

Pyridinium tosylate

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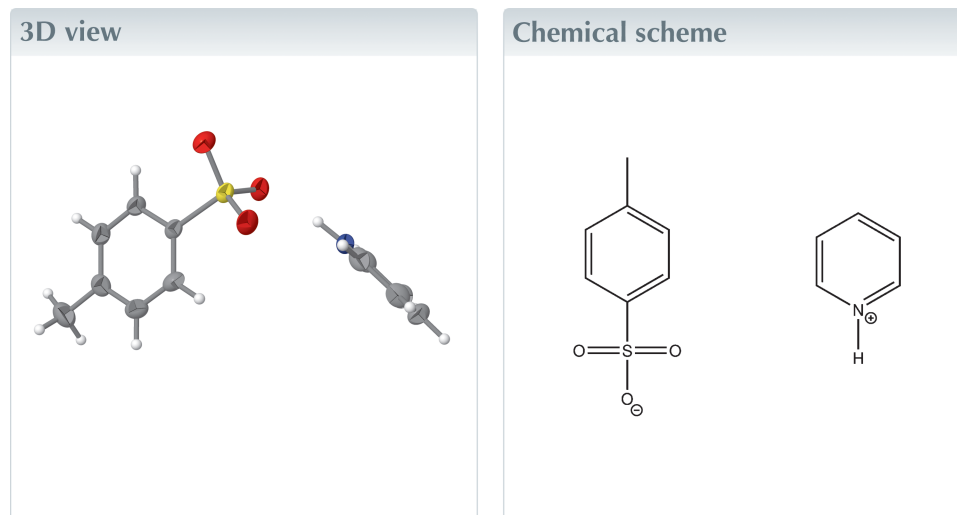
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Keywords: crystal structure; hydrogen bond; pyridinium salt.

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Structural data: full structural data are available from iucrdata.iucr.org

The title compound (systematic name: pyridinium 4-methylbenzenesulfonate), $C_5H_6N^+ \cdot C_7H_7O_3S^-$, is the pyridinium salt of *para*-toluenesulfonic acid. In the crystal, classical $N-H \cdots O$ hydrogen bonds as well as $C-H \cdots O$ contacts connect the cationic and anionic entities into sheets lying parallel to the *ab* plane.



Structure description

Many fundamental synthesis reactions in preparative organic chemistry make use of activated reagents to allow for the faster and easier production of certain key compounds or to avoid the presence of cumbersome equilibrium reactions. A prime example for this finding is a series of derivatives of carboxylic acids such as esters and amides that – instead of employing the free acid as starting material – are often more conveniently obtained by using the pertaining carboxylic anhydride or acyl chloride or bromide as starting materials (Becker *et al.*, 2000). One downside of this increased reactivity is the frequent need to use auxiliary reagents that can mitigate potential side effects of the byproducts produced, most notably basic reagents that can act as acid scavengers to prevent undesired hydrolysis effects. Among the more common ingredients used in the latter context are amines such as triethylamine or pyridine whose onium salts can often conveniently be removed from reaction mixtures in organic solvents by means of simple filtration. Occasionally, however, some of the material tenaciously migrates through many steps of purification procedures and can manifest as lingering impurity in the assumed final product. To prevent the waste of valuable data-collection time on diffractometers for future researchers, it is of importance to report the structures even of such undesired compounds as a reference point for the broader scientific community, as done previously by us for ammonium formate (Hosten & Betz, 2014), ammonium phenyl glyoxylate (Hosten & Betz, 2015) as well as the chlorides (Maritz *et al.*, 2021; Muller *et al.*, 2021*a,b,c*) and tosylate salts (Moleko *et al.*, 2015) of a number of protonated amines. Furthermore, the molecular and crystal structures of the non-radioactive halogenide salts

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O11$	0.93 (3)	1.81 (3)	2.724 (2)	166 (3)
$C21-H21\cdots O13^i$	0.95	2.41	3.306 (2)	157
$C22-H22\cdots O12^{ii}$	0.95	2.36	3.117 (2)	136
$C24-H24\cdots O13^{iii}$	0.95	2.35	3.202 (2)	149
$C25-H25\cdots O12$	0.95	2.54	3.259 (3)	133
$C25-H25\cdots O11^{iii}$	0.95	2.36	3.194 (2)	147

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

of the pyridinium cation are apparent in the literature (Boenigk & Mootz, 1988; Mootz & Hocken, 1989; Klooster *et al.*, 2019; Owczarek *et al.*, 2012).

