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Structural Studies of Tris(dialkylamino)sulfonium (TAS) Fluorosilicates

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ABSTRACT

The crystal structures of two pentavalent silicon anions are discussed. The structure of $[SiMe_3F_2]^-$ **1** *shows a trigonal bipyramidal structure with the fluorines in apical positions. The Si–F bond distances are the longest known of this type. The crystal structure of fluorosilicate* **2** *(1,1-diphenyl-1-fluoro-3,3-bis[trifluoromethyl]-1,3-dihydro-2,1-benzoxasilole[ion 1-]) is distorted toward a rectangular structure along the Berry pseudorotation coordinate. The lone Si–F bond distance in* **2** *is much shorter than that in* **1**. *The ab initio calculations on a variety of pentavalent fluorinated silicon anions are reported, and good agreement with the experimental data are found. Fluoride affinities for the fluorosilanes are reported and are in reasonable agreement with the experimental values where known. The fluoride affinity of the tetra-coordinated species is related to the length of the Si–F bond in the pentavalent anion.*

INTRODUCTION

Pentacoordinate and hexacoordinate silicon species have been recognized for many years, and a growing number of attractive synthetic processes are now understood in terms of penta- or hexacoordinate silicon intermediates [1–3]. The anion acceptor properties of tetracoordinate silicon compounds are highly ligand dependent, and bidentate or highly electron-withdrawing ligands generally facilitate formation of the higher coordination number species.

Penta- and hexacoordinate silicate complexes are, of course, potential anion donors and can transfer an anion to other acceptors. The class of fluorosilicate anions $[R_4SiF]^-$ and their tetracoordinate precursors (R_4Si) exemplifies this behavior. Trimethyldifluorosilicate, $[Me_3SiF_2]^-$, is an exceptionally potent source of fluoride ion. This species has been isolated only with tris(dialkylamino)sulfonium (TAS) as counter cation [4a], and the molecular structure and bonding of TAS has previously been discussed [4b]. The ion pair $[Me_2N)_3S]^+[Me_3SiF_2]^-$ differs significantly (reactivity, solubility, etc.) from other fluoride ion donor systems, such as CsF [5], crown ether/KF, or alkylammonium fluorides [5]. It has been used to

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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generate a variety of unusual isolable, polyfluorinated anionic species [6–8], as well as reactive intermediates involved in group transfer polymerization of methacrylates [3a] and other processes [9]. The unique properties of TAS trimethyldifluorosilicate have been used to advantage in other areas of sulfur and sulfur-nitrogen chemistry, leading to a large number of differently coordinated sulfur-containing anions [10–12]. The outstanding fluoride-ion donor properties of the $[Me_3SiF_2]^-$ ion warranted a full structural characterization, and we report herein the results of X-ray crystallographic and computational studies on this and closely related pentacoordinate species.

EXPERIMENTAL SECTION

TAS-trimethyldifluorosilicate (TAS-**1**) was prepared according to the literature method [4,12]. Single crystals were obtained by condensing 50 mL of dry ether (dried over $LiAlH_4$) to 0.5 g of **1** in 10 mL MeCN (dried over P_4O_{10}), kept at −25°C, at a pressure of 500 mbar N_2 over a period of 3 days. The solvent mixture was decanted and the crystals dried quickly under vacuum. Colorless crystals were removed from the reaction vessel under dry N_2 in a glove box and filled into 0.3–0.7 mm Lindemann capillaries.

Relative Fluoride Affinities of Substituted Silanes

The relative fluoride affinities of silanes **7**, **8**, and **9** in CD_3CN were established using NMR, as described here for **7** and **8**.

A mixture of TAS-**5** (82 mg, 0.15 mmol) and silane **7** (64 mg, 0.15 mmol) was dissolved in CD_3CN (0.6 mL) for NMR analyses at 25°C. ^1H NMR showed the following signals and relative areas: $\delta = 8.26$–8.10 (1H), 7.95–7.78 (4H), 7.7–7.05 (18H), 0.68 (3H), 2.70 (18H, TAS); no CH_3 signal due to **5** (0.18) was observed. ^{19}F NMR showed $\delta = -74.1$ (singlet) and −75.39 (center of nearly coalesced A_3B_3 pattern for silane **8**).

