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

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.095
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title structure, $C_7H_{14}ClN_2^+ \cdot BF_4^- \cdot CDCl_3$, 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 C—D···F interaction.

Comment

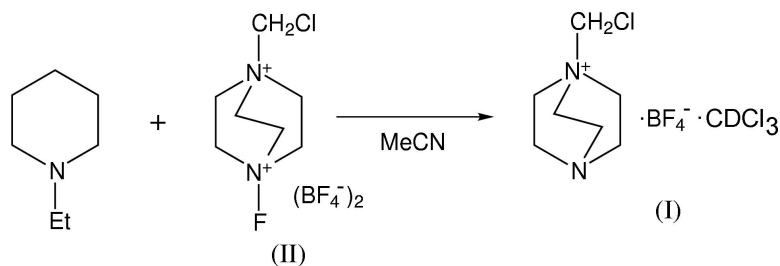In the course of our studies of electrophilic fluorination methodology (Chambers et al., 2004), 1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate deuterochloroform solvate, (I), was obtained as a by-product in the reaction of 'Selectfluor', (II), with N-ethylpiperidine. Compound (I) was obtained by recrystallization from deuterochloroform. 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 Cl1/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 deuterochloroform molecule. The solvent molecule and the anion are linked by a C6—D···F1 hydrogen bond (Table 2) The N—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 deuterochloroform solution of the non-volatile residue at room temperature.

organic papers

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

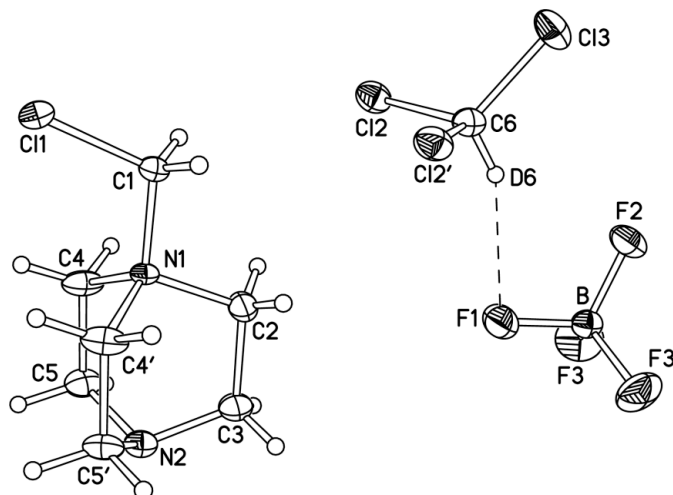| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—D6$\cdots$F1	0.90 (4)	2.28 (4)	3.123 (4)	156 (3)

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) Å and C—D distances of 0.90 (4) Å.

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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Chambers, R. D., Holling, D., Sandford, G., Batsanov, A. S. & Howard, J. A. K. (2004). *J. Fluorine Chem.* **125**, 661–671.
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supporting information

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Crystal data

$C_7H_{14}ClN_2^+ \cdot BF_4^- \cdot CDCl_3$	$F(000) = 744$
$M_r = 368.84$	$D_x = 1.725$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo *Kα* radiation, $λ = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 884 reflections
$a = 22.368$ (3) Å	$θ = 12.2–25.4°$
$b = 8.4961$ (11) Å	$μ = 0.86$ mm^{-1}
$c = 7.4726$ (10) Å	$T = 120$ K
$V = 1420.1$ (3) Å^3	Plate, colourless
$Z = 4$	$0.50 × 0.20 × 0.06$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer	16850 measured reflections
Radiation source: fine-focus sealed tube	2037 independent reflections
Graphite monochromator	1760 reflections with $I > 2σ(I)$
Detector resolution: 8 pixels mm^{-1}	$R_{int} = 0.045$
ω scans	$θ_{max} = 29.1°$, $θ_{min} = 1.8°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = −30→30$
	$k = −11→11$
$T_{min} = 0.672$, $T_{max} = 0.950$	$l = −10→10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2σ(F^2)] = 0.040$	All H-atom parameters refined
$wR(F^2) = 0.095$	$w = 1/[σ^2(F_o^2) + (0.0364P)^2 + 1.1232P]$
$S = 1.21$	where $P = (F_o^2 + 2F_c^2)/3$
2037 reflections	$(Δ/σ)_{max} = 0.001$
134 parameters	$Δρ_{max} = 0.73$ e Å^{-3}
0 restraints	$Δρ_{min} = −0.46$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. The data collection nominally covered full sphere of reciprocal space, by a combination of 5 sets of *ω* scans; each set at different *φ* and/or 2*θ* angles and each scan (20 sec exposure) covering 0.3° in *ω*. Crystal to detector distance 4.41 cm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.25564 (3)	0.2500	0.34874 (9)	0.01955 (16)
N1	0.33556 (10)	0.2500	0.6221 (3)	0.0139 (4)
N2	0.35116 (11)	0.2500	0.9627 (3)	0.0189 (5)
C1	0.33068 (12)	0.2500	0.4210 (4)	0.0180 (5)
H1	0.3499 (9)	0.157 (3)	0.379 (3)	0.014 (5)*
C2	0.40138 (13)	0.2500	0.6669 (4)	0.0305 (8)
H2	0.4162 (12)	0.151 (4)	0.617 (4)	0.046 (9)*
C3	0.40859 (14)	0.2500	0.8711 (4)	0.0254 (6)
H3	0.4297 (10)	0.160 (3)	0.904 (4)	0.027 (7)*
C4	0.30739 (11)	0.1057 (2)	0.7039 (3)	0.0234 (4)
H41	0.2661 (12)	0.113 (3)	0.677 (4)	0.028 (7)*
H42	0.3276 (12)	0.018 (4)	0.651 (4)	0.042 (8)*
C5	0.31737 (10)	0.1104 (2)	0.9081 (3)	0.0218 (4)
H51	0.2774 (11)	0.111 (3)	0.964 (4)	0.027 (7)*
H52	0.3387 (11)	0.022 (3)	0.943 (4)	0.031 (7)*
F1	0.57683 (8)	0.2500	0.6439 (3)	0.0376 (5)
F2	0.65427 (8)	0.2500	0.4503 (3)	0.0317 (4)
F3	0.66116 (7)	0.11659 (19)	0.7124 (2)	0.0437 (4)
B	0.63872 (15)	0.2500	0.6307 (4)	0.0205 (6)
Cl2	0.48099 (2)	0.07856 (6)	0.26682 (7)	0.02478 (14)
Cl3	0.56793 (4)	0.2500	0.05699 (11)	0.0326 (2)
C6	0.52554 (13)	0.2500	0.2552 (4)	0.0216 (5)
D6	0.5509 (15)	0.2500	0.349 (5)	0.019 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0222 (3)	0.0214 (3)	0.0150 (3)	0	−0.0041 (2)	0
N1	0.0171 (10)	0.0161 (10)	0.0086 (9)	0	−0.0007 (8)	0
N2	0.0243 (11)	0.0173 (11)	0.0152 (10)	0	−0.0005 (9)	0
C1	0.0187 (12)	0.0241 (14)	0.0112 (11)	0	0.0005 (10)	0
C2	0.0164 (13)	0.060 (2)	0.0147 (13)	0	−0.0011 (11)	0
C3	0.0239 (14)	0.0385 (18)	0.0140 (13)	0	−0.0032 (11)	0
C4	0.0417 (12)	0.0143 (9)	0.0142 (9)	−0.0067 (9)	−0.0015 (8)	0.0001 (7)
C5	0.0322 (10)	0.0181 (9)	0.0150 (8)	−0.0039 (8)	−0.0018 (8)	0.0046 (7)
F1	0.0254 (9)	0.0646 (15)	0.0228 (9)	0	0.0009 (8)	0
F2	0.0347 (10)	0.0394 (11)	0.0210 (9)	0	0.0080 (8)	0
F3	0.0573 (10)	0.0285 (8)	0.0452 (9)	0.0129 (7)	−0.0061 (7)	0.0111 (7)

