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1,2,3,3-Tetramethyl-7-nitro-3,4-dihydroisoquinolinium tetrafluoroborate

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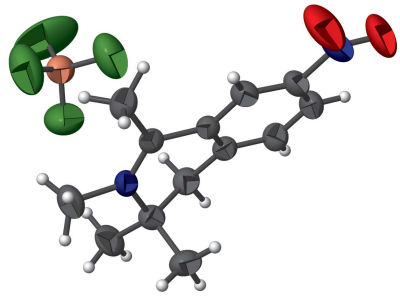
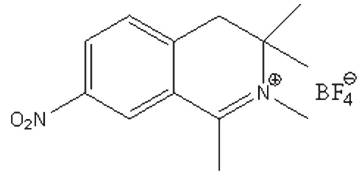
Structural data: full structural data are available from iucrdata.iucr.org

The title salt, $C_{13}H_{17}N_2O_2^+\cdot BF_4^-$, was prepared by the methylation of the imine with Meerwein salt in dichloromethane. The asymmetric unit comprises a 1,3,3-trimethyl-7-nitro-3,4-dihydroisoquinolinium cation and a tetrafluoroborate anion. The coordination around the boron atom in the tetrafluoroborate anion is tetrahedral. The heterocyclic ring adopts a half-chair conformation. The crystal packing is governed by means of C—H···F contacts, which lead to the formation of a three-dimensional network.

3D view



Chemical scheme



Structure description

The iminium function is an important functional group in organic synthesis (Bohé & Kammoun, 2002, 2004). As a result of its enhanced electrophilic character, the iminium functional group usually reacts easily with a wide range of nucleophiles.

Peracid oxidation of an iminium salt (I^+) leads to oxaziridinium (Ox^+). Catalytic oxidation methods through the iminium salt have been described (Hanquet & Lusinchi, 1993). Oxidation of the iminium salt with a peracid involves the nucleophilic properties in a two-step mechanism: nucleophilic attack by the iminium peracid leading to a *gem*-amino perester, followed by intramolecular nucleophilic substitution; this reaction resembles that of the peracid oxidation of imines leading to oxaziridines (Ogata & Sawaki, 1973). We report here the synthesis and the crystal structure determination of a new iminium salt, $C_{13}H_{17}N_2O_2^+\cdot BF_4^-$.

The asymmetric unit comprises a BF_4^- anion and a 1,2,3,3-tetramethyl-7-nitro-3,4-dihydroisoquinolinium cation (Fig. 1). The B atom in the isolated BF_4^- anion is coordinated by four fluoride anions with B—F bond lengths in the range 1.281 (5)–1.387 (5) Å and a F—B—F angle range of 104.8 (3)–113.3 (4)°. The heterocyclic ring adopts a half-

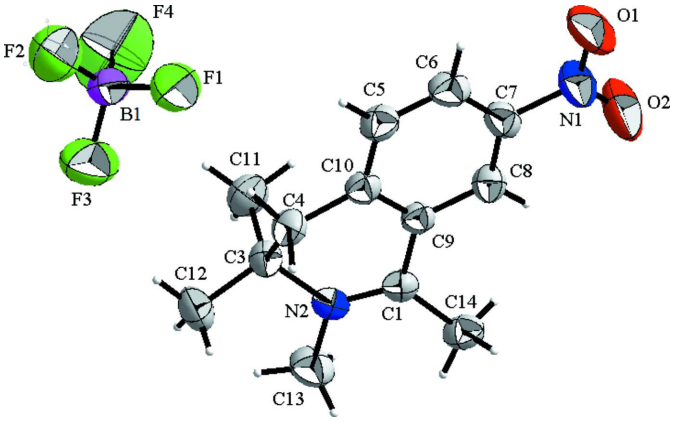


Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

chair conformation (r.m.s. deviation = 0.189 Å). It subtends an angle of 15.49 (3)° with the aromatic ring.

In the crystal, the organic cations are linked to the BF_4^- anions through C—H···F contacts (Table 1 and Fig. 2).