In a similar fashion, a mixture of silane **8** (52 mg, 0.14 mmol) and silicate TAS-**2** (100 mg, 0.17 mmol) was dissolved in CD_3CN (0.6 mL). ^1H NMR showed $\delta = 0.68$ (s, 3H), 2.75 (s, 18H), 8.3–7.0 (23H); no signal for CH_3 of TAS **5** was observed. ^{19}F $\{^1H\}$ NMR showed $\delta = -74.13$ (s), −75.41 (center of nearly coalesced A_3B_3 pattern for silane **8**).

Thus, within our NMR detection limits, the reaction below proceeds completely to the right as written.

$$\text{TAS-}\mathbf{5} + \mathbf{7} \rightarrow \mathbf{8} + \text{TAS-}\mathbf{2}$$

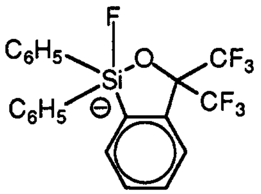
Crystal Data

The X-ray data were collected in profile fitting mode [13] at room temperature on a Siemens-Stoe diffractometer equipped with a graphite monochromator. The structure of **1** was solved by direct methods with the program SHELX 86 [14a] and refined by SHELX 76 [14b]; experimental details are given in Table 1. The positions of the hydrogen atoms were fixed, assuming ideal tetrahedral geometries and $r(C–H) = 0.96$ Å. The isotropic temperature factors for H were set at 0.08 Å [2].

TABLE 1 X-ray Crystallography Parameters for TAS-1 and TAS-2

Parameter	*1*	*2*
Formula	$SSiF_2N_3C_9H_{27}$	$SSiF_7ON_3C_{27}H_{32}$
Formula weight	275.5	607.727
Crystal system	monoclinic	triclinic
Space group	$P2_1/m$	$P1$
a(Å)	7.773(4)	10.218(4)
b(Å)	11.788(8)	15.441(7)
c(Å)	8.804(5)	9.741(4)
α(deg)	90	106.14(3)
β(deg)	94.25(4)	107.57(3)
γ(deg)	90	87.17(4)
V(Å^3)	804.5	1406.45
Z	2	2
ρ (calcd) (gcm^{-3})	2.27	1.435
Crystal Dimension (mm)	0.2 × 0.3 × 0.5	0.19 × 0.06 × 0.35
Temperature	20°C	−100°C
2θ max	45	55
Total data	1286	6596
Unique data	1108	6233
Data $I > p\sigma(I)$	874 ($p = 3$)	3987 ($p = 2$)
Parameters	82	489
R	0.067	0.048
R_w	0.068	0.052
Residual ρ max e/Å^3	−0.6	0.3

Experimental details of the preparation and structure determination of TAS 1,1-diphenyl-1-fluoro-3, 3-bis[trifluoromethyl]-1, 3-dihydro-2,1-benzoxasilole[ion 1-] (**2**) were reported earlier [5]. In that article, however, no detailed structural information on the anion **2** was reported, so we present the results here. The crystal information is also given in Table 1 [15].



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Calculations

The calculations were done with the program GRADSCF[16] on Cray Research computer systems. Geometries were gradient optimized [17]. Because of the very low torsion modes about the Si–C bonds for **1**, it was necessary to use tight op-

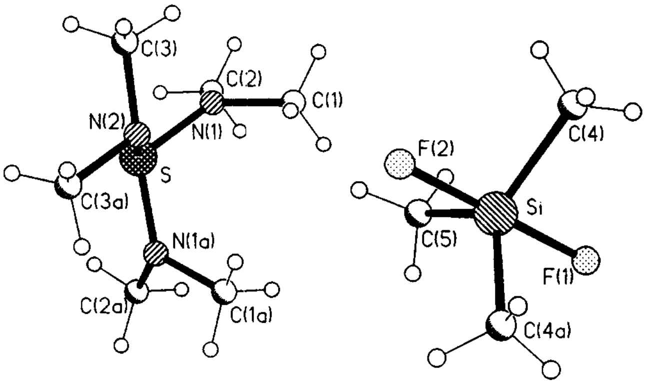


FIGURE 1 Crystallographic structure for TAS-1.

timization criteria. Force fields were calculated by using analytic second-derivative techniques [18]. Correlation corrections were done at the MP-2 level [19] in the valence space at the optimized SCF geometries. The basis set for the calculations is of polarized double-zeta quality [20], except for the H atoms on **1** which did not have polarization functions.

