

Suchada Chantrapromma,^{a*}
Pumsak Ruanwas,^a Hoong-Kun
Fun^{b*} and P. S. Patil^c^aDepartment of Chemistry, Faculty of Science,
Prince of Songkla University, Hat-Yai, Songkhla
90112, Thailand, ^bX-ray Crystallography Unit,
School of Physics, Universiti Sains Malaysia,
11800 USM, Penang, Malaysia, and
^cDepartment of Studies in Physics, Mangalore
University, Mangalagangothri, Mangalore 574
199, IndiaCorrespondence e-mail: suchada.c@psu.ac.th,
hkfun@usm.my

Key indicators

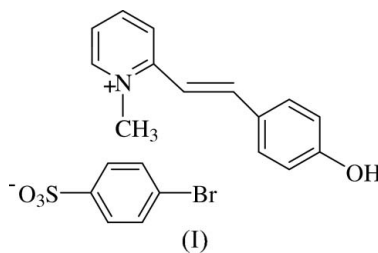
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.024
 wR factor = 0.058
Data-to-parameter ratio = 21.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-(4-Hydroxystyryl)-1-methylpyridinium
4-bromobenzenesulfonate

The title compound, $\text{C}_{14}\text{H}_{14}\text{NO}^+ \cdot \text{C}_6\text{H}_4\text{BrSO}_3^-$, (I), crystallizes in a non-centrosymmetric space group and exhibits non-linear optical properties. The second-harmonic generation (SHG) effect of (I) is about 0.14 times that of urea. The cation is almost planar and exists in an *E* configuration. The pyridinium and benzene rings of the cation make a dihedral angle of $4.52(8)^\circ$. The dihedral angles between the benzene ring of the anion and the mean planes through the pyridinium and benzene rings of the cation are $67.06(8)$ and $71.56(8)^\circ$, respectively. In the crystal structure, the cations and anions are linked by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds and weak $\text{C}-\text{H} \cdots \text{O}$ interactions into a three-dimensional network. $\text{C}-\text{H} \cdots \pi$ interactions are also observed in the crystal structure.

Received 29 October 2006
Accepted 2 November 2006

Comment

A variety of organic non-linear optical (NLO) materials, such as aromatic compounds with non-localized π -electron systems with a large dipole moment, have been synthesized and reported (Crasta *et al.*, 2004; Feng *et al.*, 2005; Hong *et al.*, 2005; Ravindrachary *et al.*, 2005; Umezawa *et al.*, 2002; Usman *et al.*, 2000). The most important criterion for these NLO materials to exhibit second-order NLO properties is for the molecules to be oriented into a non-centrosymmetric environment (Williams, 1984). Our continuing research on NLO materials (Rahman *et al.*, 2003; Jindawong *et al.*, 2005; Chantrapromma *et al.*, 2005; 2006; Fun *et al.*, 2006) has led us to synthesize the title compound, (I), and its structure determination was carried out in order to obtain detailed information on the three-dimensional structure and crystal packing, which are related to the NLO properties.



Compound (I) crystallizes in the non-centrosymmetric monoclinic space group $P2_1$. The second-harmonic generation (SHG) of (I) was measured by the classical powder method developed by Kurtz & Perry (1968) and was found to be about 0.14 times that of urea.

The asymmetric unit of (I) contains a $\text{C}_{14}\text{H}_{14}\text{NO}^+$ cation and a $\text{C}_6\text{H}_4\text{BrSO}_3^-$ anion (Fig. 1). Bond lengths and angles in both cation and anion are in normal ranges (Allen *et al.*, 1987) and

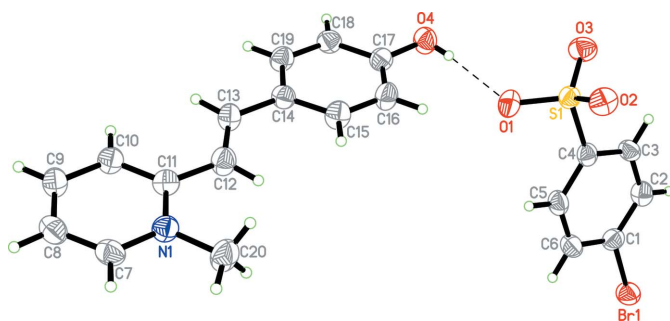


Figure 1

The asymmetric unit of (I), showing 80% probability displacement ellipsoids and the atom-numbering scheme. The dashed line indicates a hydrogen bond.