Synthesis and crystallization

The title salt (1) was prepared by methylation of the imine nitrate (2) (500 mg, 2.5 mmol) with Meerwein salt in dichloromethane (15 ml) (Fig. 3). Imine (2) has been described by Kammoun *et al.* (2012), as obtained from the commercially available tertiary alcohol (4). The mixture was stirred at room temperature for 8 h. The concentrate was chromatographed on silica gel, with dichloromethane as eluent (yield 42%). m.p. 426 K.

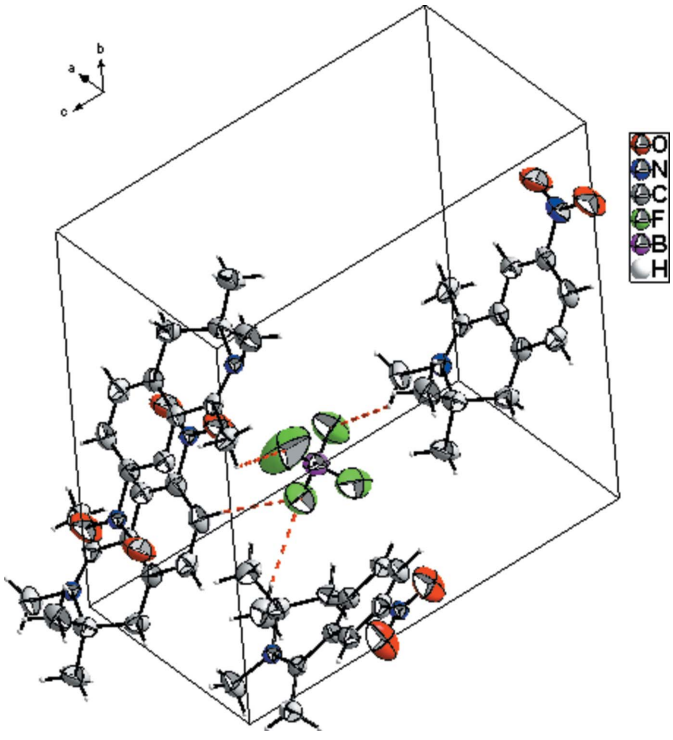


Figure 2
Detail of title compound showing the way (dashed lines) in which the $[BF_4]^-$ anion interacts with neighbouring organic cations. Displacement ellipsoids are drawn at the 50% probability level for the B and F atoms.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14C···F3^{i}	0.96	2.38	3.012 (4)	124
C12—H12B···F2	0.96	2.48	3.329 (5)	148
C4—H4A···F4^{ii}	0.97	2.46	3.419 (4)	168

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{17}N_2O_2^+\cdot BF_4^-$
M_r	320.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	7.7265 (2), 13.4792 (4), 14.5827 (3)
β (°)	96.073 (1)
V (Å^3)	1510.22 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.37 × 0.33 × 0.22
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2008)
T_{min}, T_{max}	0.964, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6335, 2752, 1794
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.068, 0.244, 1.05
No. of reflections	2770
No. of parameters	203
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.47

Computer programs: *SMART* and *SAINT* (Bruker, 1998), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

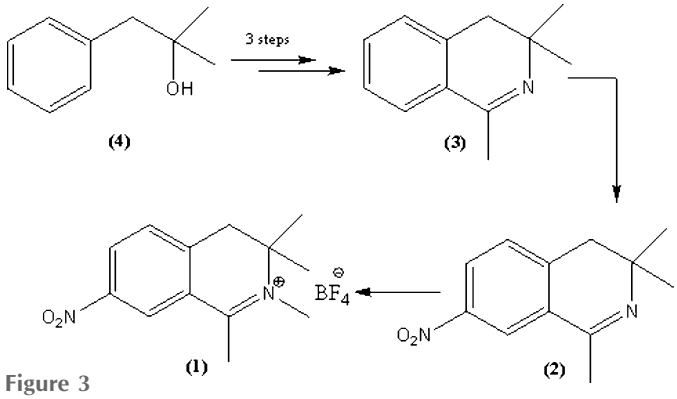


Figure 3
Reaction scheme.

