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 2-Hydroxypyridinium *p*-toluenesulfonate

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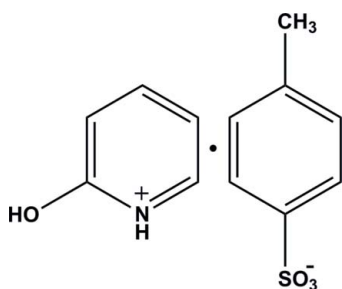
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.046; wR factor = 0.111; data-to-parameter ratio = 15.9.

In the title molecular salt, $\text{C}_5\text{H}_6\text{NO}^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$, the cations and anions are connected by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, forming [100] chains.

Related literature

For general background on ferroelectric frameworks, see: Zhang *et al.* (2008, 2009, 2010). For related salts containing *p*-toluenesulfonate anions, see: Helvenston *et al.* (2006); Collier *et al.* (2006); Koshima *et al.* (2001).



Experimental

Crystal data

 $\text{C}_5\text{H}_6\text{NO}^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$
 $M_r = 267.29$

 Orthorhombic, *Pbca*
 $a = 10.293$ (2) Å

 $b = 14.484$ (3) Å

 $c = 15.708$ (3) Å

 $V = 2341.8$ (8) Å³
 $Z = 8$

 Mo $K\alpha$ radiation

 $\mu = 0.28$ mm⁻¹
 $T = 293$ K

 $0.3 \times 0.3 \times 0.2$ mm

Data collection

 Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.489$, $T_{\max} = 1.000$

 23178 measured reflections
 2688 independent reflections
 2239 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.111$
 $S = 1.09$

2688 reflections

169 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
O1—H1⋯O2	0.89 (4)	1.66 (4)	2.523 (2)	160 (3)
N1—H1 <i>D</i> ⋯O4 ⁱ	0.86	1.86	2.704 (2)	166

 Symmetry code: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2431).

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supplementary materials

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2-Hydroxypyridinium *p*-toluenesulfonate

Yu Jin

Comment

Several crystal structures of *p*-toluenesulfonate have been reported previously (Helvenston *et al.*, 2006; Collier *et al.*, 2006; Koshima *et al.*, 2001). As an extension of this research, we report here the synthesis and the crystal structure of the title complex.

Until now, researchers have found that molecular motion can cause a rotation of the local structure to give rise to the formation of reversible structural phase transition from high-temperature disordered fashion to low temperature ordered fashion. Reversible structural phase transition is caused by many kinds of factors. Hydrogen-bonding interactions come to be the most common factor. Transition for hydrogen-bonding interactions from high-temperature disordered state to low temperature ordered state allows reversible structural phase transition. The compound reported here could have a tendency to hold such transition as a result of numerous hydrogen-bonding interactions in its crystal structure. The transition from the disordered arrangement to the ordered one gives rise to sharp change in the physical properties of these compounds. Only few compounds in which the components can be arranged in a disordered status at a relative high temperature and in an ordered one at a relative low temperature have been found until now (Zhang *et al.*, 2008, 2009, 2010). As part of our search for simple ferroelectric compounds we have investigated the title compound and report its room temperature structure.

The asymmetric unit, containing one anion and one cation, is shown in Fig. 1 with the hydrogen bonds listed in Table 1. The compound remains stable as a result of the existence of numerous hydrogen-bonding interactions formed in the crystal. These interactions tie the cations and anions together in a complex spatial geometry (Fig. 2).

Experimental

$C_5H_6ON^+ \cdot C_7H_7O_3S^-$ was formed from a mixture of C_5H_5ON (95.1 mg, 1.00 mmol), $C_7H_7SO_3H$ (172 mg, 1.00 mmol), and distilled water (5 mL), which was stirred a few minutes at room temperature, giving a clear transparent solution. After evaporation for a few days, block colourless crystals suitable for X-ray diffraction were obtained in about 71% yield and filtered and washed with distilled water.

Refinement

H atoms bound to C and N atoms were placed at idealized positions [C—H = 0.93–0.96 Å, N—H = 0.86 Å] and allowed to ride on their parent atoms with $U_{iso} = 1.5 U_{eq}(C1)$ for the methyl group and $U_{iso} = 1.2 U_{eq}(\text{carrier atom})$ otherwise. Hydroxyl H atom was found in a difference map and refined freely.

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for

publication: *SHELXL97* (Sheldrick, 2008).

