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1-[(Methylsulfonyl)oxy]pyridin-1-ium methanesulfonate

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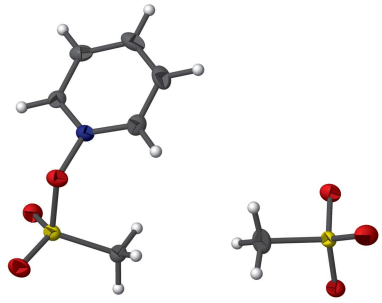
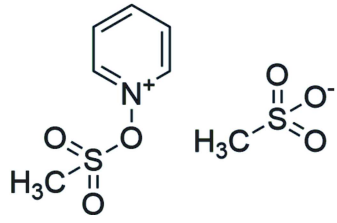
Structural data: full structural data are available from iucrdata.iucr.org

The title molecular salt, $C_6H_8NO_3S^+\cdot CH_3O_3S^-$, consists of a cationic sulfonated pyridine *N*-oxide moiety and a methanesulfonate anion. An N—O bond length of 1.4004 (15) Å is observed in the cation. In the crystal, weak C—H···O interactions link the components into a three-dimensional network.

3D view



Chemical scheme



Structure description

Zhen-Chu & Stang (1984) reported the synthesis of 1-{[(trifluoromethyl)sulfonyl]-oxy}pyridin-1-ium trifluoromethanesulfonate from pyridine *N*-oxide and trifluoromethanesulfonic anhydride. The reactivity of *O*-sulfonyl pyridinium salts toward nucleophiles and their substitution of the 2-position as reaction products were described by Umemoto *et al.* (1996). Rössler *et al.* (2019) reported the photochemical application of 1-{[(trifluoromethyl)sulfonyl]oxy}pyridin-1-ium trifluoromethanesulfonate, which allows direct amination of arenes and heteroarenes.

Here, we report the formation of 1-[(methylsulfonyl)oxy]pyridin-1-ium methanesulfonate, $C_6H_8NO_3S^+\cdot CH_3O_3S^-$, obtained from the reaction of pyridine-*N*-oxide and methanesulfonic anhydride. Its molecular structure (Fig. 1) consists of a cationic sulfonated pyridine *N*-oxide moiety and a methanesulfonate anion. The N—O bond length of 1.4004 (15) Å is similar to that observed in 1-{[(trifluoromethyl)sulfonyl]oxy}pyridin-1-ium trifluoromethanesulfonate [N—O = 1.4095 (11) Å; Rössler *et al.*, 2019]. Furthermore, O1 is 0.19 Å out of the pyridinium plane in the title compound and the N1—O1—S1—C6 torsion angle is 66.72 (11)°.

In the crystal, the components are linked by C—H···O interactions into a three-dimensional network (Table 1); the C5—H5···O4 bond with H···O = 2.19 Å is notably short.

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O5^{i}	0.95	2.29	3.1745 (19)	154
C3—H3···O4^{ii}	0.95	2.35	3.132 (2)	139
C4—H4···O2^{iii}	0.95	2.42	3.254 (2)	146
C5—H5···O4^{iv}	0.95	2.19	3.1008 (19)	159
C6—H6A···O5^{v}	0.98	2.39	3.1840 (19)	137
C6—H6B···O5^{i}	0.98	2.38	3.3023 (19)	157
C6—H6C···O6^{vi}	0.98	2.36	3.261 (2)	152