RESULTS

*Crystal Structures of Silicate Salts TAS-***1** *and TAS-***2**

Figures 1 and 2 show the atomic labeling of TAS-**1** and TAS-**2**. Selected bond distances and angles for **1** and **2** are listed in Table 2 and 3. The data for the $[(Me_2N)_3S]^+$ ion in TAS-**1** and TAS-**2** agree very well with those reported for other TAS salts [5].

The $[Me_3SiF_2]^-$ ion **1** exhibits the expected TBP geometry (Figure 1) with fluorine atoms in the apical positions. The F(1)-Si-F(2) angle is essentially linear (179.7(2)°), and the Si–F bond lengths are identical within the limits of error. The Si is slightly shifted from the plane of the three carbon atoms toward F(1) by 0.02 Å which leads to F-Si-C bond angles that deviate from 90° and C-Si-C bond angles that deviate from 120°. Both the cation and anion lie on a mirror plane.

TABLE 2 Geometry Parameters for the Anion **1**[a]

Parameter	*Calcd*[b]	*Expt*[c]
r(Si–F1)	1.751	1.758(4)
r(Si–F2)	1.757	1.755(4)
r(Si–C1)	1.918	1.874(5)
r(Si–C2)	1.919	1.873(8)
r(Si–C3)	1.919	1.874(5)
r(C1–H1)	1.086(0.4)	—
r(C1–H2)	1.091(−121.4)	—
r(C1–H3)	1.090(122.2)	—
r(C2–H4)	1.086(−179.1)	—
r(C2–H5)	1.091(−57.2)	—
r(C2–H6)	1.091(59.1)	—
r(C3–H7)	1.087(6.8)	—
r(C3–H8)	1.090(−114.4)	—
r(C3–H9)	1.090(129.2)	—
θ(F1–Si–F2)	179.7	179.7(2)
θ(F1–Si–C1)	91.5	90.9(2)
θ(F1–Si–C2)	88.6	89.7(3)
θ(F1–Si–C3)	91.2	90.9(2)
θ(F2–Si–C1)	88.8	88.9(2)
θ(F2–Si–C2)	91.2	90.6(2)
θ(F2–Si–C3)	88.7	88.9(2)
θ(C1–Si–C2)	119.8	120.8(2)
θ(C1–Si–C3)	120.0	118.4(3)
θ(C2–Si–C3)	120.2	120.8(2)
θ(Si–C1–H1)	113.4	—
θ(Si–C1–H2)	110.2	—
θ(Si–C1–H3)	110.1	—
θ(Si–C2–H4)	113.5	—
θ(Si–C2–H5)	110.1	—
θ(Si–C2–H6)	110.1	—
θ(Si–C3–H7)	113.4	—
θ(Si–C3–H8)	109.8	—
θ(Si–C3–H9)	110.4	—

[a] Bond distances in Å. Bond angles in degrees.
[b] Values in parentheses are the torsions about the Si–C bond with respect to **1**.
[c] R(C–H) = 0.96 Å. Tetrahedral geometry assumed at C.

The anion **2** also exhibits the expected TBP structure, with the electronegative elements in apical positions. However, because of the different ligands, the structure is distorted toward a rectangular pyramid structure (RP) along the Berry pseudo-rotation coordinate with C(10) acting as a pivot (F(1)Si(1)O(1) = 171.2(1)°, C(4)Si(1)O(16) = 134.8(1)°). This distortion is more pronounced than that observed in $[(C_6H_5)_2(1\text{-}C_{10}H_7)SiF_2]^-$ [21]. The Si–C bond distances average 1.913 Å, and the Si–F bond distance is 1.707 Å. The Si–O distance is 1.850 Å. Thus, the Si–F is significantly shorter than when two F atoms are bonded to the Si, and clearly the Si–O bond is much longer than the Si–F bond.

