Supporting Information

SF₄•N(C₂H₅)₃: The First Conclusively Characterized SF₄ Adduct with an Organic Base

James T. Goettel, Praveen Chaudhary, Paul Hazendonk, Hélène P. A. Mercier, Michael Gerken

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 F₂ 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 SF₄ was vacuum-distilled onto the frozen triethylamine at –196 °C. Upon melting of SF₄ at –120°C, triethylamine reacted with SF₄ forming a clear colourless solution. The sample was warmed to –90°C to ensure complete reaction, and excess SF₄ was removed under dynamic vacuum, yielding 0.10 g of a white solid, i.e., SF₄•N(C₂H₅)₃ (0.48 mmol). Molecular Weight: 209.25 g mol⁻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 CFCl₃ at room temperature. In the ^19F NMR spectrum in SF₄ at –78 °C, trace amounts of SOF₂ (70.9 ppm) and SF₆ (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 SF₄ 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. The crystals were centered on a Bruker SMART APEX II diffractometer, controlled by the APEX2 Graphical User Interface software. The program SADABS was used for scaling of diffraction data, the application of a decay correction, and a multi-scan absorption correction. C₁₀H₁₅F₄NS: formula weight Mᵣ = 209.25 g cm⁻³, clear colourless plate (0.020 x 0.080 x 0.100 mm³), triclinic, P₁, Z = 2, a = 6.880(5), b = 7.764(5), c = 9.793(6) Å, α = 73.128(7)°, β = 80.178(7)°, γ = 72.893(5)°, V = 476.4(5) Å³, ρcalc = 1.39 g cm⁻³, 2θmax λ(MoKα) = 0.71073 Å, 153(2) K, 5542 reflections, 2148 unique reflections
($R_{	ext{int}} = 0.0737$), absorption coefficient ($\mu = 0.351 \, \text{mm}^{-1}$), $R_1 = 0.0374$, $wR_2= 0.0882$. 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\(_4\cdot\text{N(C}_2\text{H}_5)_3\) were calculated at the density functional theory (DFT) level by use of the B3LYP\(^6\) 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 level 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 nearly 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.

---

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 SF₄, N(C₂H₅)₃ and F₄SN(C₂H₅)₃ (B3LYP/cc-pVTZ). Bands associated with the SF₄ moiety are highlighted.

<table>
<thead>
<tr>
<th></th>
<th>SF₄</th>
<th>N(C₂H₅)₃</th>
<th>SF₄·N(C₂H₅)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>expt</td>
<td>calcd</td>
<td>assignment</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3098(53)</td>
<td>3100(17)</td>
<td>3127(19)</td>
<td>νₐ(CH₃)</td>
</tr>
<tr>
<td>3094(39)</td>
<td>3091(68)</td>
<td>3087(48)</td>
<td></td>
</tr>
<tr>
<td>3087(48)</td>
<td>3085(86)</td>
<td>3059(70)</td>
<td></td>
</tr>
<tr>
<td>3064(116)</td>
<td>3026(25)</td>
<td>3028(144)</td>
<td></td>
</tr>
<tr>
<td>2967(73)</td>
<td>2988 sh</td>
<td>2981(41)</td>
<td></td>
</tr>
<tr>
<td>2934(100)</td>
<td>2926 sh</td>
<td>2948(36)</td>
<td></td>
</tr>
<tr>
<td>2871(60)</td>
<td>2895(40)</td>
<td>2854(17)</td>
<td></td>
</tr>
<tr>
<td>2776(18)</td>
<td>2734(15)</td>
<td>2748(4)</td>
<td>Δₐ(CH₃) / Δ(CH₂)</td>
</tr>
<tr>
<td>2709(17)</td>
<td>2718(4)</td>
<td>2718(4)</td>
<td></td>
</tr>
<tr>
<td>1523(1)</td>
<td>1508(2)</td>
<td>1489(4)</td>
<td>δₐ(CH₃)</td>
</tr>
<tr>
<td>1512(12)</td>
<td>1498(6)</td>
<td>1469sh</td>
<td>δₐ(CH₃)</td>
</tr>
<tr>
<td>1501(2)</td>
<td>1488(9)</td>
<td>1445(29)</td>
<td>Δₐ(CH₃) / Δ(CH₂)</td>
</tr>
<tr>
<td>1447 sh</td>
<td>1490(10)</td>
<td>1490(10)</td>
<td></td>
</tr>
<tr>
<td>1455(54)</td>
<td>1495(11)</td>
<td>1497(27)</td>
<td></td>
</tr>
<tr>
<td>1483(5)</td>
<td>1488(9)</td>
<td>1445(29)</td>
<td></td>
</tr>
<tr>
<td>1407(15)</td>
<td>1401(14)</td>
<td>1380(13)</td>
<td></td>
</tr>
<tr>
<td>1409(1)</td>
<td>1398(1)</td>
<td>1368(3)</td>
<td></td>
</tr>
<tr>
<td>1368(3)</td>
<td>1382(1)</td>
<td>1363(7)</td>
<td></td>
</tr>
<tr>
<td>1376(3)</td>
<td>1316(1)</td>
<td>1301(6)</td>
<td></td>
</tr>
<tr>
<td>1302(4)</td>
<td>1324(6)</td>
<td>1292(14)</td>
<td></td>
</tr>
<tr>
<td>1203(4)</td>
<td>1239(1)</td>
<td>1203(4)</td>
<td></td>
</tr>
</tbody>
</table>

