

N-Fluoropyridinium trifluoromethanesulfonate and 1-fluoro-2,4,6-trimethoxy-1,3,5-triazinium hexafluoroantimonate: the first experimental determination of the F—N⁺ bond length involving *sp*² nitrogen

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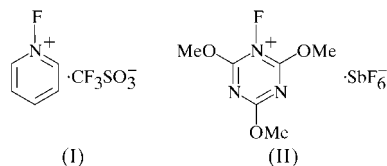
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The structures of *N*-fluoropyridinium trifluoromethanesulfonate, C₅H₅FN⁺·CF₃O₃S[−], (I), and 1-fluoro-2,4,6-trimethoxy-1,3,5-triazinium hexafluoroantimonate, (C₆H₉FN₃O₃)[SbF₆], (II), are presented. The N—F bond lengths in (I), a well known electrophilic fluorinating agent, and its novel analogue, (II), are 1.357 (4) and 1.354 (4) Å, respectively.

Comment

Prior to this study, the chloro analogue of the title triazine, (II), *viz.* [(ClCN)₃F][AsF₆] (Schleyer *et al.*, 1993), was the only F—N sp^{2+} -containing molecule to be reported by X-ray diffraction. However, the investigators rejected their experimental N—F⁺ bond length of 1.11 Å, due to the cations being severely disordered, and proposed, instead, a value of 1.314 Å, which they obtained from quantum-chemical calculations at the HF/6-31+G* level. This computed length was confirmed subsequently (Broschag *et al.*, 1994) and improved more recently using MP2 (1.360 Å) and B3LYP (1.349 Å) theory level calculations (Fraenk *et al.*, 2001). These latter values



show excellent agreement with the N—F⁺ length of 1.354 (4) Å established in the current study for the title triazinyl derivative, (II) (Fig. 2 and Table 2). At 1.357 (4) Å, the analogous bond in 1-fluoropyridinium trifluoromethanesulfonate, (I) (Fig. 1 and Table 1), is identical within experimental error, and also shows good agreement with the

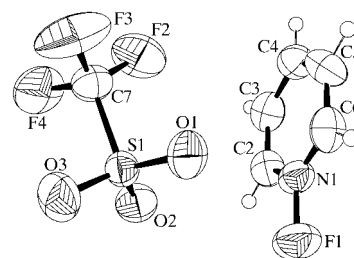


Figure 1

A view of the structure of (I) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

computed values of 1.323 (RHF level), 1.370 (MP2) and 1.357 Å (B3LYP) (Fraenk *et al.*, 2001).

Comparison of the title structures, (I) and (II), with their respective neutral precursors, pyridine (Mootz & Wussow, 1981) and trimethoxy-1,3,5-triazine (Główska & Iwanicka, 1989), reveals changes to the ring geometry that are similar to those seen on protonation. As expected, involvement of the N-atom lone pair in a covalent bond to F⁺ has significantly expanded the C—N—F bond angle in both (I) and (II). As a consequence, the remaining ring angles have also changed, the magnitude of the difference diminishing on traversing the ring away from the F site in the order *meta* > *ortho* > *para* (Table 3).

In the case of the pyridinium derivative, (I), a small contraction of the average ring bonds of between 0.024 and 0.010 Å can also be detected on forming the F⁺ adduct. In contrast, the bond-length changes in methoxytriazinyl, (II), are more complex and are strongly influenced by the OMe substituents, which are conjugated with the ring delocalization system. In the parent triazine, the OMe groups and the ring are coplanar, due to the molecule lying on a crystallographic mirror plane. Molecule (II) is also nearly planar, as shown by the C_{Me}—O—C—N torsion angles of 1.5 (6), −1.0 (6) and 1.3 (6)°. Also, like the parent molecule, the ring C—N bonds