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

Synthesis and crystallization

Following a modified literature procedure of Rössler *et al.* (2019), a stirred solution of pyridine *N*-oxide (3.00 g, 31.6 mmol, 1.0 eq.) in DCM (100 ml) was treated dropwise with a solution of methanesulfonic anhydride (7.13 g, 37.9 mmol, 1.3 eq.) in DCM at −30°C. After complete addition, the reaction mixture was stirred for 2 h and allowed to warm to room temperature. The white precipitate was filtered and washed with fresh DCM (30 ml). Additional drying *in vacuo* yields the title compound (6.40 g, 23.8 mmol, 75%). Colourless needles suitable for X-ray crystal structure analysis were obtained by cooling a warm saturated acetonitrile solution to −30°C (Caution: heating to > 50°C leads to decomposition of the title compound.). ^{1}H NMR (400 MHz, acetonitrile-d_3) δ 8.7 (*s*, 2H), 8.1 (*s*, 1H), 7.9 (*s*, 2H), 3.5 (*s*, 2H), 2.6 (*s*, 3H). ^{13}C NMR (101 MHz, acetonitrile-d_3) δ 140.62, 129.10, 41.78, 39.65. IR (ATR, neat, cm^{-1}): 3108 (*w*), 3013 (*w*), 2986 (*w*), 2943 (*w*), 1606 (*w*), 1479 (*w*), 1428 (*w*), 1381 (*m*), 1330 (*w*), 1315 (*w*), 1289 (*w*), 1182 (*s*), 1163 (*s*), 1144 (*m*), 1040 (*s*), 1002 (*m*), 984 (*s*), 818 (*m*), 789 (*s*), 762 (*s*), 672 (*m*), 655 (*s*), 602 (*w*), 554 (*s*), 520 (*s*), 507 (*s*), 489 (*m*), 456 (*m*), 421 (*m*).

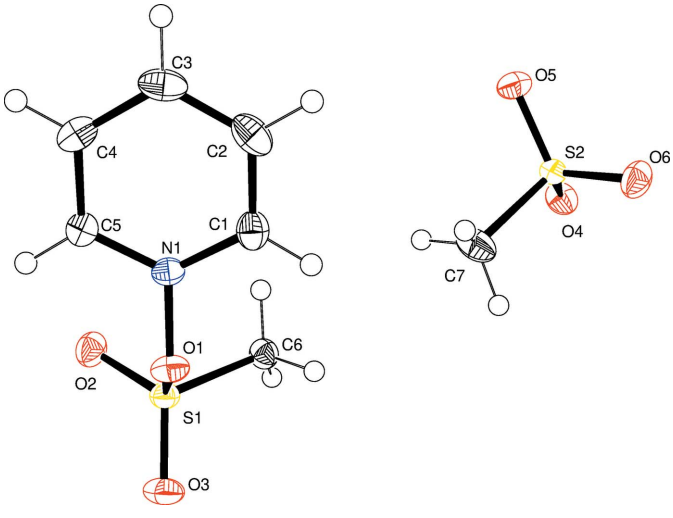


Figure 1
Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_8NO_3S^+\cdot CH_3O_3S^-$
M_r	269.29
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	7.9335 (3), 7.6255 (3), 18.3875 (7)
β (°)	99.0734 (14)
V (Å^3)	1098.47 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.50
Crystal size (mm)	0.36 × 0.08 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.84, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27689, 3400, 2732
R_{int}	0.033
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.718
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.098, 1.05
No. of reflections	3400
No. of parameters	147
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.29

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Analysis (%) calculated for $C_7H_{11}NO_6S_2$: C, 31.22; H, 4.12; N, 5.20; S, 23.81. Found: C, 31.02; H, 4.61; N, 4.93; S, 23.62.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

IUCrData (2021). **6**, x211026 [https://doi.org/10.1107/S2414314621010269]