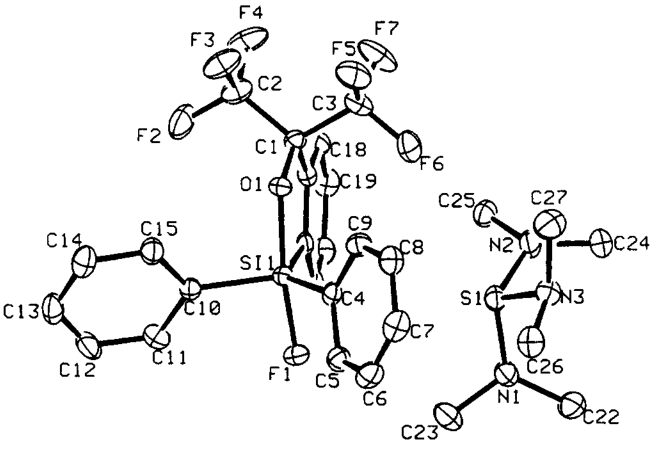


FIGURE 2 Crystallographic structure for TAS-2.

TABLE 3 Geometry Parameters for **2**

Interatomic Distances (Å)					
Si(1)-F(1)	1.707(2)	C(1)-O(1)	1.371(4)	C(10)-C(15)	1.398(4)
Si(1)-O(1)	1.850(2)	C(1)-C(2)	1.541(4)	C(11)-C(12)	1.391(5)
Si(1)-C(4)	1.927(3)	C(1)-C(3)	1.543(4)	C(12)-C(13)	1.374(6)
Si(1)-C(10)	1.902(3)	C(1)-C(17)	1.533(4)	C(13)-C(14)	1.374(5)
Si(1)-C(16)	1.909(3)	C(4)-C(5)	1.407(4)	C(14)-C(15)	1.394(5)
C(2)-F(2)	1.330(4)	C(4)-C(9)	1.394(5)	C(16)-C(17)	1.394(4)
C(2)-F(3)	1.340(4)	C(5)-C(6)	1.395(5)	C(16)-C(21)	1.401(4)
C(2)-F(4)	1.348(4)	C(6)-C(7)	1.381(5)	C(17)-C(18)	1.406(4)
C(3)-F(5)	1.337(4)	C(7)-C(8)	1.381(5)	C(18)-C(19)	1.380(5)
C(3)-F(6)	1.335(4)	C(8)-C(9)	1.399(5)	C(19)-C(20)	1.390(5)
C(3)-F(7)	1.352(4)	C(10)-C(11)	1.402(4)	C(20)-C(21)	1.389(4)

Intermolecular Angles (°)			
F(1)-Si(1)-O(1)	171.2(1)	F(7)-C(3)-C(1)	113.4(3)
F(1)-Si(1)-C(4)	91.0(1)	O(1)-C(1)-C(2)	108.1(2)
F(1)-Si(1)-C(10)	93.2(1)	O(1)-C(1)-C(3)	108.1(2)
F(1)-Si(1)-C(16)	89.4(1)	O(1)-C(1)-C(17)	109.8(2)
O(1)-Si(1)-C(4)	89.6(1)	C(2)-C(1)-C(3)	110.4(3)
O(1)-Si(1)-C(10)	94.6(1)	C(2)-C(1)-C(17)	111.0(2)
O(1)-Si(1)-C(16)	83.9(1)	C(3)-C(1)-C(17)	109.5(3)
C(4)-Si(1)-C(10)	113.0(1)	C(5)-C(4)-C(9)	115.7(3)
C(4)-Si(1)-C(16)	134.8(1)	C(4)-C(5)-C(6)	122.4(3)
C(10)-Si(1)-C(16)	112.1(1)	C(5)-C(6)-C(7)	120.0(3)
Si(1)-O(1)-C(1)	119.3(2)	C(6)-C(7)-C(8)	119.4(3)
Si(1)-C(4)-C(5)	119.2(2)	C(7)-C(8)-C(9)	120.0(3)
Si(1)-C(4)-C(9)	125.0(2)	C(4)-C(9)-C(8)	122.5(3)
Si(1)-C(10)-C(11)	121.1(2)	C(11)-C(10)-C(15)	116.6(3)
Si(1)-C(10)-C(15)	122.3(2)	C(10)-C(11)-C(12)	121.6(3)
Si(1)-C(16)-C(17)	115.1(2)	C(11)-C(12)-C(13)	120.3(4)
Si(1)-C(16)-C(21)	127.0(2)	C(12)-C(.13)-C(14)	119.7(3)
F(2)-C(2)-F(3)	106.5(3)	C(13)-C(14)-C(15)	120.3(4)
F(2)-C(2)-F(4)	106.8(3)	C(10)-C(15)-C(14)	121.6(3)
F(3)-C(2)-F(4)	106.3(3)	C(17)-C(16)-C(21)	117.6(3)
F(5)-C(3)-F(6)	107.1(3)	C(1)-C(17)-C(16)	111.7(3)
F(5)-C(3)-F(7)	106.3(3)	C(1)-C(17)-C(18)	126.5(3)
F(6)-C(3)-F(7)	106.2(3)	C(16)-C(17)-C(18)	121.8(3)
F(2)-C(2)-C(1)	110.9(3)	C(17)-C(18)-C(19)	118.8(3)
F(3)-C(2)-C(1)	112.3(3)	C(18)-C(19)-C(20)	120.7(3)
F(4)-C(2)-C(1)	113.7(3)	C(19)-C(20)-C(21)	119.8(3)
F(5)-C(3)-C(1)	113.1(3)	C(16)-C(21)-C(20)	121.2(3)
F(6)-C(3)-C(1)	110.4(3)		