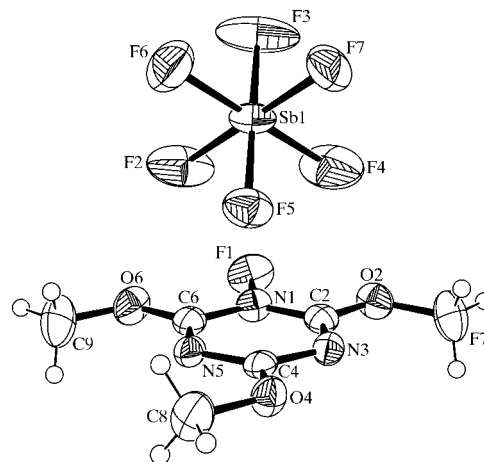


Figure 2

A view of the structure of (II) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

trans to OMe are considerably longer [1.349 (6), 1.344 (5) and 1.356 (6) Å] than the *cis* bonds [1.291 (5), 1.327 (5) and 1.292 (5) Å]. However, the C_{3h} symmetry of (MeOCN)₃ is lost in (II), because both OMe groups flanking the F-bonded N atom point away from F. Consequently, both N—C bonds to the F-bonded N atom are of the longer type [1.349 (6) and 1.356 (6) Å].

The fluoropyridinium and fluorotriazinium structures, (I) and (II), also differ in their crystal packing. Whereas there are no significant short interionic contacts in (I) (apart from three C—H...O contacts), in (II), each SbF₆[−] anion is sandwiched between two [(MeOCN)₃F]⁺ rings, and participates in several short interionic C...F contacts in the range 2.83 (1)–2.89 (1) Å. The three-point contact and central location of the [SbF₆][−] anion above one ring (Fig. 2) is reminiscent of the interaction between [SbF₆][−] and the central aromatic C₆ ring in hexaazaoctadecahydrovoronene tetrakis(hexafluoroantimonate) acetonitrile solvate (Miller *et al.*, 1990).

Experimental

A sample of (I) with appropriate NMR properties was prepared by an adaptation of the one-pot procedure of Umemoto *et al.* (1991) via direct flow fluorination of pyridine and LiOTf in MeCN at 238 K (Banks *et al.*, 1996). Suitable crystals were obtained by recrystallization from dry tetrahydrofuran (m.p. 459 K; literature value: 458–460 K). Analysis, found: C 28.9, H 1.9, N 5.6%; calculated for C₆H₅F₄NO₃S: C 29.1, H 2.0, N 5.7%. In order to prepare (II) (Banks & Besheesh, 2002), a homogeneous mixture of 2,4,6-trimethoxy-1,3,5-triazine (0.50 g, 2.92 mmol), hexafluoroantimonic acid (0.69 g, 2.92 mmol) and hexafluoro-2-propanol (80 ml) were placed in a Pyrex flow-fluorination reactor (Banks *et al.*, 1996). This mixture was cooled to 268 K, stirred vigorously and treated with a 1:9 (v/v) F₂/N₂ blend (flow rate 130 ml min^{−1}) until the exit gas gave a strong positive test (KI) for fluorine. The resulting colourless solution was concentrated under reduced pressure (volume reduced to about 10 ml) and then mixed with dry diethyl ether (50 ml), causing a brilliant-white crystalline solid to precipitate. This solid was collected by suction filtration, washed with dry diethyl ether (30 ml) and dried *in vacuo* to give a material which was identified by elemental and NMR analyses as 1-fluoro-2,4,6-trimethoxy-1,3,5-triazinium hexafluoroantimonate, (II) (1.22 g, 2.86 mmol, 98%; m.p. 484 K, decomposition). ¹H NMR (CD₃CN, TMS, δ): 4.59 (s, 2 × OCH₃), 4.44 (s, 1 × OCH₃); ¹⁹F NMR (CD₃CN, TFA, δ): 18.9 (*br s*, NF⁺), −20.75 to −79.95 (complex, SbF₆⁺). Elemental analysis, calculated for C₆H₆F₇N₃O₃Sb: C 17.0, H 2.1, N 9.9, Sb 28.6%; found: C 17.1, H 1.9, N 9.5, Sb 28.9%. Crystals of (I) and (II) suitable for X-ray analysis were grown by vapour diffusion of Et₂O into MeCN solutions.

Compound (I)

Crystal data

C ₅ H ₅ FN ⁺ ·CF ₃ O ₃ S [−]	$D_x = 1.742 \text{ Mg m}^{-3}$
$M_r = 247.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 6.027 (2) \text{ \AA}$	$\theta = 8.4\text{--}16.1^\circ$
$b = 12.901 (4) \text{ \AA}$	$\mu = 0.39 \text{ mm}^{-1}$
$c = 12.490 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 103.96 (3)^\circ$	Prism, colourless
$V = 942.5 (5) \text{ \AA}^3$	$0.40 \times 0.25 \times 0.25 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (Å, °) for (I).

