$T = 273\ (2)$ K
$V = 2221.50\ (13)$ Å^3	Needle, colorless
$Z = 4$	$0.50 \times 0.24 \times 0.10$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	3913 independent reflections
	3138 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(SADABS; Bruker, 2005)	$h = -8 \rightarrow 8$
$T_{min} = 0.948$, $T_{max} = 0.982$	$k = -26 \rightarrow 26$
17716 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 1.1272P]$
$wR(F^2) = 0.107$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3913 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
301 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.4402 (17)	O5—C11	1.362 (2)
S1—O2	1.4453 (17)	N1—C16	1.339 (3)
S1—O1	1.4600 (15)	N1—C20	1.412 (3)
S1—C3	1.780 (2)	N1—C26	1.461 (3)
O4—C10	1.363 (2)	C14—C15	1.324 (3)
C12—C13—C14	122.02 (18)	N1—C16—C15	119.73 (19)
C25—O4—C10—C9	7.5 (3)	O4—C10—C11—C12	−178.86 (18)
C25—O4—C10—C11	−174.14 (19)	C13—C14—C15—C16	−178.1 (2)
C8—C9—C10—O4	177.0 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5A$\cdots$O1^i	0.82	1.83	2.653 (2)	177
C5—H5B$\cdots$O2^{ii}	0.93	2.59	3.504 (3)	167
C12—H12A$\cdots$O3^i	0.93	2.57	3.490 (3)	171
C23—H23A$\cdots$O5^{iii}	0.93	2.58	3.219 (3)	126
C25—H25D$\cdots$O2^{iv}	0.96	2.47	3.269 (3)	141
C26—H26A$\cdots$O3^i	0.96	2.37	3.163 (3)	140
C26—H26C$\cdots$Cg1^v	0.96	2.58	3.458 (2)	153

Symmetry codes: (i) x, y, z; (ii) $x - 1, y, z$; (iii) $x, y, z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x, -y, -z + 2$.

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_{iso}(H) values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms, and $1.2U_{eq}$(C) for the remaining H atoms.

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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