are comparable with those observed in a closely related structure (Chantrapromma *et al.*, 2006). The cation is almost planar, as indicated by the dihedral angle between the pyridinium (N1/C7–C11) and benzene (C14–C19) rings of $4.52(8)^\circ$ [$3.46(8)^\circ$ in Chantrapromma *et al.*, 2006], and exists in an *E* configuration with respect to the C12=C13 double bond [$1.345(2) \text{ \AA}$, *cf.* $1.323(3) \text{ \AA}$ in Chantrapromma *et al.*, 2006]. The C11–C12–C13–C14 torsion angle is $179.58(17)^\circ$. The methyl substituent is coplanar with the pyridinium ring, as evidenced by the C20–N1–C7–C8 torsion angle of $179.22(17)^\circ$. The benzene ring (C1–C6) of the anion makes a dihedral angle of $67.06(8)^\circ$ with the pyridinium ring and a dihedral angle of $71.56(8)^\circ$ with the benzene ring of the cation.

In the solid state, the cations and anions of (I) are individually arranged into chains along the *c* axis. These cationic and anionic chains are individually stacked down the *a* axis into cationic and anionic sheets, respectively. These cationic and anionic sheets are arranged alternately along the *b* axis, and are interconnected through O–H...O hydrogen bonds and C–H...O interactions to form a three-dimensional molecular network (Fig. 2 and Table 2). The crystal structure is stabilized by these interactions as well as by the C–H... π interactions involving the C1–C6 benzene ring of the anion (centroid Cg1) (Table 2).

Experimental

2-(4-Hydroxystyryl)-1-methylpyridinium iodide (compound *A*) was synthesized according to our previously reported method (Chantrapromma *et al.*, 2006). Silver(I) 4-bromobenzenesulfonate (compound *B*) was synthesized by mixing 4-bromobenzenesulfonylchloride (2.56 g, 10.0 mmol) in hot CH_3OH (20 ml) and sodium hydroxide (0.42 g, 10.0 mmol) in hot CH_3OH (20 ml). A colourless solution formed, which contained a precipitate of sodium chloride which was filtered off; the solution was then evaporated. The residue was dissolved in water mixed with CH_2Cl_2 (35 ml, 4:3, *v/v*). The excess dichloromethane was then evaporated and the residue was dissolved in hot CH_3OH (30 ml), followed by the addition of a solution of sodium hydroxide (0.42 g, 10.0 mmol) and silver nitrate (1.71 g, 10.0 mmol) in hot CH_3OH (80 ml). The solid nitrate in the resulting solution was then filtered off and discarded. Compound *B* was

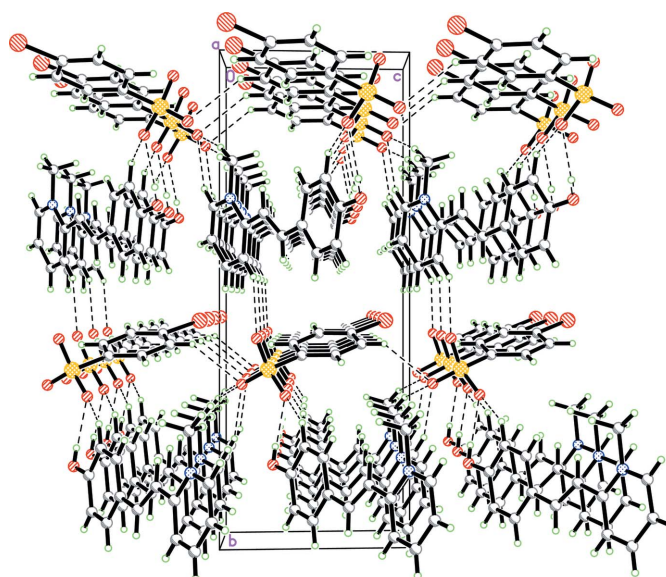


Figure 2

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

obtained after allowing the resulting filtrate to stand in air for several days.

The title compound was synthesized by mixing compound *A* (0.17 g, 0.5 mmol) in hot CH_3OH (30 ml) and compound *B* (0.18 g, 0.5 mmol) in hot CH_3OH (30 ml). The mixture immediately yielded a yellow solid of silver iodide. After stirring the mixture for *ca* 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated to yield a purple solid. Purple block-shaped single crystals of (I) were obtained by recrystallization from CH_3OH after several days (m.p. 513–516 K).

