

1-Chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate deuteriochloroform solvate

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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.040
 wR factor = 0.095
Data-to-parameter ratio = 15.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title structure, $\text{C}_7\text{H}_{14}\text{ClN}_2^+\cdot\text{BF}_4^-\cdot\text{CDCl}_3$, comprises 1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane cations, BF_4^- anions and CDCl_3 solvent molecules, each having C_s crystallographic symmetry. The cation has a staggered conformation and the anion and solvent molecule are connected *via* a $\text{C}-\text{D}\cdots\text{F}$ interaction.

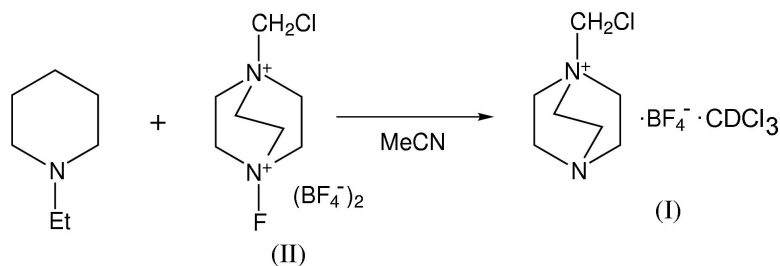
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Comment

In the course of our studies of electrophilic fluorination methodology (Chambers *et al.*, 2004), 1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate deuteriochloroform solvate, (I), was obtained as a by-product in the reaction of 'Selectfluor', (II), with *N*-ethylpiperidine. Compound (I) was obtained by recrystallization from deuteriochloroform. The crystal structure of solvent-free 1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate has been reported previously by Banks *et al.* (1993).



The cation, anion and solvent molecule (Fig. 1 and Table 1) all lie on a crystallographic mirror plane, which passes through atoms C11/N1/N2/C1–C3 of the cation (which, therefore, has a staggered conformation around the N1–C1 bond), atoms B, F1 and F2 of the anion, and atoms C6, Cl3 and D of the deuteriochloroform molecule. The solvent molecule and the anion are linked by a $\text{C6}-\text{D}\cdots\text{F1}$ hydrogen bond (Table 2). The $\text{N}-\text{C}$ bonds at quaternized atom N1 are longer by 0.047 (4) Å than at N2.

Experimental

A mixture comprising (II) (3.5 g, 12.1 mmol) and *N*-ethylpiperidine (1.0 g, 11.1 mmol) in acetonitrile was heated at reflux temperature 355 K for 18 h. The reaction mixture appeared dark red in colour. On completion of the reaction, the mixture was poured into water and extracted with dichloromethane (3×100 ml). The organic phase was dried with magnesium sulfate. After evaporation, the crude product was purified by distillation on a Kugelrohr apparatus. Crystals of X-ray quality were grown from a deuteriochloroform solution of the non-volatile residue at room temperature.

Crystal data

$C_7H_{14}ClN_2^+ \cdot BF_4^- \cdot CDCl_3$
 $M_r = 368.84$
 Orthorhombic, *Pnma*
 $a = 22.368 (3) \text{ \AA}$
 $b = 8.4961 (11) \text{ \AA}$
 $c = 7.4726 (10) \text{ \AA}$
 $V = 1420.1 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.725 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 884 reflections
 $\theta = 12.2\text{--}25.4^\circ$
 $\mu = 0.86 \text{ mm}^{-1}$
 $T = 120 (2) \text{ K}$
 Plate, colourless
 $0.50 \times 0.20 \times 0.06 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{\min} = 0.672$, $T_{\max} = 0.950$
 16850 measured reflections

2037 independent reflections
 1760 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 29.1^\circ$
 $h = -30 \rightarrow 30$
 $k = -11 \rightarrow 11$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.095$
 $S = 1.21$
 2037 reflections
 134 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 1.1232P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cl1—C1	1.763 (3)	F1—B	1.388 (4)
N1—C1	1.507 (3)	F2—B	1.393 (4)
N1—C4	1.507 (2)	F3—B	1.381 (2)
N1—C2	1.510 (4)	Cl2—C6	1.767 (2)
N2—C3	1.456 (4)	Cl3—C6	1.759 (3)
N2—C5	1.464 (2)		
C1—N1—C4	111.96 (13)	N1—C1—Cl1	111.99 (18)
C1—N1—C2	107.0 (2)	N1—C2—C3	108.8 (2)
C4—N1—C2	108.54 (14)	N2—C3—C2	112.0 (2)
C3—N2—C5	108.94 (15)	N1—C4—C5	108.63 (17)
C5—N2—C5 ⁱ	108.2 (2)	N2—C5—C4	111.79 (17)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C6-D6 \cdots F1$	0.90 (4)	2.28 (4)	3.123 (4)	156 (3)

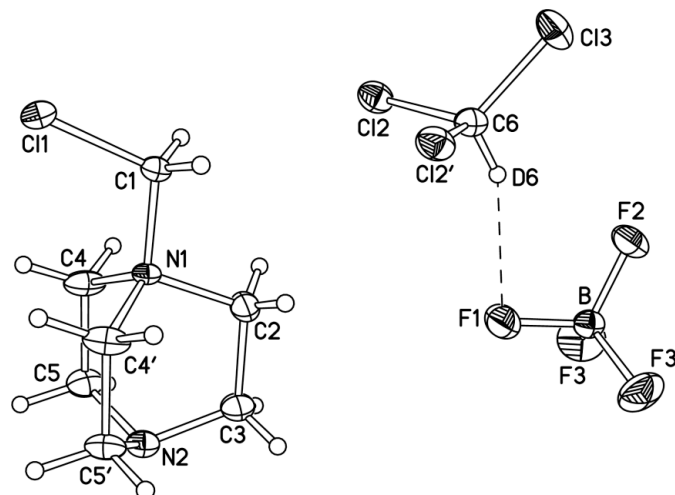


Figure 1

Twice the asymmetric unit of (I), showing atomic displacement ellipsoids (at the 50% probability level) and the D—F hydrogen bond (dashed line). Primed atoms are generated by the reflection operation $(x, \frac{1}{2} - y, z)$.

All H and D atoms were refined isotropically with C—H bond distances in the range 0.93 (3)–0.99 (3) \AA and C—D distances of 0.90 (4) \AA .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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