Spectroscopic analysis,^{1}H NMR (300 MHz, $CDCl_3$, p.p.m): 1.61 (s, 6*H*, 2Me 3); 3.13 (*s*, 3H, Me 1); 3.54 (*s*, 2H, CH_2 4); 3.91 (*s*, *N*—Me); 7.83 (*d*, *J* = 8.1, 1H aromatic H); 8.62 (*dd*, *J* = 8.1, *J* = 2.1, 1H, aromatic H); 8.86 (*d*, *J* = 2.1, 1H, aromatic H). ^{13}C NMR (75 MHz, $CDCl_3$, p.p.m): 21.15; 24.07; 38.82; 39.94; 64.61; 148.56; 125.82; 130.85; 131.13; 129.49; 143.97; 177.33. SM (FAB): 233 ($M^{+\cdot}$-tetrafluoroborate); 217 ($M^{+\cdot}$−16); 187 ($M^{+\cdot}$−46). Recrystallization from ether/hexane solution afforded colourless crystals suitable for X-ray diffraction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160619 [doi:10.1107/S2414314616006192]

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Crystal data

$C_{13}H_{17}N_2O_2^+\cdot BF_4^-$
M_r = 320.09
Monoclinic, $P2_1/c$
a = 7.7265 (2) Å
b = 13.4792 (4) Å
c = 14.5827 (3) Å
β = 96.073 (1)°
V = 1510.22 (7) Å^3
Z = 4
$F(000)$ = 664
D_x = 1.408 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1794 reflections
θ = 2.9–22.6°
μ = 0.13 mm^{-1}
T = 296 K
Prism, colourless
0.37 × 0.33 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008)
T_{min} = 0.964, T_{max} = 0.983
6335 measured reflections
2752 independent reflections
1794 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.4°, θ_{min} = 3.5°
h = −9→9
k = −11→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.244
S = 1.05
2770 reflections
203 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1509P)^2 + 0.3904P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
B1	0.2682 (5)	0.5714 (3)	0.8190 (3)	0.0555 (10)
F1	0.3487 (4)	0.5895 (3)	0.74005 (18)	0.1084 (10)
F2	0.3127 (4)	0.4785 (2)	0.8479 (2)	0.1080 (10)
F3	0.1023 (4)	0.5791 (3)	0.8052 (4)	0.191 (2)
F4	0.3427 (5)	0.6376 (2)	0.88258 (18)	0.1151 (11)
O1	0.8422 (5)	0.6099 (3)	0.37772 (18)	0.0962 (11)
O2	0.9054 (5)	0.7123 (3)	0.4856 (2)	0.1028 (12)
N1	0.8482 (4)	0.6332 (3)	0.4566 (2)	0.0636 (8)
N2	0.7341 (3)	0.48461 (19)	0.83658 (15)	0.0406 (6)
C1	0.7342 (3)	0.5531 (2)	0.77464 (18)	0.0378 (7)
C3	0.7267 (4)	0.3756 (2)	0.8128 (2)	0.0468 (8)
C4	0.6195 (4)	0.3635 (2)	0.7200 (2)	0.0485 (8)
H4A	0.6279	0.2953	0.6996	0.073*
H4B	0.4983	0.3770	0.7270	0.073*
C5	0.6784 (4)	0.4035 (3)	0.5566 (2)	0.0505 (8)
H5	0.6421	0.3402	0.5377	0.061*
C6	0.7323 (4)	0.4693 (3)	0.4932 (2)	0.0536 (8)
H6	0.7312	0.4518	0.4315	0.064*
C7	0.7881 (4)	0.5620 (3)	0.52354 (19)	0.0474 (8)
C8	0.7896 (4)	0.5919 (2)	0.6134 (2)	0.0440 (7)
H8	0.8275	0.6550	0.6317	0.053*
C9	0.7324 (3)	0.5249 (2)	0.67690 (18)	0.0377 (7)
C10	0.6776 (3)	0.4307 (2)	0.64861 (19)	0.0414 (7)
C11	0.9148 (4)	0.3407 (3)	0.8092 (3)	0.0645 (10)
H11A	0.9654	0.3758	0.7614	0.097*
H11B	0.9157	0.2708	0.7967	0.097*
H11C	0.9811	0.3536	0.8675	0.097*
C12	0.6383 (5)	0.3166 (3)	0.8838 (2)	0.0675 (10)
H12A	0.6206	0.2495	0.8628	0.101*
H12B	0.5279	0.3463	0.8918	0.101*
H12C	0.7105	0.3168	0.9415	0.101*
C13	0.7541 (5)	0.5110 (3)	0.9354 (2)	0.0617 (10)
H13A	0.8347	0.5651	0.9455	0.093*
H13B	0.7975	0.4548	0.9711	0.093*
H13C	0.6433	0.5304	0.9538	0.093*
C14	0.7380 (4)	0.6597 (2)	0.8001 (2)	0.0508 (8)
H14A	0.6595	0.6712	0.8458	0.076*
H14B	0.7030	0.6990	0.7464	0.076*
H14C	0.8538	0.6779	0.8246	0.076*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.051 (2)	0.057 (3)	0.059 (2)	−0.0020 (18)	0.0109 (16)	0.0062 (19)
F1	0.130 (2)	0.128 (3)	0.0682 (16)	−0.0274 (18)	0.0188 (15)	0.0026 (15)

