## Supporting Information

for

# "The Synthesis and Structural Analysis of 2-Quinuclidonium Tetrafluoroborate" 

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Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Norcamphor, 3-chloroperbenzoic acid ( $m$-CPBA), lithium aluminum hydride, sodium azide, trifluoroacetic acid (TFA), trifluoromethanesulfonimide, di-tertbutyl dicarbonate $\left(\mathrm{Boc}_{2} \mathrm{O}\right)$ and tetrafluoroboric acid in $\mathrm{Et}_{2} \mathrm{O}$ solution were purchased from Sigma-Aldrich Chemical Company and used as received. p-Toluenesulfonyl chloride was purchased from EM Science Inc. and purified prior to use. Triethylamine was purchased from Sigma-Aldrich Chemical Company and freshly distilled prior to use. Trifluoromethanesulfonic acid was purchased from SynQuest Laboratories, Inc. and used as received. 1,1-Dihydro-1,1,1-triacetoxy-1,2-benzoiodooxol-3(1H)-one (Dess-Martin periodinane, DMP) was prepared by known method ${ }^{1}$. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F 254 precoated plates $(0.25 \mathrm{~mm})$ and visualized by UV fluorescence quenching, anisaldehyde or $\mathrm{KMnO}_{4}$ staining. ICN Silica gel (particle size $0.032-0.063 \mathrm{~mm}$ ) was used for flash chromatography. Optical rotations were measured with a Jasco P-1010 polarimeter at $589 \mathrm{~nm} .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$, NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz and 75 MHz , respectively). ${ }^{1} \mathrm{H}$ NMR spectra were reported relative to $\mathrm{Me}_{4} \mathrm{Si}\left(\delta 0.0 \mathrm{ppm}\right.$ ) or residual $\mathrm{CHCl}_{3}$ ( $\delta 7.26 \mathrm{ppm}$ ) or $\mathrm{CHD}_{2} \mathrm{CN}$ ( $\delta 1.94 \mathrm{ppm}$ ). ${ }^{13} \mathrm{C}$ NMR were reported relative to $\mathrm{CDCl}_{3}(\delta 77.0 \mathrm{ppm})$ and $\mathrm{CD}_{3} \mathrm{CN}(\delta 118.69 \mathrm{ppm})$, respectively. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption $\left(\mathrm{cm}^{-1}\right)$. High resolution mass spectra were obtained from the Caltech Mass Spectral Facility.

## Procedure for the Synthesis of Ketoazide (7).

## 2-Oxabicyclo[3.2.1]octan-3-one (10); CAS \# 5724-61-8 ${ }^{2}$

To a mixture of $m$-CPBA $(77 \%, 28.8 \mathrm{~g}, 129 \mathrm{mmol})$ and $\mathrm{NaHCO}_{3}(20.7 \mathrm{mmol}, 246 \mathrm{mmol})$ in DCM $(800 \mathrm{~mL})$ was slowly added a solution of norcamphor $9(13.5 \mathrm{~g}, 123 \mathrm{mmol})$ in DCM ( 200 mL ) over 10 min at $20^{\circ} \mathrm{C}$. After stirring for 20 h at $20^{\circ} \mathrm{C}$, the reaction mixture was filtered to remove insoluble material and the filtrate was concentrated in vacuo to give a pale yellow oil, which was dissolved with AcOEt ( 200 mL ) and washed $10 \%$ aqueous solution of $\mathrm{Na}_{2} \mathrm{SO}_{3}(100 \mathrm{~mL})$. The aqueous layer was extracted with AcOEt repeatedly ( $2 \times 100 \mathrm{~mL}$ ) and the combined organic layers were washed with saturated aqueous $\mathrm{NaHCO}_{3}$ solution ( 100 mL ), brine $(100 \mathrm{~mL})$, dried over $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure to afford a crude pale yellow semi solid ( 15.3 g ). A solution of a crude product (include $10 \%$ of undesired isomer) in $\mathrm{DCM}(100 \mathrm{~mL})$ was washed with aqueous 1 M NaOH repeatedly ( 1 x 100 $\mathrm{mL}, 2 \times 50 \mathrm{~mL}$ ), brine ( 100 mL ), dried over $\mathrm{MgSO}_{4}$ and concentrated in vacuo to give $12.2 \mathrm{~g}(79 \%$ yield) of desired bicyclic lactone 10 as a pale yellow semi solid. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHZ}, \mathrm{CDCl}_{3}$ ) $\delta 4.86(\mathrm{~m}, 1 \mathrm{H})$, $2.73(\mathrm{ddd}, J=18.3,4.8,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.55(\mathrm{~m}, 1 \mathrm{H}), 2.48(\mathrm{dt}, J=18.3,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.17(\mathrm{~m}, 1 \mathrm{H}), 2.04-$ $1.85(\mathrm{~m}, 3 \mathrm{H}), 1.80-1.60(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.8(\mathrm{C}=\mathrm{O}), 80.9(\mathrm{CHO}), 40.6\left(\mathrm{CH}_{2}\right)$, $35.8\left(\mathrm{CH}_{2}\right), 32.4\left(\mathrm{CH}_{2}\right), 31.8(\mathrm{CH}), 29.2\left(\mathrm{CH}_{2}\right)$; IR (Neat film, NaCl$) 2945,1730,1375,1223,1196,1129$, 1069, 1016, 1000, $978 \mathrm{~cm}^{-1}$; HRMS (EI) $\mathrm{m} / \mathrm{z}$ calc'd for $\mathrm{C}_{7} \mathrm{H}_{10} \mathrm{O}_{2}\left[\mathrm{M}^{+}\right]: 126.0681$, found 126.0679.

