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Bis[4-(2-nitrobenzenesulfonamido)-pyridinium] hexafluorosilicate

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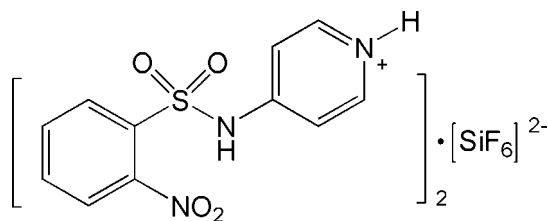
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Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.043; wR factor = 0.111; data-to-parameter ratio = 14.5.

In the title compound, $2\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_4\text{S}^+\cdot\text{SiF}_6^{2-}$, the short C—N distance [1.386 (2) Å] is indicative of a slight conjugation of N with the π electrons of the pyridinium ring, and with those of the sulfonyl group. The dihedral angle between the benzene and pyridinium rings is 77.48 (7)°. The crystal structure is stabilized by N—H...F and C—H...F hydrogen bonds. The Si atom of the anion lies on a special position.

Related literature

For zwitterionic forms of *N*-arylbenzenesulfonamides, see: Li *et al.* (2007); Yu & Li (2007). For reference geometric data, see: Allen *et al.* (1987). Damiano *et al.* (2007) describe the use of pyridinium derivatives for the construction of supra-molecular architectures.



Experimental

Crystal data

 $2\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_4\text{S}^+\cdot\text{SiF}_6^{2-}$ $M_r = 702.65$

Monoclinic, $C2/c$
 $a = 22.691$ (5) Å
 $b = 8.524$ (2) Å
 $c = 14.776$ (3) Å
 $\beta = 110.95$ (3)°
 $V = 2669$ (1) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.35$ mm⁻¹
 $T = 113$ (2) K
 $0.22 \times 0.16 \times 0.04$ mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MS, 2005)
 $T_{\min} = 0.927$, $T_{\max} = 0.986$

10620 measured reflections
3064 independent reflections
2456 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.111$
 $S = 1.06$
3064 reflections
212 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...F1 ⁱ	0.86 (3)	1.96 (3)	2.789 (2)	162 (3)
N2—H2N...F1 ⁱⁱ	0.73 (3)	1.97 (3)	2.690 (2)	171 (3)
C4—H4...F2 ⁱ	0.95	2.35	3.141 (2)	141
C5—H5...F3 ⁱⁱ	0.95	2.50	3.426 (3)	165

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

Data collection: *CrystalClear* (Rigaku/MS, 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: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2077).

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supplementary materials

Acta Cryst. (2008). E64, o2405 [doi:10.1107/S1600536808038191]

Bis[4-(2-nitrobenzenesulfonamido)pyridinium] hexafluorosilicate

A.-R. Wang

Comment

Organic pyridinium salts have been widely used in the construction of supramolecular architectures (Damiano *et al.*, 2007). As part of our ongoing studies of supramolecular chemistry involving the pyridinium rings (Li *et al.*, 2007), herein we report the crystal structure of the title compound, 4-(2-nitrophenylsulfonylamino)pyridinium hexafluorosilicate (Fig. 1).

In the cations of the title compound the short C—N distance [N2—C1 = 1.386 (2) Å] has a value between those of a typical C=N double and C—N single bond (1.47–1.50 Å and 1.34–1.38 Å, respectively; Allen *et al.*, 1987). This might be indicative of a slight conjugation of N with π electrons of the pyridinium ring, and with those of the sulfonyl group. The dihedral angle between the benzene ring and the pyridinium ring is 77.48 (7)°. The crystal structure is stabilized by N—H \cdots F and C—H \cdots F hydrogen bonds (Table 1).

Experimental

A solution of 2-nitrobenzenesulfonyl chloride (2.2 g, 10 mmol) in CH₂Cl₂ (10 ml) was added dropwise to a suspension of 4-aminopyridine (0.9 g, 10 mmol) in CH₂Cl₂ (10 ml) at room temperature with stirring. The reaction mixture was stirred overnight. The yellow solid obtained was washed with warm water to obtain the title compound in a yield of 55.3%. A colorless single crystal suitable for X-ray analysis was obtained by slow evaporation of a fluorosilicic acid (10%) solution at room temperature over a period of a week.

Refinement

The N-bound H atoms were located in a difference density Fourier map and freely refined. The C-bound H atoms were positioned geometrically (C—H = 0.95 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

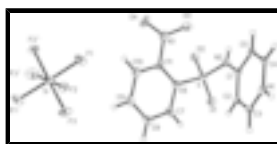


Fig. 1. View of one molecule of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level (arbitrary spheres for the H atoms). [Symmetry code: (i) $-x + 2, y, -z + 3/2$.]