The asymmetric unit of the title compound, $C_5H_6N^+ \cdot C_7H_7O_3S^-$, is shown in Fig. 1 and consists of one complete ion pair. The S–O bond lengths in the anion are found in the narrow range of 1.4525 (14)–1.4682 (14) Å, which is in agreement with full resonant delocalization of the anionic charge over all three oxygen atoms. All other bond lengths and angles are found in good agreement with other tosylates whose molecular and crystal structures were determined on grounds of diffraction studies conducted on single crystals and whose metrical parameters have been deposited with the Cambridge Structural Database (Allen, 2002). The least-squares planes as defined by the non-hydrogen atoms of the cation as well as the intracyclic carbon atoms of the tosylate anion intersect at an angle of 74.44 (10)°, *i.e.* the two separate aromatic systems in the asymmetric unit are orientated almost perpendicular to one another.

In the crystal, classical N–H⋯O hydrogen bonds are observed as well as C–H⋯O contacts whose range falls by more than 0.1 Å below the sum of van der Waals radii of the atoms participating in them (Table 1). While the classical hydrogen bonds are established by the pnictogen-bonded hydrogen atom as donor and one of the oxygen atoms of the sulfato group as acceptor, the C–H⋯O contacts are supported by each of the aromatic hydrogen atoms of the cation except for the one in *para* position to the protonated nitrogen atom. All three sulfur-bonded oxygen atoms act as acceptors in for the latter contacts. In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for the classical hydrogen bonds is *D* on the unary level while the C–H⋯O contacts require a *DDDD*

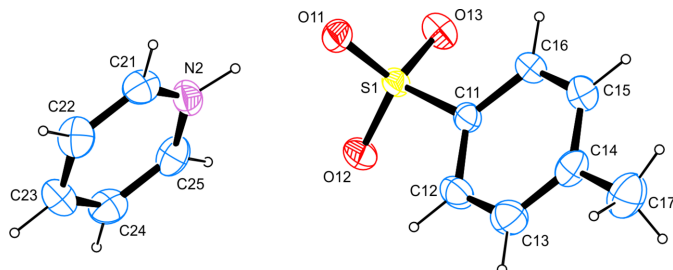


Figure 1
The molecular structure of the title compound, with anisotropic displacement ellipsoids drawn at 50% probability level.

Table 2
Experimental details.

Crystal data	$C_5H_6N^+ \cdot C_7H_7O_3S^-$
Chemical formula	251.29
M_r	Orthorhombic, $P2_12_12_1$
Crystal system, space group	200
Temperature (K)	5.8868 (2), 8.8927 (4), 22.8226 (9)
a, b, c (Å)	1194.75 (8)
V (Å ³)	4
Z	Mo $K\alpha$
Radiation type	0.27
μ (mm ⁻¹)	0.57 × 0.39 × 0.34
Crystal size (mm)	
Data collection	Bruker APEXII CCD
Diffractometer	Numerical (SADABS; Krause <i>et al.</i> , 2015)
Absorption correction	0.904, 1.000
T_{min}, T_{max}	11137, 2972, 2903
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	0.013
R_{int}	0.668
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.072, 1.08
No. of reflections	2972
No. of parameters	160
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.27, -0.26
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.21 (8)

Computer programs: APEX2 and SAINT (Bruker, 2010), SHELXS97, SHELXL97 and SHELXTL (Sheldrick, 2008).

descriptor on the same level. Overall, the intermolecular contacts connect the ions of the title compound into sheets lying parallel the the *ab* plane. A depiction of the pattern is shown in Fig. 2. Aromatic π – π stacking is not a prominent feature in the crystal structure of the title compound with the shortest intercentroid distance between two aromatic systems measuring 4.9276 (12) Å for the anion and its symmetry-generated equivalent.