## 3-(2-Hydroxyethyl)cyclopentanol (11); CAS \# 61478-09-9 ${ }^{3}$

To a stirred suspension of $\mathrm{LiAlH}_{4}(3.67 \mathrm{~g}, 96.7 \mathrm{mmol})$ in dry $\mathrm{Et}_{2} \mathrm{O}(300 \mathrm{~mL})$ was slowly added a solution of a bicyclic lactone $10(12.2 \mathrm{~g}, 96.7 \mathrm{mmol})$ in dry $\mathrm{Et}_{2} \mathrm{O}(100 \mathrm{~mL})$ over 10 min at $0{ }^{\circ} \mathrm{C}$. After stirring for 1 h at ambient temperature, the reaction was quenched by the addition of saturated aqueous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ solution ( 50 mL ) at $0{ }^{\circ} \mathrm{C}$ and the mixture was stirred for $30 \mathrm{~min} . \mathrm{MgSO}_{4}(30 \mathrm{~g})$ was added to the white suspension and the resulting mixture was stirred for further 30 min . The insoluble white solid was separated by filtration and the filtrate was concentrated in vacuo to afford 12.3 g ( $98 \%$ yield) of desired diol 11 as a colorless oil. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}$ ) $\delta 4.23(\mathrm{br} \mathrm{s}, 2 \mathrm{H}), 4.02(\mathrm{~m}, 1 \mathrm{H}), 3.36(\mathrm{t}, J=6.6$ $\mathrm{Hz}, 2 \mathrm{H}), 1.95(\mathrm{~m}, 1 \mathrm{H}), 1.78(\mathrm{~m}, 1 \mathrm{H}), 1.68-1.52(\mathrm{~m}, 2 \mathrm{H}), 1.52-1.38(\mathrm{~m}, 3 \mathrm{H}), 1.24(\mathrm{~m}, 1 \mathrm{H}), 1.00(\mathrm{~m}, 1 \mathrm{H}) ;$ ${ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}\right) \delta 71.7(\mathrm{CHOH}), 60.1\left(\mathrm{CH}_{2} \mathrm{OH}\right), 42.0\left(\mathrm{CH}_{2}\right), 39.8\left(\mathrm{CH}_{2}\right), 34.9\left(\mathrm{CH}_{2}\right), 34.4$ $(\mathrm{CH}), 30.0\left(\mathrm{CH}_{2}\right)$; IR (Neat film, NaCl$) 3326,2946,1435,1346,1054,1007 \mathrm{~cm}^{-1}$; HRMS (EI) $\mathrm{m} / \mathrm{z}$ calc'd for $\mathrm{C}_{7} \mathrm{H}_{12} \mathrm{O}\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}\right]^{+}: 112.0888$, found 112.0898.

## 2-(3-Hydroxycyclopentyl)ethyl 4-methylbenzenesulfonate (12).

To a solution of diol $11(3.05 \mathrm{~g}, 23.5 \mathrm{mmol})$ in $\mathrm{DCM}(50 \mathrm{~mL})$ was added $\mathrm{TsCl}(4.94 \mathrm{~g}, 25.9 \mathrm{mmol})$ and $\mathrm{Et}_{3} \mathrm{~N}(3.61 \mathrm{~mL}, 25.9 \mathrm{mmol})$ at ambient temperature. After stirring for 48 h at ambient temperature, the resulting suspension was concentrated in vacuo and the residue was purified by the flash column chromatography (eluent, hexanes/AcOEt) to give 4.93
$\mathrm{g}\left(74 \%\right.$ yield) of desired monotosylate 12 as a colorless oil. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.74(\mathrm{~d}, J$ $=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.21(\mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{t}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}), 2.23(\mathrm{~s}, 1 \mathrm{H})$, $2.01(\mathrm{~m}, 1 \mathrm{H}), 1.84(\mathrm{~m}, 1 \mathrm{H}), 1.76-1.48(\mathrm{~m}, 5 \mathrm{H}), 1.30(\mathrm{~m}, 1 \mathrm{H}), 1.07(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $144.6(\mathrm{ArC}), 132.8(\mathrm{ArC}), 129.7(\mathrm{Ar} \mathrm{CH}), 127.7(\mathrm{Ar} \mathrm{CH}), 73.1(\mathrm{CHOH}), 69.8\left(\mathrm{CH}_{2} \mathrm{OTs}\right), 41.5\left(\mathrm{CH}_{2}\right)$, $35.2\left(\mathrm{CH}_{2}\right), 35.0\left(\mathrm{CH}_{2}\right), 34.3(\mathrm{CH}), 29.7\left(\mathrm{CH}_{2}\right), 21.5\left(\mathrm{ArCH}_{3}\right)$; IR (Neat film, NaCl$) 3379,2953,1598$, 1446, 1356, 1176, 1097, 1041, 996, 959, 886, 816, 767, $665 \mathrm{~cm}^{-1}$; HRMS (FAB, Pos.) m/z calc'd for $\mathrm{C}_{14} \mathrm{H}_{21} \mathrm{O}_{4} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}: 285.1161$, found 285.1169.