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Crystal data

$C_6H_8NO_3S^+·CH_3O_3S^-$
M_r = 269.29
Monoclinic, $P2_1/c$
a = 7.9335 (3) Å
b = 7.6255 (3) Å
c = 18.3875 (7) Å
β = 99.0734 (14)°
V = 1098.47 (7) Å^3
Z = 4
$F(000)$ = 560
D_x = 1.628 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8765 reflections
θ = 2.2–30.6°
μ = 0.50 mm^{-1}
T = 150 K
Needle, colourless
0.36 × 0.08 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.84, T_{max} = 0.96
27689 measured reflections
3400 independent reflections
2732 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 30.7°, θ_{min} = 2.2°
h = −11→11
k = −10→10
l = −26→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.05
3400 reflections
147 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.5052P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7438 (2)	0.3898 (2)	0.41962 (9)	0.0246 (3)
H1	0.710677	0.472427	0.381358	0.030*
C2	0.6250 (2)	0.3078 (3)	0.45464 (10)	0.0314 (4)
H2	0.507103	0.332900	0.440638	0.038*
C3	0.6775 (2)	0.1881 (2)	0.51058 (10)	0.0297 (4)
H3	0.595713	0.131149	0.534962	0.036*
C4	0.8495 (2)	0.1523 (2)	0.53060 (9)	0.0248 (3)
H4	0.886377	0.070444	0.568762	0.030*
C5	0.96647 (19)	0.2354 (2)	0.49509 (8)	0.0203 (3)
H5	1.085198	0.213089	0.508170	0.024*
C6	0.95043 (19)	0.3470 (2)	0.27306 (8)	0.0215 (3)
H6A	0.993775	0.324167	0.226919	0.032*
H6B	0.886302	0.457327	0.268887	0.032*
H6C	0.875225	0.250804	0.282868	0.032*
C7	0.5041 (2)	0.4202 (3)	0.19949 (11)	0.0349 (4)
H7A	0.549811	0.518471	0.174279	0.052*
H7B	0.583596	0.321159	0.202500	0.052*
H7C	0.489657	0.456406	0.249278	0.052*
N1	0.90840 (16)	0.34870 (16)	0.44154 (7)	0.0182 (2)
O1	1.02878 (14)	0.45125 (15)	0.41284 (6)	0.0228 (2)
O2	1.18327 (14)	0.19494 (16)	0.36976 (7)	0.0269 (3)
O3	1.23496 (15)	0.50071 (17)	0.33542 (7)	0.0295 (3)
O4	0.33727 (14)	0.30518 (17)	0.07686 (6)	0.0259 (3)
O5	0.24872 (14)	0.20919 (15)	0.19056 (6)	0.0252 (2)
O6	0.19265 (15)	0.50693 (16)	0.14815 (7)	0.0285 (3)
S1	1.12073 (5)	0.36235 (5)	0.34493 (2)	0.01954 (10)
S2	0.30549 (4)	0.35686 (5)	0.15000 (2)	0.01779 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0256 (7)	0.0232 (8)	0.0244 (8)	0.0051 (6)	0.0019 (6)	−0.0025 (6)
C2	0.0202 (7)	0.0375 (10)	0.0370 (9)	0.0025 (7)	0.0063 (7)	−0.0092 (8)
C3	0.0301 (8)	0.0286 (9)	0.0345 (9)	−0.0074 (7)	0.0174 (7)	−0.0081 (7)
C4	0.0364 (9)	0.0188 (7)	0.0211 (7)	−0.0004 (6)	0.0103 (6)	−0.0008 (6)
C5	0.0234 (7)	0.0191 (7)	0.0185 (7)	0.0017 (6)	0.0037 (5)	−0.0021 (5)
C6	0.0213 (7)	0.0232 (8)	0.0196 (7)	−0.0004 (6)	0.0018 (5)	−0.0006 (6)
C7	0.0247 (8)	0.0409 (11)	0.0374 (10)	−0.0099 (8)	−0.0006 (7)	−0.0060 (8)
N1	0.0205 (6)	0.0158 (6)	0.0191 (6)	−0.0019 (5)	0.0058 (5)	−0.0019 (5)
O1	0.0279 (5)	0.0188 (5)	0.0228 (5)	−0.0065 (4)	0.0080 (4)	−0.0023 (4)
O2	0.0254 (6)	0.0273 (6)	0.0288 (6)	0.0067 (5)	0.0068 (5)	0.0053 (5)
O3	0.0290 (6)	0.0309 (7)	0.0301 (6)	−0.0125 (5)	0.0092 (5)	0.0003 (5)
O4	0.0234 (5)	0.0336 (7)	0.0218 (5)	0.0011 (5)	0.0066 (4)	−0.0027 (5)
O5	0.0286 (6)	0.0198 (6)	0.0284 (6)	−0.0039 (5)	0.0082 (5)	0.0022 (5)
O6	0.0326 (6)	0.0242 (6)	0.0304 (6)	0.0097 (5)	0.0098 (5)	0.0047 (5)