Bis[4-(2-nitrobenzenesulfonamido)pyridinium] hexafluorosilicate

Crystal data

$2\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_4\text{S}^+\cdot\text{SiF}_6^{2-}$

$M_r = 702.65$

$F_{000} = 1432$

$D_x = 1.749 \text{ Mg m}^{-3}$

supplementary materials

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 22.691\ (5)\ \text{\AA}$

$b = 8.524\ (2)\ \text{\AA}$

$c = 14.776\ (3)\ \text{\AA}$

$\beta = 110.95\ (3)^\circ$

$V = 2669\ (1)\ \text{\AA}^3$

$Z = 4$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3772 reflections

$\theta = 1.9\text{--}27.5^\circ$

$\mu = 0.35\ \text{mm}^{-1}$

$T = 113\ (2)\ \text{K}$

Block, colourless

$0.22 \times 0.16 \times 0.04\ \text{mm}$

Data collection

Rigaku Saturn CCD area-detector diffractometer

Radiation source: rotating anode

Monochromator: confocal

Detector resolution: $7.31\ \text{pixels mm}^{-1}$

$T = 113(2)\ \text{K}$

ω and φ scans

Absorption correction: multi-scan (CrystalClear; Rigaku/MSO, 2005)

$T_{\min} = 0.927$, $T_{\max} = 0.986$

10620 measured reflections

3064 independent reflections

2456 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 1.9^\circ$

$h = -22 \rightarrow 29$

$k = -10 \rightarrow 11$

$l = -18 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.111$

$S = 1.06$

3064 reflections

212 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 1.0092P]$

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

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

$\Delta\rho_{\max} = 0.38\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.49\ \text{e \AA}^{-3}$

Extinction correction: none

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. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculat-

ing R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R- factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.61983 (2)	0.29097 (5)	0.52758 (4)	0.01969 (15)
O1	0.58452 (8)	0.32136 (18)	0.42794 (11)	0.0273 (4)
O2	0.63133 (8)	0.13308 (16)	0.56235 (12)	0.0282 (4)
O3	0.69576 (9)	0.3188 (2)	0.75056 (13)	0.0473 (5)
O4	0.78705 (10)	0.2230 (3)	0.7737 (2)	0.0843 (10)
N1	0.56160 (8)	0.8430 (2)	0.63088 (13)	0.0192 (4)
H1N	0.5583 (14)	0.942 (3)	0.639 (2)	0.052 (9)*
N2	0.58416 (9)	0.3725 (2)	0.59405 (14)	0.0194 (4)
H2N	0.5795 (14)	0.315 (3)	0.628 (2)	0.043 (9)*
N3	0.74149 (10)	0.3008 (2)	0.72703 (15)	0.0363 (5)
C1	0.57577 (9)	0.5317 (2)	0.60418 (14)	0.0167 (4)
C2	0.57532 (9)	0.6398 (2)	0.53308 (14)	0.0177 (4)
H2	0.5800	0.6058	0.4748	0.021*
C3	0.56798 (9)	0.7955 (2)	0.54852 (15)	0.0193 (4)
H3	0.5674	0.8704	0.5006	0.023*
C4	0.56074 (9)	0.7410 (2)	0.70051 (14)	0.0195 (4)
H4	0.5555	0.7784	0.7577	0.023*
C5	0.56742 (9)	0.5837 (2)	0.68832 (14)	0.0185 (4)
H5	0.5664	0.5109	0.7364	0.022*
C6	0.69299 (10)	0.3905 (2)	0.55358 (15)	0.0192 (4)
C7	0.70103 (11)	0.4743 (2)	0.47788 (16)	0.0258 (5)
H7	0.6675	0.4795	0.4169	0.031*
C8	0.75749 (12)	0.5503 (3)	0.49066 (18)	0.0309 (5)
H8	0.7620	0.6078	0.4385	0.037*
C9	0.80672 (11)	0.5435 (3)	0.57748 (19)	0.0307 (5)
H9	0.8451	0.5965	0.5854	0.037*
C10	0.80059 (10)	0.4591 (3)	0.65379 (18)	0.0295 (5)
H10	0.8347	0.4530	0.7141	0.035*
C11	0.74405 (10)	0.3839 (3)	0.64084 (16)	0.0249 (5)
Si	1.0000	0.65155 (9)	0.7500	0.01731 (19)
F1	0.94232 (7)	0.64561 (14)	0.79977 (10)	0.0303 (3)
F2	0.96119 (6)	0.51233 (14)	0.67115 (9)	0.0265 (3)
F3	0.96052 (7)	0.79039 (14)	0.67359 (9)	0.0333 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0207 (3)	0.0158 (3)	0.0229 (3)	−0.0010 (2)	0.0083 (2)	−0.00471 (19)
O1	0.0294 (9)	0.0304 (8)	0.0199 (8)	−0.0032 (7)	0.0060 (6)	−0.0071 (6)
O2	0.0324 (9)	0.0145 (7)	0.0426 (10)	0.0012 (7)	0.0196 (8)	−0.0020 (7)
O3	0.0360 (11)	0.0728 (14)	0.0333 (11)	0.0026 (10)	0.0127 (8)	0.0205 (10)
O4	0.0312 (11)	0.112 (2)	0.104 (2)	0.0222 (13)	0.0172 (12)	0.0855 (17)

