## *Supporting Information*

# $SF_4 \cdot N(C_2H_5)_3$: The First Conclusively Characterized $SF_4$ Adduct with an Organic Base

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## *Experimental Section*

**General**: All volatile materials were handled (a) on a Pyrex vacuum line equipped with glass/Teflon J. Young valves and (b) a vacuum line constructed of nickel, stainless steel, and FEP. Reaction vessels and NMR sample tubes were fabricated from ¼-in. o.d. and 4-mm o.d. FEP tubing, respectively, and outfitted with Kel-F valves. All reaction vessels and sample tubes were rigorously dried under dynamic vacuum followed by treatment with > 1 atm of $F_2$ gas.

Triethylamine (Sigma Aldrich) was dried by vacuum distillation onto freshly cut sodium, followed by vacuum distillation onto dry 4A molecular sieves. Sulfur tetrafluoride (Ozark-Mahoning Co.) was purified by passing the gas through a column of activated charcoal. Traces of thionyl fluoride and sulfur hexafluoride were present in the sulfur tetrafluoride, but did not interfere with the chemistry.

**Adduct Formation**: Triethylamine (0.048 g, 0.47 mmol) was vacuum distilled into a ¼-in. FEP reactor equipped with a Kel-F valve. Large excess of $SF_4$ was vacuum-distilled onto the frozen triethylamine at –196 °C. Upon melting of $SF_4$ at –120°C, triethylamine reacted with $SF_4$ forming a clear colourless solution. The sample was warmed to –90°C to ensure complete reaction, and excess $SF_4$ was removed under dynamic vacuum, yielding 0.10 g of a white solid, i.e., $SF_4 \bullet N(C_2H_5)_3$ (0.48 mmol). Molecular Weight: 209.25 $gmol^{-1}$.

**NMR spectroscopy:** All NMR spectra were recorded unlocked on a 300 MHz Bruker Avance II NMR spectrometer equipped with a 5-mm broad band probe. Fluorine-19 (282.404 MHz) NMR spectra were referenced externally to neat $CFCl_3$ at room temperature. In the $^{19}F$ NMR spectrum in $SF_4$ at –78 °C, trace amounts of $SOF_2$ (70.9 ppm) and $SF_6$ (55.8 ppm) were observed.

**Raman spectroscopy** All Raman spectra were recorded on a Bruker RFS 100 FT Raman spectrometer with a quartz beam splitter, a liquid-nitrogen cooled Ge detector, and R-496 temperature accessory. The actual usable Stokes range was 50 to 3500 $cm^{-1}$. The 1064-nm line of an Nd:YAG laser was used for excitation of the sample. The Raman spectra were recorded at –110°C with a spectral resolution of 2 $cm^{-1}$ using laser powers of 150 mW.

**X-ray crystallography:** Crystals were grown by slow evaporation of excess $SF_4$ at –118°C in a ¼-in. o.d. FEP reactor and allowed to warm to –90 °C. After no change in pressure was observed, the reactor was backfilled with nitrogen and stored in a cryo-bath set at –60°C for three days. Crystals were mounted at low temperature under a stream of dry cold nitrogen as previously described.[1] The crystals were centered on a Bruker SMART APEX II diffractometer, controlled by the APEX2 Graphical User Interface software.[2] The program SADABS[3] was used for scaling of diffraction data, the application of a decay correction, and a multi-scan absorption correction. $C_6H_{15}F_4NS$: formula weight $M_r$ = 209.25 g $cm^{-3}$, clear colourless plate (0.020 x 0.080 x 0.100 $mm^3$), triclinic, $P\bar{1}$, $Z = 2$, $a = 6.880(5)$, $b = 7.764(5)$, $c = 9.793(6)$ Å, $\alpha = 73.128(7)°$, $\beta = 80.178(7)°$, $\gamma = 72.893(5)°$, V = 476.4(5) $Å^3$, $\rho_{calcd}$ = 1.459 $gcm^{-3}$, $2\theta_{max}$ $\lambda(Mo_{K\alpha})$ = 0.71073 Å, 153(2) K, 5542 reflections, 2148 unique reflections