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
<table>
<thead>
<tr>
<th>ν(SF&lt;sub&gt;2&lt;/sub&gt;,&lt;sub&gt;aq&lt;/sub&gt;)</th>
<th>ν(SF&lt;sub&gt;2&lt;/sub&gt;,&lt;sub&gt;aq&lt;/sub&gt;)</th>
<th>ν(SF&lt;sub&gt;2&lt;/sub&gt;,&lt;sub&gt;aq&lt;/sub&gt;)</th>
<th>ν(SF&lt;sub&gt;2&lt;/sub&gt;,&lt;sub&gt;aq&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>892</td>
<td>856(13)[102]</td>
<td>826 (64)</td>
<td>805(76)[130]</td>
</tr>
<tr>
<td>867</td>
<td>825(4)[170]</td>
<td>737(21)</td>
<td>735(7)[9]</td>
</tr>
<tr>
<td>730</td>
<td>703(1)[630]</td>
<td>936(2)</td>
<td>924(3)[19]</td>
</tr>
<tr>
<td>558</td>
<td>535(12)[3]</td>
<td>483(6)</td>
<td>340(&lt;1)[11]</td>
</tr>
<tr>
<td>532</td>
<td>494(3)[19]</td>
<td>475(3)[2]</td>
<td>414(&lt;1)[2]</td>
</tr>
<tr>
<td>475</td>
<td>436(1)[&lt;0.1]</td>
<td>345(2)</td>
<td>290(32)[&lt;1]</td>
</tr>
<tr>
<td>353</td>
<td>327(&lt;0.1)[10]</td>
<td>336(3)[&lt;1]</td>
<td>331(7)</td>
</tr>
<tr>
<td>228</td>
<td>211(&lt;1)[1]</td>
<td>227(&lt;0.1)[&lt;0.1]</td>
<td>198(4)</td>
</tr>
<tr>
<td>184(&lt;1)[2]</td>
<td>154(11)</td>
<td>158(&lt;1)[&lt;1]</td>
<td>128(10)</td>
</tr>
<tr>
<td>114(&lt;1)[&lt;1]</td>
<td>110(7)</td>
<td>102(1)[&lt;1]</td>
<td>94(&lt;1)[&lt;1]</td>
</tr>
<tr>
<td>84(&lt;1)[&lt;1]</td>
<td>83(&lt;1)[4]</td>
<td>70(&lt;1)[5]</td>
<td>55(&lt;1)[&lt;0.1]</td>
</tr>
<tr>
<td>1085(21)</td>
<td>1085(9)[3]</td>
<td>1072(9)</td>
<td>1089(5)[8]</td>
</tr>
<tr>
<td>1066(23)</td>
<td>1080(5)[39]</td>
<td>1058(15)</td>
<td>1072(5)[21]</td>
</tr>
<tr>
<td>1021(4)</td>
<td>1056(1)[9]</td>
<td>1048(10)</td>
<td>1055(4)[5]</td>
</tr>
<tr>
<td>1000(8)</td>
<td>1001(8)[11]</td>
<td>1009(21)</td>
<td>1011(16)[12]</td>
</tr>
<tr>
<td>919(15)</td>
<td>924(4)[2]</td>
<td>917(7)</td>
<td>923(3)[2]</td>
</tr>
<tr>
<td>901(10)</td>
<td>905(4)[2]</td>
<td>907(10)</td>
<td>914(5)[1]</td>
</tr>
<tr>
<td>814(&lt;1)[2]</td>
<td>802(&lt;1)[2]</td>
<td>829(&lt;1)[&lt;1]</td>
<td>810(&lt;1)[&lt;1]</td>
</tr>
<tr>
<td>ν(C–C) / ν(C–N)</td>
<td>ν(CH&lt;sub&gt;3&lt;/sub&gt;) / ν(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>ν(CH&lt;sub&gt;3&lt;/sub&gt;) / ν(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>ν(CH&lt;sub&gt;3&lt;/sub&gt;) / ν(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>ρ(CH&lt;sub&gt;3&lt;/sub&gt;) / ρ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>ρ(CH&lt;sub&gt;3&lt;/sub&gt;) / ρ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>ρ(CH&lt;sub&gt;3&lt;/sub&gt;) / ρ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>ρ(CH&lt;sub&gt;3&lt;/sub&gt;) / ρ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>δ(NCC)</td>
<td>δ(C–C) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>δ(CH&lt;sub&gt;3&lt;/sub&gt;) / δ(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
</tbody>
</table>

