Structure of the 1:1 Adduct of Di-*tert*-butylfluorosilanol and Pyridine *N*-Oxide, C$_8$H$_{19}$FOSi.C$_5$H$_5$NO

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Abstract. $M_r = 273.4$, triclinic, $P\bar{1}$, $a = 6.581$ (2), $b = 9.168$ (3), $c = 13.484$ (4) Å, $\alpha = 84.62$ (2), $\beta = 76.22$ (2), $\gamma = 83.63$ (2)°, $V = 783.3$ (4) Å^3, $Z = 2$, $D_x = 1.159$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.15$ mm^{-1}, $F(000) = 296$, $T = 153$ K, $R = 0.064$ for 2944 observed reflections. The silanol and pyridine *N*-oxide are linked by a hydrogen bond [O···O = 2.630 (6) Å, Si–O···O = 127.6 (4), N–O···O = 117.2 (4)°]. The electron-withdrawing fluoro substituent causes the Si–O bond to be much shorter than those in other hydrogen-bonded silanols. The adduct formation does not affect the normal tetrahedral coordination of Si.

Introduction. Bifunctionally substituted silanes Bu$_2$SiXY (Bu = *tert*-butyl; X, Y = OH or NH$_2$) do not easily undergo condensation reactions, in contrast to homologous compounds with less bulky alkyl substituents (Sommer & Tyler, 1954; Weidenbruch, Pesel & Hieu, 1980). The fluorosilanol Bu$_2$SiFOH (Klingebiel, 1981*a*,*b*) is also stable at room temperature, and is not hydrolysed on long exposure to the atmosphere. We have been unable, however, to determine its crystal structure. It sublimes rapidly at room temperature. A brief examination on a diffractometer indicated an *I*-centred tetragonal cell, but the broad reflections made a detailed study impossible. Examination at 100 K showed a reduced Laue symmetry, with a possible phase change and consequent twinning.

Bu$_2$SiFOH forms a 1:1 adduct with pyridine *N*-oxide when the two reagents are heated briefly in petroleum ether solution; the yield is quantitative (Bentmann, 1981). The adduct is stable, but its melting point is only 319 K. For this reason, data collection was carried out at 153 K. There is no evidence of any phase change between room temperature and this temperature.

Experimental. Crystals from CH$_2$Cl$_2$, sealed in capillaries, 0.5 × 0.3 × 0.3 mm, Nicolet $P2_1$ diffractometer, unit-cell parameters refined from setting angles of 12 reflections with $17 < 2\theta < 32°$, $\omega/2\theta$ data collection, scan speed 4–30° min^{-1} in 2θ, background measurements for one-quarter of the scan time at each end of the scan, 3410 reflections with $2\theta < 54°$, range of *hkl*: h 0→8, k –11→11, l –17→17, no significant intensity variation for one standard reflection, no absorption corrections, $R_{int} = 0.013$ (00*l* reflections only), 3395 unique reflections, 2944 with $F > 6\sigma(F)$; automatic multisolution direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.00071F^2$, H atoms constrained to give C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring external bisectors, U(H) = 1.2U_{eq}(C), OH freely refined, anisotropic thermal parameters for non-H atoms, no extinction correction, scattering factors from *International Tables for X-ray Crystallography* (1974), 185 parameters, $R = 0.064$, $wR = 0.118$, slope of normal probability plot = 2.00, $(\Delta/\sigma)_{max} = 0.034$, $(\Delta/\sigma)_{mean} = 0.007$, largest peak in final difference map = 0.57 e Å^{-3}, largest hole = –0.39 e Å^{-3}, program system used: *SHELXTL* (Sheldrick, 1978).

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular structure is shown in Fig. 1.

The fluorosilanol and pyridine *N*-oxide molecules are held together by an O–H···O hydrogen bond. The hydroxy H atom is very imprecisely located, but the short O···O distance, together with the angles at the two O atoms, clearly demonstrate this interaction. The normal tetrahedral coordination of Si is not affected by the adduct formation. The Si–O bond is considerably

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* Tables of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39170 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 10^4)$