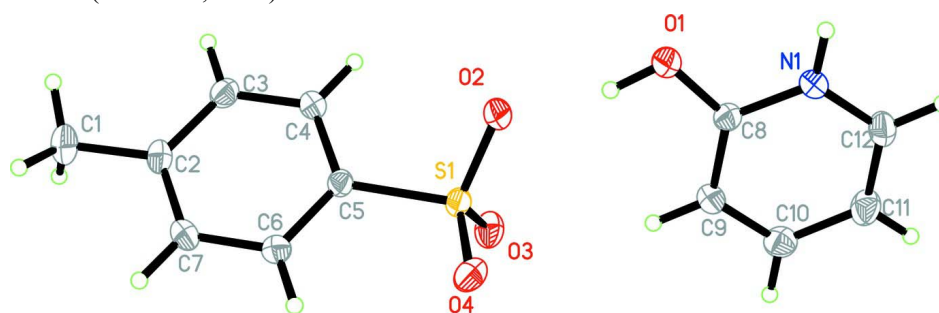


Figure 1

The structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

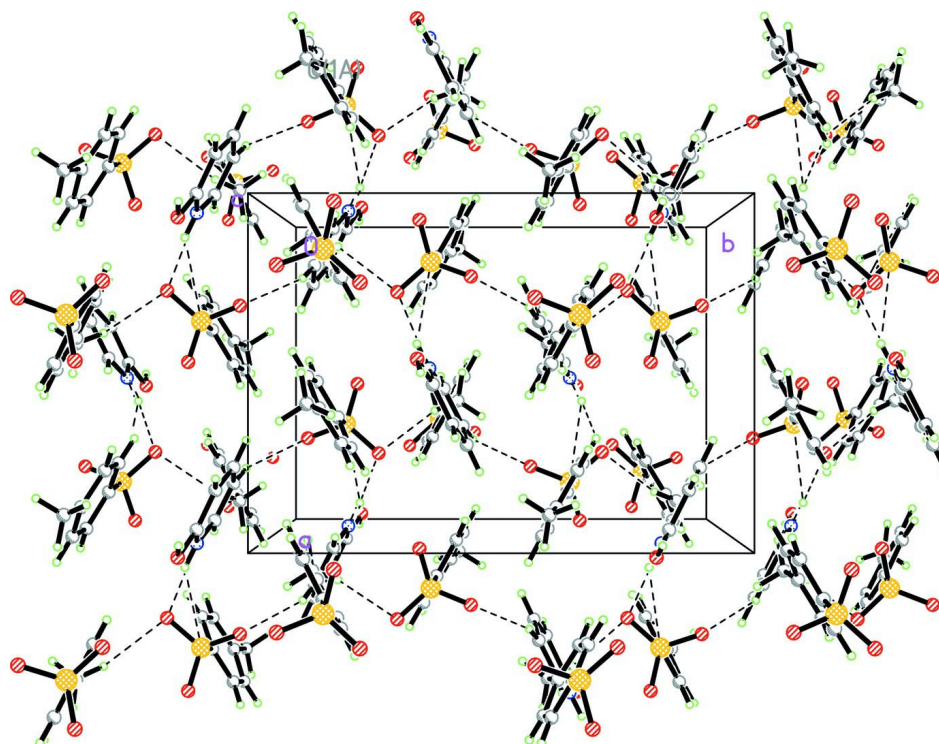


Figure 2

Part of the crystal structure of the title compound viewed along the *c* axis. Intermolecular interactions are shown as dashed lines.

2-Hydroxypyridinium *p*-toluenesulfonate

Crystal data

$C_5H_6NO^+ \cdot C_7H_7O_3S^-$

$M_r = 267.29$

Orthorhombic, *Pbca*

Hall symbol: $-P\ 2ac\ 2ab$

$a = 10.293\ (2)\ \text{\AA}$

$b = 14.484\ (3)\ \text{\AA}$

$c = 15.708\ (3)\ \text{\AA}$

$V = 2341.8\ (8)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1120$

$D_x = 1.516\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3450 reflections

$\theta = 6.2\text{--}55.3^\circ$

$\mu = 0.28 \text{ mm}^{-1}$
 $T = 293 \text{ K}$

Block, colourless
 $0.3 \times 0.3 \times 0.2 \text{ mm}$

Data collection

Rigaku Mercury CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.489$, $T_{\max} = 1.000$