supplementary materials

N1	0.0217 (9)	0.0125 (8)	0.0228 (10)	0.0012 (7)	0.0073 (7)	-0.0012 (7)
N2	0.0221 (9)	0.0136 (8)	0.0242 (10)	0.0014 (7)	0.0104 (7)	0.0011 (7)
N3	0.0227 (10)	0.0443 (13)	0.0350 (12)	-0.0019 (9)	0.0019 (9)	0.0175 (10)
C1	0.0135 (9)	0.0149 (9)	0.0205 (10)	-0.0005 (8)	0.0045 (7)	-0.0011 (8)
C2	0.0195 (10)	0.0196 (10)	0.0138 (10)	0.0015 (8)	0.0060 (8)	-0.0017 (8)
C3	0.0184 (10)	0.0182 (10)	0.0195 (10)	0.0009 (8)	0.0048 (8)	0.0026 (8)
C4	0.0178 (10)	0.0244 (10)	0.0165 (10)	0.0018 (9)	0.0064 (8)	-0.0008 (8)
C5	0.0177 (10)	0.0195 (10)	0.0182 (10)	-0.0008 (8)	0.0063 (8)	0.0003 (8)
C6	0.0202 (10)	0.0168 (9)	0.0219 (11)	0.0020 (8)	0.0092 (8)	-0.0028 (8)
C7	0.0293 (12)	0.0270 (11)	0.0237 (12)	0.0011 (10)	0.0126 (9)	-0.0029 (9)
C8	0.0367 (14)	0.0297 (12)	0.0359 (14)	-0.0016 (11)	0.0247 (11)	-0.0002 (10)
C9	0.0225 (11)	0.0292 (11)	0.0457 (15)	-0.0018 (10)	0.0184 (10)	-0.0011 (11)
C10	0.0187 (11)	0.0289 (11)	0.0377 (14)	0.0019 (10)	0.0060 (9)	0.0040 (10)
C11	0.0216 (11)	0.0230 (10)	0.0295 (12)	0.0044 (9)	0.0083 (9)	0.0044 (9)
Si	0.0263 (4)	0.0132 (4)	0.0144 (4)	0.000	0.0098 (3)	0.000
F1	0.0431 (8)	0.0202 (6)	0.0393 (8)	0.0036 (6)	0.0292 (7)	0.0010 (5)
F2	0.0306 (7)	0.0222 (6)	0.0233 (7)	-0.0018 (6)	0.0056 (5)	-0.0054 (5)
F3	0.0505 (9)	0.0225 (7)	0.0248 (7)	0.0093 (6)	0.0110 (6)	0.0072 (5)

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

S—O1	1.426 (2)	C4—H4	0.9500
S—O2	1.431 (2)	C5—H5	0.9500
S—N2	1.634 (2)	C6—C11	1.393 (3)
S—C6	1.779 (2)	C6—C7	1.393 (3)
O3—N3	1.216 (3)	C7—C8	1.387 (3)
O4—N3	1.214 (3)	C7—H7	0.9500
N1—C3	1.338 (3)	C8—C9	1.368 (3)
N1—C4	1.353 (3)	C8—H8	0.9500
N1—H1N	0.86 (3)	C9—C10	1.385 (3)
N2—C1	1.386 (2)	C9—H9	0.9500
N2—H2N	0.73 (3)	C10—C11	1.385 (3)
N3—C11	1.477 (3)	C10—H10	0.9500
C1—C2	1.395 (3)	Si—F3 ⁱ	1.6597 (14)
C1—C5	1.395 (3)	Si—F3	1.6597 (14)
C2—C3	1.367 (3)	Si—F2	1.6756 (13)
C2—H2	0.9500	Si—F2 ⁱ	1.6756 (13)
C3—H3	0.9500	Si—F1 ⁱ	1.7161 (13)
C4—C5	1.368 (3)	Si—F1	1.7161 (13)
O1—S—O2	120.30 (10)	C7—C6—S	116.81 (16)
O1—S—N2	109.10 (10)	C8—C7—C6	120.7 (2)
O2—S—N2	104.47 (10)	C8—C7—H7	119.7
O1—S—C6	105.83 (10)	C6—C7—H7	119.7
O2—S—C6	109.54 (10)	C9—C8—C7	120.8 (2)
N2—S—C6	106.98 (10)	C9—C8—H8	119.6
C3—N1—C4	122.20 (18)	C7—C8—H8	119.6
C3—N1—H1N	118 (2)	C8—C9—C10	119.9 (2)
C4—N1—H1N	120 (2)	C8—C9—H9	120.0

