

## Experimental

### General

NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT NMR spectrometer, with  $\text{CFCl}_3$  as reference for  $^{19}\text{F}$  NMR. GC/MS was performed on a Hewlett-Packard 5890A gas chromatograph with an H.-P. 5971 mass selective detector. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR instrument. Melting points were measured with a Thomas-Hoover Unimelt capillary melting point apparatus without correction. Elemental analyses were done by Atlantic Microlab, Inc. High resolution mass spectra were obtained from the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois and the Mass Spectrometry Center, University of Massachusetts, Amherst. The X-ray crystal structures were determined by Dr. Victor G. Young, Jr. at the X-ray Crystallographic Laboratory, University of Minnesota.

### 11-Aza-11-benzyl-7,7,8,8,9,9,10,10-octafluoroquadricyclo[4.2.2.1<sup>2,5</sup>.0<sup>1,6</sup>]undec-3-ene (5)

To a flame dried 500 mL round-bottom flask was added freshly activated Zn (67.7 g, 1.04 g at), N-benzylpyrrole<sup>1</sup> (8.18 g, 52.0 mmol), dibromide **4** (20.0 g, 52.0 mmol) and 200 mL dry acetonitrile. The system was flushed with  $\text{N}_2$  for 3 minutes, then a small crystal of  $\text{I}_2$  was added to the mixture. The flask was placed in a water-cooled ultrasonic bath and shaken under nitrogen for 1 hour using a modified kugelrohr motor.  $^{19}\text{F}$  NMR of the resulting yellow solution showed complete conversion to the desired adduct **5**. The mixture was filtered and the residue was

washed with  $\text{CH}_2\text{Cl}_2$  (40 mL  $\times$  2). After evaporation of the combined filtrate, the residue was purified by flash chromatography on silica gel (hexane: $\text{CH}_2\text{Cl}_2$  = 10:1) to give product **5** as yellowish crystals (16.8 g, 67%): mp 99-101 °C; IR (KBr,  $\text{cm}^{-1}$ ): 2860, 1499, 1459, 1331, 1218, 1166, 1093;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -111.2, -114.2 (AB q,  $J=227$  Hz, 4F); -112.5, -118.3 (AB q,  $J=217$  Hz, 4F),  $J_{\text{FF,endo}} = 52$  Hz,  $J_{\text{F(exo)H}} = 7$  Hz;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26 (m, 5H), 6.35 (d,  $J=7$  Hz, 2H), 4.31 (s, 2H), 3.49 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.5, 134.7, 129.4, 128.5, 127.8, 66.0, 49.5.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $^{19}\text{F}$  decoupled)  $\delta$  115.4, 114.1, 59.9. Anal. calcd for  $\text{C}_{17}\text{H}_{11}\text{F}_8\text{N}$ : C, 53.55; H, 2.91; N, 3.67. Found C, 53.51; H, 2.90; N, 3.53.

#### Octafluorobicyclo[2.2.0]hex-1(4)-ene (**6**).

Adduct **5** (0.32 g, 0.83 mmol) was placed in a flame-dried 5 mL round-bottom flask, which was connected to a pyrolysis apparatus consisting of a 15 mm O.D. pyrex tube enclosed in a 55 cm long tube furnace. The outlet of the tube was connected to an ice-cold U-trap followed by a liquid  $\text{N}_2$ -cooled U-trap. The furnace was heated to 275 °C, then **5** was allowed to sublime slowly into the hot zone under reduced pressure (60 mTorr). N-benzylpyrrole was intercepted in the ice water trap, and alkene **6** was collected in the liquid  $\text{N}_2$  trap. After all of the adduct had sublimed, the liquid  $\text{N}_2$  trap was disconnected under  $\text{N}_2$  and quickly stoppered. Upon warming, the alkene was a colorless liquid (0.154 g, 82%), mp 19-20 °C, bp 52.5 °C.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -99.07 (s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  175.8 (C=C), 121.6 ( $\text{CF}_2$ ). IR (vapor,  $\text{cm}^{-1}$ ) 1312, 1234, 1184, 886, 827. MS

m/e 205 ( $\text{C}_6\text{F}_7^+$ ), 174 ( $\text{C}_5\text{F}_6^+$ ), 155 ( $\text{C}_5\text{F}_5^+$ , base), 124 ( $\text{C}_4\text{F}_4^+$ ), 93 ( $\text{C}_3\text{F}_3^+$ ), 69 ( $\text{CF}_3^+$ ). HRMS calcd for  $\text{C}_6\text{F}_8$  223.9880; found 223.9872. It can be stored in a refrigerator for long periods without decomposition.