($R_{\mathrm{int}} = 0.0737$), absorption coefficient ($\mu$ = 0.351 mm$^{-1}$), $R_1$ = 0.0374, $wR_2$= 0.0882. Program SHELXS-97 (Sheldrick, 2008)[4] was used for both solution and refinement. A structure solution was obtained by direct methods. CCDC 883511 contains the crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Computational Methods.** The optimized geometries and frequencies of $SF_4{\cdot}N(C_2H_5)_3$ were calculated at the density functional theory (DFT) level by use of the B3LYP[5] method. The aug-cc-pVTZ basis sets for sulfur, fluorine, nitrogen, carbon and hydrogen were used.[6] Quantum-chemical calculations were carried out using the programs Gaussian 09.[5] The geometries were fully optimized using analytical gradient methods. The vibrational frequencies were calculated at the B3LYP leve using the appropriate minimized structure, and the vibrational mode descriptions were assigned with the aid of Gaussview.[7] The geometries of two isomers, one with a mearly square planar $SF_4$ geometry and one with retention of the $SF_4$ seesaw geometry, were investigated. Both converged to the same square pyramidal geometry also observed experimentally.

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[1] M. Gerken, D. A. Dixon and G. J. Schrobilgen, *Inorg. Chem.* 2000, **39**, 4244-4255.

[2] *APEX* 2, Version 2.2-0; Bruker AXS Inc.: Madison, WI, 2007.

[3] G. M. Sheldrick, *SADABS*, Version 2007/4; Bruker AXS Inc.; Madison, WI, 2007.

[4] G. M. Sheldrick, *SHELXTL97*, University of Göttingen, Germany, 2007.

[5] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[6] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis set Database, version 2/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Science Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352.

[7] *GaussView*, release 3.0; Gaussian Inc.; Pittsburgh, PA, 2003.

**Table S1.** Observed and Calculated Frequencies for $SF_4$, $N(C_2H_5)_3$ and $F_4SN(C_2H_5)_3$ (B3LYP/cc-pVTZ). Bands associated with the $SF_4$ moiety are highlighted.