## 3-(2-Azidoethyl)cyclopentanol (13).

To a solution of tosylate $12(9.48 \mathrm{~g}, 33.3 \mathrm{mmol})$ in dry DMF $(33 \mathrm{~mL})$ was added sodium azide ( 2.28 $\mathrm{g}, 35.0 \mathrm{mmol}$ ) and the mixture was heated with stirring for 1 h . After the reaction mixture was cooled with ice bath, $\mathrm{Et}_{2} \mathrm{O}(50 \mathrm{~mL})$ was added to this mixture and this suspension was stirred for 10 min . The precipitate was filtered off and the filtrate was concentrated in vacuo. The crude residue was purified by
flash $\mathrm{SiO}_{2}$ column chromatography to afford 4.78 g ( $92 \%$ yield) of azidoalcohol $\mathbf{1 3}$ as a colorless oil. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 4.32(\mathrm{~m}, 1 \mathrm{H}), 3.28(\mathrm{t}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.18(\mathrm{ddd}, J=12.9,8.1,6.3 \mathrm{~Hz}, 1 \mathrm{H})$, $2.00-1.60(\mathrm{~m}, 7 \mathrm{H}), 1.51-1.34(\mathrm{~m}, 1 \mathrm{H}), 1.19$ (dddd, $J=12.9,8.7,5.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR $(75 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 72.9(\mathrm{CHOH}), 50.3\left(\mathrm{CH}_{2}\right), 41.6\left(\mathrm{CH}_{2}\right), 35.3(\mathrm{CH}), 35.2\left(\mathrm{CH}_{2}\right), 34.9\left(\mathrm{CH}_{2}\right), 29.7\left(\mathrm{CH}_{2}\right)$; IR $(\mathrm{Neat}$ film, NaCl ) 3351, 2948, 2097, 1439, 1343, 1265, 1103, $997 \mathrm{~cm}^{-1}$; HRMS (FAB, Pos.) $\mathrm{m} / \mathrm{z}$ calc'd for $\mathrm{C}_{7} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}[\mathrm{M}+\mathrm{H}]^{+}: 156.1137$, found 156.1128 .

## 3-(2-Azidoethyl)cyclopentanone (7).

To a suspension of DMP ( $3.73 \mathrm{~g}, 8.80 \mathrm{mmol}$ ) in DCM ( 20 mL ) was slowly added a solution of azidoalcohol $13(1.24 \mathrm{~g}, 8.00 \mathrm{mmol})$ in $\mathrm{DCM}(20 \mathrm{~mL})$ over 5 min at $0^{\circ} \mathrm{C}$. The resulting reaction mixture was stirred at ambient temperature until complete consumption of 13. After 1 h stirring, the mixture was diluted with 100 mL of $\mathrm{Et}_{2} \mathrm{O}$ and the insoluble material was removed by filtration. The filtrate was then washed with 100 mL of saturated aqueous $\mathrm{NaHCO}_{3}$ solution and the aqueous layer was extracted with 50 mL of $\mathrm{Et}_{2} \mathrm{O}$. The combined organic layers were washed with water, brine, dried over $\mathrm{MgSO}_{4}$ and concentrated in vacuo. The crude residue was purified by flash $\mathrm{SiO}_{2}$ column chromatography to afford $1.14 \mathrm{~g}\left(7.44 \mathrm{mmol}, 93 \%\right.$ yield) of ketoazide 7 as a colorless oil; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 3.36(\mathrm{t}, \mathrm{J}$ $=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.50-2.10(\mathrm{~m}, 5 \mathrm{H}), 1.90-1.70(\mathrm{~m}, 3 \mathrm{H}), 1.54(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 218.5$ $(\mathrm{C}=\mathrm{O}), 49.8\left(\mathrm{CH}_{2}\right), 44.7\left(\mathrm{CH}_{2}\right), 38.3\left(\mathrm{CH}_{2}\right), 34.5(\mathrm{CH}), 34.4\left(\mathrm{CH}_{2}\right), 29.3\left(\mathrm{CH}_{2}\right)$; IR (Neat film, NaCl$)$ 2933, 2098, 1741, 1458, 1405, 1357, 1265, $1161 \mathrm{~cm}^{-1}$; HRMS (EI) $m / z$ calc'd for $\mathrm{C}_{7} \mathrm{H}_{11} \mathrm{~N}_{3} \mathrm{O}\left[\mathrm{M}^{+}\right]:$ 153.0902 , found 153.0899 .