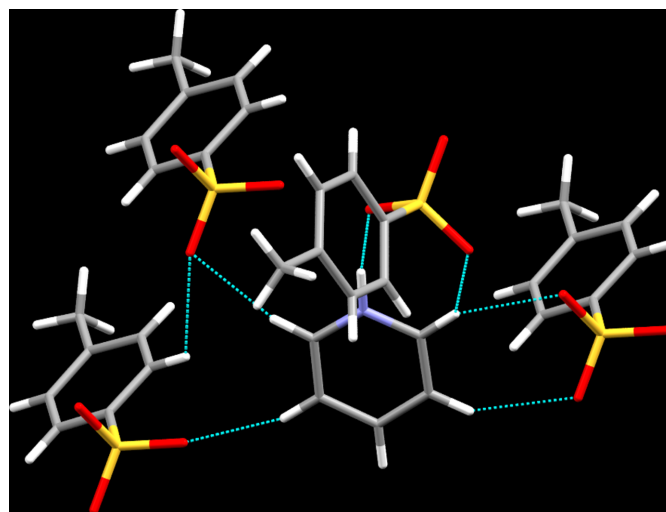


Figure 2
Intermolecular contacts, viewed approximately along [001].

Synthesis and crystallization

After an initial unintentional isolation of the crystalline compound from a different synthesis product the compound was targeted by reacting a slight excess of liquid pyridine with solid tosylic acid in solvent-free conditions. Crystals of the title compound in the form of colourless blocks suitable for the diffraction study were obtained upon free evaporation of the reaction mixture at room temperature.

Refinement

Data collection and crystallographic data are summarized in Table 2. The crystal used for data collection was found to be an inversion twin with a volume ratio of 79.3:20.7.

Acknowledgements

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full crystallographic data

IUCrData (2024). **9**, x240831 [<https://doi.org/10.1107/S2414314624008319>]

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Pyridinium 4-methylbenzenesulfonate

Crystal data

$C_5H_6N^+ \cdot C_7H_7O_3S^-$

$M_r = 251.29$

Orthorhombic, $P2_12_12_1$

$a = 5.8868$ (2) Å

$b = 8.8927$ (4) Å

$c = 22.8226$ (9) Å

$V = 1194.75$ (8) Å³

$Z = 4$

$F(000) = 528$

$D_x = 1.397$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9608 reflections

$\theta = 2.5$ – 28.3°

$\mu = 0.27$ mm⁻¹

$T = 200$ K

Block, colourless

$0.57 \times 0.39 \times 0.34$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: numerical

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.904$, $T_{\max} = 1.000$

11137 measured reflections

2972 independent reflections

2903 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.013$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -7 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -30 \rightarrow 30$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.072$

$S = 1.08$

2972 reflections

160 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2 + 0.2871P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Absolute structure: Refined as an inversion

twin.