F2	0.130 (2)	0.083 (2)	0.112 (2)	0.0264 (17)	0.0151 (17)	0.0179 (16)
F3	0.0461 (15)	0.166 (4)	0.361 (7)	0.0160 (17)	0.017 (2)	0.006 (4)
F4	0.173 (3)	0.104 (2)	0.0725 (17)	−0.043 (2)	0.0317 (17)	−0.0150 (15)
O1	0.141 (3)	0.107 (3)	0.0437 (16)	−0.011 (2)	0.0243 (16)	0.0114 (15)
O2	0.162 (3)	0.085 (2)	0.0617 (18)	−0.036 (2)	0.0108 (18)	0.0212 (17)
N1	0.0783 (19)	0.066 (2)	0.0452 (17)	−0.0030 (17)	0.0016 (13)	0.0150 (15)
N2	0.0372 (12)	0.0493 (16)	0.0356 (12)	0.0008 (10)	0.0055 (9)	−0.0009 (11)
C1	0.0309 (12)	0.0423 (17)	0.0399 (15)	0.0012 (11)	0.0028 (10)	−0.0021 (13)
C3	0.0507 (16)	0.0419 (18)	0.0484 (17)	0.0017 (14)	0.0082 (13)	0.0065 (14)
C4	0.0541 (17)	0.0399 (17)	0.0520 (18)	−0.0047 (14)	0.0076 (13)	−0.0033 (14)
C5	0.0611 (18)	0.0451 (19)	0.0448 (17)	−0.0004 (15)	0.0032 (14)	−0.0102 (14)
C6	0.0631 (19)	0.062 (2)	0.0354 (15)	0.0081 (16)	0.0028 (13)	−0.0053 (15)
C7	0.0495 (16)	0.056 (2)	0.0364 (15)	0.0045 (14)	0.0049 (12)	0.0081 (14)
C8	0.0446 (15)	0.0432 (18)	0.0434 (16)	−0.0011 (13)	0.0009 (12)	0.0024 (13)
C9	0.0379 (13)	0.0397 (17)	0.0352 (14)	0.0042 (12)	0.0028 (10)	−0.0004 (12)
C10	0.0399 (14)	0.0424 (18)	0.0417 (15)	0.0031 (12)	0.0028 (11)	−0.0021 (13)
C11	0.0592 (19)	0.063 (2)	0.071 (2)	0.0185 (17)	0.0071 (16)	0.0095 (19)
C12	0.087 (2)	0.061 (2)	0.057 (2)	−0.006 (2)	0.0190 (18)	0.0169 (18)
C13	0.074 (2)	0.074 (3)	0.0367 (16)	−0.0028 (19)	0.0026 (14)	−0.0035 (16)
C14	0.0532 (17)	0.048 (2)	0.0516 (17)	−0.0037 (14)	0.0090 (13)	−0.0123 (15)