As shown in Figure 2, the cation fits into a pocket formed by the phenyl rings, with the closest approach being the interaction of S(1) with F(6) (positive S with negative F) which is 3.58 Å. This distance is larger than the sum of the van der Waals radii. The crystal packing is otherwise dominated by F···F interactions.

Electronic Structure of 1

The initial calculations were done with the conformer with C_{3h} symmetry. This geometry had three imaginary frequencies (at 59*i*(e) and 30.6*i* cm^{-1} corresponding to rotation of the three CH_3 groups), and thus it is not even a transition state on the potential energy surface. The optimized geometry is derived from the C_{3h} geometry by three 90° rotations about the SiC bonds to yield a structure where two CH_3 groups have a C–H bond approximately eclipsing one SiF bond and the other group has a C–H bond eclipsing the other Si–F bond. This is the same configuration as found in the X-ray analysis. The surface for torsion about the Si–C bonds is very flat, however, with the C_{3h} structure only 0.20 kcal/mol above the optimized structure at the SCF level, and this energy difference is reduced to 0.15 kcal/mol at the MP-2 level.

The calculated and experimental structures show quite good agreement, with the calculated bond distances for the SiC bonds being 0.045 Å longer than the experimental values. The calculated Si–F bond lengths, in contrast, are in essentially exact agreement with the experimental values. The C_{3h} structure has almost the same geometry parameters as the optimum structure with $r(\text{Si–F}) = 1.753$ Å, $r(\text{Si–C}) = 1.919$ Å, $r(\text{C–H}_{ip}) = 1.093$ Å, and $r(\text{C–H}_{op}) = 1.088$ Å [22].

The calculated vibrational spectrum is given as supplementary material. The three torsions about the Si–C bonds are at 27, 58, and 67 cm^{-1}. The most intense transition is predicted to be the asymmetric Si–F stretch at 637 cm^{-1} (I = 267 km/mol) which, when scaled, would be predicted to be observed near 575 cm^{-1}. The symmetric Si–F stretch is calculated at 453 cm^{-1}, with a scaled value near 410 cm^{-1}.

The charge distribution for $SiMe_3F_2^-$ shows the Si to be quite positive at +1.66 e and the fluorines to be negative at −0.65 e. The remaining negative charge is on the CH_3 groups, and each CH_3 group has −0.45 e (the charge on the C is −0.88 e).

DISCUSSION

Tris(dialkylamino)sulfonium trialkyldifluorosilicates are formed in the terminal step of a series of reactions which occur when SF_4 is treated with aminosilanes using stoichiometry 1:3 (Equation 1) [4].

$$SF_4 + 3\,(R_2N)SiMe_3 \rightarrow [(R_2N)_3S]^+\,[Me_3SiF_2]^- + 2Me_3SiF \qquad (1)$$

Although a tris(dialkylamino)fluorosulfurane structure might have been anticipated, based upon known chemistry (e.g., dialkylaminosulfur trifluoride and congeners [23]), no direct evidence for the formation of such sulfuranes has been obtained. Presumably, the three dialkylamino ligands are responsible for decreasing the acceptor properties of the central sulfur atom sufficiently that an alternative fluoride ion acceptor species (Me_3SiF) appears strong by comparison. Changes in S–N and S–F bond lengths for the series $(Me_2N)_nSF_{4-n}$ ($n = 0, 1, 2$) are consistent with the notion that the S–F bond in $(Me_2N)_3SF$ should be quite weak [24].

