C17	0.3903 (2)	0.5705 (4)	0.2854 (2)	0.0466
C18	0.6010 (2)	0.3862 (5)	0.1326 (2)	0.0496
C19	0.6937 (3)	0.1047 (10)	0.4787 (3)	0.1038
C20	0.6389 (3)	0.6185 (5)	0.3698 (3)	0.0632
C21	0.3749 (3)	−0.1621 (7)	0.0645 (3)	0.0698

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

O6—C13	1.219 (4)	C7—C8	1.387 (4)
C1—C2	1.570 (4)	C8—C9	1.526 (4)
C1—C14	1.528 (4)	C9—C10	1.549 (4)
C1—C15	1.550 (4)	C10—C11	1.512 (4)
C2—C3	1.540 (4)	C11—C12	1.347 (4)
C3—C4	1.397 (4)	C11—C15	1.539 (4)
C3—C8	1.411 (4)	C12—C13	1.484 (4)
C4—C5	1.389 (5)	C12—C18	1.509 (5)
C5—C6	1.374 (5)	C13—C14	1.504 (4)
C6—C7	1.373 (5)		
O1—C1—C2	105.8 (2)	O4—C9—C10	107.6 (2)
O1—C1—C14	108.7 (2)	C8—C9—C10	109.9 (2)
O1—C1—C15	107.7 (2)	O5—C10—C9	107.9 (2)
C2—C1—C14	113.9 (2)	O5—C10—C11	115.5 (2)
C2—C1—C15	111.7 (2)	C9—C10—C11	109.9 (2)
C14—C1—C15	108.9 (2)	C10—C11—C12	119.2 (2)
O2—C2—C1	109.3 (2)	C10—C11—C15	121.2 (2)
O2—C2—C3	112.5 (2)	C12—C11—C15	118.9 (2)
C1—C2—C3	118.1 (2)	C11—C12—C13	119.6 (3)
C2—C3—C4	121.1 (2)	C11—C12—C18	125.8 (3)
C2—C3—C8	121.3 (2)	C13—C12—C18	114.3 (2)
C4—C3—C8	117.5 (3)	O6—C13—C12	121.4 (3)
O3—C4—C3	116.3 (3)	O6—C13—C14	119.6 (3)
O3—C4—C5	121.8 (3)	C12—C13—C14	118.7 (2)
C3—C4—C5	121.9 (3)	C1—C14—C13	115.6 (2)
C4—C5—C6	119.2 (3)	C1—C15—C11	105.3 (2)
C5—C6—C7	120.5 (3)	C1—C15—C16	111.4 (2)
C6—C7—C8	121.1 (3)	C1—C15—C17	110.7 (2)
C3—C8—C7	119.8 (3)	C11—C15—C16	116.9 (2)
C3—C8—C9	122.4 (2)	C11—C15—C17	108.1 (2)
C7—C8—C9	117.5 (3)	C16—C15—C17	104.4 (3)
O4—C9—C8	109.7 (2)		
C14—C1—C2—C3	46.1 (3)	C8—C9—C10—C11	50.7 (3)
C15—C1—C2—C3	−77.8 (3)	C9—C10—C11—C12	−99.7 (3)
C2—C1—C14—C13	−85.7 (3)	C9—C10—C11—C15	70.6 (3)
C15—C1—C14—C13	39.6 (3)	C10—C11—C15—C1	−116.5 (3)
C2—C1—C15—C11	63.5 (3)	C12—C11—C15—C1	53.8 (3)
C14—C1—C15—C11	−63.2 (3)	C11—C12—C13—O6	172.9 (3)
C1—C2—C3—C8	92.7 (3)	C11—C12—C13—C14	−12.9 (4)
C2—C3—C8—C9	−10.0 (4)	O6—C13—C14—C1	173.5 (3)
C3—C8—C9—C10	−82.0 (3)	C12—C13—C14—C1	−0.9 (4)

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 71260 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1058]

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Acta Cryst. (1993). C**49**, 1804–1806

Quinuclidine–Trifluoromonoborane: a (1/1) Lewis Base–Lewis Acid Complex

R. E. Banks, M. K. Besheesh, R. G. Pritchard and I. Sharif

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

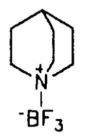
(*Received* 10 *February* 1993; *accepted* 13 *April* 1993)

Abstract

In quinuclidine-trifluoroborane a crystallographic mirror plane bisects the staggered quinuclidine and boron trifluoride groups. The B—N distance [1.601 (7) Å] is identical to that in pyridine-trifluoroborane [1.602 (4) Å; Topel, Hensen & Bats (1984). *Acta Cryst.* C**40**, 828-830] despite the markedly lower basicity of the aromatic amine [pK_a 5.25 (H_2O, 298 K) *versus* 10.95 for quinuclidine].

Comment

Several novel *N*-fluoroquinuclidinium salts 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. The title molecule (I) was prepared in order to determine if changes occur in the quinuclidine moiety on lone-pair donation to a typical Lewis acid. Although the C—N bonds of the title molecule [1.486 (6) and 2×1.514 (5) Å] are longer than the 1.472 Å assumed for quinuclidine (Fourme, 1979) it is impossible to relate these differences to lone-pair donation as both quinuclidine geometries fall in a range defined by known complexes. These complexes include bis(quinuclidine)Br$^+$ (Blair, Parris, Hii & Brock, 1983), bis(quinuclidine)I$^+$ (Brock, Fu, Blair, Chen & Lovell, 1988) and a quinuclidine-carbon tetrabromide charge-transfer complex (Blackstock, Lorand & Kochi, 1987).