23178 measured reflections
 2688 independent reflections
 2239 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$
 $h = -13 \rightarrow 13$
 $k = -18 \rightarrow 18$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.111$
 $S = 1.09$
 2688 reflections
 169 parameters
 0 restraints
 0 constraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.2062P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0347 (16)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5889 (2)	0.09901 (16)	0.81599 (13)	0.0461 (6)
H1A	0.6382	0.0453	0.8315	0.069*
H1B	0.4989	0.0890	0.8291	0.069*
H1C	0.6203	0.1514	0.8473	0.069*
C2	0.6034 (2)	0.11654 (13)	0.72297 (12)	0.0322 (4)
C3	0.5108 (2)	0.08731 (14)	0.66618 (13)	0.0356 (5)
H3	0.4365	0.0580	0.6862	0.043*
C4	0.52611 (19)	0.10060 (14)	0.58087 (12)	0.0335 (5)
H4	0.4625	0.0804	0.5431	0.040*
C5	0.63523 (18)	0.14370 (13)	0.55080 (12)	0.0277 (4)
C6	0.72725 (19)	0.17508 (14)	0.60638 (12)	0.0318 (4)
H6	0.8007	0.2055	0.5863	0.038*
C7	0.7102 (2)	0.16122 (13)	0.69220 (13)	0.0342 (5)
H7	0.7728	0.1827	0.7301	0.041*
C8	0.53344 (18)	0.14460 (13)	0.19333 (12)	0.0309 (4)
C9	0.65239 (19)	0.10354 (14)	0.20266 (13)	0.0352 (5)
H9	0.6890	0.0961	0.2564	0.042*
C10	0.7158 (2)	0.07393 (14)	0.13220 (14)	0.0401 (5)
H10	0.7970	0.0464	0.1378	0.048*
C11	0.6624 (2)	0.08387 (17)	0.05305 (14)	0.0446 (5)
H11	0.7052	0.0622	0.0049	0.054*

C12	0.5470 (2)	0.12556 (16)	0.04656 (14)	0.0424 (5)
H12	0.5097	0.1342	−0.0068	0.051*
N1	0.48537 (16)	0.15481 (12)	0.11587 (10)	0.0344 (4)
H1D	0.4112	0.1814	0.1101	0.041*
O1	0.45846 (14)	0.17554 (12)	0.25338 (10)	0.0446 (4)
H1	0.498 (3)	0.167 (2)	0.303 (2)	0.095 (12)*
O2	0.53381 (14)	0.17679 (12)	0.40618 (9)	0.0477 (4)
O3	0.70545 (15)	0.06576 (10)	0.41196 (9)	0.0426 (4)
O4	0.75191 (14)	0.22574 (10)	0.42828 (8)	0.0397 (4)
S1	0.65917 (5)	0.15323 (3)	0.44102 (3)	0.03132 (18)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0660 (16)	0.0449 (13)	0.0273 (11)	−0.0031 (11)	0.0006 (10)	−0.0002 (9)
C2	0.0433 (11)	0.0285 (10)	0.0247 (9)	0.0050 (8)	−0.0003 (8)	−0.0014 (7)
C3	0.0343 (11)	0.0397 (11)	0.0326 (10)	−0.0038 (9)	0.0056 (9)	−0.0006 (9)
C4	0.0306 (10)	0.0415 (11)	0.0286 (10)	−0.0020 (8)	−0.0021 (8)	−0.0025 (9)
C5	0.0277 (9)	0.0317 (10)	0.0238 (9)	0.0053 (7)	0.0003 (7)	−0.0008 (7)
C6	0.0293 (10)	0.0340 (10)	0.0322 (10)	−0.0016 (8)	0.0004 (8)	0.0006 (8)
C7	0.0358 (11)	0.0358 (10)	0.0310 (10)	−0.0011 (8)	−0.0075 (8)	−0.0037 (8)
C8	0.0290 (10)	0.0348 (10)	0.0290 (10)	−0.0036 (8)	0.0013 (8)	0.0003 (8)
C9	0.0335 (11)	0.0398 (11)	0.0321 (10)	0.0004 (8)	−0.0045 (8)	0.0026 (9)
C10	0.0370 (11)	0.0381 (11)	0.0451 (12)	0.0086 (9)	0.0020 (9)	0.0002 (10)
C11	0.0507 (13)	0.0492 (13)	0.0338 (11)	0.0092 (11)	0.0069 (10)	−0.0043 (10)
C12	0.0469 (13)	0.0534 (13)	0.0269 (10)	0.0036 (10)	−0.0019 (9)	−0.0005 (10)
N1	0.0289 (8)	0.0432 (10)	0.0309 (9)	0.0013 (7)	−0.0033 (7)	0.0022 (7)
O1	0.0335 (8)	0.0702 (11)	0.0302 (8)	0.0100 (7)	0.0000 (6)	−0.0018 (8)
O2	0.0349 (8)	0.0804 (12)	0.0276 (7)	0.0126 (8)	−0.0024 (6)	0.0046 (8)
O3	0.0529 (9)	0.0417 (9)	0.0331 (8)	0.0064 (7)	0.0033 (7)	−0.0075 (6)
O4	0.0386 (8)	0.0428 (8)	0.0377 (8)	0.0030 (6)	0.0099 (6)	0.0051 (7)
S1	0.0296 (3)	0.0402 (3)	0.0241 (3)	0.0057 (2)	0.00163 (18)	0.0007 (2)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.491 (3)	C8—N1	1.322 (2)
C1—H1A	0.9600	C8—C9	1.369 (3)
C1—H1B	0.9600	C9—C10	1.355 (3)
C1—H1C	0.9600	C9—H9	0.9300
C2—C7	1.364 (3)	C10—C11	1.367 (3)
C2—C3	1.373 (3)	C10—H10	0.9300
C3—C4	1.363 (3)	C11—C12	1.336 (3)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.369 (3)	C12—N1	1.330 (3)
C4—H4	0.9300	C12—H12	0.9300
C5—C6	1.366 (3)	N1—H1D	0.8600
C5—S1	1.7474 (19)	O1—H1	0.89 (4)
C6—C7	1.374 (3)	O2—S1	1.4425 (15)
C6—H6	0.9300	O3—S1	1.4284 (15)
C7—H7	0.9300	O4—S1	1.4333 (16)