## Intramolecular Schmidt Reaction of Ketoazide (7) with TFA.

A solution of ketoazide $7(235 \mathrm{mg}, 1.54 \mathrm{mmol})$ in TFA ( 3 mL ) was stirred for 3 h at $60^{\circ} \mathrm{C}$ under dry nitrogen atmosphere. After cooling, 3 mL of dry MeOH was added to the reaction mixture and this mixture was stirred for further 1 h at ambient temperature. The resulting mixture was concentrated in vacuo to give a mixture of amino ester TFA salts ( $\mathbf{1 4}$ and $\mathbf{1 5}$ ). This amino ester was then treated with $(\mathrm{Boc})_{2} \mathrm{O}\left(0.46 \mathrm{~mL}, 3.08 \mathrm{mmol}, 2.0\right.$ eq.) in $\mathrm{CHCl}_{3}(3 \mathrm{~mL})$ and sat. $\mathrm{NaHCO}_{3}$ aq. ( 3 mL ). After 14 h stirring, the aqueous phase of the reaction mixture was separated and extracted with $\mathrm{CHCl}_{3}$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$ and concentrated under the reduced pressure to give crude oil, which was purified by flash column chlomatography (eluent; Hexanes-AcOEt) to give 222 mg of Boc protected amino ester 16 ( $56 \%$ yield) and 134 mg of 17 ( $34 \%$ yield) as a colorless oil. Spectra data for $\mathbf{1 6} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 4.07$ (br d, $J=13.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), $3.67(\mathrm{~s}, 3 \mathrm{H}), 2.71(\mathrm{~m}, 2 \mathrm{H}), 2.24(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H})$, $1.92(\mathrm{~m}, 1 \mathrm{H}), 1.73-1.58(\mathrm{~m}, 3 \mathrm{H}), 1.45(\mathrm{~s}, 9 \mathrm{H}), 1.26-1.06(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 172.7$ $\left(\mathrm{CO}_{2} \mathrm{CH}_{3}\right), 154.6\left(\mathrm{NCO}_{2} t-\mathrm{Bu}\right), 79.2\left(C\left(\mathrm{CH}_{3}\right)_{3}\right)$, $51.3\left(\mathrm{CO}_{2} \mathrm{CH}_{3}\right), 43.5\left(\mathrm{NCH}_{2}\right), 40.7\left(\mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 32.9$ $(\mathrm{CH}), 31.6\left(\mathrm{CHCH}_{2} \mathrm{CH}_{2} \mathrm{~N}\right)$, 28.3 $\left(\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$; IR (Neat film, NaCl$) 2976,2931,2851,1739,1694,1424$, 1366, 1315, 1289, 1241, 1161, 1122, 1014, 968, 950, 866, $770 \mathrm{~cm}^{-1}$; HRMS (EI) $\mathrm{m} / \mathrm{z}$ calc'd for $\mathrm{C}_{13} \mathrm{H}_{23} \mathrm{NO}_{4}\left[\mathrm{M}^{+}\right]: 257.1627$, found 257.1616. Spectra data for $17 ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.68(\mathrm{~s}$, $3 \mathrm{H}), 3.53$ (dd, $J=10.5,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.45(\mathrm{~m}, 1 \mathrm{H}), 3.24$ (ddd, $J=10.5,9.6,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.87$ (dd, $J=$ $10.5,9.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.34(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 2.10(\mathrm{~m}, 1 \mathrm{H}), 1.99(\mathrm{~m}, 1 \mathrm{H}), 1.71(\mathrm{q}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.45(\mathrm{~s}$, $9 \mathrm{H}), 1.45(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 173.5\left(\mathrm{CO}_{2} \mathrm{CH}_{3}\right), 154.4\left(\mathrm{NCO}_{2} t \mathrm{Bu}\right), 78.9\left(C\left(\mathrm{CH}_{3}\right)_{3}\right)$, $51.5\left(\mathrm{CO}_{2} \mathrm{CH}_{3}\right), 51.0\left(\mathrm{NCH}_{2} \mathrm{CH}\right), 45.4\left(\mathrm{NCH}_{2} \mathrm{CH}_{2}\right)$, $38.0\left(\mathrm{NCH}_{2} \mathrm{CH}\right), 32.5\left(\mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 31.1$
 $1479,1405,1366,1258,1170,1124,882,773 \mathrm{~cm}^{-1}$; HRMS (EI) $m / z$ calc'd for $\mathrm{C}_{13} \mathrm{H}_{23} \mathrm{NO}_{4}\left[\mathrm{M}^{+}\right]:$ 257.1627, found 257.1623 .