(I)

Interestingly, the title compound is isomorphous with the 1:1 complex formed by quinuclidine with sulfur trioxide (Kubas, Larson & Ryan, 1979) [$P2_1/m$, a = 7.955 (4), b = 8.829 (3), c = 6.100 (4) Å, β = 96.03 (4)°].

Acta Crystallographica Section C
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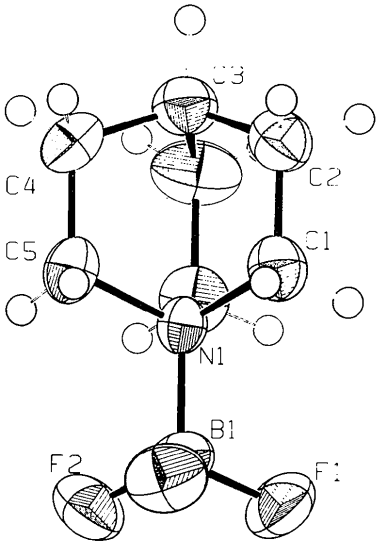

Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).

Experimental

Crystal data

$C_7H_{13}N^+.BF_3^-$
M_r = 178.99
Monoclinic
$P2_1/m$
a = 7.905 (3) Å
b = 8.796 (3) Å
c = 6.167 (2) Å
β = 93.91 (3)°
V = 427.8 (5) Å^3
Z = 2

D_x = 1.389 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 11.16-26.64°
μ = 0.1202 mm^{-1}
T = 296.0 K
Plate
0.40 × 0.40 × 0.20 mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
785 measured reflections
720 independent reflections
440 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.033
$\theta_{\rm max}$ = 23.97°

$h = 0 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -7 \rightarrow 7$
3 standard reflections monitored every 150 reflections intensity variation: none

Refinement

Refinement on F
Final R = 0.0473
wR = 0.0322
S = 2.789
440 reflections
91 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\rm max}$ = 0.0022
$\Delta\rho_{\rm max}$ = 0.15216 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.15044 e Å^{-3}
Extinction correction: not applied
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection and cell refinement: *CAD-4 Diffractometer Control Software* (Enraf-Nonius, 1989). 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)

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

	x	y	z	$U_{\rm eq}$
F1	0.3239 (3)	0.1213 (3)	0.2780 (3)	0.0700
F2	0.3755 (4)	0.2500	−0.0281 (5)	0.0684
N1	0.5916 (5)	0.2500	0.2688 (7)	0.0380
C1	0.6217 (8)	0.2500	0.5092 (10)	0.0535
C2	0.8092 (8)	0.2500	0.579 (1)	0.0584
C3	0.9123 (8)	0.2500	0.3843 (10)	0.0584
C4	0.8646 (5)	0.3895 (7)	0.2464 (9)	0.0765
C5	0.6775 (6)	0.3883 (6)	0.1798 (8)	0.0571
B1	0.3930 (8)	0.2500	0.198 (1)	0.0533

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

F1—B1	1.364 (4)	C1—C2	1.516 (8)
F2—B1	1.392 (8)	C2—C3	1.499 (8)
N1—C1	1.486 (6)	C3—C4	1.525 (5)
N1—C5	1.514 (5)	C4—C5	1.508 (6)
N1—B1	1.601 (7)		
C1—N1—C5	108.5 (3)	C4—C3—C4	107.1 (6)
C1—N1—B1	111.0 (4)	C3—C4—C5	110.3 (4)
C5—N1—C5	106.9 (5)	N1—C5—C4	111.2 (4)
C5—N1—B1	110.9 (3)	F1—B1—F1	112.2 (6)
N1—C1—C2	111.8 (5)	F1—B1—F2	110.3 (4)
C1—C2—C3	110.2 (5)	F1—B1—N1	108.1 (3)
C2—C3—C4	108.7 (4)	F2—B1—N1	107.5 (5)

Quinuclidine-trifluoroborane was prepared by adding boron trifluoride etherate (26.3 mmol) to a stirred solution of quinuclidine (26.3 mmol) in HPLC-grade acetonitrile (30 ml) using dry-box (N_2) techniques. Evaporation of the product under reduced pressure followed by recrystallization from acetone/ethyl acetate (1:1 v/v) gave an analytically pure white sample (found C 46.2, H 7.5, N 7.6%; $C_7H_{13}BF_3N$ requires C 46.9, H 7.3, N 7.8%), m.p. 437-439 K in 70% yield [literature m.p. 434-437 K (VanPaasschen & Geanangel, 1976)]. Crystals suitable for X-ray work were obtained by allowing ethyl acetate vapour to diffuse into a solution of the compound 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 71249 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1050]

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Acta Cryst. (1993). C**49**, 1806–1807

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

R. E. Banks, R. G. Pritchard and I. Sharif

*Department of Chemistry, University of Manchester
Institute of Science and Technology, PO Box 88,
Manchester M60 1QD, England*

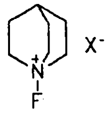
(*Received* 10 *February* 1993; *accepted* 13 *April* 1993)

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)].

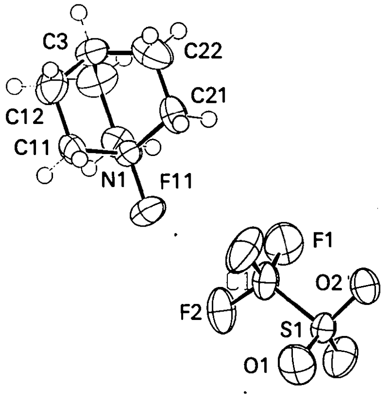


Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).

Experimental

Crystal data

$C_7H_{13}FN^+.CF_3O_3S^-$
$M_r = 279.25$
Mo *Kα* radiation
$\lambda = 0.71069$ Å