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4′-Hydroxy-3′-methoxy-*N*-methyl-4-stilbazolium Tosylate Hydrate, $C_{15}H_{16}NO_2^+.C_7H_7O_3S^-.H_2O$

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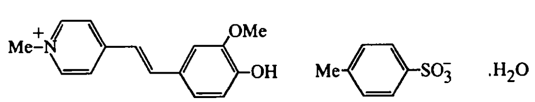
Abstract

In the cation of the title compound, 4-[2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-tolylsulfonate hydrate, the pyridyl ring makes a dihedral angle of 3.63 (5)° with the phenyl ring. The phenyl ring in the anion makes a dihedral angle of 86.3 (2)° with the best mean plane of the cation. Layers of cations and anions are interleaved and connected by hydrogen bonds to the water molecule.

Comment

During our systematic search of organic salts for non-linear optical purposes, we isolated the title compound, (I). Comparison of its structure with those of very similar compounds (Marder, Perry & Tiemann, 1990; Okada *et al.*, 1990) showed no significant differences in the molecular geometry. The cation is basically planar. The torsion angle about the double bond between the two rings in the cation is 178.1 (2)°. The maximum deviation of the non-H atoms from the mean plane (Nardelli, 1983) through the backbone atoms in the two rings and the vinyl linker is 0.110 (1) Å. The hydroxy group is out of the plane [10.3 (3)°], possibly because of stereochemical hindrance of the methoxy group in its *ortho* position.



(I)

The phenyl ring in the anion is planar within 0.01 Å and makes a dihedral angle of 86.3 (2)° with the mean plane of the cation. There are layers of cations near $x = \frac{1}{2}$ and layers of anions near $x = 0$ (and 1). The water of crystallization (O6) connects these two layers through hydrogen bonds (see Table 2). Also, the negatively charged sulphonate group in the anion is near the positively charged N atom of the cation. When viewed down **a**, the arrangement of cations is herringbone-like. Within the cation layers, the closest distance between the planes of antiparallel cations is 3.514 (3) Å, showing the existence of π–π interactions. There is also a short contact between cations, namely $N\cdots H^i$—$O4^i$ of 3.459 (3) Å [symmetry code: (i) $-1-x, y-\frac{1}{2}, \frac{1}{2}-z$]. Table 3 also shows short intermolecular contacts which appear to be C—H···O hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Krishnamohan Sharma & Desiraju, 1994).

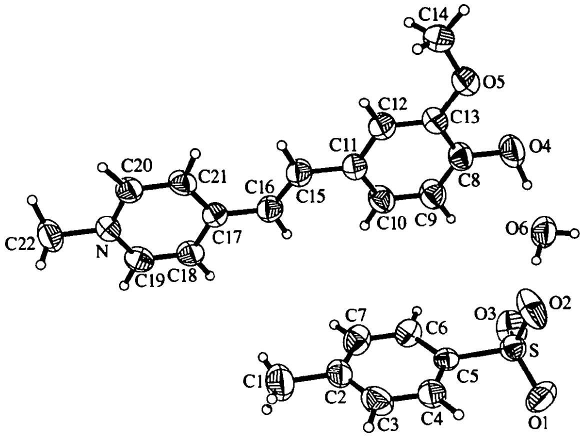


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

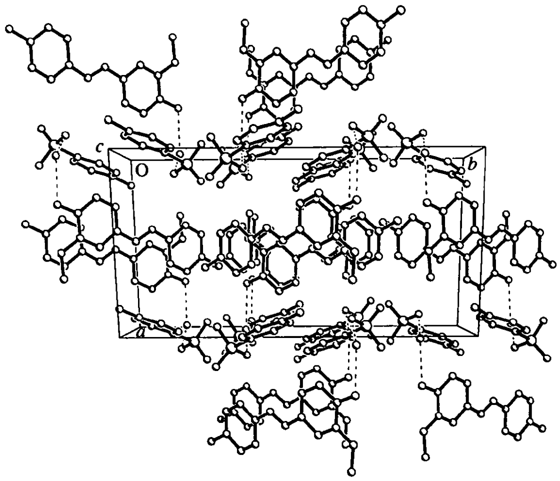


Fig. 2. Packing diagram viewed down the *c* axis.

Experimental

1,4-Dimethylpyridinium iodide (4.72 g; prepared from CH_3I and γ-methylpyridine) and 4-hydroxy-3-methoxybenzaldehyde (3.64 g) in 10 ml methanol were heated to 353 K for 8 h. The product was recrystallized twice from ethanol–water (2:1), dissolved in water again (0.74 g in 100 ml) and treated with a saturated solution of silver *p*-tolylsulphonate, added dropwise with stirring at 363 K over 20 min. The title compound was separated, recrystallized twice and crystals were grown from methanol–water (10:1) by slow evaporation.

Crystal data

$C_{15}H_{16}NO_2^+.C_7H_7O_3S^-.H_2O$
$M_r = 431.49$
Monoclinic
$P2_1/c$
$a = 10.9520\,(10)$ Å
$b = 19.853\,(2)$ Å
$c = 10.4960\,(10)$ Å
$\beta = 111.450\,(10)^\circ$
$V = 2124.1\,(4)$ Å^3
$Z = 4$
$D_x = 1.349$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 2$–25°
$\mu = 0.191$ mm^{-1}
$T = 295\,(2)$ K
Block
0.46 × 0.46 × 0.46 mm
Orange–red

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$
Absorption correction: none
3962 measured reflections
3743 independent reflections
2394 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0165$

$\theta_{\rm max} = 25^\circ$
$h = -13 \rightarrow 12$
$k = -23 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: 2.23%

Refinement

Refinement on F^2
$R(F) = 0.0399$
$wR(F^2) = 0.1048$
$S = 0.902$
3743 reflections
372 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.007$

$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0197 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

S—O1	1.428 (2)	N—C22	1.481 (3)
S—O3	1.437 (2)	C11—C15	1.465 (3)
S—O2	1.438 (2)	C15—C16	1.318 (3)
S—C5	1.767 (2)	C16—C17	1.456 (3)
O4—C8	1.356 (3)		

Table 2. *Intermolecular contacts (Å)*

O4···O6	2.671 (3)	C9···O6	3.270 (4)
O6···O3	2.835 (3)	C4···O2$^{\rm ii}$	3.323 (3)
O6···O1$^{\rm i}$	3.082 (3)	C19···O1$^{\rm iii}$	3.225 (3)
O6···O2$^{\rm i}$	3.098 (3)	C22···O4$^{\rm iv}$	3.251 (4)

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Extended Conformation of Putrescine Occurring on a Center of Symmetry in its 1:2 Complex with Malonic Acid

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Abstract

The 1,4-butane diammonium (putrescine) ion co-crystalizes with propanedioic acid (malonic acid) monoanions in space group *Pcab* (1,4-butane diammonium hydrogen propanedioate, $C_4H_{14}N_2^{2+}.2C_3H_3O_4^-$). One of the carboxylate moieties of malonic acid is protonated. The asymmetric unit of the crystal contains one molecule of malonic acid and half a molecule of putrescine. All three H atoms of the putrescine amino groups participate in hydrogen bonding.