## 2-Trifluoromethyl-1,3-dioxolane<sup>2</sup>

To a dried Schlenk flask equipped with a finger condenser (acetonitrile bath,  $-45\text{ }^\circ\text{C}$ ) was added 2-chloroethanol (15.0 g, 0.186 mol) and pentane (30 mL). The flask was cooled to  $-78\text{ }^\circ\text{C}$  and gaseous trifluoroacetaldehyde generated by dropwise addition of trifluoroacetaldehyde methyl hemiacetal (30.0 g, 0.230 mol) to polyphosphoric acid (110.0 g) at  $130\text{--}150\text{ }^\circ\text{C}$  was condensed in the flask. After all of the aldehyde had condensed, the side arm of the flask was closed and the mixture was warmed to room temperature slowly with stirring. When bubbling inside the finger condenser ceased, potassium carbonate (25.0 g, 0.181 mol) was added slowly and the mixture was stirred for 20 h under  $\text{N}_2$ . Water (100 mL) was added and the aqueous layer was extracted with pentane (70 mL  $\times$  3). The dried ( $\text{MgSO}_4$ ) pentane solution was fractionally distilled very carefully to give 2-trifluoromethyl-1,3-dioxolane as a colorless liquid (17.6 g, 67%): bp  $88\text{--}91\text{ }^\circ\text{C}$ ;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -83.6;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (q,  $J=4.5\text{ Hz}$ , 1H), 4.12 (m, 2H), 4.08 (m, 2H).

## 2-(Difluoromethylene)-1,3-dioxolane (7)

To a flame-dried 50 mL Schlenk flask was added anhydrous ether (6 mL) and 2-trifluoromethyl-1,3-dioxolane (130 mg, 0.915 mmol). The solution was cooled to -78 °C and *n*-BuLi (2.5 M in hexane, 1.98 mL, 4.95 mmol) was added. After being stirred at -78 °C for 6 hours, the mixture was vacuum transferred (60 mTorr, temperature as low as possible) and the distillate was trapped with liquid N<sub>2</sub>. [Caution: The Schlenk flask should be attached to a N<sub>2</sub> bubbler and have its contents quenched, e.g. with *t*-butanol, before warming.] Because ketene acetal **7** was found to have a boiling point close to that of ether, its ether/hexane solution was used directly in the next step. Yield, 50-70%. <sup>19</sup>F NMR (ether/hexane) δ -137.9 (s); GC/MS: *m/e* 122 (M<sup>+</sup>), 103 (C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>F<sup>+</sup>), 85, 43, 28 (base, C<sub>2</sub>H<sub>4</sub><sup>+</sup>).

### 2,2-Ethylenedioxyperfluorotricyclo[2.2.2.0<sup>1,4</sup>]octane (**3**)

The solution of 2-(difluoromethylene)-1,3-dioxolane (**7**) from the previous step was added to octafluorobicyclo[2.2.0]hex-1(4)ene (**6**) (150 mg, 0.670 mmol) in 2 mL anhydrous ether. <sup>19</sup>F NMR spectrum showed that the reaction completed immediately and that all of the alkene **6** was consumed. Evaporation of the solvent gave the [2.2.2]propellane (212 mg, 100% yield) as a colorless solid. Mp 48-50 °C; <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ -104.1(s, 2F); -106.6, -107.0 (AB q, J=228 Hz, 4F); -106.7, -107.4 (AB q, J=224 Hz, 4F); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.25 (m, 2H), 4.21 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.7Hz, <sup>19</sup>F decoupled) δ 119.6 (s), 115.5 (s), 115.0 (s), 111 (s), 66.9 (t,

$J=154$  Hz), 53.2 (s), 51.5 (s); IR (film,  $\text{cm}^{-1}$ ) 2961, 1305, 1235, 949, 847; HRMS (CI) calcd for  $\text{C}_{10}\text{H}_5\text{O}_2\text{F}_{10}$  ( $\text{M}+\text{H}^+$ ) 347.0130; found 347.0127.

