

Azhar A. Rahman,^a
Ibrahim Abdul Razak,^a
Hoong-Kun Fun,^{a*}
Pornchai Saene,^b
Boonwasana Jindawong,^b
Suchada Chantrapromma^b and
Chatchanok Karalai^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bDepartment of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.065
wR factor = 0.155
Data-to-parameter ratio = 13.1

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

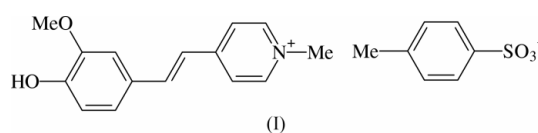
4-[(4-Hydroxy-3-methoxyphenyl)ethenyl]-N-methylpyridinium *p*-toluenesulfonate

In the title compound, $\text{C}_{15}\text{H}_{16}\text{NO}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$, the cation is almost planar and makes a dihedral angle of $83.1(1)^\circ$ with the benzene ring of the anion. In the crystal structure, alternate layers of anions and cations are interconnected by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi$ interactions.

Received 3 October 2003
Accepted 15 October 2003
Online 23 October 2003

Comment

A number of organic compounds have shown non-linear optical properties (Marder *et al.*, 1991). Several of them, such as single crystals of stilbazolium *p*-toluenesulfonate derivatives, are useful materials for applications in optical switching, telecommunications, data storage and photonics through the frequency doubling effect (Marder *et al.*, 1991; Jones, 1997). This second-order non-linear effect requires a non-centrosymmetric structure of the bulk materials. However, a large number of organic compounds are unusable for such applications because they tend to crystallize in centrosymmetric arrangements. Benzenesulfonate is most frequently used to cocrystallize with cations to form compounds which are expected to have non-linear optical properties. Our interest in searching for non-linear optical compounds had led us to synthesize the title compound, (I); its structure is reported here. Unfortunately (I) crystallized in space group $P\bar{1}$ and does not exhibit non-linear optical properties.



In the title compound (Fig. 1), the cation is nearly planar, the dihedral angle between the benzene and pyridinium rings

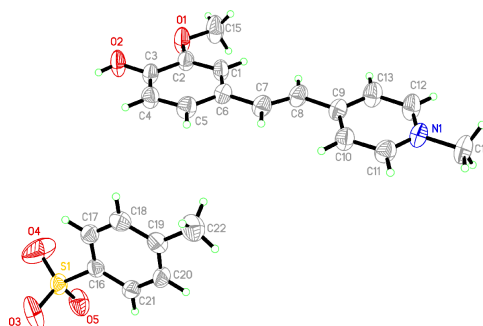


Figure 1

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

being 6.2 (2)°. The benzene ring in the anion makes a dihedral angle of 83.1 (1)° with the mean plane of the cation. The bond lengths and angles (Table 1) in both the cation and anion are comparable to those reported, for a closely related structure, by Zhang *et al.* (1997).

In the solid state, the cations are interlinked through C14—H14C··O2(1 + x, y, 1 + z) interactions to form chains. Adjacent chains are arranged in a parallel fashion to form cationic layers parallel to the *ac* plane. Inversion-related anions are linked together by C17—H17··O4(−x, 1 − y, 1 − z) interactions to form dimers. In the crystal structure, the molecules form alternate layers of cations and anions stacked along the *b* axis. In addition to the electrostatic interactions, the cationic and anionic layers are interconnected through O2—H1O··O3(−x, 1 − y, 1 − z) hydrogen bonds and a number of C—H··O interactions (Table 2). The crystal structure is further stabilized by C—H··π interactions involving the benzene ring of the anion (Table 2).

Experimental

Silver *p*-toluenesulfonate (compound *A*) was synthesized from a solution (1:1:1 molar ratio) of *p*-toluenesulfonic acid (2.01 g, 10.57 mmol), sodium hydroxide (0.43 g, 10.75 mmol) and silver nitrate (1.79 g, 10.54 mmol) in hot methanol (Okada *et al.*, 1990). The mixture was stirred for *ca* 5 min and the white compound *A* was precipitated during stirring (2.0 g, 67%). 4-[4-Hydroxy-3-methoxyphenyl]ethenyl]-*N*-methylpyridinium iodide (compound *B*) was synthesized from a mixture (1:1:1 molar ratio) of *N*-4-dimethylpyridinium iodide (2.00 g, 8.51 mmol), vanillin (1.30 g, 8.50 mmol) and piperidine (0.85 g, 8.60 mmol) in methanol under reflux for 2 h under a nitrogen atmosphere. The solid which formed was filtered off, washed with 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 *B* (0.26 g, 0.72 mmol) in hot methanol (20 ml) and a solution of compound *A* (0.21 g, 0.75 mmol) in hot methanol (40 ml). The mixture turned yellow and cloudy immediately. After stirring for 0.5 h, the precipitate of silver iodide was filtered off and the filtrate was evaporated to give a red gum. The red gum was dissolved in ethanol to give red single crystals of (**1**) after allowing the resulting solution to stand in air for a few days (m.p. 468–469 K).