N1—F1	1.357 (4)	C3—C4	1.350 (6)
N1—C2	1.322 (6)	C4—C5	1.385 (7)
N1—C6	1.315 (6)	C5—C6	1.367 (7)
C2—C3	1.347 (7)		
F1—N1—C2	118.4 (4)	C2—C3—C4	118.9 (4)
F1—N1—C6	115.0 (4)	C3—C4—C5	119.3 (4)
C2—N1—C6	126.7 (4)	C4—C5—C6	121.6 (4)
N1—C2—C3	119.0 (4)	N1—C6—C5	114.6 (4)

Data collection

Rigaku AFC-6S diffractometer	$R_{\text{int}} = 0.034$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 25.3^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -7 \rightarrow 0$
$T_{\text{min}} = 0.809$, $T_{\text{max}} = 0.905$	$k = 0 \rightarrow 15$
1824 measured reflections	$l = -14 \rightarrow 14$
1658 independent reflections	3 standard reflections every 150 reflections
890 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.31P]$
$R(F) = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
1658 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
136 parameters	
H-atom parameters constrained	

Compound (II)

Crystal data

(C ₆ H ₆ FN ₃ O ₃)[SbF ₆]	$D_x = 2.119 \text{ Mg m}^{-3}$
$M_r = 425.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 7.616 (2) \text{ \AA}$	$\theta = 8.1\text{--}11.4^\circ$
$b = 11.843 (3) \text{ \AA}$	$\mu = 2.16 \text{ mm}^{-1}$
$c = 14.924 (3) \text{ \AA}$	$T = 203 (2) \text{ K}$
$\beta = 97.43 (2)^\circ$	Plate, colourless
$V = 1334.9 (6) \text{ \AA}^3$	$0.30 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Nonius MACH3 diffractometer	$R_{\text{int}} = 0.025$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -8 \rightarrow 2$
$T_{\text{min}} = 0.686$, $T_{\text{max}} = 0.803$	$k = 0 \rightarrow 14$
3200 measured reflections	$l = -17 \rightarrow 17$
2335 independent reflections	3 standard reflections every 150 reflections
1799 reflections with $I > 2\sigma(I)$	intensity decay: none

Table 2

Selected geometric parameters (Å, °) for (II).

F1—N1	1.353 (4)	N1—C2	1.349 (6)
O2—C2	1.290 (5)	N1—C6	1.356 (6)
O2—C7	1.466 (6)	N3—C2	1.291 (5)
O4—C4	1.291 (5)	N3—C4	1.344 (5)
O4—C8	1.454 (5)	N5—C4	1.327 (5)
O6—C6	1.285 (5)	N5—C6	1.292 (5)
O6—C9	1.463 (6)		
F1—N1—C2	119.2 (4)	C4—N5—C6	116.1 (4)
F1—N1—C6	119.2 (4)	N1—C2—N3	120.2 (4)
C2—N1—C6	121.6 (4)	N3—C4—N5	127.1 (4)
C2—N3—C4	115.4 (4)	N1—C6—N5	119.6 (4)

Table 3

Comparative ring angles (°) for the title adducts and their non-fluorinated analogues.

Aromatic ring	C—N—C	<i>meta</i>	<i>ortho</i>	<i>para</i>
[(C ₅ H ₅ N)F] [†]	126.7	116.9	120.2	119.4
C ₅ H ₅ N‡	116.6	123.7	118.6	118.8
(MeOCN) ₃ §	113.7	126.6	113.2	126.9
[(MeOCN) ₃ F] [†]	121.6	120.0	115.8	127.1

† This work. ‡ Mootz & Wussow (1981). § Główska & Iwanicka (1989).

Refinement

Refinement on F^2

$R(F) = 0.034$

$wR(F^2) = 0.071$

$S = 1.06$

2335 reflections

181 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 1.7485P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.98 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.66 \text{ e } \text{Å}^{-3}$$

H atoms were treated as riding, with C—H distances of 0.93 and 0.97 Å.

For compound (I), data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). For compound (II), data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1153). Services for accessing these data are described at the back of the journal.

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