#### **1H, 4H-2,2-Ethylenedioxyperfluorobicyclo[2.2.2]octane (8)**

To a round bottom flask was added [2.2.2]propellane **3** (30.0 mg, 0.087 mmol) and a solution of tetrabutylammonium iodide (1.5 g, 4.1 mmol) in 4 mL anhydrous acetonitrile. The reaction completed instantly. Pentane (40 mL) then was added and the resulting solution was washed with water (30 mL  $\times$  4). The dried pentane solution ( $\text{Na}_2\text{SO}_4$ ) was evaporated and the residue was purified by flash chromatography on silica gel (pentane:  $\text{CH}_2\text{Cl}_2$  = 3:1) to afford **8** as a white solid (24.5 mg, 81%): mp 96-97 °C;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -105.3 (m, 2F); -108.4, -109.1 (AB q,  $J=270$  Hz, 4F); -109.8 (m, 4F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.20 (m, 2H), 4.17 (m, 2H), 3.45 (m, 1H), 3.12 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.7 Hz,  $^{19}\text{F}$  decoupled)  $\delta$  115.4, 112.3, 111.9, 102.7, 66.6 (t,  $J=153$  Hz), 52.9 (d,  $J=148$  Hz), 52.1 (d,  $J=147$  Hz); IR (film,  $\text{cm}^{-1}$ ) 2917, 1347, 1198, 1100, 947, 984; HRMS calcd for  $\text{C}_{10}\text{H}_6\text{O}_2\text{F}_{10}$  348.0208; found 348.0170.

#### **4H-2,2-Ethylenedioxyperfluorobicyclo[2.2.2]octane (9)**

To tetrabutylammonium fluoride trihydrate (2.00 g, 6.34 mmol), which was dried at 37 °C (60 mTorr) for 4 h, was added [2.2.2]propellane **3** (50.0 mg, 0.145 mmol) in 3 mL anhydrous acetonitrile. The reaction completed instantly, and the mixture was diluted with pentane (60 mL),

then washed with water (40 mL  $\times$  4). The dried pentane ( $\text{Na}_2\text{SO}_4$ ) was evaporated and the residue was purified by flash chromatography on silica gel (pentane: $\text{CH}_2\text{Cl}_2$  = 3:1) to give adduct **9** as colorless solid (42.0 mg, 79%): mp 58-60 °C;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -107.3 (m, 2F); -110.8 (m, 4F); -120.8, -121.2 (AB q,  $J$ =268 Hz, 4F); -219.0 (s, 1F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.27 (m, 2H), 4.21 (m, 2H), 3.55 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.7 Hz,  $^{19}\text{F}$  decoupled)  $\delta$  113.7, 110.8, 110.6, 103.3, 89.1, 67.8 (t,  $J$ =153 Hz), 51.0 (d,  $J$ =148 Hz); IR (film,  $\text{cm}^{-1}$ ) 2917, 1335, 1262, 1210, 952, 898; HRMS calcd for  $\text{C}_{10}\text{H}_5\text{O}_2\text{F}_{11}$  366.0114; found 366.0117.

## 2,2-Ethylenedioxy-1-iodo-4-methylperfluorobicyclo[2.2.2]octane (**16**)

To a flame-dried 50 mL Schlenk flask was added propellane **3** (110 mg, 0.318 mmol), freshly distilled  $\text{CH}_3\text{I}$  (0.6 mL, 10 mmol) and tetrabutylammonium iodide (23.5 mg, 0.0636 mmol) in 3 mL dry acetonitrile under  $\text{N}_2$ . The reaction completed immediately. Pentane (80 mL) was added and the resulting solution was washed with water (40 mL  $\times$  4). The dried pentane ( $\text{Na}_2\text{SO}_4$ ) was evaporated and the residue was purified by flash chromatography on silica gel (pentane:  $\text{CH}_2\text{Cl}_2$  = 3:1) to give adduct **16** as a colorless solid (96.2 mg, 62%): mp 194-196 °C;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -102.0, -104.8 (AB q,  $J$ =256 Hz, 4F); -110.5 (m, 2F); -114.9 (m, 4F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.36 (m, 2H), 4.20 (m, 2H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.7 Hz,  $^{19}\text{F}$  decoupled)  $\delta$  113.4, 111.6, 110.5, 104.3, 67.6 (t,  $J$ =156 Hz), 53.7 (q,  $J$ =4.5 Hz), 50.6, 2.86 (q,  $J$ =134 Hz); IR (film,  $\text{cm}^{-1}$ ) 2919, 1194, 1113, 1036, 956, 858; GC/MS  $m/e$  361 ( $\text{M}^+-\text{I}$ ), 346 ( $\text{M}^+-\text{I}$ ,

CH<sub>3</sub>), 317, 234, 177, 122 (base, C<sub>4</sub>H<sub>4</sub>F<sub>2</sub>O<sub>2</sub>); HRMS calcd for C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>F<sub>10</sub>I 487.9331; found 487.9290. Though the isomer **17** was not purified, these spectral data were obtained: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.16 (m, 4H), 1.52 (s, 3H); GC/MS m/e 361 (M<sup>+</sup>-I), 346 (M<sup>+</sup>-I, CH<sub>3</sub>), 327 (M<sup>+</sup>-I, CH<sub>3</sub>, F), 303, 253, 225, 113, 69 (CF<sub>3</sub><sup>+</sup>).