Crystal data

C ₁₅ H ₁₆ NO ₂ ⁺ ·C ₇ H ₇ O ₃ S [−]	<i>Z</i> = 2
<i>M_r</i> = 413.47	<i>D_x</i> = 1.376 Mg m ^{−3}
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 9.7154 (16) Å	Cell parameters from 4331 reflections
<i>b</i> = 10.4598 (17) Å	<i>θ</i> = 2.1–27.7°
<i>c</i> = 10.6997 (18) Å	<i>μ</i> = 0.20 mm ^{−1}
<i>α</i> = 110.436 (4)°	<i>T</i> = 293 (2) K
<i>β</i> = 94.184 (4)°	Block, red
<i>γ</i> = 98.581 (3)°	0.38 × 0.20 × 0.18 mm
<i>V</i> = 998.3 (3) Å ³	

Data collection

Siemens SMART CCD area-detector diffractometer	3518 independent reflections
<i>ω</i> scans	3251 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	<i>R</i> _{int} = 0.023
<i>T</i> _{min} = 0.896, <i>T</i> _{max} = 0.966	<i>θ</i> _{max} = 25.0°
10593 measured reflections	<i>h</i> = −11 → 11
	<i>k</i> = −12 → 12
	<i>l</i> = −12 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.065
wR(*F*²) = 0.155
S = 1.11
 3518 reflections
 269 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.884P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.63 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

S1—O4	1.410 (3)	N1—C12	1.336 (4)
S1—O5	1.422 (2)	N1—C11	1.336 (4)
S1—O3	1.452 (3)	N1—C14	1.474 (4)
S1—C16	1.773 (3)	C6—C7	1.457 (4)
O1—C2	1.357 (3)	C7—C8	1.324 (4)
O1—C15	1.425 (4)	C8—C9	1.456 (4)
O2—C3	1.349 (3)		
O4—S1—O5	113.7 (2)	O4—S1—C16	107.18 (15)
O4—S1—O3	114.4 (2)	O5—S1—C16	106.58 (13)
O5—S1—O3	109.93 (18)	O3—S1—C16	104.29 (14)
C1—C6—C7—C8	1.2 (5)	C7—C8—C9—C10	3.7 (5)
C6—C7—C8—C9	−177.7 (3)		

Table 2

Hydrogen-bonding 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>
O2—H1O···O3 ⁱ	0.81 (4)	1.79 (4)	2.567 (4)	160 (4)
C10—H10···O5 ⁱⁱ	0.93	2.35	3.266 (5)	170
C14—H14B···O3 ⁱⁱⁱ	0.96	2.60	3.501 (5)	157
C14—H14C···O2 ^{iv}	0.96	2.43	3.378 (5)	167
C17—H17···O4 ⁱ	0.93	2.45	3.186 (5)	136
C13—H13···Cg1 ^v	0.93	2.59	3.479 (3)	161
C15—H15A···Cg1 ^{vi}	0.96	2.83	3.616 (4)	140

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $1+x, y-1, z$; (iv) $1+x, y, 1+z$; (v) $1-x, -y, 1-z$; (vi) $x, y-1, z-1$. Cg1 denotes the centroid of benzene ring C16–C21.

The C-bound H atoms were positioned geometrically and were treated as riding on their parent atoms, with C—H distances of 0.93 (aromatic) and 0.96 Å (methyl); *U*_{iso}(H) = 1.5*U*_{eq}(C) for the methyl H atoms and 1.2*U*_{eq}(C) for other H atoms. A rotating group model was used for the methyl groups. The hydroxyl H atom was located in a difference map and its *x*, *y*, *z* and *U*_{eq} parameters were refined freely [the O—H distance is 0.81 (4) Å]. Owing to the large fraction of weak data at higher angles, the 2θ maximum was limited to 50°.

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, 1990).

This work received partial financial support from Prince of Songkla University and the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry, Royal Thai Government. PS and BJ thank the Natural Products from Mangrove Plants and Synthetic Materials Research Unit, PSU. The authors thank the

Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 304/PFIZIK/670011.

References

- Jones, W. (1997). *Organic Molecular Solids: Properties and Application*. New York: CRC Press.
- Marder, S. R., Stucky, G. D. & Sohn, J. E. (1991). *Materials for Nonlinear Optics: Chemical Perspectives*. Washington, DC: Am. Chem. Soc. Symposium Series No. 455.
- Okada, S., Masaki, A., Matsuda, H., Nakanishi, H., Kato, M., Muramatsu, R. & Otsuka, M. (1990). *Jpn. J. Appl. Phys.* **29**, 1112–1115.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Zhang, D. C., Zhang, T. Z., Zhang, Y. Q., Fei, Z. H. & Yu, K. B. (1997). *Acta Cryst.* **C53**, 364–365.