## Procedure for the Synthesis of 2-Quinuclidonium tetrafluoroborate $\left(\mathbf{1} \cdot \mathbf{H B F}_{4}\right)$.

A 10 mL tube equipped with stir bar and three-way stopcock was flame-dried under vacuum, backfilled with dry nitrogen, and charged with ketoazide $7(306 \mathrm{mg}, 2.00 \mathrm{mmol}, 1.0$ equiv) and dry ether $(4 \mathrm{~mL})$. To this solution was added ethereal $\mathrm{HBF}_{4}(54 \mathrm{wt} \%, 0.55 \mathrm{~mL}, 4.00 \mathrm{mmol}, 2.0$ equiv $)$ at $0{ }^{\circ} \mathrm{C}$ and the resulting mixture was stirred at ambient temperature until gas evolution ceased ( 3 h ). The supernatant of the resulting suspension was removed by syringe and the remaining white solid was washed with dry ether ( $3 \times 3 \mathrm{~mL}$ ) and dried under vacuum. The resulting crude solid was then dissolved with 4 mL of dry acetonitrile and this solution was transferred to a 10 mL test tube, which was placed in septum sealed 200 mL Erlenmeyer flask. Dry $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$ was then added to Erlenmeyer flask outside of the tube, and the resulting flask was settled in a desiccator $\left(\mathrm{P}_{2} \mathrm{O}_{5}\right)$ at ambient temperature until the crystals were formed (6 days). After the mother liquor was removed by syringe, the solid was washed with dry $\mathrm{Et}_{2} \mathrm{O}$ ( 3 x 5 mL ) and dried under vacuum to afford $164 \mathrm{mg}(0.770 \mathrm{mmol}, 38 \%$ yield) of 2-quinuclidonium tetrafluoroborate $\mathbf{1} \cdot \mathbf{H B F}_{4}$ as a colorless crystals; mp $185-200{ }^{\circ} \mathrm{C}$ dec.; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, \mathrm{TMS}=0 \mathrm{ppm}$ ) $\delta 8.02$ (br, $\left.1 \mathrm{H}, \mathrm{N}^{+} H\right), 3.85-3.60\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{NCH}_{2}\right), 2.99\left(\mathrm{~d}, J=3.0 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{COCH}_{2}\right), 2.51$ (sept. $J=3.0 \mathrm{~Hz}, 1 \mathrm{H}$, $\mathrm{CH}_{2} \mathrm{CH}$ ), 2.10-1.90 (m, 4H, CH2CH); ${ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, \mathrm{CD}_{3} \mathrm{CN}=118.69 \mathrm{ppm}\right) \delta 175.9$ $(C=0), 48.1\left(\mathrm{CH}_{2}\right), 40.1\left(\mathrm{CH}_{2}\right), 25.7(\mathrm{CH}), 22.7\left(\mathrm{CH}_{2}\right)$; IR $(\mathrm{KBr}) 3168,2981,1822,1468,1398,1336$, 1312, 948, 823, 799, 766, $716 \mathrm{~cm}^{-1}$; HRMS (FAB, Pos.) $m / z$ calc'd for $\mathrm{C}_{7} \mathrm{H}_{12} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+} 126.0919$, found 126.0920. The obtained 2-quinuclidonium tetrafluoroborate $\mathbf{1} \cdot \mathbf{H B F}_{4}$ was recrystallized from $\mathbf{C H}_{3} \mathbf{C N}$ $\mathrm{Et}_{2} \mathrm{O}$ to provide suitable crystals for X-ray analysis.

## Procedure for the Reactivity Study of $\left(\mathbf{1} \cdot \mathbf{H B F}_{\mathbf{4}}\right)$ with 5 equiv of $\mathbf{D}_{\mathbf{2}} \mathbf{O}$.

To an oven dried NMR tube ( 8 inch ) equipped with septum was charged $\mathbf{1} \cdot \mathbf{H B F}_{4}(13.4 \mathrm{mg}, 0.0629$ $\mathrm{mmol})$ and 0.75 mL of acetonitrile- $\mathrm{d}_{3}$ under $\mathrm{N}_{2}$ atmosphere. To this was added $\mathrm{D}_{2} \mathrm{O}(5.7 \mu \mathrm{~L}, 0.315 \mathrm{mmol}$, 5.0 equiv) in one portion. After the cap was wrapped in parafilm, the tube was well shaken and the resulting tube was transferred to the probe of NMR spectrometer operating at ambient temperature. The ratio of $\mathbf{1} \cdot \mathbf{H B F}_{4}$ to product amino acid was determined by the integral values of ${ }^{1} \mathrm{H}$ NMR spectra.

## References

1. Dess, D. B.; Martin, J. C. J. Am. Chem. Soc. 1991, 113, 7277.
2. House, H. O.; Haack, J. L.; McDaniel, W. C.; VanDerveer, D. J. Org. Chem. 1983, 48, 1643.
3. Jung, M. E.; Speltz, L. M. J. Am. Chem. Soc. 1976, 98, 7882.

## X-ray crystallographic structure of $\mathbf{1} \cdot \mathbf{H B F}_{\mathbf{4}}$



Figure 1. ORTEP drawing of $\mathbf{1} \cdot \mathbf{H B F}_{\mathbf{4}}$ (shown with $50 \%$ probability ellipsoids, $\mathrm{BF}_{4}{ }^{-}$is omitted for clarity)

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 296767.

Table 1. Crystal data and structure refinement for $\mathbf{1 \cdot H B F}_{4}$ (CCDC 296767).

Empirical formula
Formula weight
Crystallization Solvent
Crystal Habit
Crystal size
Crystal color
$\left[\mathrm{C}_{7} \mathrm{H}_{12} \mathrm{NO}\right]^{+} \mathrm{BF}_{4}^{-}$
212.99

Acetonitrile/diethylether
Block
$0.30 \times 0.26 \times 0.20 \mathrm{~mm}^{3}$
Colorless

## Data Collection

## Table 1 (cont.)

## Structure solution and Refinement

| Structure solution program | Bruker XS v6.12 |
| :--- | :--- |
| Primary solution method | Direct methods |
| Secondary solution method | Difference Fourier map |
| Hydrogen placement | Geometric positions |
| Structure refinement program | Bruker XL v6.12 |
| Refinement method | Full matrix least-squares on F ${ }^{2}$ |
| Data / restraints / parameters | $6413 / 7 / 281$ |
| Treatment of hydrogen atoms | Riding |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 3.203 |
| Final R indices [I>2 $\sigma(\mathrm{I}), 4707$ reflections] | $\mathrm{R} 1=0.0831, w \mathrm{R} 2=0.1590$ |
| R indices (all data) | $\mathrm{R} 1=0.1122, w \mathrm{R} 2=0.1667$ |
| Type of weighting scheme used | Sigma |
| Weighting scheme used | $w=1 / \sigma^{2}\left(\mathrm{Fo}^{2}\right)$ |
| Max shift/error | 0.002 |
| Average shift/error | 0.000 |
| Absolute structure parameter | $1.4(13)$ |
| Largest diff. peak and hole | 1.434 and $-1.240 \mathrm{e} . \AA^{\AA}-3$ |

## Special Refinement Details

This compound crystallizes in the orthorhombic space group $P c a 2_{1}$ with $Z=8$. Interestingly, it has been reported that very high correlation coefficients can be observed during least-squares refinement if certain conditions are present. ${ }^{1}$ In addition to two molecules in the asymmetric unit, these two molecules need to be related by a local center of symmetry and that center needs to lie near $x=1 / 8$ and $y=1 / 4$. If these conditions are met; and they are here, then the correlation coefficients between atoms related by the local center will be very high and consequently the standard uncertainty of parameters derived from least-squares will also be high. Therefore the errors presented in this report are uncharacteristically high considering the quality of the data. These conditions also give rise to high R-factors and Goodness-of-fit. However, the connectivity of the molecule is unambiguous.