The known Si–C and Si–F bond distances in phenyl- and methylfluorosilanes and the related silicates formed by F^- addition are listed in Table 4. Successive replacement of F by carbon ligands in SiF_4 leads to a lengthening of the Si–F bond by 0.01–0.015 Å for each F that is substituted. A similar result has been found for the simple fluorosilanes SiF_nH_m [30]. The only known phenyl substituted structure is that of $PhSiF_3$, **3**. The Si–F bond in **3** is the same as that in $MeSiF_3$, whereas the Si–C bond is 0.006 Å shorter in **3**. This is significantly less than the normal differences found in comparing lengths to an sp^3 carbon and an sp^2 one. The longest known Si–F bond is found in $[SiMe_3F_2]^-$. Because this structure was determined at room temperature, these values should be corrected for thermal motion which results in even longer Si–F bonds. For **1**, the librationally corrected Si–F bond lengths are 1.784 Å and 1.773 Å.

A surprising result is the much larger Si–C distance in the phenyl as compared to the methyl derivatives. This may be a steric effect, as the structure of $[PhMeSiF_3]^-$ shows that the bond from Si to the methyl group is almost 0.04 Å shorter than that from Si to the phenyl group [21]. A steric effect due to interactions of the ortho-hydrogens is suggested, because phenyl will better stabilize negative charge as compared to methyl. Thus, the Si–C bond distance would be shorter with the phenyl substituent if only this effect were working; however, the evidence is in opposition to this. A similar trend, although not as pronounced, is also found in the isoelectronic fluorophosphoranes; e.g., in $PhPF_4$, the P–C bond is 1.796 Å [31a], and, in $MePF_4$, the P–C bond is 1.780 Å [31b].

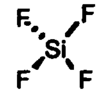
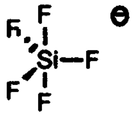
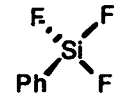
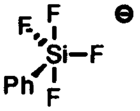
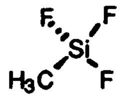
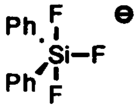
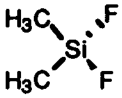
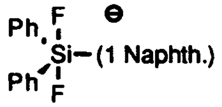
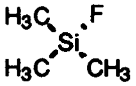
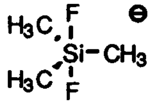
In order to obtain more structural comparisons for this pentavalent silicon anion, we optimized the structures of $[SiF_2H_3]^-$ and $[SiF_5]^-$ in D_{3h} symmetry. The Si–F bond lengths for $[SiF_5]^-$ are 1.658 Å for the axial position and 1.620 Å for the equatorial. The experimental values [26] are 1.646 Å for the axial Si–F distance and 1.591 Å for the equatorial. The Si–F bond in $[SiF_2H_3]^-$ is 1.734 Å, and the Si–H bond is 1.497 Å. Comparison with the structure of $[SiF_2(CH_3)_3]^-$ shows that the axial Si–F bond is longest with CH_3 as an equatorial substituent and shortest with F as an equatorial substituent. The structure of $[SiH_3OHF]^-$ **4** was also calculated for comparison to **1** and **2**. The structure of **4** has Si–F and Si–OH bond distances of 1.742 and 1.788 Å, respectively. These distances differ by less than 0.05 Å, as compared to the difference of 0.14 Å found for **2**. Clearly, the oxygen atom is in a different environment in **2** than in **4**. Of course, the $C(CF_3)_2$ group is not the same as a proton, and the placement of the O in a five-membered ring in **2** also could account for part of the difference ($\theta(\text{SiOC}) = 119.3°$ in **2** vs. $\theta(\text{SiOH}) = 112.0°$ in **4**). This suggests that the O atom in **2** is less electronegative than the O atom in **4**. This accounts for the longer Si–O distance in **2** ($\Delta r(\text{Si-O}) = 0.062$ Å) and, as a consequence, the shorter Si–F distance in **2** ($\Delta r(\text{Si-F}) = -0.035$ Å) as compared to **4**.