| $SF_4$[a] | | | $N(C_2H_5)_3$ | | $SF_4 \cdot N(C_2H_5)_3$ | | |
|---|---|---|---|---|---|---|---|
| exptl | calcd | assignment[b] | exptl[c] | calcd | exptl[d] | calcd | assignment[b] |
| | | | | 3098(53)[53] | | 3127(19)[11] | $\nu_{as}(CH_3)$ |
| | | | | 3100(17)[41] | | 3116(21)[26] | |
| | | | | 3094(21)[39] | 3000 sh | 3114(12)[32] | $\nu_{as}(CH_3)$ / $\nu_{as}(CH_2)$ |
| | | | | 3091(68)[45] | 2994 (25) | 3105(55)[42] | |
| | | | | 3087(48)[23] | | 3100(45)[8] | |
| | | | 2967(73) | 3085(86)[33] | 2981 (41) | 3095(87)[29] | |
| | | | | 3059(70)[17] | | 3091(71)[2] | |
| | | | | 3064(116)[7] | 2970 (20) | 3084(54)[4] | |
| | | | | 3026(25)[24] | | 3062(90)[5] | $\nu_s(CH_2)$ |
| | | | 2934(100) | 3045(122)[18] | | 3053(30)[6] | $\nu_{as}(CH_2)$ |
| | | | 2926 sh | 3031(225)[25] | 2948 (36) | 3045(280)[9] | $\nu_{as}(CH_3)$ |
| | | | 2898 sh | 3029(193)[22] | 2933 (26) | 3045(19)[27] | |
| | | | | | 2914 (15) | | |
| | | | | 3028(144)[29] | 2899 (15) | 3038(191)[26] | |
| | | | 2871(60) | 2912(181)[134] | 2881 (25) | 2974(119)[58] | $\nu_{as}(CH_2)$ |
| | | | 2795(40) | 2905(30)[27] | 2854 (17) | 2949(135)[61] | |
| | | | 2776(18) | | | | combination modes |
| | | | 2750(18) | | | | |
| | | | 2734(15) | | 2748 (4) | | |
| | | | 2709(17) | | 2718 (4) | | |
| | | | | 1523(1)[1] | | 1525(1)[3] | $\delta_{as}(CH_3)$ / $\delta(CH_2)$ |
| | | | | 1508(2)[3] | 1489(4) | 1515(2)[3] | |
| | | | | 1512(2)[12] | | 1513(<1)[5] | |
| | | | | 1498(6)[4] | 1469sh | 1506(4)[4] | |
| | | | | 1501(2)[1] | 1461(42) | 1505(10)[4] | |
| | | | | 1490(10)[2] | | 1500(8)[2] | |
| | | | 1455(54) | 1495(11)[1] | | 1497(2)[7] | $\delta_{as}(CH_3)$ |
| | | | 1447 sh | 1488(9)[5] | | 1495(2)[10] | $\delta_{as}(CH_3)$ / $\delta(CH_2)$ |
| | | | | 1483(5)[4] | 1445(29) | 1490(18)[3] | |
| | | | | 1414(<1)[17] | | 1429(<1)[18] | $\delta_s(CH_3)$ / $\rho_w(CH_2)$ |
| | | | | 1419(<1)[13] | | 1423(3)[8] | |
| | | | | 1407(<1)[4] | 1394(5) | 1418(5)[3] | |
| | | | | 1401(<1)[14] | 1380 (13)[e] | 1411(1)[17] | |
| | | | | 1398(<1)[4] | | 1405(<1)[1] | |
| | | | 1368(3) | 1382(1)[13] | 1363(7) | 1395(3)[4] | |
| | | | | 1367(3)[12] | 1336(8) | 1365(5)[3] | $\rho_t(CH_2)$ |
| | | | | 1316(<1)[2] | 1301(6)[e] | 1331(2)[2] | |
| | | | 1292(14) | 1324(6)[20] | 1293(10) | 1321(7)[8] | |
| | | | 1203(4) | 1239(1)[24] | 1197(6) | 1226(4)[13] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| | | | | 1232(<1)[17] | 1184(2) | 1211(1)[16] | |
| | | | | 1155(2)[9] | 1156(26) | 1179(15)[7] | |
| | | | | 1114(4)[26] | 1101(5) | 1123(2)[12] | |
| | | | | 1103(2)[5] | 1091(16) | 1106(7)[9] | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1085(21) | 1085(9)[3] | 1072(9) | 1089(5)[8] | $\nu(C{-}C)$ / $\nu(C{-}N)$ |
| | | | 1066(23) | 1080(5)[39] | 1058(15) | 1072(5)[21] | |
| | | | 1021(4) | 1056(1)[9] | 1048(10) | 1055(4)[5] | |