### 1-[Difluoro-2-(2-methoxy-1,3-dioxolanyl)methyl]-4*H*-perfluorobicyclo[2.2.0]hexane (**18**)

Anhydrous methanol (3 mL) was added to [2.2.2]propellane **3** (50.0 mg, 0.145 mmol) and the resulting solution was allowed to stand at room temperature overnight. After removal of methanol, the residue was crystallized from pentane to give orthoester **18** as colorless crystals (51.3 mg, 94%): mp 83-84 °C; <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ -109.5 (m, 2F); -111.0, -112.4 (AB q, J=223 Hz, 4F); -113.1, -113.5 (AB q, J=230 Hz, 4F); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.30 (m, 2H), 4.21 (m, 2H), 3.95 (m, 1H), 3.42 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.7 Hz, <sup>19</sup>F decoupled) δ 117.9, 115.5, 114.9, 114.3, 67.1 (t, J=153 Hz), 60.1, 50.0 (d, J=164 Hz), 49.1 (q, J=145 Hz); IR (neat, cm<sup>-1</sup>) 2958, 1265; HRMS calcd for C<sub>10</sub>H<sub>5</sub>O<sub>2</sub>F<sub>10</sub> (M<sup>+</sup>-OCH<sub>3</sub>) 347.0130; found 347.0122.

### 2-Hydroxyethyl difluoro[1-(4*H*-perfluorobicyclo[2.2.0]hexyl)]acetate (**20**)

A solution of distilled water (0.5 mL) in acetonitrile (4 mL) was added to [2.2.2]propellane **3** (100 mg, 0.289 mmol) and the resulting solution was allowed to stand at room temperature for 24 h. The acetonitrile was evaporated and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> (40 mL). The dried

solution ( $\text{Na}_2\text{SO}_4$ ) was evaporated and the residue was purified by flash chromatography on silica gel (ether as eluent) to afford hydroxyester **20** as colorless liquid (100 mg, 95%). IR (neat,  $\text{cm}^{-1}$ ): 3390, 1782, 1765, 1348, 1268, 1188;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -105.0 (m, 2F); -110.6 (d,  $J=226$  Hz, 2F); -115.1 (d,  $J=226$  Hz, 2F); -112.3, -112.9 (AB q,  $J=225$  Hz, 4F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.51 (t,  $J=4.5$  Hz, 2H), 4.13 (m, 1H), 3.95 (t,  $J=4.5$  Hz, 2H), 1.88 (br, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.7 Hz,  $^{19}\text{F}$  decoupled)  $\delta$  160.7, 115.2, 114.4, 109.9, 69.5 (t,  $J=150$  Hz), 60.3 (t,  $J=143$  Hz), 58.7, 50.5 (d,  $J=164$  Hz); HRMS calcd for  $\text{C}_{10}\text{H}_6\text{O}_3\text{F}_{10}$  364.0157; found 364.0164.

## 2-Bromoethyl difluoro[1-(4-bromoperfluorobicyclo[2.2.0]hexyl)]acetate (**22**)

To a solution of [2.2.2]propellane **3** (80 mg, 0.23 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (5 mL) was added  $\text{Br}_2$  (0.2 mL, 4 mmol). The resulting solution remained in the dark for two days. After evaporation of solvent and excess  $\text{Br}_2$ , the residue was purified by a flash chromatography on silica gel (pentane:  $\text{CH}_2\text{Cl}_2$  = 3:1) to afford bromoester **22** as colorless liquid (110 mg, 94%). IR (neat,  $\text{cm}^{-1}$ ): 1789, 1770, 1320, 1255, 1180;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -104.7 (m, 2F), -106.8 (d,  $J=211$  Hz, 2F), -113.6 (d,  $J=211$  Hz, 2F), -110.8 (d,  $J=224$  Hz, 2F), -115.3 (d,  $J=224$  Hz, 2F);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.70 (t,  $J=6.0$  Hz, 2H), 3.59 (t,  $J=6.0$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125.7 Hz,  $^{19}\text{F}$  decoupled)  $\delta$  159.9, 114.0, 113.5, 110.4, 67.4 (t,  $J=153$  Hz), 63.6, 57.9, 26.4 (t,  $J=153$  Hz); HRMS (CI) calcd for  $\text{C}_{10}\text{H}_5\text{O}_2\text{Br}_2\text{F}_{10}$  ( $\text{M}+\text{H}^+$ ) 504.8497; found 504.8412.



