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Key indicators

Single-crystal X-ray study
T = 297 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.043
wR factor = 0.110
Data-to-parameter ratio = 21.7

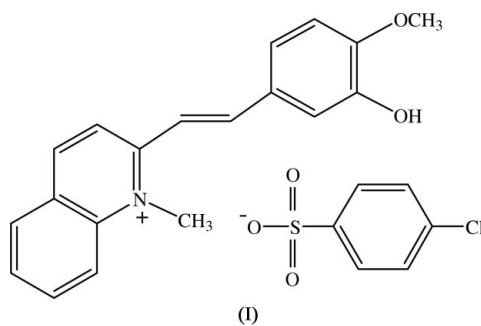
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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

The title compound, $\text{C}_{19}\text{H}_{18}\text{NO}_2^+ \cdot \text{C}_6\text{H}_4\text{ClO}_3\text{S}^-$, exhibits non-linear optical properties. The cation is almost planar and the benzene ring of the anion makes dihedral angles of 48.97 (6) and 51.63 (7)° with the mean planes through the quinolinium system and the benzene ring of the cation, respectively. The anions are linked by $\text{C}-\text{H} \cdots \text{O}$ interactions, forming a chain along the *a* axis, while the cations are stacked along the *a* axis. The anionic chains and the cationic stacks are alternately arranged.

Comment

Several organic compounds show non-linear optical (NLO) properties and are useful materials for applications in optical switching, optical communications, data storage and laser technology (Chemla & Zyss, 1987; Crasta *et al.*, 2004; Feng *et al.*, 2005; Hong *et al.*, 2005; Williams, 1984). The second-order non-linear effect requires a non-centrosymmetric structure of the bulk materials. The design of organic materials for non-linear effects is based on molecular units containing highly delocalized π -electrons; they should have electron-donor and electron-acceptor groups on opposite ends of the molecules at appropriate positions on the ring to enhance conjugation effects. For a second-order non-linear effect, ionic organic crystals are of interest because they exhibit large β values at the molecular level, possess high values for hardness and have high melting points. Their crystal structures can also be controlled by changing the counter-ions (Nogi *et al.*, 2000). Benzenesulfonate is most frequently used to co-crystallize with cations to form compounds which are expected to have second-order non-linear optical properties. Our continuing research on NLO materials (Rahman *et al.*, 2003; Jindawong, Chantrapromma, Fun, Yu & Karalai, 2005; Jindawong, Chantrapromma, Fun, & Karalai, 2005; Chantrapromma *et al.*, 2005) has led us to synthesize the title compound, (I).



The X-ray study of (I) was carried out in order to obtain detailed information on its crystal structure. This paper reports the synthesis and structure of (I) which is a new ionic

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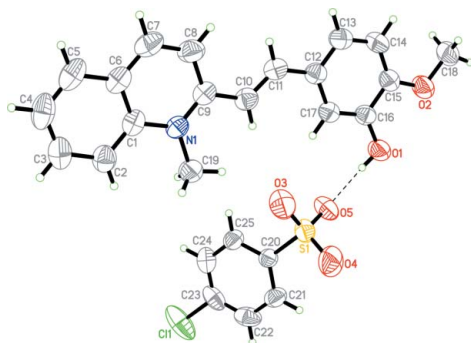


Figure 1

The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering. The dashed line indicates an O—H...O hydrogen bond.

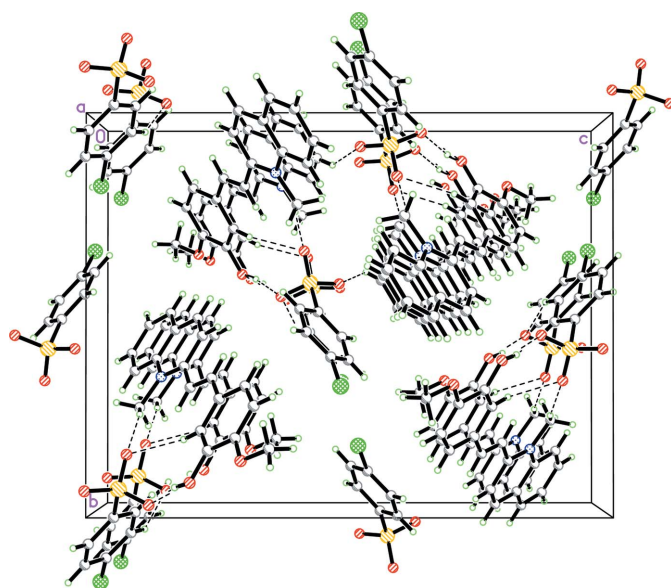


Figure 2

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

organic NLO compound which crystallized in the non-centrosymmetric space group $P2_12_12_1$. The second harmonic generation (SHG) measurement of (I) was made in accordance with the classical powder method developed by Kurtz and Perry (1968). It was found that the SHG effect of the crystal of (I) is about 0.85 times that of urea.

The asymmetric unit of (I) consists of a $C_{19}H_{18}NO_2^+$ cation and a $C_6H_4ClO_3S^-$ anion (Fig. 1). 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 related structures (Rahman *et al.*, 2003; Jindawong, Chantrapromma, Fun, Yu & Karalai, 2005; Jindawong, Chantrapromma, Fun, & Karalai, 2005; Chantrapromma *et al.*, 2005). The cation is almost planar, the dihedral angle between the benzene and quinolinium rings being $2.8(1)^\circ$. The H atoms attached to C10 and C11 are *trans* to each other; thus the cation exists in an *E* configuration [the C9—C10—C11—C12 torsion angle is $179.61(18)^\circ$]. The benzene ring in the 4-chlorobenzenesulfonate anion makes dihedral angles of

$48.97(6)^\circ$ and $51.63(7)^\circ$, respectively, with the quinolinium system and the benzene ring of the cation.