C1—N2—S	126.70 (16)	C10—C9—H9	120.0
C1—N2—H2N	122 (2)	C11—C10—C9	119.0 (2)
S—N2—H2N	110 (2)	C11—C10—H10	120.5
O4—N3—O3	123.2 (2)	C9—C10—H10	120.5
O4—N3—C11	117.7 (2)	C10—C11—C6	122.2 (2)
O3—N3—C11	119.09 (19)	C10—C11—N3	115.0 (2)
N2—C1—C2	122.01 (19)	C6—C11—N3	122.8 (2)
N2—C1—C5	118.34 (18)	F3 ⁱ —Si—F3	89.03 (10)
C2—C1—C5	119.64 (18)	F3 ⁱ —Si—F2	178.59 (7)
C3—C2—C1	118.97 (19)	F3—Si—F2	90.59 (7)
C3—C2—H2	120.5	F3 ⁱ —Si—F2 ⁱ	90.59 (7)
C1—C2—H2	120.5	F3—Si—F2 ⁱ	178.59 (7)
N1—C3—C2	120.30 (19)	F2—Si—F2 ⁱ	89.82 (9)
N1—C3—H3	119.8	F3 ⁱ —Si—F1 ⁱ	90.21 (7)
C2—C3—H3	119.8	F3—Si—F1 ⁱ	92.20 (7)
N1—C4—C5	119.82 (19)	F2—Si—F1 ⁱ	88.45 (7)
N1—C4—H4	120.1	F2 ⁱ —Si—F1 ⁱ	89.16 (7)
C5—C4—H4	120.1	F3 ⁱ —Si—F1	92.20 (7)
C4—C5—C1	119.02 (19)	F3—Si—F1	90.21 (7)
C4—C5—H5	120.5	F2—Si—F1	89.16 (7)
C1—C5—H5	120.5	F2 ⁱ —Si—F1	88.45 (7)
C11—C6—C7	117.3 (2)	F1 ⁱ —Si—F1	176.62 (9)
C11—C6—S	125.73 (17)		
O1—S—N2—C1	-65.8 (2)	O2—S—C6—C7	131.78 (16)
O2—S—N2—C1	164.31 (18)	N2—S—C6—C7	-115.54 (17)
C6—S—N2—C1	48.2 (2)	C11—C6—C7—C8	-1.3 (3)
S—N2—C1—C2	24.9 (3)	S—C6—C7—C8	-177.48 (17)
S—N2—C1—C5	-155.30 (16)	C6—C7—C8—C9	0.6 (3)
N2—C1—C2—C3	-178.80 (19)	C7—C8—C9—C10	0.4 (3)
C5—C1—C2—C3	1.4 (3)	C8—C9—C10—C11	-0.6 (3)
C4—N1—C3—C2	-1.5 (3)	C9—C10—C11—C6	-0.1 (3)
C1—C2—C3—N1	0.3 (3)	C9—C10—C11—N3	-178.4 (2)
C3—N1—C4—C5	0.9 (3)	C7—C6—C11—C10	1.0 (3)
N1—C4—C5—C1	0.7 (3)	S—C6—C11—C10	176.86 (17)
N2—C1—C5—C4	178.30 (18)	C7—C6—C11—N3	179.2 (2)
C2—C1—C5—C4	-1.9 (3)	S—C6—C11—N3	-5.0 (3)
O1—S—C6—C11	-175.15 (18)	O4—N3—C11—C10	-43.6 (3)
O2—S—C6—C11	-44.1 (2)	O3—N3—C11—C10	132.9 (2)
N2—S—C6—C11	68.6 (2)	O4—N3—C11—C6	138.1 (3)
O1—S—C6—C7	0.70 (18)	O3—N3—C11—C6	-45.4 (3)

Symmetry codes: (i) $-x+2, y, -z+3/2$.

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>
N1—H1N \cdots F1 ⁱⁱ	0.86 (3)	1.96 (3)	2.789 (2)	162 (3)

supplementary materials

N2—H2N \cdots F1 ⁱⁱⁱ	0.73 (3)	1.97 (3)	2.690 (2)	171 (3)
C4—H4 \cdots F2 ⁱⁱ	0.95	2.35	3.141 (2)	141
C5—H5 \cdots F3 ⁱⁱⁱ	0.95	2.50	3.426 (3)	165

Symmetry codes: (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x+3/2, y-1/2, -z+3/2$.

Fig. 1

