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(2*Z*)-3-(4-Hydroxyphenyl)-2-(pyridinium-4-yl)-acrylonitrile *p*-toluenesulfonate

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In the structure of the title compound, $C_{15}H_{13}N_2O^+\cdot C_7H_7O_3S^-$, the cation has a *Z* geometry about the ethylene bridge that links the heterocyclic and aromatic rings. The skeleton of the cation is slightly non-planar; the dihedral angles between the ethylene linkage and the pyridinium ring and *p*-hydroxyphenyl ring are 9.2 (1) and 2.0 (1)°, respectively. In the crystal structure, the cations are stacked along the *b* axis, with a head-to-tail orientation, and weak intermolecular C—H···N hydrogen bonds link the cations into chains along the *a* axis. In addition, intermolecular O—H···O and C—H···O hydrogen bonds between cations and anions link two such chains together with a mean interplanar distance of 3.23 Å between cations.

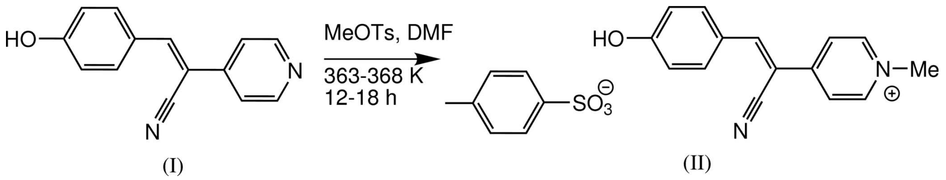
Key indicators

Single-crystal X-ray study
T = 213 K
Mean σ(C–C) = 0.004 Å
R factor = 0.056
wR factor = 0.170
Data-to-parameter ratio = 14.1

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

Comment

The present investigation is a continuation of our work that includes the synthesis and structural studies of polarized organic compounds with potential nonlinear optical properties (Huang *et al.*, 1999; Nesterov, Antipin *et al.*, 2000; Nesterov, Kislyi *et al.*, 2000; Wang *et al.*, 2001; Helvenston *et al.*, 2005). These compounds may have applications in nonlinear optical, electrooptical, photorefractive and optical limiting materials (Zyss *et al.*, 1994; Kuzyk & Dirk, 1998; Kaino *et al.*, 2002). The title compound, (II), was synthesized by the reaction of (2*Z*)-3-(4-hydroxyphenyl)-2-(pyridin-4-yl)acrylonitrile, (I), with methyl *p*-toluenesulfonate in dry dimethylformamide (DMF).



The cation of the title salt has a *Z*-geometry about the ethylene bridge which links the heterocyclic and aromatic rings (Fig. 1). Most of the geometric parameters in the cation are very similar to the standard values (Allen *et al.*, 1987) and our previous work (Helvenston *et al.*, 2005). The molecular skeleton of (II) is slightly non-planar: the dihedral angle between the ethylene linkage and the pyridinium ring is 9.2 (1)°, and that between this linkage and the *p*-hydroxyphenyl ring is 2.0 (1)°. In the cation, there are short intramolecular contacts (H5*A*···H8*A* = 2.02 Å and H10*A*···C1 = 2.44 Å) that are less than the sum of the van der Waals radii of the corresponding atoms (Rowland & Taylor, 1996). The reason for the slight nonplanarity of the cation may be to avoid such unfavorable steric interactions, and because of this

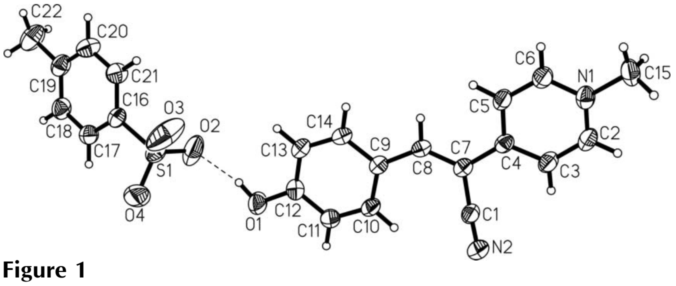


Figure 1
The asymmetric unit of (II), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles of arbitrary small radius and the dashed line indicates an intermolecular O—H···O hydrogen bond.