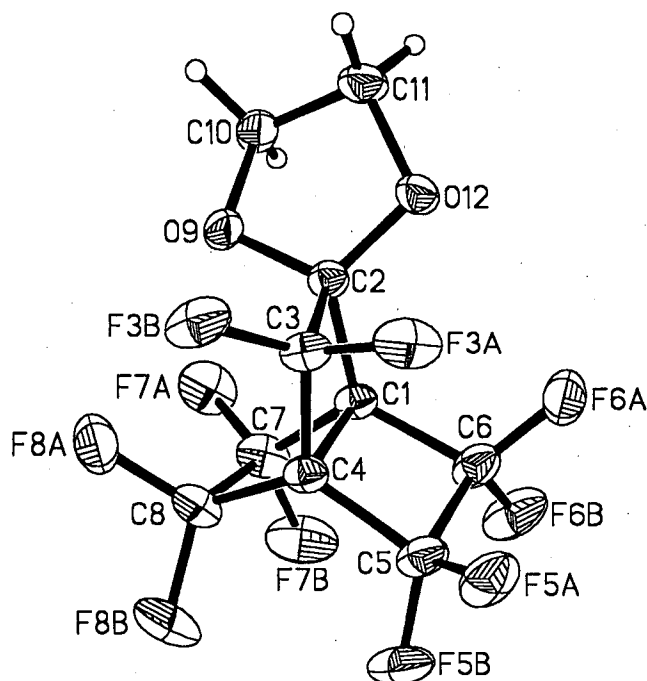
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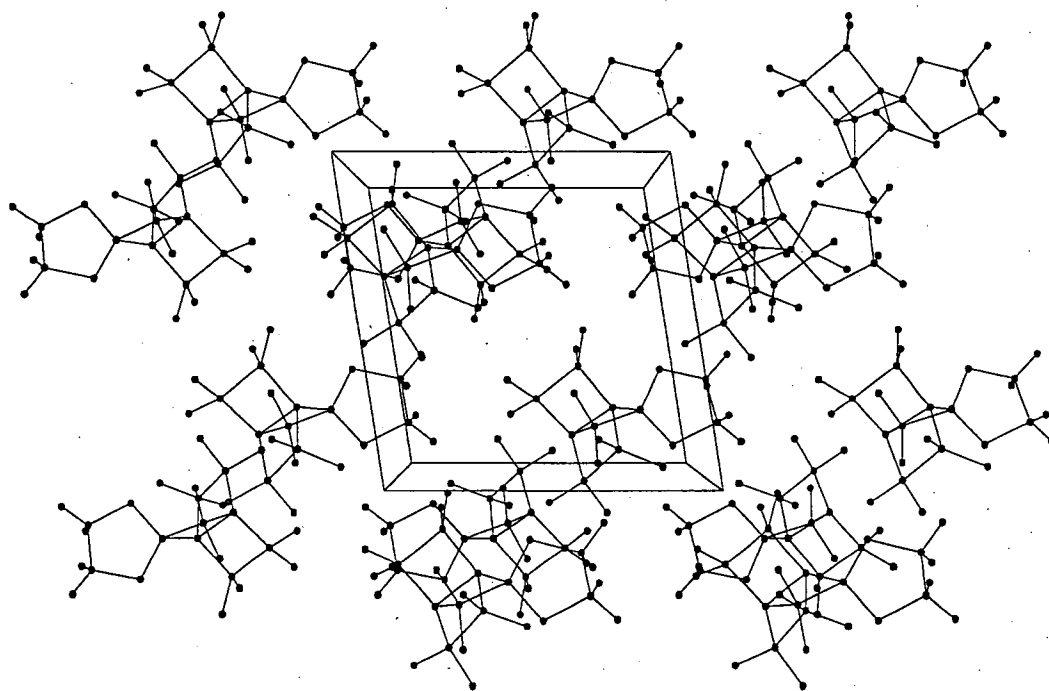
REFERENCE NUMBER: 02271a

### Crystal Structure Report for Propellane 3

$C_{10}H_4F_{10}O_2$



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#### Data collection

A crystal (approximate dimensions  $0.40 \times 0.38 \times 0.15 \text{ mm}^3$ ) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART system for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from one sets of 85 frames. This produced an initial orientation matrix determined from 203 reflections. The data collection was carried out using MoK $\alpha$  radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 3.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.68 Å. Three major sections of frames were collected with 0.30° steps in  $\omega$  at 4 different  $\phi$  settings and a detector position of -32° in  $2\theta$ . The intensity data were corrected for absorption and decay (SADABS).<sup>1</sup> Final cell constants were calculated from 2845 strong reflections from the actual data collection after integration (SAINT 6.35A, 1999).<sup>2</sup> Please refer to Table 1 for additional crystal and refinement information.

#### Structure solution and refinement

The structure was solved using SHELXS-86<sup>3</sup> and refined using SHELXL-97.<sup>3</sup> The space group  $P2_1/n$  was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to  $R1 = 0.0374$  and  $wR2 = 0.1088$  ( $F^2$ , all data).