C8—O1	1.299 (2)		
C2—C1—H1A	109.5	O1—C8—C9	127.14 (19)
C2—C1—H1B	109.5	N1—C8—C9	118.81 (18)
H1A—C1—H1B	109.5	C10—C9—C8	118.75 (19)
C2—C1—H1C	109.5	C10—C9—H9	120.6
H1A—C1—H1C	109.5	C8—C9—H9	120.6
H1B—C1—H1C	109.5	C9—C10—C11	121.1 (2)
C7—C2—C3	118.42 (18)	C9—C10—H10	119.5
C7—C2—C1	120.61 (19)	C11—C10—H10	119.5
C3—C2—C1	120.97 (19)	C12—C11—C10	118.3 (2)
C4—C3—C2	120.99 (19)	C12—C11—H11	120.8
C4—C3—H3	119.5	C10—C11—H11	120.8
C2—C3—H3	119.5	N1—C12—C11	120.4 (2)
C3—C4—C5	119.90 (18)	N1—C12—H12	119.8
C3—C4—H4	120.0	C11—C12—H12	119.8
C5—C4—H4	120.0	C8—N1—C12	122.64 (18)
C6—C5—C4	120.00 (18)	C8—N1—H1D	118.7
C6—C5—S1	120.44 (15)	C12—N1—H1D	118.7
C4—C5—S1	119.49 (15)	C8—O1—H1	109 (2)
C5—C6—C7	119.34 (19)	O3—S1—O4	112.53 (9)
C5—C6—H6	120.3	O3—S1—O2	112.76 (10)
C7—C6—H6	120.3	O4—S1—O2	111.68 (10)
C2—C7—C6	121.31 (18)	O3—S1—C5	107.00 (9)
C2—C7—H7	119.3	O4—S1—C5	106.83 (9)
C6—C7—H7	119.3	O2—S1—C5	105.48 (9)
O1—C8—N1	114.05 (18)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots O2	0.89 (4)	1.66 (4)	2.523 (2)	160 (3)
N1—H1D \cdots O4 ⁱ	0.86	1.86	2.704 (2)	166
O1—H1 \cdots S1	0.89 (4)	2.73 (4)	3.6139 (18)	169 (3)
N1—H1D \cdots S1 ⁱ	0.86	2.75	3.4747 (18)	143

Symmetry code: (i) $x-1/2, y, -z+1/2$.