*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. The abbreviations denote symmetric (s), asymmetric (as), stretch (ν), bend (δ), twist (ρ), wagging (ρ<sub>wa</sub>), rock (ρ<sub>rock</sub>), and TEA (triethylamine). Numbering of fluorine atoms is shown in Figure 1b. The Raman spectrum was recorded in a 5-mm glass NMR tube at −110 °C. 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<sup>–1</sup>. Overlap with signal from FEP sample tube.
Table S2. Calculated<sup>a</sup> Geometrical Parameters for N(C₂H₅)_3 and SF₄·N(C₂H₅)_3.

<table>
<thead>
<tr>
<th></th>
<th>N(C₂H₅)_3</th>
<th>SF₄</th>
<th>SF₄·N(C₂H₅)_3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond Lengths (Å)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N–C₁</td>
<td>1.464</td>
<td>1.478</td>
<td></td>
</tr>
<tr>
<td>N–C₃</td>
<td>1.463</td>
<td>1.477</td>
<td></td>
</tr>
<tr>
<td>N–C₅</td>
<td>1.462</td>
<td>1.477</td>
<td></td>
</tr>
<tr>
<td>C₁–C₂</td>
<td>1.536</td>
<td>1.532</td>
<td></td>
</tr>
<tr>
<td>C₃–C₄</td>
<td>1.527</td>
<td>1.526</td>
<td></td>
</tr>
<tr>
<td>C₅–C₆</td>
<td>1.525</td>
<td>1.524</td>
<td></td>
</tr>
<tr>
<td>N---S₁</td>
<td></td>
<td>2.626</td>
<td></td>
</tr>
<tr>
<td>S₁–F₁</td>
<td>1.576</td>
<td>1.586</td>
<td></td>
</tr>
<tr>
<td>S₁–F₂</td>
<td>1.575</td>
<td>1.607</td>
<td></td>
</tr>
<tr>
<td>S₁–F₃</td>
<td>1.682</td>
<td>1.710</td>
<td></td>
</tr>
<tr>
<td>S₁–F₄</td>
<td>1.682</td>
<td>1.714</td>
<td></td>
</tr>
<tr>
<td><strong>Bond Angles (deg)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁–N–C₃</td>
<td>113.3</td>
<td>110.9</td>
<td></td>
</tr>
<tr>
<td>C₁–N–C₅</td>
<td>114.8</td>
<td>114.3</td>
<td></td>
</tr>
<tr>
<td>C₃–N–C₅</td>
<td>112.8</td>
<td>112.3</td>
<td></td>
</tr>
<tr>
<td>N–C₁–C₂</td>
<td>117.2</td>
<td>116.9</td>
<td></td>
</tr>
<tr>
<td>N–C₃–C₄</td>
<td>113.3</td>
<td>115.4</td>
<td></td>
</tr>
<tr>
<td>N–C₅–C₆</td>
<td>113.9</td>
<td>115.1</td>
<td></td>
</tr>
<tr>
<td>C₁–N---S₁</td>
<td>105.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃–N---S₁</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅–N---S₁</td>
<td>112.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N---S₁–F₁</td>
<td>82.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N---S₁–F₂</td>
<td>176.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N---S₁–F₃</td>
<td>92.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N---S₁–F₄</td>
<td>89.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F₁–S₁–F₂</td>
<td>101.3</td>
<td>94.6</td>
<td></td>
</tr>
<tr>
<td>F₁–S₁–F₃</td>
<td>87.7</td>
<td>87.0</td>
<td></td>
</tr>
<tr>
<td>F₁–S₁–F₄</td>
<td>87.7</td>
<td>86.9</td>
<td></td>
</tr>
<tr>
<td>F₂–S₁–F₃</td>
<td>87.7</td>
<td>88.9</td>
<td></td>
</tr>
<tr>
<td>F₂–S₁–F₄</td>
<td>87.7</td>
<td>88.9</td>
<td></td>
</tr>
<tr>
<td>F₃–S₁–F₄</td>
<td>172.7</td>
<td>173.3</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> The B3LYP/aug-cc-pVTZ level was used.
Figure S1. Calculated geometries of N(C₂H₅)₃ and SF₄·N(C₂H₅)₃ (B3LYP/aug-cc-pVTZ)