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N-Fluoroquinuclidinium Trifluoromethanesulfonate (Triflate): a Novel Electrophilic Fluorinating Agent

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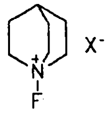
Abstract

The N—F bond length of 1.407 (6) Å in the title molecule is close to the value of 1.37 (2) Å found in 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) [Banks, Sharif & Pritchard (1993). *Acta Cryst.* C**49**, 492-495]. Both these bonds are substantially longer than those in $NF_4^+.BF_4^-$, which range from 1.265 (9) to 1.321 (10) Å [Christie, Lind, Thorup, Russell, Fawcett & Bau (1988). *Inorg. Chem.* **27**, 2450-2454].

Comment

Several novel *N*-fluoroquinuclidinium salts (I) have been synthesized recently (Banks, Du Boisson, Morton & Tsiliopoulos, 1988; Banks & Sharif, 1991) as part of the continuing search for safe, easily handled, non-gaseous electrophilic fluorinating agents for use in organic synthesis (Furin, 1989). In connection with mechanistic studies of the mode of action of these salts, and the stereochemistry involved (Banks, Mohialdin-Khaffaf & Sharif, 1993), the molecular parameters of the trifluoromethanesulfonate (triflate) salt (I) ($X^- = CF_3SO_3^-$) have been determined.



(I)

$X^- = CF_3SO_2O^-$, F^-, BF_4^-
$CF_3CO_2^-$, $C_3F_7CO_2^-$

The barrel-shaped quinuclidine moiety is bisected top-to-bottom by a crystallographic mirror plane. Its dimensions are close to those of a recently determined quinuclidine–boron trifluoride adduct (Banks, Besheesh, Pritchard & Sharif, 1993).

While the N^+—F bond [1.407 (6) Å] in *N*-fluoroquinuclidinium trifluoromethanesulfonate is substantially longer than any of those in tetrafluoroammonium tetrafluoroborate [1.265 (9)–1.321 (10) Å (Christie, Lind, Thorup, Russell, Fawcett & Bau, 1988)], it is close to that found in 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), the only other *N*-fluoroammonium salt to have been examined crystallographically [1.37 (2) Å (Banks, Sharif & Pritchard, 1993)]. Interestingly, the longer bonds agree well with N—F distances observed in several *N*,*N*-difluoroamino compounds (*i.e.* tertiary amines), *e.g.* 2,4,6-$(NO_2)_3C_6H_2NF_2$ [1.391, 1.404 Å (Batail & Grandjean, 1975)], 2,4-$(NO_2)_2C_6H_3NF_2$ [1.380–1.415 Å (Batail, Louër, Grandjean, Dudragne & Michaud, 1976)] and 4-BrC_6H_5-$(C_6H_5)_2CNF_2$ [1.407, 1.417 Å (Surles, Bumgardner & Bordner, 1975)].

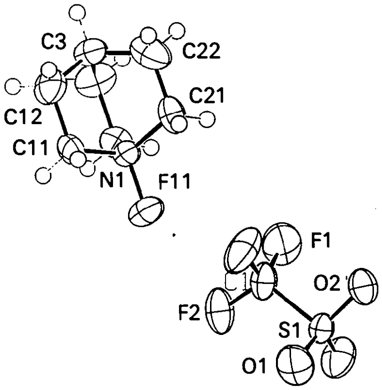


Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).

Experimental

Crystal data

$C_7H_{13}FN^+.CF_3O_3S^-$
$M_r = 279.25$

Mo *Kα* radiation
$\lambda = 0.71069$ Å

Orthorhombic
Pnma
$a = 13.407\ (9)$ Å
$b = 8.483\ (8)$ Å
$c = 9.940\ (8)$ Å
$V = 1130\ (3)$ Å^3
$Z = 4$
$D_x = 1.640$ Mg m^{-3}

Cell parameters from 22 reflections
$\theta = 26.81\text{-}39.14°$
$\mu = 0.3239$ mm^{-1}
$T = 296$ K
Triangular prism
$0.40 \times 0.20 \times 0.20$ mm
Colourless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.7$, $T_{\max} = 1.0$
1187 measured reflections
1187 independent reflections
729 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.00$
$\theta_{\max} = 25.0089°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections
monitored every 150 reflections
intensity variation: -11.00%

Refinement

Refinement on F
Final $R = 0.0557$
$wR = 0.0718$
$S = 2.692$
729 reflections
92 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0006$

$\Delta\rho_{\max} = 0.45290$ e Å^{-3}
$\Delta\rho_{\min} = -0.42011$ e Å^{-3}
Extinction correction: Zachariasen type 2 Gaussian isotropic
Extinction coefficient: 8.94×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*; *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*; *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.5185 (4)	0.2500	0.6562 (5)	0.0383
C3	0.4830 (6)	0.2500	0.9016 (6)	0.0512
C11	0.4594 (4)	0.3947 (5)	0.6860 (5)	0.0459
C12	0.4397 (5)	0.3948 (6)	0.8372 (6)	0.0678
C21	0.6161 (5)	0.2500	0.7259 (8)	0.0522
C22	0.5949 (8)	0.2500	0.8764 (8)	0.0810
F11	0.5372 (3)	0.2500	0.5170 (4)	0.0623
S1	0.8299 (1)	0.2500	0.1808 (2)	0.0390
F1	0.7440 (3)	0.3760 (4)	0.3891 (3)	0.0938
F2	0.6441 (3)	0.2500	0.2608 (5)	0.0799
O1	0.8104 (3)	0.1098 (4)	0.1073 (3)	0.0705
O2	0.9207 (4)	0.2500	0.2584 (5)	0.0710
C1	0.7363 (5)	0.2500	0.3114 (8)	0.0518

Table 2. *Geometric parameters* (Å, °)

N1—C11	1.491 (5)	C3—C22	1.52 (1)
N1—C21	1.481 (8)	C11—C12	1.526 (7)
N1—F11	1.407 (6)	C21—C22	1.52 (1)
C3—C12	1.502 (7)		
C11—N1—C11	110.9 (5)	C12—C3—C22	108.2 (4)
C11—N1—C21	112.1 (3)	N1—C11—C12	106.8 (4)
C11—N1—F11	106.9 (3)	C3—C12—C11	110.6 (5)
C21—N1—F11	107.6 (5)	N1—C21—C22	107.1 (6)
C12—C3—C12	109.7 (7)	C3—C22—C21	110.2 (6)

N-Fluoroquinuclidinium trifluoromethanesulfonate was prepared by passing neat fluorine at a pressure of 10–20 mmHg (1 mmHg = 133.322 Pa) into cold (238 K) dry acetonitrile (200 cm^3) containing equimolar quantities of quinuclidine (21.4 mmol) and lithium trifluoromethanesulfonate (21.4 mmol) (Banks & Sharif, 1991) until the calculated amount had been absorbed (5.5 h). The reaction mixture was filtered to remove lithium fluoride and then evaporated; the residual solid was taken up in AnalaR acetone and *N*-fluoroquinuclidinium trifluoromethanesulfonate (99% crude, 88% pure yield) precipitated by the addition of ethyl acetate. A sample of the analytically pure (C, H, F, N, S combustion analysis) product thus isolated was then recrystallized by allowing ethyl acetate vapour to diffuse into its solution in AnalaR acetone.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71248 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1049]

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