Crystal data

$\text{C}_{14}\text{H}_{14}\text{NO}^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$
 $M_r = 448.32$
 Monoclinic, $P2_1$
 $a = 6.2827(1) \text{ \AA}$
 $b = 19.5377(3) \text{ \AA}$
 $c = 7.5025(1) \text{ \AA}$
 $\beta = 95.923(1)^\circ$
 $V = 916.01(2) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.625 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 2.38 \text{ mm}^{-1}$
 $T = 100.0(1) \text{ K}$
 Block, purple
 $0.48 \times 0.39 \times 0.31 \text{ mm}$

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.394$, $T_{\max} = 0.522$
 (expected range = 0.360–0.477)

15947 measured reflections
 5286 independent reflections
 5107 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 30.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.058$
 $S = 1.07$
 5286 reflections
 249 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 0.0214P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 with 2427 Friedel pairs
 Flack parameter: 0.013 (4)

Table 1

Selected geometric parameters (Å, °).

Br1—C1	1.9034 (17)	S1—C4	1.7771 (18)
S1—O2	1.4535 (13)	N1—C20	1.474 (2)
S1—O3	1.4551 (14)	O4—C17	1.358 (2)
S1—O1	1.4671 (13)	C12—C13	1.345 (2)
C20—N1—C7—C8	179.22 (17)	C11—C12—C13—C14	179.58 (17)

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1—C6 benzene ring.

<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>
O4—H1O4...O1	0.71 (3)	1.98 (3)	2.6833 (18)	171 (3)
C5—H5A...O1	0.93	2.58	2.921 (2)	102
C6—H6A...O3 ⁱ	0.93	2.49	3.206 (2)	134
C7—H7A...O3 ⁱⁱ	0.93	2.26	3.132 (2)	156
C10—H10A...O2 ⁱⁱⁱ	0.93	2.46	3.111 (2)	127
C16—H16A...O1	0.93	2.41	3.091 (2)	130
C20—H20A...O3 ⁱⁱ	0.96	2.34	3.254 (2)	158
C16—H16A...Cg1 ^{iv}	0.93	3.24	3.9330 (19)	133
C19—H19A...Cg1 ^v	0.93	2.72	3.6245 (19)	165

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

The hydroxyl H atom was located in a difference map and refined isotropically. The remaining H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.96 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$, where $x = 1.5$ for hydroxyl and Me H atoms and $x = 1.2$ for all other 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).

The authors thank the Thailand Toray Science Foundation for a Science and Technology Research Grant. The authors also thank Prince of Songkla University, the Malaysian Government, and Universiti Sains Malaysia for Scientific Advancement Grant Allocation (SAGA) No. 304/PFIZIK/653003/A118.

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* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chantrapromma, S., Jindawong, B., Fun, H.-K., Anjum, S. & Karalai, C. (2005). *Acta Cryst. E61*, o2096–o2098.
- Chantrapromma, S., Ruanwas, P., Jindawong, B., Razak, I. A. & Fun, H.-K. (2006). *Acta Cryst. E62*, o875–o877.
- 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.
- Fun, H.-K., Rodwatcharapiban, P., Jindawong, B. & Chantrapromma, S. (2006). *Acta Cryst. E62*, o2725–o2727.
- 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., Yu, X.-L. & Karalai, C. (2005). *Acta Cryst. E61*, o1340–o1342.
- Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
- Rahman, A. A., Razak, I. A., Fun, H.-K., Saene, P., Jindawong, B., Chantrapromma, S. & Karalai, C. (2003). *Acta Cryst. E59*, o1798–o1800.
- Ravindrachary, V., Crasta, V., Bhajantri, R. F. & Poojari, B. (2005). *J. Cryst. Growth*, **275**, e313–e318.
- Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Umezawa, H., Tsuji, K., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2002). *Opt. Mater.* **21**, 75–78.
- Usman, A., Okada, S., Oikawa, H. & Nakanishi, H. (2000). *Chem. Mater.* **22**, 1162–1170.
- Williams, D. J. (1984). *Angew. Chem. Int. Ed. Engl.* **23**, 690–703.