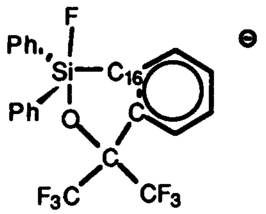
The fluoride affinity of a molecule A is defined by the negative of ΔH for Reaction 2.

$$A + F^- \rightarrow AF^- \qquad (2)$$

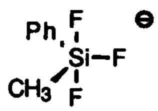
Although it is possible to calculate the absolute binding energy of a proton to a molecule quite accurately [32], it is very difficult to calculate the absolute fluoride affinity directly because of the difficulty in calculating the absolute electron affinity of F. However, one can calculate the relative fluoride affinity [33] quite well by following the same procedure one would employ to measure a relative fluoride affinity, for example, in an ion cyclotron resonance spectrometer. The absolute fluoride affinity of CF_2O is well-established as 42.6 kcal/mol

TABLE 4 Structural Data of Aryl- and Alkyl-fluorosilanes and Their Related Fluorosilicates

 SiF = 1.56 Å[25]	 SiF_{ax} = 1.646 Å SiF_{eq} = 1.591 Å $F_{ax}SiF_{ax}$ = 180°[28]		
 SiF = 1.572 Å, SiC = 1.822 Å[27]	 SiF_{ax} = 1.669 Å SiF_{eq} = 1.602 Å SiC = 1.871 Å $F_{ax}SiF_{ax}$ = 174.6[28]	 SiF = 1.570 Å SiC = 1.8728 Å[29]	$MeSiF_4^-$
Ph_2SiF_2	 SiF_{ax} = 1.688 Å SiF_{eq} = 1.648 Å SiC = 1.893 Å $F_{ax}SiF_{ax}$ = 172.4°[26]	 SiF = 1.586 Å SiC = 1.836 Å[29]	$Me_2SiF_3^-$
Ph_3SiF	 SiF = 1.720 Å SiCPh = 1.915 Å $F_{ax}SiF_{ax}$ = 176.4°[21]	 SiF = 1.600 Å SiC = 1.848 Å[29]	 SiF = 1.756 Å SiC = 1.874 Å $F_{ax}SiF_{ax}$ = 179.7° (this work)



SiF = 1.707 Å SiCPh = 1.927 Å SiC_{16} = 1.990 Å
SiO = 1.850 Å FSiO = 171.2°
(this work)



SiF = 1.695 Å SiC_{Ph} = 1.882 Å
SiC_{CH3} = 1.845 Å $F_{ax}SiF_{ax}$ = 175.6°[21]

[34]. We thus calculate our values relative to this molecule from ΔE for Reaction 3.

$$[CF_3O]^- + A \rightarrow CF_2O + [AF]^- \qquad (3)$$

The fluoride affinities are summarized in Table 5. The fluoride affinity of $SiMe_3F$ is slightly less than that of CF_2O, as determined from experiment. The calculated fluoride affinity of SiH_3F is comparable to that of CF_2O. The fluoride affinity of SiF_4 is much higher, and there is good agreement between the experimental and theoretical values considering the lack of compounds with high fluoride affinities which can be used in the bracketing experiments. The fluoride affinity of the silanol is much lower

TABLE 5 Fluoride Affinities in kcal/mol

Molecule	*ΔE(RXN 3)* *SCF*	*ΔE(RXN 3)* *MP2*	*FA*[a]
COF_2	0.0	0.0	42.6 [33]
SiF_4	−24.9	−24.2	66.8 (60 ± 4) [35]
$SiHF_3$	−15.6	−15.4	58.0
SiH_2F_2	−8.0	−8.6	51.2
SiH_3F	0.5	−0.6	43.2 (38.2)[b] [34]
SiH_3OH	12.2	10.2	32.5
SiH_4	18.8	19.5	23.1

[a] Experimental values in parentheses. FA(COF_2) from experiment, FA = fluoride affinity.
[b] $SiMe_3F$

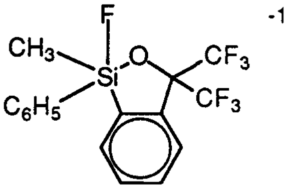
than that of SiH_3F, showing that F can stabilize fluoride addition to Si better than OH. The fluoride affinity of SiH_4 is significantly lower than that of SiH_3OH, consistent with OH being more able to stabilize addition of F^- to Si as compared to H.