| | | | 1000(8) | 1001(8)[11] | 1009(21) | 1011(16)[12] | |
| | | | 919(15) | 924(4)[2] | 917(7) | 923(3)[2] | $\rho_r(CH_3)$ / $\rho_t(CH_2)$ |
| | | | 901(10) | 905(4)[2] | 907(10) | 914(5)[1] | $\nu(C{-}C)$ / $\nu(C{-}N)$ / $\rho_r(CH_3)$ |
| | | | | 814(<1)[2] | | 829(3)[<1] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| | | | | 802(<1)[2] | | 810(<1)[3] | |
| 892 | 856(13)[102] | $\nu_s(SF_{2,eq})$ | | | 826 (64)<br>816(100) | 805(76)[130] | $\nu(S{-}F_1)$ |
| | | | | 783(<1)[4] | | 790(<1)[5] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| | | | 737(21) | 735(7)[9] | 736(57)[e] | 724(24)[233] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| 867 | 825(4)[170] | $\nu_{as}(SF_{2,eq})$ | | | 691(90) | 741(59)[266] | $\nu(S{-}F_2)$ |
| 730 | 703(<1)[630] | $\nu_{as}(SF_{2,ax})$ | | | 606(7) | 644(1)[467] | $\nu(S{-}F_3) - \nu(S{-}F_4)$ |
| | | | 535(3) | 531(2)[6] | 558(22) | 552(4)[14] | $\delta(NCC)$ |
| 558 | 535(12)[3] | $\nu_s(SF_{2,ax})$ | | | 498(32) | 505(7)[<1] | $\nu(S_1{-}F_3) + \nu(S_1{-}F_4)$ |
| 532 | 494(3)[19] | $\delta_{sc}(SF_{2,eq}) + \delta_{sc}(SF_{2,ax})$ | | | 513(11) | 481(2)[31] | $\delta(F_1S_1F_2) + \delta(F_3S_1F_4)$ |
| | | | 483(6)<br>474(6) | 475(3)[2] | 491(18)<br>484(27) | 476(4)[5] | $\delta(CNC)$ |
| 532 | 500(<1)[<1] | $\delta_{rocking}(SF_{2,eq})$ | | | | 473(2)[11] | $\delta(F_1S_1F_3) - \delta(F_1S_1F_4) + \rho_w(F_1S_1F_2)$ |
| | | | 440(13)<br>427(11) | 414(<1)[2] | 430(6) | 425(1)[10] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| 475 | 436(1)[<0.1] | $\tau(SF_2)$ | | | | 388(<1)[1] | $\rho_t(F_1S_1F_2) + \delta(F_2S_1F_3) - \delta(F_2S_1F_4)$ |
| 353 | 327(<0.1)[10] | $\delta_{sc,\ out\text{-}of\text{-}plane}(SF_{2,ax})$ | | | 353(4) | 346(1)[4] | $\rho_r(F_1S_1F_2) + \rho_w(F_3S_1F_4)$ / $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| | | | 345(2) | 336(3)[<1] | | 340(<1)[11] | $\rho_r(CH_3)$ / $\rho_r(CH_2)$ |
| | | | | 297(<1)[1] | 331(7) | 307(2)[1] | |
| | | | | 279(<1)[<1] | | 268(<1)[<1] | |
| 228 | 211(<1)[1] | $\delta_{sc}(SF_{2,eq}) - \delta_{sc}(SF_{2,ax})$ | | | 290(32)[e] | 255(4)[<1] | $\delta(F_1S_1F_2) + \rho_w(F_3S_1F_4)$ |
| | | | | 227(<0.1)[<0.1] | | 252(<1)[<1] | $\rho_r(CH_3)$ |
| | | | | 214(<1)[<0.1] | 198(4) | 222(<1)[1] | |
| | | | | 184(<1)[2] | | 214(<1)[3] | |
| | | | | | 154(11) | 158(<1)[1] | $\rho_t(S_1F_1F_2) + \rho_t(TEA)$ |
| | | | | | 142(15) | 127(<1)[<1] | $\rho_t(TEA)$ |
| | | | | | | 119(<1)[<1] | |
| | | | | | 128(10) | 109(1)[1] | $\rho_t(TEA)$ |
| | | | | 114(<1)[<1] | 110(7) | 102(<1)[<1] | $\rho_r(TEA)$ |
| | | | | | | 94(<1)[<1] | $\rho_t(S_1F_1F_2) - \rho_r(TEA)$ |
| | | | | 84(<1)[<1] | | 83(<1)[4] | $\rho_t(S_1F_3F_4) - \rho_t(TEA)$ |
| | | | | | | 70(<1)[5] | $\nu(S_1{-}N)$ |
| | | | | 55(<1)[<0.1] | | 30(<1)[<0.1] | $\rho_t(S_1F_2F_3F_4) - \rho_t(TEA)$ |