Refinement of $\mathrm{F}^{2}$ against ALL reflections. The weighted R -factor ( $w \mathrm{R}$ ) 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 $F^{2}>$ $2 \sigma\left(\mathrm{~F}^{2}\right)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $\mathrm{F}^{2}$ are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.
All esds (except the esd in the dihedral angle between two 1.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.

[^0]

Figure 2. Crystal packing of $\mathbf{1} \cdot \mathbf{H B F}_{\mathbf{4}}$.

Table 2. Atomic coordinates ( $\mathbf{x} \mathbf{1 0}^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \mathbf{x} 10^{\mathbf{3}}\right.$ ) for $1 \cdot \mathrm{HBF}_{4}$ (CCDC 296767). $\mathrm{U}(\mathrm{eq})$ is defined as the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | X | y | Z | $\mathrm{U}_{\text {eq }}$ | Occ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| O(1A) | 4301(2) | 411(3) | 1929(2) | 17(1) | 1 |
| N(1A) | 6163(3) | 120(3) | 1883(2) | 17(1) | 1 |
| C(1A) | 5100(3) | 311(4) | 2278(2) | 9(1) | 1 |
| C(2A) | 5257(3) | 346(4) | 3079(2) | 12(1) | 1 |
| C(3A) | 6441(3) | 177(4) | 3244(3) | 17(1) | 1 |
| C(4A) | 6848(3) | -1533(5) | 2935(2) | 20(1) | 1 |
| C(5A) | 6656(3) | -1563(4) | 2113(2) | 19(1) | 1 |
| C(6A) | 6895(3) | 1584(5) | 2069(2) | 21(1) | 1 |
| C(7A) | 7075(3) | 1626(5) | 2877(2) | 20(1) | 1 |
| O(1B) | 1805(3) | 4894(4) | 682(2) | 54(1) | 1 |
| N(1B) | 3636(3) | 4873(3) | 717(2) | 19(1) | 1 |
| C(1B) | 2590(4) | 4902(5) | 340(3) | 38(1) | 1 |
| C(2B) | 2751(4) | 5013(6) | -462(3) | 44(2) | 1 |
| C(3B) | 3962(4) | 5053(4) | -630(3) | 23(1) | 1 |
| C(4B) | 4467(4) | 3401(6) | -344(2) | 28(1) | 1 |
| C(5B) | 4307(3) | 3329(5) | 496(2) | 26(1) | 1 |
| C(6B) | 4270(3) | 6501(5) | 553(2) | 21(1) | 1 |
| C(7B) | 4457(4) | 6611(5) | -265(2) | 27(1) | 1 |
| B(1A) | 9178(4) | 4903(4) | 2571(3) | 17(1) | 1 |
| F(1A) | 9462(2) | 3292(3) | 2643(2) | 59(1) | 1 |
| F(2A) | 8220(2) | 5116(3) | 2201(2) | 38(1) | 1 |
| F(3A) | 9069(2) | 5789(4) | 3231(2) | 40(1) | 1 |
| $\mathrm{F}(4 \mathrm{~A})$ | 9968(2) | 5789(3) | 2178(1) | 29(1) | 1 |
| B(1B) | 6695(5) | 21(5) | 34(4) | 24(1) | 1 |
| F(1B) | 5723(2) | -120(3) | 408(2) | 37(1) | 1 |
| F(2B) | 6510(4) | 762(8) | -633(3) | 36(2) | 0.472(7) |
| F(3B) | 7443(5) | 824(8) | 433(3) | 50(2) | 0.472(7) |
| F(4B) | 7048(5) | -1648(8) | -141(4) | 56(2) | 0.472(7) |
| F(2C) | 6866(6) | 1795(8) | 173(6) | 126(4) | 0.528(7) |
| F(3C) | 7481(6) | -768(9) | 379(5) | 94(3) | 0.528(7) |
| $\mathrm{F}(4 \mathrm{C})$ | 6572(5) | -464(12) | -643(3) | 72(3) | 0.528(7) |

Table 3. Bond lengths $[\AA \AA]$ and angles $\left[{ }^{\circ}\right]$ for $\mathbf{1 \cdot} \mathrm{HBF}_{4}$ (CCDC 296767).

| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | $1.192(4)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | $1.168(6)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})$ | $1.504(5)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})$ | $1.484(6)$ |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | $1.512(5)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | $1.524(5)$ |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | $1.526(5)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | $1.529(5)$ |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | $1.495(5)$ | $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | $1.499(7)$ |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | $1.518(5)$ | $\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | $1.547(7)$ |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | $1.539(5)$ | $\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | $1.523(6)$ |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | $1.539(5)$ | $\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | $1.530(6)$ |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | $1.540(6)$ | $\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | $1.567(6)$ |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | $1.511(6)$ | $\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | $1.533(6)$ |


| $\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(1 \mathrm{~A})$ | $1.314(4)$ | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(3 \mathrm{C})$ | $1.325(9)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(2 \mathrm{~A})$ | $1.390(6)$ | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{C})$ | $1.316(9)$ |
| $\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(3 \mathrm{~A})$ | $1.410(6)$ | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(3 \mathrm{~B})$ | $1.346(8)$ |
| $\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(4 \mathrm{~A})$ | $1.409(5)$ | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{~B})$ | $1.381(9)$ |
|  |  | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(1 \mathrm{~B})$ | $1.404(7)$ |
|  |  | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{~B})$ | $1.413(7)$ |
|  |  | $\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{C})$ | $1.424(8)$ |


| $\mathrm{C}(6 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | $110.3(3)$ | $\mathrm{C}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | $111.8(3)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | $110.3(3)$ | $\mathrm{C}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | $110.6(3)$ |
| $\mathrm{C}(5 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})$ | $107.8(3)$ | $\mathrm{C}(5 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | $108.5(3)$ |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})$ | $130.2(3)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{N}(1 \mathrm{~B})$ | $119.1(4)$ |
| $\mathrm{O}(1 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | $118.6(3)$ | $\mathrm{O}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | $130.5(5)$ |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(1 \mathrm{~A})-\mathrm{N}(1 \mathrm{~A})$ | $111.2(3)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | $110.3(4)$ |
| $\mathrm{C}(1 \mathrm{~A})-\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | $109.1(3)$ | $\mathrm{C}(1 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})$ | $109.3(4)$ |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | $108.9(3)$ | $\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | $110.6(4)$ |
| $\mathrm{C}(2 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | $110.5(3)$ | $\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | $109.0(4)$ |
| $\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | $107.6(4)$ | $\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(2 \mathrm{~B})$ | $108.6(4)$ |
| $\mathrm{C}(3 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})$ | $109.2(3)$ | $\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})$ | $108.6(4)$ |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(5 \mathrm{~A})-\mathrm{C}(4 \mathrm{~A})$ | $109.2(3)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(5 \mathrm{~B})-\mathrm{C}(4 \mathrm{~B})$ | $108.0(3)$ |
| $\mathrm{N}(1 \mathrm{~A})-\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})$ | $109.5(3)$ | $\mathrm{N}(1 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})$ | $108.8(3)$ |
| $\mathrm{C}(6 \mathrm{~A})-\mathrm{C}(7 \mathrm{~A})-\mathrm{C}(3 \mathrm{~A})$ | $110.1(3)$ | $\mathrm{C}(3 \mathrm{~B})-\mathrm{C}(7 \mathrm{~B})-\mathrm{C}(6 \mathrm{~B})$ | $109.3(4)$ |


| $\mathrm{F}(1 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(2 \mathrm{~A})$ | $113.5(4)$ | $\mathrm{F}(3 \mathrm{C})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{C})$ | $114.3(7)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{F}(1 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(3 \mathrm{~A})$ | $114.1(5)$ | $\mathrm{F}(3 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{~B})$ | $114.3(5)$ |
| $\mathrm{F}(2 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(3 \mathrm{~A})$ | $106.5(4)$ | $\mathrm{F}(3 \mathrm{C})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(1 \mathrm{~B})$ | $111.7(6)$ |
| $\mathrm{F}(1 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(4 \mathrm{~A})$ | $109.4(4)$ | $\mathrm{F}(4 \mathrm{C})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(1 \mathrm{~B})$ | $110.1(5)$ |
| $\mathrm{F}(2 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(4 \mathrm{~A})$ | $107.0(4)$ | $\mathrm{F}(3 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(1 \mathrm{~B})$ | $111.6(6)$ |
| $\mathrm{F}(3 \mathrm{~A})-\mathrm{B}(1 \mathrm{~A})-\mathrm{F}(4 \mathrm{~A})$ | $105.9(3)$ | $\mathrm{F}(2 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(1 \mathrm{~B})$ | $109.1(5)$ |
|  |  | $\mathrm{F}(3 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{~B})$ | $109.7(6)$ |
|  |  | $\mathrm{F}(2 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{~B})$ | $103.6(6)$ |
|  | $\mathrm{F}(1 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(4 \mathrm{~B})$ | $108.1(4)$ |  |
|  | $\mathrm{F}(3 \mathrm{C})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{C})$ | $104.6(6)$ |  |
|  |  | $\mathrm{F}(4 \mathrm{C})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{C})$ | $118.0(7)$ |
|  | $\mathrm{F}(1 \mathrm{~B})-\mathrm{B}(1 \mathrm{~B})-\mathrm{F}(2 \mathrm{C})$ | $96.7(5)$ |  |