#### Structure description

The structure was found as predicted.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 160 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the current SHELXTL suite of programs.

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<sup>1</sup> An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst. A* 51, 33 - 38 (1995).

<sup>2</sup> SAINT V6.1, Bruker Analytical X-Ray Systems, Madison, WI.

<sup>3</sup> SHELXTL-Plus V5.10, Bruker Analytical X-Ray Systems, Madison, WI.

Table 1. Crystal data and structure refinement for 02271a.

Identification code	02271a	
Empirical formula	C <sub>10</sub> H <sub>4</sub> F <sub>10</sub> O <sub>2</sub>	
Formula weight	346.13	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 <sub>1</sub> /n	
Unit cell dimensions	a = 8.9462(17) Å	α = 90°.
	b = 14.060(3) Å	β = 98.692(4)°.
	c = 8.9621(16) Å	γ = 90°.
Volume	1114.3(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	2.063 Mg/m <sup>3</sup>	
Absorption coefficient	0.250 mm <sup>-1</sup>	
F(000)	680	
Crystal habit and color	Colorless, Block	
Crystal size	0.40 x 0.38 x 0.15 mm <sup>3</sup>	
Theta range for data collection	2.72 to 31.61°.	
Index ranges	-13 ≤ h ≤ 13, 0 ≤ k ≤ 20, 0 ≤ l ≤ 13	
Reflections collected	10310	
Independent reflections	3732 [R(int) = 0.0257]	
Observed Reflections	2943	
Completeness to theta = 31.61°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9634 and 0.9065	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3732 / 0 / 199	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices [I > 2sigma(I)]	R1 = 0.0374, wR2 = 0.0996	
R indices (all data)	R1 = 0.0495, wR2 = 0.1088	
Largest diff. peak and hole	0.482 and -0.225 e.Å <sup>-3</sup>	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 02271a.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
C1	2697(1)	1726(1)	7710(1)	20(1)
C2	2816(1)	774(1)	6778(1)	20(1)
F3A	2299(1)	-255(1)	8805(1)	36(1)
F3B	4610(1)	-294(1)	8376(1)	37(1)
C3	3388(1)	265(1)	8324(1)	23(1)
C4	3611(1)	1233(1)	9140(1)	21(1)
F5A	1842(1)	939(1)	10941(1)	39(1)
F5B	2879(1)	2326(1)	10980(1)	41(1)
C5	2412(2)	1583(1)	10095(1)	28(1)
F6A	211(1)	1312(1)	8236(1)	41(1)
F6B	825(1)	2787(1)	8614(1)	47(1)
C6	1374(2)	1904(1)	8607(1)	29(1)
F7B	3628(1)	3305(1)	8371(1)	47(1)
F7A	4492(1)	2670(1)	6481(1)	42(1)
C7	3968(2)	2475(1)	7762(2)	30(1)
F8A	6084(1)	1396(1)	8388(1)	41(1)
F8B	5650(1)	2330(1)	10189(1)	45(1)
C8	4995(2)	1861(1)	8964(1)	30(1)
O9	3966(1)	787(1)	5908(1)	25(1)
C10	3232(1)	818(1)	4361(1)	26(1)
C11	1848(2)	224(1)	4444(1)	30(1)
O12	1505(1)	456(1)	5931(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for 02271a.

C1-C7	1.5462(18)	F6A-C6	1.3347(18)
C1-C6	1.5483(17)	F6B-C6	1.3352(16)
C1-C4	1.5731(15)	F7B-C7	1.3430(16)
C1-C2	1.5900(15)	F7A-C7	1.3323(16)
C2-O12	1.3723(14)	C7-C8	1.5659(19)
C2-O9	1.3815(13)	F8A-C8	1.3390(16)
C2-C3	1.5744(16)	F8B-C8	1.3376(15)
F3A-C3	1.3403(15)	O9-C10	1.4427(14)
F3B-C3	1.3418(14)	C10-C11	1.5051(18)
C3-C4	1.5435(16)	C10-H10A	0.9900
C4-C8	1.5478(17)	C10-H10B	0.9900
C4-C5	1.5498(16)	C11-O12	1.4490(15)
F5A-C5	1.3308(16)	C11-H11A	0.9900
F5B-C5	1.3393(15)	C11-H11B	0.9900
C5-C6	1.5722(17)		
C7-C1-C6	119.36(10)	C3-C4-C8	120.15(10)
C7-C1-C4	89.20(9)	C3-C4-C5	119.38(10)
C6-C1-C4	89.57(8)	C8-C4-C5	120.44(10)
C7-C1-C2	118.82(10)	C3-C4-C1	89.30(8)
C6-C1-C2	121.78(10)	C8-C4-C1	89.50(9)
C4-C1-C2	89.41(8)	C5-C4-C1	89.55(8)
O12-C2-O9	109.86(9)	F5A-C5-F5B	107.75(10)
O12-C2-C3	118.44(10)	F5A-C5-C4	117.11(11)
O9-C2-C3	109.39(9)	F5B-C5-C4	113.26(11)
O12-C2-C1	116.44(9)	F5A-C5-C6	116.77(12)
O9-C2-C1	113.55(9)	F5B-C5-C6	111.69(11)
C3-C2-C1	87.60(8)	C4-C5-C6	89.56(8)
F3A-C3-F3B	107.31(10)	F6A-C6-F6B	107.92(11)
F3A-C3-C4	112.13(10)	F6A-C6-C1	113.43(10)
F3B-C3-C4	116.99(10)	F6B-C6-C1	117.62(12)
F3A-C3-C2	112.04(10)	F6A-C6-C5	111.77(11)
F3B-C3-C2	116.81(9)	F6B-C6-C5	115.70(11)
C4-C3-C2	91.07(8)	C1-C6-C5	89.64(9)