B	0.0247 (15)	0.0180 (14)	0.0187 (14)	0	−0.0002 (12)	0
Cl2	0.0308 (3)	0.0220 (2)	0.0216 (2)	0.00027 (19)	0.00304 (19)	0.00215 (19)
Cl3	0.0323 (4)	0.0371 (4)	0.0285 (4)	0.000	0.0129 (3)	0
C6	0.0236 (13)	0.0245 (14)	0.0166 (12)	0	−0.0011 (11)	0

Geometric parameters (Å, º)

Cl1—C1	1.763 (3)	C4—H42	0.96 (3)
N1—C1	1.507 (3)	C4—C5	1.543 (3)
N1—C4	1.507 (2)	C5—H52	0.93 (3)
N1—C2	1.510 (4)	C5—H51	0.99 (3)
N2—C3	1.456 (4)	F1—B	1.388 (4)
N2—C5	1.464 (2)	F2—B	1.393 (4)
C1—H1	0.95 (2)	F3—B	1.381 (2)
C2—H2	0.98 (3)	Cl2—C6	1.767 (2)
C2—C3	1.535 (4)	Cl3—C6	1.759 (3)
C3—H3	0.93 (3)	C6—D6	0.90 (4)
C4—H41	0.95 (3)		
C1—N1—C4	111.96 (13)	H41—C4—N1	105.3 (17)
C4^i—N1—C4	108.8 (2)	H42—C4—N1	105.6 (18)
C1—N1—C2	107.0 (2)	H41—C4—C5	110.6 (17)
C4—N1—C2	108.54 (14)	H42—C4—C5	111.1 (19)
C3—N2—C5	108.94 (15)	N1—C4—C5	108.63 (17)
C5—N2—C5^i	108.2 (2)	H52—C5—H51	110 (2)
H1^i—C1—H1	112 (3)	H52—C5—N2	108.0 (17)
H1—C1—N1	107.2 (14)	H51—C5—N2	110.3 (16)
H1—C1—Cl1	109.3 (13)	H52—C5—C4	109.5 (17)
N1—C1—Cl1	111.99 (18)	H51—C5—C4	106.8 (15)
H2^i—C2—H2	119 (4)	N2—C5—C4	111.79 (17)
H2—C2—N1	104.2 (17)	F3^i—B—F3	110.3 (3)
H2—C2—C3	110.2 (19)	F3—B—F1	109.34 (18)
N1—C2—C3	108.8 (2)	F3—B—F2	109.68 (18)
H3^i—C3—H3	110 (3)	F1—B—F2	108.5 (2)
H3—C3—N2	108.8 (15)	Cl3—C6—Cl2	110.21 (11)
H3—C3—C2	108.5 (16)	Cl2^i—C6—Cl2	111.04 (16)
N2—C3—C2	112.0 (2)	Cl3—C6—D6	109 (2)
H41—C4—H42	115 (2)	Cl2—C6—D6	108.4 (11)
C2—N1—C1—Cl1	180.0		

Symmetry code: (i) *x*, −*y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C6—D6⋯F1	0.90 (4)	2.28 (4)	3.123 (4)	156 (3)