In the crystal structure, atoms O3 and O4 of the anion are involved in C—H...O weak interactions, while atom O5 is involved in both weak C—H...O interactions and O—H...O hydrogen bonds (Table 2). The anions are linked by C—H...O interactions, forming a chain along the *a* axis. The cations are stacked along the *a* axis in such a way that the centroid-centroid distance between the N1/C1/C6—C9 ring at (*x*, *y*, *z*) and the C12—C17 ring at ($1 + x$, *y*, *z) is $3.620(1)\text{Å}$, indicating π — π interactions. The anionic chains and the cationic stacks are alternately arranged (Fig. 2).*

Experimental

2-(4-Methoxy-3-hydroxystyryl)-1-methylquinolinium iodide (compound A) was prepared from a mixture (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (3.0 g, 10.05 mmol), isovanillin (1.6 g, 10.05 mmol) and piperidine (1.00 ml, 10.00 mmol) in methanol (50 ml) under reflux for 2 h under a nitrogen atmosphere. The resulting solid was filtered off, washed with diethyl ether and crystallized from methanol to give red-brown crystals of compound A (2.80 g, 64% yield). Silver(I) 4-chlorobenzenesulfonate (compound B) was synthesized by mixing a solution (1:2:1 molar ratio) of 4-chlorobenzenesulfonyl chloride (5.0 g, 19.57 mmol), sodium hydroxide (1.6 g, 39.14 mmol) and silver nitrate (3.3 g, 19.57 mmol) in hot methanol (30 ml). The title compound was synthesized by mixing a solution (1:1 molar ratio) of compound A (0.28 g, 0.67 mmol) and compound B (0.20 g, 0.67 mmol) in hot methanol (50 ml). The mixing immediately yielded yellow solid silver iodide. The precipitate of silver iodide was removed and the resulting solution was evaporated to yield a red-orange solid of the title compound. Orange single crystals suitable for X-ray data collection were obtained by recrystallization from methanol after several days at room temperature (m.p. 535–536 K).

Crystal data

$C_{19}H_{18}NO_2^+ \cdot C_6H_4ClO_3S^-$
 $M_r = 483.96$
 Orthorhombic, $P2_12_12_1$
 $a = 6.9503(1)\text{Å}$
 $b = 15.6916(2)\text{Å}$
 $c = 20.4365(3)\text{Å}$
 $V = 2228.83(5)\text{Å}^3$

$Z = 4$
 $D_x = 1.442\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.30\text{ mm}^{-1}$
 $T = 297(2)\text{ K}$
 Block, orange
 $0.51 \times 0.31 \times 0.31\text{ mm}$

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.860$, $T_{\max} = 0.910$

28163 measured reflections
 6533 independent reflections
 4956 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\max} = 30.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.110$
 $S = 1.04$
 6533 reflections
 301 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.2404P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30\text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -0.36\text{ e Å}^{-3}$
 Absolute structure: Flack (1983),
 2836 Friedel pairs
 Flack parameter: 0.05 (6)

Table 1

Selected geometric parameters (Å, °).

S1—O3	1.4293 (17)	S1—C20	1.7708 (19)
S1—O4	1.4385 (18)	N1—C9	1.343 (3)
S1—O5	1.4631 (16)	N1—C1	1.404 (2)
C15—O2—C18	117.12 (18)	C10—C11—C12	127.12 (19)
C9—C10—C11—C12	179.61 (18)	C18—O2—C15—C16	−179.91 (18)
C18—O2—C15—C14	−0.2 (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—H1...O5	0.82	1.81	2.625 (2)	176
C3—H3...O4 ⁱ	0.93	2.40	3.183 (3)	142
C17—H17...O3	0.93	2.51	3.413 (3)	164
C19—H19A...O3	0.96	2.32	3.194 (3)	151
C21—H21...O4	0.93	2.57	2.916 (3)	103
C24—H24...O5 ⁱⁱ	0.93	2.49	3.322 (3)	149

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

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 hydroxy and methyl H atoms, and $1.2U_{\text{eq}}(\text{C})$ 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: *SAINTE* (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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References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bruker (2005). *APEX2* (Version 1.27), *SAINTE* (Version 7.12a) and *SADABS* (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Anjum, S. & Karalai, C. (2005). *Acta Cryst. E61*, o2096–o2098.
- Chemla, D. S. & Zyss, J. (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*. New York: Academic Press.
- Crasta, V., Ravindrachary, V., Bhajantri, R. F. & Gonsalves, R. (2004). *J. Cryst. Growth*, **267**, 129–133.
- Feng, X. J., Chantrapromma, S., Fun, H.-K. & Tian, Y.-P. (2005). *Acta Cryst. E61*, m1077–m1079.
- Flack, H. D. (1983). *Acta Cryst. A39*, 876–881.
- Hong, H., Park, J. W., Lee, K. S. & Yoon, C. S. (2005). *J. Cryst. Growth*, **277**, 509–517.
- Jindawong, B., Chantrapromma, S., Fun, H.-K. & Karalai, C. (2005). *Acta Cryst. E61*, o3237–o3239.
- Jindawong, B., Chantrapromma, S., Fun, H.-K., Yu, X.-L. & Karalai, C. (2005). *Acta Cryst. E61*, o1340–o1342.
- Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
- Nogi, K., Nogi, K., Usman, A., Tsuji, K., Duan, X. M., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2000). *Nonlinear Optics*, **24**, 35–40.
- Rahman, A. A., Razak, I. A., Fun, H.-K., Saene, P., Jindawong, B., Chantrapromma, S. & Karalai, C. (2003). *Acta Cryst. E59*, o1798–o1800.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Williams, D. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 690–703.