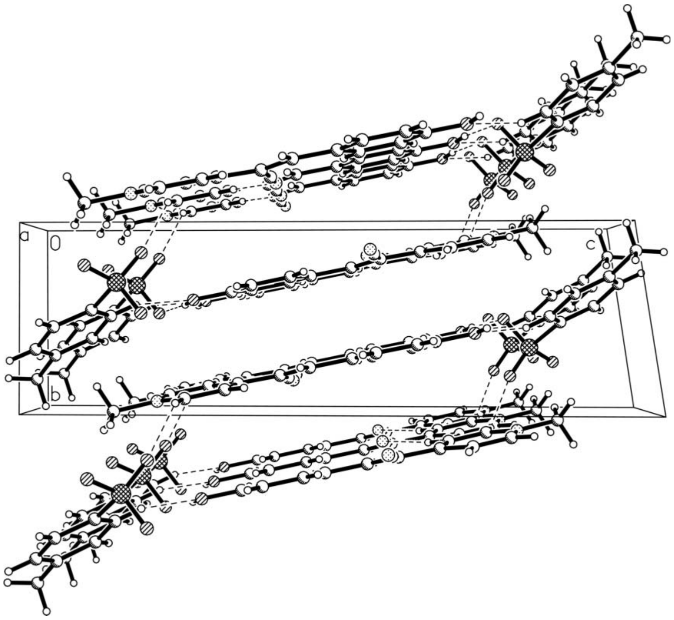


Figure 2
Projection of the crystal packing of (II) along the *a* axis. Dashed lines are intermolecular O—H···O, C—H···N and C—H···O hydrogen bonds.

only slight non-planarity of (II), bond conjugation is still observed. The substituted benzene ring has a slightly quinoidal structure and the C4—C7, C7—C8 and C8—C9 bond lengths (Table 1) are slightly different from the standard values (Allen *et al.*, 1987).

In the crystal structure, the cations are stacked along the *b* axis with head-to-tail orientation. Intermolecular C—H···N hydrogen bonds link the cations into chains along the *a* axis. In addition, intermolecular O—H···O and C—H···O hydrogen bonds between cations and anions link two such chains together with a mean interplanar distance of 3.23 Å between cations (Fig. 2).

Experimental

Compound (I) (0.35 g, 1.57 mmol), methyl *p*-toluenesulfonate (MeOTs, 0.47 ml, 2.35 mmol, 1.5 excess) and dry DMF (approximately 15–20 ml) were placed in a 50 ml round-bottomed flask. The mixture was heated to 363–368 K while stirring under nitrogen; after about 2 h a yellow precipitate appeared and the reaction was allowed to continue overnight. The solution was then removed from the heat and allowed to cool; the precipitate was filtered off and washed with Et_2O to remove any residual DMF. The crystals were dried under vacuum. The pure product had a yield of 89% (m.p. 554 K). For X-ray analysis, crystals were obtained by slow isothermic evaporation of an ethanol solution of (II).

Crystal data

$C_{15}H_{13}N_2O^+ \cdot C_7H_7O_3S^-$
$M_r = 408.47$
Triclinic, $P\overline{1}$
$a = 6.9959\ (15)$ Å
$b = 7.4103\ (16)$ Å
$c = 21.343\ (5)$ Å
$\alpha = 84.138\ (3)^\circ$
$\beta = 85.684\ (3)^\circ$
$\gamma = 62.749\ (2)^\circ$
$V = 978.0\ (4)$ Å^3
$Z = 2$
$D_x = 1.387$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.20$ mm^{-1}
$T = 213\ (2)$ K
Prism, yellow
0.45 × 0.35 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.925$, $T_{\max} = 0.962$
6597 measured reflections
3792 independent reflections
2891 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.170$
$S = 1.00$
3792 reflections
268 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1088P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.339 (3)	C7—C8	1.355 (3)
C4—C7	1.460 (3)	C8—C9	1.440 (3)
C4—C7—C8—C9	179.5 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2	0.86 (5)	1.73 (5)	2.578 (3)	167 (3)
C5—H5*A*···N2$^{\rm i}$	0.94	2.52	3.454 (4)	172
C6—H6*A*···O3$^{\rm ii}$	0.94	2.30	3.039 (4)	136
C21—H21*A*···O1$^{\rm i}$	0.94	2.39	3.248 (4)	151

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y, -z + 1$.

All C-bound H atoms were placed in geometrically calculated positions and refined using a riding model, with C—H distances of 0.94 Å for aromatic and ethylene H atoms, and 0.97 Å for CH_3 groups, and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$, or $1.5U_{\rm eq}(C)$ for methyl H atoms. The H atom of the OH group was found in a difference Fourier synthesis and was refined isotropically.

Data collection: *SMART APEX* (Bruker, 2003); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*;

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program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2001); software used to prepare material for publication: *SHELXL97*.

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