Absolute structure parameter: 0.21 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin. The N-bonded H atom was located in a difference map and refined freely. The aromatic carbon-bound H atoms were placed in calculated positions (C—H = 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The H atoms of the methyl group were allowed to rotate but not to tip around the C—C bond to best fit the experimental electron density with $U(\text{H})$ set to $1.5U_{\text{eq}}(\text{C})$.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.59831 (7)	0.68244 (5)	0.67195 (2)	0.02552 (11)
O11	0.5179 (3)	0.56756 (15)	0.71323 (6)	0.0338 (3)
O12	0.5035 (3)	0.82991 (15)	0.68422 (6)	0.0367 (3)
O13	0.8442 (2)	0.68221 (16)	0.66646 (6)	0.0345 (3)
N2	0.1743 (3)	0.6291 (2)	0.78954 (7)	0.0330 (4)
C11	0.4869 (3)	0.62497 (19)	0.60326 (8)	0.0257 (3)
C12	0.2780 (3)	0.6787 (2)	0.58477 (9)	0.0335 (4)
H12	0.200255	0.752191	0.607339	0.040*
C13	0.1821 (4)	0.6250 (3)	0.53319 (10)	0.0390 (5)
H13	0.039834	0.663586	0.520560	0.047*
C14	0.2902 (4)	0.5162 (2)	0.49988 (9)	0.0357 (4)
C15	0.5018 (4)	0.4649 (2)	0.51834 (9)	0.0369 (4)
H15	0.580051	0.392004	0.495557	0.044*
C16	0.6006 (4)	0.5186 (2)	0.56962 (8)	0.0331 (4)
H16	0.745310	0.482637	0.581603	0.040*
C17	0.1802 (5)	0.4560 (3)	0.44461 (10)	0.0515 (6)
H17A	0.185227	0.533185	0.413990	0.077*
H17B	0.021716	0.429478	0.452787	0.077*
H17C	0.262372	0.366456	0.431323	0.077*
C21	0.0159 (4)	0.5375 (2)	0.81078 (9)	0.0345 (4)
H21	0.032091	0.431632	0.806892	0.041*
C22	−0.1711 (4)	0.5966 (2)	0.83835 (9)	0.0375 (5)
H22	−0.286699	0.532290	0.853071	0.045*
C23	−0.1893 (4)	0.7505 (3)	0.84444 (10)	0.0374 (5)
H23	−0.317615	0.793002	0.863489	0.045*
C24	−0.0202 (4)	0.8426 (2)	0.82274 (9)	0.0362 (4)
H24	−0.029529	0.948643	0.827267	0.043*
C25	0.1609 (4)	0.7788 (2)	0.79463 (9)	0.0351 (5)
H25	0.277146	0.840648	0.778725	0.042*
H2	0.297 (5)	0.594 (3)	0.7673 (12)	0.054 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0293 (2)	0.02035 (18)	0.02696 (19)	0.00397 (16)	0.00644 (17)	0.00092 (16)
O11	0.0426 (8)	0.0287 (7)	0.0301 (6)	0.0043 (6)	0.0093 (6)	0.0064 (5)
O12	0.0488 (8)	0.0249 (6)	0.0364 (7)	0.0115 (6)	0.0066 (6)	−0.0023 (6)
O13	0.0295 (6)	0.0324 (6)	0.0417 (7)	0.0001 (5)	0.0046 (5)	−0.0054 (6)
N2	0.0307 (8)	0.0418 (9)	0.0265 (7)	0.0042 (7)	0.0012 (6)	−0.0062 (7)

C11	0.0274 (8)	0.0227 (7)	0.0270 (8)	0.0012 (6)	0.0070 (7)	0.0037 (6)
C12	0.0261 (8)	0.0338 (9)	0.0407 (10)	0.0044 (8)	0.0068 (7)	0.0008 (9)
C13	0.0289 (9)	0.0449 (12)	0.0433 (11)	0.0019 (8)	0.0006 (9)	0.0057 (9)
C14	0.0388 (11)	0.0389 (11)	0.0294 (9)	-0.0051 (9)	0.0009 (8)	0.0073 (8)
C15	0.0423 (11)	0.0369 (10)	0.0316 (9)	0.0076 (9)	0.0051 (8)	-0.0028 (8)
C16	0.0341 (9)	0.0337 (9)	0.0316 (8)	0.0104 (8)	0.0041 (8)	-0.0001 (7)
C17	0.0554 (15)	0.0636 (16)	0.0356 (11)	-0.0051 (13)	-0.0077 (10)	0.0004 (11)
C21	0.0447 (11)	0.0244 (9)	0.0345 (9)	-0.0013 (8)	-0.0069 (8)	-0.0036 (7)
C22	0.0370 (10)	0.0334 (10)	0.0423 (11)	-0.0134 (8)	0.0044 (9)	0.0015 (8)
C23	0.0315 (10)	0.0385 (11)	0.0422 (11)	0.0040 (8)	0.0039 (9)	-0.0069 (9)
C24	0.0480 (11)	0.0216 (8)	0.0390 (10)	-0.0030 (7)	-0.0055 (9)	-0.0015 (8)
C25	0.0370 (11)	0.0377 (10)	0.0305 (9)	-0.0133 (8)	0.0000 (8)	0.0050 (7)

Geometric parameters (Å, °)