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Si	1633 (1)	7815 (1)	7324 (1)	201 (2)
F	4016 (3)	7507 (2)	7445 (2)	357 (6)
O(1)	153 (4)	6962 (3)	8274 (2)	325 (7)
H(1)	46 (100)	6215 (67)	8285 (53)	1035 (217)*
C(1)	1694 (5)	7068 (3)	6067 (2)	271 (9)
C(2)	2501 (6)	5424 (4)	6129 (3)	406 (12)
C(3)	−492 (7)	7192 (5)	5843 (4)	520 (15)
C(4)	3189 (7)	7842 (4)	5178 (3)	474 (13)
C(5)	913 (5)	9832 (3)	7491 (2)	273 (9)
C(6)	2409 (10)	10796 (5)	6768 (4)	737 (21)
C(7)	983 (8)	10106 (4)	8590 (3)	501 (15)
C(8)	−1315 (8)	10271 (5)	7370 (5)	792 (24)
O(2)	−480 (3)	4155 (2)	8491 (2)	376 (8)
N	−2423 (4)	3819 (3)	8858 (2)	245 (7)
C(9)	−3034 (5)	3321 (3)	9849 (3)	273 (9)
C(10)	−5035 (5)	2929 (3)	10234 (2)	281 (9)
C(11)	−6447 (5)	3048 (3)	9610 (3)	302 (10)
C(12)	−5804 (4)	3573 (4)	8600 (2)	290 (9)
C(13)	−3782 (4)	3957 (3)	8232 (2)	267 (9)

* Isotropic.

Fig. 1. Structure of the adduct, showing the atom-labelling scheme.

Table 2. *Bond lengths* (Å) *and angles* (°)

Si—F	1·606 (2)	Si—O(1)	1·609 (2)
Si—C(1)	1·877 (3)	Si—C(5)	1·878 (3)
O(1)—H(1)	0·695 (64)	C(1)—C(2)	1·543 (4)
C(1)—C(3)	1·529 (6)	C(1)—C(4)	1·530 (5)
C(5)—C(6)	1·508 (6)	C(5)—C(7)	1·538 (5)
C(5)—C(8)	1·519 (7)	O(2)—N	1·316 (3)
N—C(9)	1·351 (4)	N—C(13)	1·358 (4)
C(9)—C(10)	1·370 (4)	C(10)—C(11)	1·385 (5)
C(11)—C(12)	1·383 (4)	C(12)—C(13)	1·377 (4)
O(1)···O(2)	2·630 (6)		
F—Si—O(1)	108·2 (1)	F—Si—C(1)	104·2 (1)
O(1)—Si—C(1)	112·5 (1)	F—Si—C(5)	105·5 (1)
O(1)—Si—C(5)	106·3 (1)	C(1)—Si—C(5)	119·5 (1)
Si—O(1)—H(1)	122·2 (51)	Si—C(1)—C(2)	107·8 (2)
Si—C(1)—C(3)	111·8 (2)	C(2)—C(1)—C(3)	108·2 (3)
Si—C(1)—C(4)	111·8 (3)	C(2)—C(1)—C(4)	108·0 (3)
C(3)—C(1)—C(4)	109·1 (3)	Si—C(5)—C(6)	113·2 (2)
Si—C(5)—C(7)	107·5 (2)	C(6)—C(5)—C(7)	107·8 (3)
Si—C(5)—C(8)	110·5 (3)	C(6)—C(5)—C(8)	109·8 (4)
C(7)—C(5)—C(8)	107·8 (4)	O(2)—N—C(9)	119·7 (3)
O(2)—N—C(13)	119·5 (3)	C(9)—N—C(13)	120·8 (2)
N—C(9)—C(10)	120·3 (3)	C(9)—C(10)—C(11)	120·0 (3)
C(10)—C(11)—C(12)	118·9 (3)	C(11)—C(12)—C(13)	119·8 (3)
N—C(13)—C(12)	120·1 (3)	Si—O(1)···O(2)	127·6 (4)
N—O(2)···O(1)	117·2 (4)		

shorter than in other hydrogen-bonded silanols (Clegg, 1983; Graalmann, Klingebiel, Clegg, Haase & Sheldrick, 1983). This can be ascribed to the electron-withdrawing fluoro substituent, which has also been observed to shorten adjacent Si—N bonds in silazanes (Clegg, Sheldrick & Stalke, 1984).

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Structure of Sucrose Octaacetate, C28H38O19, at 173 K

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Abstract. $M_r = 678 \cdot 60$, orthorhombic, $P2_1 2_1 2_1$, $a = 18 \cdot 350$ (7), $b = 21 \cdot 441$ (6), $c = 8 \cdot 350$ (5) Å, $V = 3285 \cdot 2$ Å³, $Z = 4$, $D_x = 1 \cdot 372$ g cm⁻³, λ(Mo $K\bar{\alpha}$) = $0 \cdot 71073$ Å, $\mu = 1 \cdot 1$ cm⁻¹, $F(000) = 1432$. Final $R = 0 \cdot 053$ for 2156 unique observed reflections. The pyranose and furanose rings are in chair ($^4C_1$) and twist ($^4T_1$) conformations respectively. The conformations about the glycosidic bonds differ by 14 and 23° from