[a] Experimental gas-phase frequencies and assignments from K. O. Christe, X. Zhang, J. A. Sheehy, R. Bau, *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348 and references therein. The calculated frequencies are essentially the same as in K. O. Christe et al., *J. Am. Chem. Soc.* **2001**, *123*, 6338-6348. [b] The abbreviations denote symmetric (s), asymmetric (as), stretch ($\nu$), bend ($\delta$), twist ($\rho_t$), wagging ($\rho_w$), rock ($\rho_{rock}$), and TEA (triethylamine). Numbering of fluorine atoms is shown in Figure 1b. [c] The Raman spectrum was recorded in a 5-mm glass NMR tube at –110 °C. [d] The Raman spectrum was recorded in a ¼-in FEP tube at –110 °C. Signals from the FEP sample tube were observed at 382(7), 750 sh, and 1214 (1) cm$^{-1}$. [e] Overlap with signal from FEP sample tube.

**Table S2.** Calculated[a] Geometrical Parameters for $N(C_2H_5)_3$ and $SF_4 \cdot N(C_2H_5)_3$.

| | $N(C_2H_5)_3$ | $SF_4$ | $SF_4 \cdot N(C_2H_5)_3$ |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| $N–C_1$ | 1.464 | | 1.478 |
| $N–C_3$ | 1.463 | | 1.477 |
| $N–C_5$ | 1.462 | | 1.477 |
| $C_1–C_2$ | 1.536 | | 1.532 |
| $C_3–C_4$ | 1.527 | | 1.526 |
| $C_5–C_6$ | 1.525 | | 1.524 |
| $N{-}{-}{-}S_1$ | | | 2.626 |
| $S_1–F_1$ | | 1.576 | 1.586 |
| $S_1–F_2$ | | 1.575 | 1.607 |
| $S_1–F_3$ | | 1.682 | 1.710 |
| $S_1–F_4$ | | 1.682 | 1.714 |
| Bond Angles (deg) | | | |
| $C_1–N–C_3$ | 113.3 | | 110.9 |
| $C_1–N–C_5$ | 114.8 | | 114.3 |
| $C_3–N–C_5$ | 112.8 | | 112.3 |
| $N–C_1–C_2$ | 117.2 | | 116.9 |
| $N–C_3–C_4$ | 113.3 | | 115.4 |
| $N–C_5–C_6$ | 113.9 | | 115.1 |
| $C_1–N{-}{-}{-}S_1$ | | | 105.5 |
| $C_3–N{-}{-}{-}S_1$ | | | 99.9 |
| $C_5–N{-}{-}{-}S_1$ | | | 112.8 |
| $N{-}{-}{-}S_1–F_1$ | | | 82.2 |
| $N{-}{-}{-}S_1–F_2$ | | | 176.6 |
| $N{-}{-}{-}S_1–F_3$ | | | 92.3 |
| $N{-}{-}{-}S_1–F_4$ | | | 89.6 |
| $F_1–S_1–F_2$ | | 101.3 | 94.6 |
| $F_1–S_1–F_3$ | | 87.7 | 87.0 |
| $F_1–S_1–F_4$ | | 87.7 | 86.9 |
| $F_2–S_1–F_3$ | | 87.7 | 88.9 |
| $F_2–S_1–F_4$ | | 87.7 | 88.9 |
| $F_3–S_1–F_4$ | | 172.7 | 173.3 |

[a] The B3LYP/aug-cc-pVTZ level was used.

**Figure S1.** Calculated geometries of $N(C_2H_5)_3$ and $SF_4 \cdot N(C_2H_5)_3$ (B3LYP/aug-cc-pVTZ)