S1—O12	1.4525 (14)	C15—C16	1.391 (3)
S1—O13	1.4527 (14)	C15—H15	0.9500
S1—O11	1.4682 (14)	C16—H16	0.9500
S1—C11	1.7745 (19)	C17—H17A	0.9800
N2—C21	1.330 (3)	C17—H17B	0.9800
N2—C25	1.339 (3)	C17—H17C	0.9800
N2—H2	0.93 (3)	C21—C22	1.373 (3)
C11—C12	1.385 (3)	C21—H21	0.9500
C11—C16	1.390 (2)	C22—C23	1.380 (3)
C12—C13	1.390 (3)	C22—H22	0.9500
C12—H12	0.9500	C23—C24	1.381 (3)
C13—C14	1.385 (3)	C23—H23	0.9500
C13—H13	0.9500	C24—C25	1.368 (3)
C14—C15	1.392 (3)	C24—H24	0.9500
C14—C17	1.516 (3)	C25—H25	0.9500
O12—S1—O13	113.63 (9)	C11—C16—C15	119.79 (19)
O12—S1—O11	112.36 (9)	C11—C16—H16	120.1
O13—S1—O11	112.06 (9)	C15—C16—H16	120.1
O12—S1—C11	106.76 (9)	C14—C17—H17A	109.5
O13—S1—C11	106.96 (8)	C14—C17—H17B	109.5
O11—S1—C11	104.32 (9)	H17A—C17—H17B	109.5
C21—N2—C25	122.43 (19)	C14—C17—H17C	109.5
C21—N2—H2	122.5 (18)	H17A—C17—H17C	109.5
C25—N2—H2	114.9 (18)	H17B—C17—H17C	109.5
C12—C11—C16	119.60 (18)	N2—C21—C22	119.67 (18)
C12—C11—S1	119.87 (14)	N2—C21—H21	120.2
C16—C11—S1	120.39 (15)	C22—C21—H21	120.2
C11—C12—C13	120.01 (19)	C21—C22—C23	119.2 (2)
C11—C12—H12	120.0	C21—C22—H22	120.4
C13—C12—H12	120.0	C23—C22—H22	120.4
C14—C13—C12	121.2 (2)	C22—C23—C24	119.8 (2)
C14—C13—H13	119.4	C22—C23—H23	120.1

C12—C13—H13	119.4	C24—C23—H23	120.1
C13—C14—C15	118.3 (2)	C25—C24—C23	118.95 (18)
C13—C14—C17	120.5 (2)	C25—C24—H24	120.5
C15—C14—C17	121.3 (2)	C23—C24—H24	120.5
C16—C15—C14	121.1 (2)	N2—C25—C24	119.96 (19)
C16—C15—H15	119.5	N2—C25—H25	120.0
C14—C15—H15	119.5	C24—C25—H25	120.0
O12—S1—C11—C12	-27.38 (17)	C13—C14—C15—C16	1.5 (3)
O13—S1—C11—C12	-149.35 (15)	C17—C14—C15—C16	-178.9 (2)
O11—S1—C11—C12	91.76 (16)	C12—C11—C16—C15	-1.2 (3)
O12—S1—C11—C16	156.98 (15)	S1—C11—C16—C15	174.43 (16)
O13—S1—C11—C16	35.00 (18)	C14—C15—C16—C11	0.1 (3)
O11—S1—C11—C16	-83.89 (16)	C25—N2—C21—C22	1.0 (3)
C16—C11—C12—C13	0.7 (3)	N2—C21—C22—C23	-1.1 (3)
S1—C11—C12—C13	-174.98 (16)	C21—C22—C23—C24	0.1 (4)
C11—C12—C13—C14	1.0 (3)	C22—C23—C24—C25	1.1 (3)
C12—C13—C14—C15	-2.0 (3)	C21—N2—C25—C24	0.3 (3)
C12—C13—C14—C17	178.4 (2)	C23—C24—C25—N2	-1.3 (3)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N2—H2...O11	0.93 (3)	1.81 (3)	2.724 (2)	166 (3)
C21—H21...O13 ⁱ	0.95	2.41	3.306 (2)	157
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