Table 4. Anisotropic displacement parameters ( $\AA^{2} \mathbf{x} \mathbf{1 0}^{4}$ ) for $1 \cdot \mathrm{HBF}_{4}$ (CCDC 296767). The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} \mathbf{a}^{* 2} \mathbf{U}^{11}+\ldots+2 h k a^{*} b^{*} \mathbf{U}^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{O}(1 \mathrm{~A})$ | 120(12) | 160(10) | 242(15) | 3(9) | -11(11) | 14(8) |
| $\mathrm{N}(1 \mathrm{~A})$ | 189(19) | 211(16) | 124(18) | 2(11) | 38(15) | 34(10) |
| C(1A) | 92(10) | 57(8) | 109(10) | -3(7) | 6(8) | -19(7) |
| C(2A) | 111(18) | 113(14) | 143(18) | -21(11) | 1(13) | 14(10) |
| C(3A) | 180(20) | 165(17) | 180(20) | -18(13) | 20(18) | 24(12) |
| C(4A) | 168(17) | 161(17) | 257(19) | 41(15) | -17(16) | 111(13) |
| $\mathrm{C}(5 \mathrm{~A})$ | 98(15) | 188(16) | 270(20) | -56(14) | 82(14) | 1(13) |
| C(6A) | 59(14) | 225(18) | 340(20) | 59(16) | 16(16) | -36(12) |
| C(7A) | 158(17) | 183(16) | 260(20) | -17(15) | -15(16) | -66(14) |
| $\mathrm{O}(1 \mathrm{~B})$ | 210(18) | 1110(30) | 302(19) | -42(18) | 48(15) | -69(15) |
| N(1B) | 120(18) | 272(17) | 170(20) | 6(12) | 29(15) | -3(10) |
| C(1B) | 250(20) | 560(30) | 330(20) | -61(18) | -42(18) | -28(18) |
| C(2B) | 320(30) | 790(40) | 210(20) | 10(20) | -40(19) | 7(19) |
| C(3B) | 200(20) | 340(20) | 150(20) | 61(13) | 29(19) | 22(13) |
| C(4B) | 390(20) | 340(20) | 122(17) | -14(16) | 7(17) | -22(17) |
| C(5B) | 400(20) | 185(17) | 190(19) | 1(15) | 8(17) | 26(16) |
| C(6B) | 260(20) | 186(17) | 170(18) | -35(13) | 47(15) | -23(14) |
| C(7B) | 350(20) | 235(19) | 230(20) | 10(16) | 63(18) | 48(16) |
| B(1A) | 150(20) | 151(18) | 200(30) | 19(13) | 30(20) | -9(11) |
| F(1A) | 211(11) | 123(9) | 1450(30) | 173(15) | 230(15) | 66(9) |
| F(2A) | 244(15) | 695(19) | 206(16) | -32(11) | -32(14) | 96(10) |
| F(3A) | 273(13) | 703(19) | 219(12) | -152(14) | -5(11) | -5(13) |
| F(4A) | 209(10) | 368(12) | 298(11) | 68(11) | 126(10) | -109(10) |
| B(1B) | 230(30) | 270(20) | 230(30) | 17(16) | 0 (20) | -15(14) |
| $F(1 B)$ | 294(16) | 592(18) | 232(17) | -60(10) | $0(14)$ | -75(10) |
| $F(2 B)$ | 330(30) | 550(40) | 220(30) | 70(30) | $30(20)$ | 40(30) |
| $F(3 B)$ | 480(30) | 490(40) | 510(40) | -100(30) | -10(30) | -160(30) |
| F(4B) | 480(40) | 400(30) | 810(50) | -180(30) | 60(30) | 90(30) |
| F(2C) | 740(50) | 230(30) | 2820(120) | 140(50) | -270(60) | -90(30) |
| $\mathrm{F}(3 \mathrm{C})$ | 550(40) | 690(50) | 1590(80) | 110(50) | -230(50) | 270(40) |
| $\mathrm{F}(4 \mathrm{C})$ | 550(40) | 1400(80) | 230(30) | -140(40) | 110(20) | -270(50) |

Table 5. Hydrogen bonds for $1 \cdot \mathrm{HBF}_{4}$ (CCDC 296767) [ $\AA$ and $\left.{ }^{\circ}\right]$.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $<(\mathrm{DHA})$ |
| :--- | :---: | :---: | :---: | :---: |
| N(1A)-H(1A) $\ldots$ F(1B) | 0.93 | 1.86 | $2.789(6)$ | 174.3 |
| N(1A)-H(1A) $\ldots$ F(3B) | 0.93 | 2.55 | $3.171(7)$ | 124.7 |
| N(1B)-H(1B) $\ldots$ F(2A) \#1 | 0.93 | 1.86 | $2.792(6)$ | 175.4 |
| N(1B)-H(1B) $\ldots$ F(4A) \#1 | 0.93 | 2.59 | $3.215(5)$ | 124.9 |

Symmetry transformations used to generate equivalent atoms:
\#1 x-1/2,-y+1,z

## Spectra data of reported compounds.


${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$

${ }^{1}$ H NMR ( 300 MHz , DMSO- $\mathrm{d}_{6}$ )

${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


SI-16
$\underbrace{2}$
${ }^{1} \mathrm{HNMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$
$\underbrace{2}$
${ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$



${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ )


$1 \cdot \mathrm{HBF}_{4}$
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ )



TV-013 $3.8 \mathrm{mg}+1.8 \mathrm{mg}$ dithranol on SS recrys w/ chloroform ref 2500 ,0300_0004.dat
Acquired: 10:56:00, March 10, 2006


[^0]:    ${ }^{1}$ Marsh, R. E., Schomaker, V. and Herbstein, F. H. Arrays with Local Centers of Symmetry in Space Groups Pca2 ${ }_{1}$ and Pna2 ${ }_{1}$. Acta Cryst., 1998, B54, 921-924.