The fluoride affinities of the fluorosilanes increase by about 8 kcal/mol per additional fluorine from SiH_3F to SiF_4. A similar result was found by Deiters and Holmes [36] at the SCF level. However, their absolute values are too large by about 10 kcal/mol, because they employ Reaction 2 to calculate the fluoride affinity. As discussed previously, this procedure is not optimal because of the difficulty in calculating the electron affinity of F (the absolute energy of F^-). Besides the value of −33.2 kcal/mol reported by Deiters and Holmes [36] for Reaction 3, values of −31.8 [37] and −29.1 [38] kcal/mol at the ab initio level have been reported. These are somewhat larger

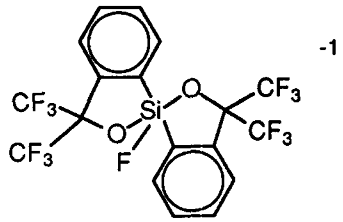
$$SiH_4 + F^- \rightarrow SiH_4F^- \qquad (3)$$

than our value of −23.1 kcal/mol from relative fluoride affinities. It is interesting to note that the MNDO value [38] of −23.8 kcal/mol is in excellent agreement with our calculated value.

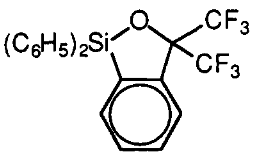
$[Me_3SiF_2]^-$ acts as a fluoride ion donor for many acceptors, and examples of silicon species available from reaction with TAS-**1** include $[Me_2SiF_3]^-$, $[MeSiF_4]^-$, $[SiF_5]^-$, $[SiF_6]^-$, and various aryl silicates $[Ar_nSiF_{5-n}]^-$, n = 1–3. Since the TAS fluorosilicates **2** [39], **5**, and **6** [39] were available from reactions of corresponding silanes **7**, **8**, and **9** with TAS $[Me_3SiF_2]$, we examined the relative fluoride affinities of silanes **7**, **8**, and **9** in solution by NMR methods. For example, treatment of fluorosilicate **5** with equimolar amounts of silane **7** resulted in essentially complete F-transfer to give silane **8** and fluorosilicate **2**. Although equilibrium constants were outside the range measurable by NMR for the pentacoordinate/tetracoordinate pairs employed, the apparent fluoride affinities increased in the order Me_3SiF < **8** < **7** < **9**.



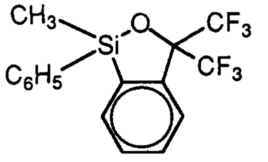
5



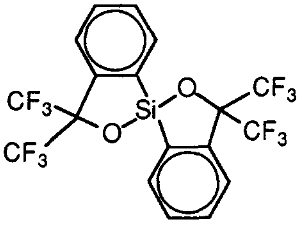
6



7



8



9

The ion $[Ph_3SiF_2]^-$ can be prepared from Ph_3SiF and $[Me_3SiF_2]^-$ (or KF/18-crown-6). Thus, the fluoride affinity of Ph_3SiF is higher than that of Me_3SiF, and this is reflected by the Si–F bond distances in the adducts which are significantly longer in $[Me_3SiF_2]^-$ than in $[Ph_3SiF_2]^-$. Although the equatorial ligands could stabilize the Si in a similar way, the steric bulk of the phenyl due to interactions of the ortho-hydrogens with the other phenyls or the axial substituents causes the Si–C distance to be longer in $[Ph_3SiF_2]^-$ than in $[Me_3SiF_2{}^-]$. As discussed earlier, this is unlikely to be an electronic effect. As a consequence, the apical F atoms can get closer to the Si and the fluoride affinity is higher. The relationship between Si–F bond distance and reactivity is also valid for **2**. As discussed earlier, the Si–F bond is shorter in **2** than in **1**, consistent with **7** having a higher fluoride affinity than $SiMe_3F$. The results in Table 4 are also consistent with this relationship between r(Si–F) in the silicate anion and the fluoride affinities. The fluoride affinities are expected to increase for $SiR_{4-n}F_n$ with increasing n, consistent with the decrease in r(Si–F) in the anion. A comparison of the fluoride affinities of SiH_3OH and **6** is also consistent with this trend. However, comparison of the calculated fluoride affinities of SiH_3OH and $SiMe_3F$ indicate that other effects are also important. Although the Si–F bond distance in **4** is shorter than that in **1**, the fluoride affinity of $SiMe_3F$ is higher than that of SiH_3OH.

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