S1	0.01875 (17)	0.01993 (19)	0.02037 (18)	−0.00212 (13)	0.00443 (13)	0.00094 (13)
S2	0.01614 (16)	0.01827 (18)	0.01905 (18)	−0.00070 (12)	0.00307 (12)	0.00026 (13)

Geometric parameters (Å, º)

C1—N1	1.3418 (19)	C6—H6B	0.9800
C1—C2	1.373 (2)	C6—H6C	0.9800
C1—H1	0.9500	C7—S2	1.7586 (17)
C2—C3	1.389 (3)	C7—H7A	0.9800
C2—H2	0.9500	C7—H7B	0.9800
C3—C4	1.383 (3)	C7—H7C	0.9800
C3—H3	0.9500	N1—O1	1.4004 (15)
C4—C5	1.371 (2)	O1—S1	1.6847 (11)
C4—H4	0.9500	O2—S1	1.4188 (12)
C5—N1	1.336 (2)	O3—S1	1.4195 (12)
C5—H5	0.9500	O4—S2	1.4610 (12)
C6—S1	1.7384 (15)	O5—S2	1.4605 (12)
C6—H6A	0.9800	O6—S2	1.4500 (12)
N1—C1—C2	117.39 (15)	S2—C7—H7B	109.5
N1—C1—H1	121.3	H7A—C7—H7B	109.5
C2—C1—H1	121.3	S2—C7—H7C	109.5
C1—C2—C3	119.94 (15)	H7A—C7—H7C	109.5
C1—C2—H2	120.0	H7B—C7—H7C	109.5
C3—C2—H2	120.0	C5—N1—C1	125.35 (14)
C4—C3—C2	119.65 (16)	C5—N1—O1	117.54 (12)
C4—C3—H3	120.2	C1—N1—O1	116.47 (13)
C2—C3—H3	120.2	N1—O1—S1	117.09 (9)
C5—C4—C3	119.68 (16)	O2—S1—O3	120.71 (7)
C5—C4—H4	120.2	O2—S1—O1	107.09 (7)
C3—C4—H4	120.2	O3—S1—O1	98.72 (7)
N1—C5—C4	117.98 (14)	O2—S1—C6	111.99 (8)
N1—C5—H5	121.0	O3—S1—C6	113.03 (8)
C4—C5—H5	121.0	O1—S1—C6	102.42 (7)
S1—C6—H6A	109.5	O6—S2—O5	112.42 (7)
S1—C6—H6B	109.5	O6—S2—O4	112.76 (7)
H6A—C6—H6B	109.5	O5—S2—O4	111.97 (7)
S1—C6—H6C	109.5	O6—S2—C7	107.14 (9)
H6A—C6—H6C	109.5	O5—S2—C7	105.72 (9)
H6B—C6—H6C	109.5	O4—S2—C7	106.25 (8)
S2—C7—H7A	109.5		
O1—N1—C1—C2	−171.14 (14)	C2—C1—N1—C5	−0.5 (2)
N1—C1—C2—C3	0.2 (3)	C2—C1—N1—O1	−171.14 (14)
C1—C2—C3—C4	0.0 (3)	C5—N1—O1—S1	85.36 (14)
C2—C3—C4—C5	0.1 (3)	C1—N1—O1—S1	−103.28 (13)
C3—C4—C5—N1	−0.3 (2)	N1—O1—S1—O2	−51.23 (11)
C4—C5—N1—C1	0.6 (2)	N1—O1—S1—O3	−177.23 (10)

C4—C5—N1—O1	171.09 (13)	N1—O1—S1—C6	66.72 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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