Geometric parameters (Å, º)

B1—F3	1.281 (5)	C5—H5	0.9300
B1—F2	1.353 (5)	C6—C7	1.379 (5)
B1—F4	1.369 (5)	C6—H6	0.9300
B1—F1	1.387 (5)	C7—C8	1.370 (4)
O1—N1	1.189 (4)	C8—C9	1.397 (4)
O2—N1	1.214 (4)	C8—H8	0.9300
N1—C7	1.477 (4)	C9—C10	1.388 (4)
N2—C1	1.292 (4)	C11—H11A	0.9600
N2—C13	1.476 (4)	C11—H11B	0.9600
N2—C3	1.510 (4)	C11—H11C	0.9600
C1—C9	1.474 (4)	C12—H12A	0.9600
C1—C14	1.484 (4)	C12—H12B	0.9600
C3—C4	1.519 (4)	C12—H12C	0.9600
C3—C12	1.523 (4)	C13—H13A	0.9600
C3—C11	1.534 (4)	C13—H13B	0.9600
C4—C10	1.485 (4)	C13—H13C	0.9600
C4—H4A	0.9700	C14—H14A	0.9600
C4—H4B	0.9700	C14—H14B	0.9600
C5—C6	1.378 (5)	C14—H14C	0.9600
C5—C10	1.392 (4)		
F3—B1—F2	109.9 (4)	C6—C7—N1	119.0 (3)
F3—B1—F4	113.3 (4)	C7—C8—C9	118.2 (3)
F2—B1—F4	108.5 (3)	C7—C8—H8	120.9
F3—B1—F1	112.6 (4)	C9—C8—H8	120.9

F2—B1—F1	107.4 (3)	C10—C9—C8	120.1 (3)
F4—B1—F1	104.8 (3)	C10—C9—C1	119.7 (3)
O1—N1—O2	123.0 (3)	C8—C9—C1	120.2 (3)
O1—N1—C7	119.0 (3)	C9—C10—C5	119.7 (3)
O2—N1—C7	118.0 (3)	C9—C10—C4	117.1 (3)
C1—N2—C13	120.1 (3)	C5—C10—C4	123.2 (3)
C1—N2—C3	122.6 (2)	C3—C11—H11A	109.5
C13—N2—C3	117.2 (3)	C3—C11—H11B	109.5
N2—C1—C9	119.4 (3)	H11A—C11—H11B	109.5
N2—C1—C14	121.2 (3)	C3—C11—H11C	109.5
C9—C1—C14	119.4 (3)	H11A—C11—H11C	109.5
N2—C3—C4	108.2 (2)	H11B—C11—H11C	109.5
N2—C3—C12	111.1 (3)	C3—C12—H12A	109.5
C4—C3—C12	107.9 (3)	C3—C12—H12B	109.5
N2—C3—C11	107.1 (2)	H12A—C12—H12B	109.5
C4—C3—C11	111.5 (3)	C3—C12—H12C	109.5
C12—C3—C11	111.0 (3)	H12A—C12—H12C	109.5
C10—C4—C3	112.5 (2)	H12B—C12—H12C	109.5
C10—C4—H4A	109.1	N2—C13—H13A	109.5
C3—C4—H4A	109.1	N2—C13—H13B	109.5
C10—C4—H4B	109.1	H13A—C13—H13B	109.5
C3—C4—H4B	109.1	N2—C13—H13C	109.5
H4A—C4—H4B	107.8	H13A—C13—H13C	109.5
C6—C5—C10	120.6 (3)	H13B—C13—H13C	109.5
C6—C5—H5	119.7	C1—C14—H14A	109.5
C10—C5—H5	119.7	C1—C14—H14B	109.5
C5—C6—C7	118.4 (3)	H14A—C14—H14B	109.5
C5—C6—H6	120.8	C1—C14—H14C	109.5
C7—C6—H6	120.8	H14A—C14—H14C	109.5
C8—C7—C6	122.9 (3)	H14B—C14—H14C	109.5
C8—C7—N1	118.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*C*···F3^{i}	0.96	2.38	3.012 (4)	124
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