F7A-C7-F7B	107.64(11)	O9-C10-C11	101.20(9)
F7A-C7-C1	117.83(11)	O9-C10-H10A	111.5
F7B-C7-C1	113.22(12)	C11-C10-H10A	111.5
F7A-C7-C8	117.35(13)	O9-C10-H10B	111.5
F7B-C7-C8	110.19(11)	C11-C10-H10B	111.5
C1-C7-C8	89.83(9)	H10A-C10-H10B	109.3
F8B-C8-F8A	107.63(11)	O12-C11-C10	102.16(10)
F8B-C8-C4	117.07(11)	O12-C11-H11A	111.3
F8A-C8-C4	113.66(11)	C10-C11-H11A	111.3
F8B-C8-C7	115.53(12)	O12-C11-H11B	111.3
F8A-C8-C7	112.93(11)	C10-C11-H11B	111.3
C4-C8-C7	89.40(9)	H11A-C11-H11B	109.2
C2-O9-C10	105.85(9)	C2-O12-C11	107.45(9)

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Symmetry transformations used to generate equivalent atoms:



Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 02271a. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C1	25(1)	20(1)	16(1)	1(1)	1(1)	4(1)
C2	22(1)	21(1)	17(1)	0(1)	2(1)	1(1)
F3A	54(1)	28(1)	27(1)	4(1)	7(1)	-13(1)
F3B	51(1)	32(1)	26(1)	1(1)	1(1)	23(1)
C3	32(1)	19(1)	19(1)	1(1)	3(1)	4(1)
C4	25(1)	20(1)	17(1)	1(1)	0(1)	3(1)
F5A	45(1)	51(1)	22(1)	7(1)	13(1)	6(1)
F5B	57(1)	38(1)	25(1)	-12(1)	1(1)	12(1)
C5	35(1)	32(1)	17(1)	-1(1)	4(1)	8(1)
F6A	25(1)	68(1)	29(1)	0(1)	7(1)	2(1)
F6B	59(1)	49(1)	34(1)	1(1)	8(1)	35(1)
C6	30(1)	36(1)	22(1)	0(1)	4(1)	14(1)
F7B	78(1)	19(1)	41(1)	-2(1)	-3(1)	-2(1)
F7A	51(1)	41(1)	34(1)	11(1)	7(1)	-16(1)
C7	41(1)	22(1)	26(1)	2(1)	1(1)	-5(1)
F8A	24(1)	59(1)	38(1)	2(1)	2(1)	0(1)
F8B	50(1)	45(1)	35(1)	-6(1)	-12(1)	-16(1)
C8	29(1)	32(1)	26(1)	-1(1)	-4(1)	-6(1)
O9	21(1)	36(1)	17(1)	-2(1)	3(1)	4(1)
C10	26(1)	36(1)	16(1)	1(1)	3(1)	2(1)
C11	35(1)	37(1)	19(1)	-6(1)	3(1)	-6(1)
O12	25(1)	37(1)	19(1)	-4(1)	3(1)	-7(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 02271a.

	x	y	z	U(eq)
H10A	3874	534	3669	31
H10B	2961	1476	4035	31
H11A	1007	403	3645	37
H11B	2066	-463	4357	37

Table 6. Torsion angles [°] for 02271a.

C7-C1-C2-O12	-138.47(11)	C6-C1-C4-C5	-9.84(10)
C6-C1-C2-O12	43.63(14)	C2-C1-C4-C5	-131.63(9)
C4-C1-C2-O12	132.77(10)	C3-C4-C5-F5A	40.88(15)
C7-C1-C2-O9	-9.38(13)	C8-C4-C5-F5A	-141.01(11)
C6-C1-C2-O9	172.73(9)	C1-C4-C5-F5A	129.82(11)
C4-C1-C2-O9	-98.14(10)	C3-C4-C5-F5B	167.24(10)
C7-C1-C2-C3	100.76(11)	C8-C4-C5-F5B	-14.66(15)
C6-C1-C2-C3	-77.13(11)	C1-C4-C5-F5B	-103.82(11)
C4-C1-C2-C3	12.00(8)	C3-C4-C5-C6	-79.25(12)
O12-C2-C3-F3A	-16.73(14)	C8-C4-C5-C6	98.85(12)
O9-C2-C3-F3A	-143.62(10)	C1-C4-C5-C6	9.69(9)
C1-C2-C3-F3A	102.22(10)	C7-C1-C6-F6A	167.19(10)
O12-C2-C3-F3B	107.62(12)	C4-C1-C6-F6A	-103.97(11)
O9-C2-C3-F3B	-19.27(14)	C2-C1-C6-F6A	-14.93(15)
C1-C2-C3-F3B	-133.43(11)	C7-C1-C6-F6B	39.95(16)
O12-C2-C3-C4	-131.19(10)	C4-C1-C6-F6B	128.78(12)
O9-C2-C3-C4	101.92(10)	C2-C1-C6-F6B	-142.17(11)
C1-C2-C3-C4	-12.24(8)	C7-C1-C6-C5	-79.14(12)
F3A-C3-C4-C8	168.97(10)	C4-C1-C6-C5	9.70(9)
F3B-C3-C4-C8	44.39(14)	C2-C1-C6-C5	98.75(11)
C2-C3-C4-C8	-76.65(11)	F5A-C5-C6-F6A	-15.09(15)
F3A-C3-C4-C5	-12.92(14)	F5B-C5-C6-F6A	-139.70(11)
F3B-C3-C4-C5	-137.50(11)	C4-C5-C6-F6A	105.35(11)
C2-C3-C4-C5	101.45(10)	F5A-C5-C6-F6B	108.96(14)
F3A-C3-C4-C1	-102.01(10)	F5B-C5-C6-F6B	-15.65(17)
F3B-C3-C4-C1	133.40(10)	C4-C5-C6-F6B	-130.61(12)
C2-C3-C4-C1	12.36(8)	F5A-C5-C6-C1	-130.28(11)
C7-C1-C4-C3	-131.08(9)	F5B-C5-C6-C1	105.11(11)
C6-C1-C4-C3	109.55(9)	C4-C5-C6-C1	-9.85(10)
C2-C1-C4-C3	-12.24(8)	C6-C1-C7-F7A	-138.96(12)
C7-C1-C4-C8	-10.92(9)	C4-C1-C7-F7A	131.98(12)
C6-C1-C4-C8	-130.29(10)	C2-C1-C7-F7A	43.09(16)
C2-C1-C4-C8	107.92(9)	C6-C1-C7-F7B	-12.14(15)
C7-C1-C4-C5	109.53(9)	C4-C1-C7-F7B	-101.20(11)

C2-C1-C7-F7B	169.92(10)	C1-C7-C8-F8B	-130.92(12)
C6-C1-C7-C8	99.85(11)	F7A-C7-C8-F8A	-17.03(16)
C4-C1-C7-C8	10.79(9)	F7B-C7-C8-F8A	-140.65(12)
C2-C1-C7-C8	-78.10(11)	C1-C7-C8-F8A	104.58(11)
C3-C4-C8-F8B	-141.73(12)	F7A-C7-C8-C4	-132.58(11)
C5-C4-C8-F8B	40.19(16)	F7B-C7-C8-C4	103.80(12)
C1-C4-C8-F8B	129.38(12)	C1-C7-C8-C4	-10.97(9)
C3-C4-C8-F8A	-15.21(15)	O12-C2-O9-C10	21.50(12)
C5-C4-C8-F8A	166.71(10)	C3-C2-O9-C10	153.10(9)
C1-C4-C8-F8A	-104.10(11)	C1-C2-O9-C10	-110.87(10)
C3-C4-C8-C7	99.67(11)	C2-O9-C10-C11	-34.56(12)
C5-C4-C8-C7	-78.41(12)	O9-C10-C11-O12	34.62(12)
C1-C4-C8-C7	10.78(9)	O9-C2-O12-C11	1.90(13)
F7A-C7-C8-F8B	107.47(14)	C3-C2-O12-C11	-124.77(11)
F7B-C7-C8-F8B	-16.15(17)	C1-C2-O12-C11	132.75(10)
		C10-C11-O12-C2	-23.15(13)

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Symmetry transformations used to generate  
equivalent atoms: