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TRENDS IN $^{19}F-^{19}F$ and $^{29}Si-^{19}F$ COUPLING CONSTANTS IN ORGANOSILICON DERIVATIVES CONTAINING SiF_2 and Si_2F_4 UNITS

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SUMMARY

Consideration of $^{19}F-^{19}F$ and $^{29}Si-^{19}F$ coupling constants in a series of organosilicon derivatives containing SiF_2 and Si_2F_4 units reveals a number of trends which are useful for structural and stereochemical assignments. For example the vicinal $^{19}F-^{19}F$ coupling constants in a number of C-SiF_2-SiF_2-C-derivatives (including straight chain compounds, disilacyclobutanes and disilacyclohexanes) show an apparent linear dependence on dihedral angle, varying in magnitude from near zero for small values of ϕ up to ca. 19 Hz for $\phi \sim 180°$. This is particularly useful for stereochemical assignments [1,2]. In addition $^{29}Si-^{19}F$ coupling constants appear to fall in quite distinct ranges ($^{1}J_{SiF} > 300$ Hz, 29 Hz $< {^{2}J_{SiF}} < 55$ Hz, $^{3}J_{SiF} < 10$ Hz). This is quite useful for structural assignments [1,6]. Reaction of SiF_2 with 1,3-cyclohexadiene give two new silicon fluorine compounds: a disilabicyclo[2,2,2]octene and an HSi_2F_5-substituted cyclohexadiene.

INTRODUCTION

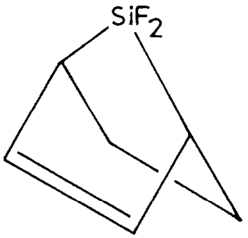
Our studies of the reactions of silicon difluoride (SiF_2) with unsaturated compounds have provided a wide variety of organosilicon fluorides [1,2]. Extensive use of ^{19}F and ^{29}Si nuclear magnetic resonance spectroscopy has been made as an aid to structure determination [1,2]. These investigations have provided a large number of $^{19}F-^{19}F$ and $^{29}Si-^{19}F$ coupling constants. These coupling constants show certain regular trends which make them very useful for the assignment of both structures and stereochemistries of new organosilicon fluoride derivatives. These trends are discussed below.

Most of the compounds discussed below are either 1,2-disilacyclobutanes or 1,2-disilacyclohexanes, both of which are produced as volatile products from the reaction of SiF_2 with olefins [1-4]. In addition, some results are reported for open chain isomers of 1,2-disilacyclohexanes and polymeric organosilicon fluorides. Finally, the ^{19}F and ^{29}Si spectra of the unusual trisilanorbornene product obtained from the reaction of SiF_2 with acetylene [5] plus the ^{19}F spectra of two new products isolated from the reaction of SiF_2 with 1,3-cyclohexadiene are discussed in detail.

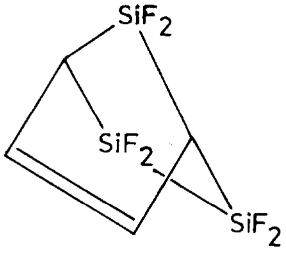
RESULTS AND DISCUSSION

Characterization of products from the reaction of SiF_2 with 1,3-cyclohexadiene

It was originally anticipated that this reaction might yield a silanorbornene derivative, I, similar to the trisilianorbornene, II, produced from the reaction of SiF_2 with acetylene [4]. Instead two other volatile silicon-containing products were formed each in *ca.* 10% yield of isolated product in addition to a small yield of benzene plus a polymer. The two volatile products could only be partially separated but this allowed assignment of individual spectral peaks to the two products.

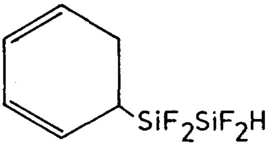


I



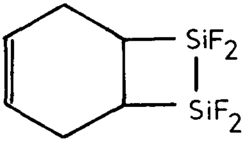
II

One product contained four non-equivalent but coupled fluorines in the range -136.6 to -142.5 ppm from $CFCl_3$. In the proton coupled ^{19}F spectrum, two of the peaks showed an additional doublet splitting of ca. 50 Hz while the other two showed smaller additional coupling. These data suggest the presence of an $H\text{-}SiF_2\text{-}SiF_2\text{-}$ unit, presumably attached to a chiral carbon to account for the non-equivalence of fluorines within an SiF_2 group. The ^1H spectrum contains a single hydrogen at δ4.94 which is a triplet of triplets, consistent with the above partial structure, plus other peaks in the region $\delta 2.1$ and $\delta 6.0$. The ^{13}C spectrum shows two aliphatic peaks, one at $\delta 21.3$ and a complex multiplet at $\delta 24.3$ plus four olefinic peaks at $\delta 123.2$, 127.3, 127.6 and 127.6. These data are only consistent with a substituted 1,3-cyclohexadiene, III:



III

IV



V

(the $HSiF_2SiF_2$ group must be attached to an sp^3 carbon to account for the fluorine non-equivalence). The second compound gave simpler spectra, including an AA'XX' F^{19} spectrum with peaks at δ-141.6 and -144.7 and a ^1H spectrum with peaks only in the aliphatic ($\delta 2.1$-2.4) and olefinic ($\delta 6.3$) regions. The ^{13}C spectrum shows aliphatic peaks at $\delta 20.2$ and $\delta 27.5$ and a single olefinic peak at $\delta 130.0$ (all with noticeable ^{19}F coupling). The most reasonable structure is a disilabicyclo[2.2.2]octene, IV. The alternative structure V is regarded as improbable since the compound was thermally stable at room temperature while 1,2-disilacyclobutane derivatives are all unstable [2a].

The ^{29}Si spectrum of the polymer showed a triplet (δ-13.1, $^1J_{SiF}$ = 321 Hz) superimposed on a triplet of triplets. This indicates the presence of both SiF_2 and Si_2F_4 units [2b,6].

Spectral analysis and tabulation of coupling constants

Spectral analysis of the ^{19}F spectra of II and 1,2-disilacyclobutanes will be discussed in some detail because they are typical of the problems in determining magnitudes and signs of ^{19}F-^{19}F coupling constants.

The structure of II has been determined by X-ray crystallography [7] and we assume that the rigid, symmetrical ring geometry is maintained in solution. The ^1H-decoupled ^{19}F spectrum (Figure 1) shows four multiplets. Multiplets B and D are assigned to the non-equivalent fluorines on the isolated silicon atom. In addition to the large geminal ^{19}F-Si-^{19}F coupling, each peak is split into a triplet due to long range coupling with either two A or two C fluorines. A and C are due to fluorines in the Si_2F_4 units. Each signal shows doublet splitting due to the long range coupling. If one ignores this latter splitting, peaks A and C make up an AA'XX' spectrum with two coupling constants essentially zero. The structure of II requires that the equivalent fluorines be on adjacent silicons in a cis arrangement. The experimental spectrum can only be reproduced with $J_{AA'}$ and $J_{XX'}$ (cis-vicinal coupling constants) both zero while J_{AX} and $J_{AX'}$ are respectively equal to 33.0 and 15.6 Hz. These represent geminal and trans-vicinal ^{19}F-^{19}F coupling constants (although not necessarily in that order). The actual assignment can be made by consideration of the ^{29}Si satellite peaks in the ^{19}F spectrum. All four fluorines in the Si_2F_4 unit are non-equivalent when one of the silicons is ^{29}Si (4.5% abundance). The two fluorines attached to ^{29}Si both show very large one bond ($^1J_{SiF}$) couplings (ca. 350 Hz) while the other two fluorines show smaller two bond ($^2J_{SiF}$) couplings. Only the larger splittings can be clearly observed (Figure 1) since the satellites due to $^2J_{SiF}$ are partially obscured by the main peaks. Selective homonuclear decoupling of the high field satellite of multiplet C collapsed the 33 Hz splitting in the high field satellite of A, confirming that the 33 Hz splitting is between two fluorines on the same Si, i.e., a geminal coupling. Thus the 15.6 Hz splitting is due to trans-vicinal coupling. The satellite peaks show no additional splitting due to cis-vicinal coupling, confirming the near zero value for this coupling. The relative signs of the geminal and trans-vicinal coupling constants cannot be determined by spectral analysis. Normally the appearance of an AA'XX' spectrum is sensitive to the relative signs of J_{AX} and $J_{AX'}$ (but insensitive to the sign of $J_{AA'}$) [8]. In this case, with $J_{AA'} \simeq J_{XX'} \simeq 0$, J_{AX} and $J_{AX'}$ become first order splittings, providing no information about relative signs. However, signs can be assigned by analogy with 1,2-disilacyclobutanes (see below).

Selective homonuclear decoupling confirmed that fluorines A and D were coupled (J_{AD} = 2 Hz), as well as B and C (J_{BC} = 2 Hz). Significant long range ^{19}F-^{19}F coupling constants are expected between spatially proximate fluorines (exo-cis) or fluorines in all-trans or W arrangement (endo-trans) [9], where cis and trans refer to the orientation of the bridge SiF_2 fluorines relative to the Si_2F_4 unit. This leaves two possible chemical shift assignments: A endo, B cis, C exo, D trans or A exo, B trans, C endo, D cis. The former is favoured on the basis of a comparison with the assigned ^{19}F resonances in perfluoronobornenes [10].

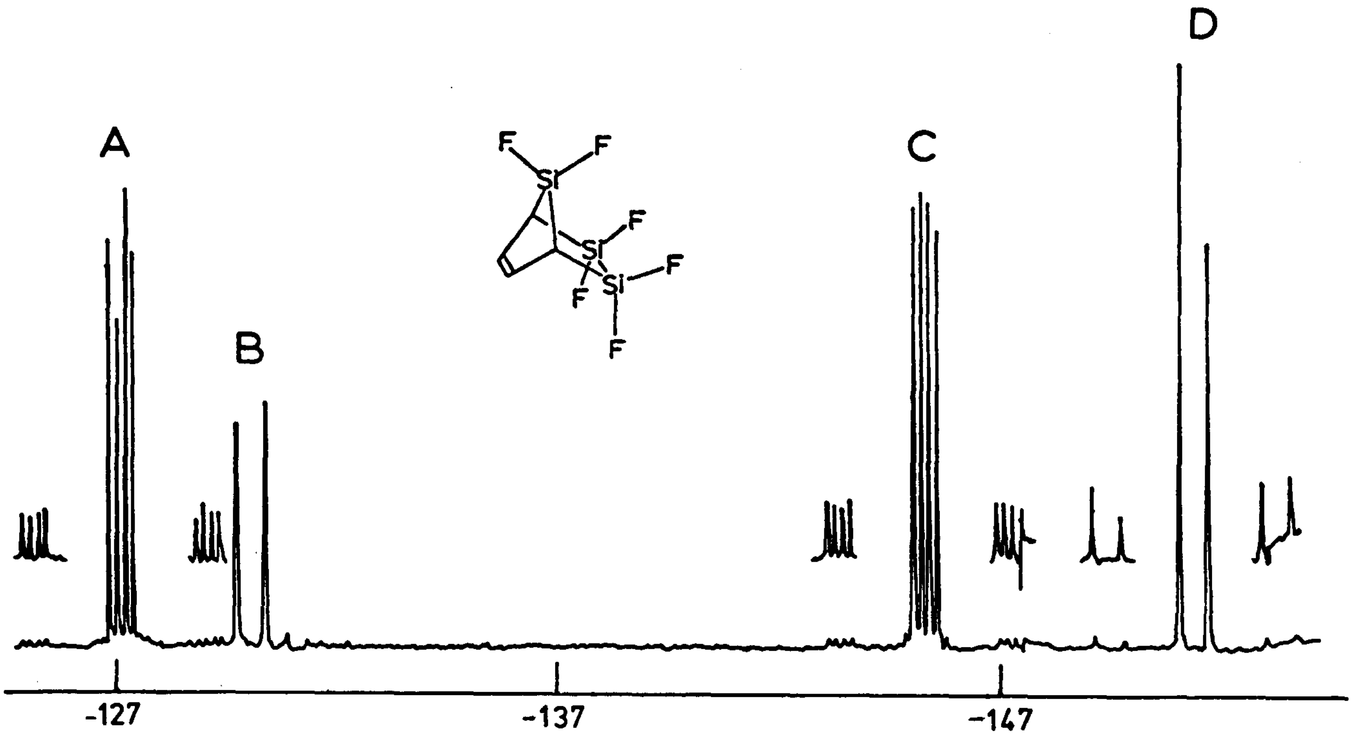
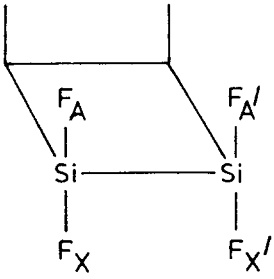


Fig. 1. ^{19}F spectrum of II with ^{1}H random noise decoupling. Expanded portions show ^{29}Si satellites. Negative chemical shifts are to high field of internal CCl_3F standard.

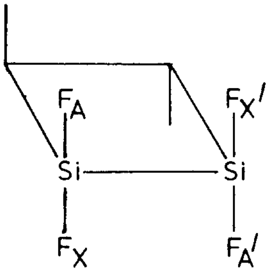
The ^{29}Si spectrum of II is shown in Figure 2. It is actually the overlap of spectra due to two ^{29}Si isotopomers, one with an isolated ^{29}Si and the other with a ^{29}Si in the Si_2F_4 unit. The spectrum is first order and is assigned as shown in Figure 2. Only the larger $^3J_{SiF}$ couplings are shown in this Figure but the smaller ones are clearly visible under optimum resolution. In fact, except for accidental degeneracies, all one hundred predicted lines are observed. The magnitudes of the Si-F coupling constants in this and other compounds can be determined directly from the first order splittings but signs cannot be determined.

Six different 1,2-disilacyclobutanes were obtained from the reaction of SiF_2 with a series of alkyl substituted olefins (ethylene, cis and trans-butene, isobutylene, propene and methylbutene) [2c]. The derivative from ethylene gave an A_4 ^{19}F spectrum (with an AA'XX' ^{29}Si satellite spectrum), the next three gave AA'XX' spectra, while the last two had four non-equivalent fluorines. In each of these two cases, the spectrum showed splittings of ca. 42 Hz, 15 Hz and 2 Hz which can be assigned as geminal, trans-vicinal and cis-vicinal couplings by comparison with II.

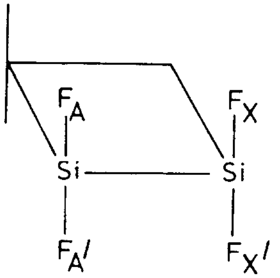
The cis-butene, trans-butene and isobutylene derivatives have different symmetries, respectively VI-VIII.



VI



VII



VIII

For example $J_{AA'}$ is respectively a cis-vicinal, a trans-vicinal and geminal coupling in VI-VIII. Spectral analysis of the three AA'XX' spectra, using the known magnitudes of the three couplings, showed that the only self-consistent solution for all three derivatives has the two vicinal couplings with the same

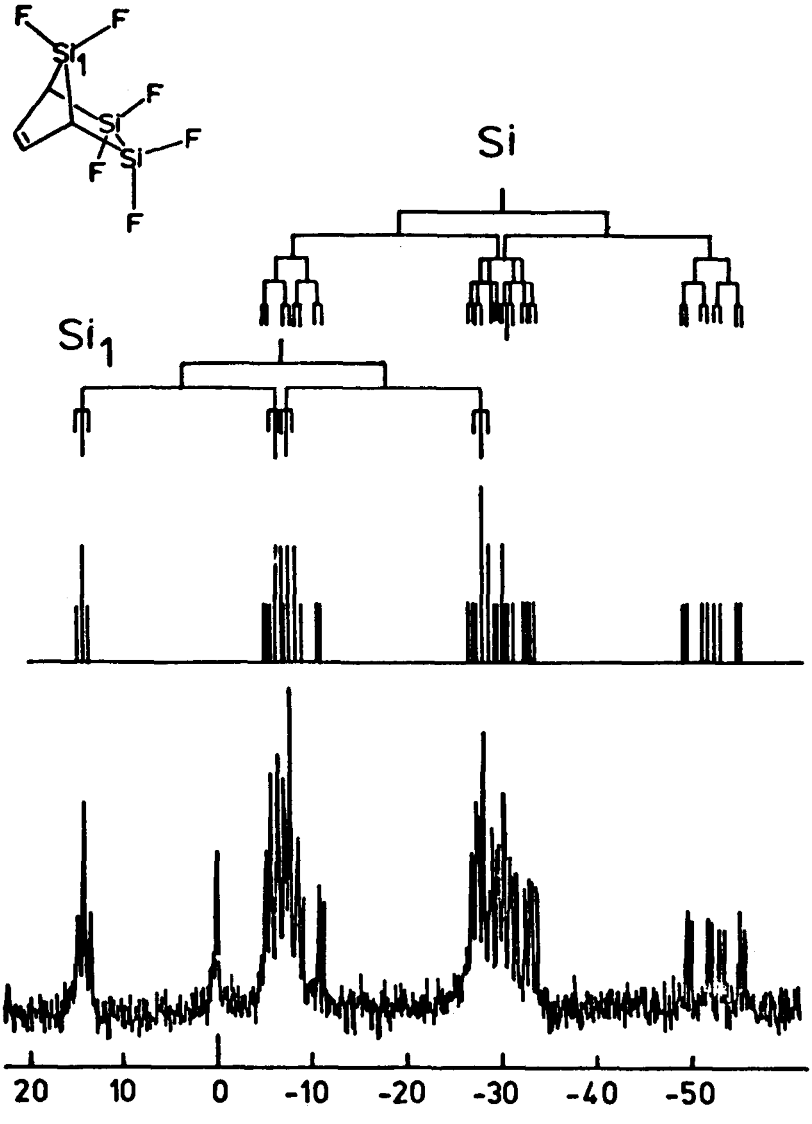
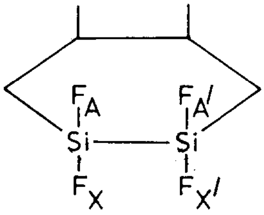


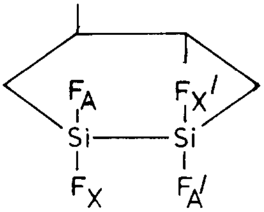
Fig. 2: ^{29}Si spectrum of II. The stick diagram corresponds to the assigned $^{1}J_{SiF}$ and $^{2}J_{SiF}$ coupling constants, as well as the larger of the $^{3}J_{SiF}$ couplings. Chemical shifts are relative to internal $^{29}Si(CH_3)_4$.

sign but with the opposite sign for the geminal coupling [1]. By analogy with the known large positive value for $^2J_{F-C-F}$ [9], the geminal coupling constant is likely positive and the vicinal coupling constants are therefore negative [2b]. However, if the geminal assignment is incorrect, then the corresponding vicinal coupling constants are positive (see below).

Similar symmetry considerations allow assignment of the coupling constants for 1,2-disilacyclohexanes. For example the reaction of propene with SiF_2 yields cis- and trans-4,5-dimethyl-1,2-disilacyclohexane [2c]. The room temperature spectra correspond to averages of two interconverting chair forms. In terms of symmetry, the averaged spectra are equivalent to those for the planar forms IX and X (corresponding respectively to cis and trans isomers).



IX



X

Analysis of the AAXX' spectra (and the ^{29}Si satellite spectra) for these and other 1,2-disilacyclohexane derivatives showed that in this case the geminal and cis-vicinal coupling constants had the same sign, opposite to that for the trans-vicinal couplings [1]. The latter are again assumed to be negative.

In many cases, the chair-to-chair interconversion of disilacyclohexanes is sufficiently slow at low temperatures (ca. -100°C) to allow direct observations of individual chair conformers and consequently the coupling between axial-axial, axial-equatorial and equatorial-equatorial fluorine pairs in chair conformers [2c]. Assignment of axial and equatorial fluorines is based on considerations of the variable temperature behavior of the ^{19}F spectra, magnitudes of $^1H-^{19}F$ coupling constants and ^{19}F chemical shifts [2c].

The spectra for open-chain derivatives were analyzed in a similar manner to that for the compounds discussed above [1].

$^{19}F-^{19}F$ and (where available) $^{29}Si-^{19}F$ coupling constants for II and IV are summarized in Table 1, coupling constants for disilacyclobutanes in Table II, for disilacyclohexanes in Table III and for straight chain compounds in Table IV.

TABLE I.

Geminal and Vicinal ^{19}F-^{19}F Coupling Constants for II and IV and ^{29}Si-^{19}F Coupling Constants (in Hz) and ^{29}Si Chemical Shifts for II.[i]

Compound	$^{2}J_{FF}$(gem)	$^{3}J_{F-F}$(cis)	$^{3}J_{F-F}$(trans)	$^{1}J_{SiF}$				$^{2}J_{SiF}$		$^{3}J_{SiF}$	δ_{Si}
				F(A)	F(B)	F(C)	F(D)	F(A)	F(C)		
II	$+33.0^{a,b}$, $+61.0^{a,c}$	<0.5	-15.6^{a}	±367	±333	±355	±354	±55.2	±34.7	$\pm10.5^{d}$, $\pm1.5^{d}$, $\pm 7.5^{e}$, $\pm2.5^{e}$	$-7.1^{f,g}$, $-31.1^{f,h}$
IV	+2.5	-1.5	-13.5	not observed							

[a] Signs assigned by analogy with 1,2-disilacyclobutanes (see text).

[b] Geminal coupling within Si_2F_4 unit.

[c] Geminal coupling within SiF_2 unit.

[d] Couplings involving ^{29}Si in bridgehead SiF_2 unit.

[e] Couplings involving ^{29}Si in Si_2F_4 unit.

[f] Chemical shifts in p.p.m. from $^{29}Si(CH_3)_4$. Highfield shifts are negative.

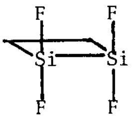
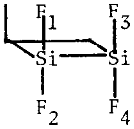
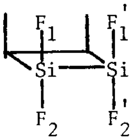
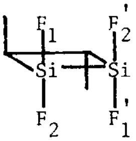
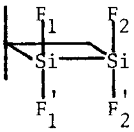
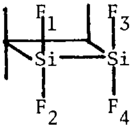
[g] Bridge SiF_2.

[h] ^{29}Si in Si_2F_4 unit.

[i] Fluorine chemical shifts are published elsewhere [2]

TABLE II.

Geminal and Vicinal $^{19}F-^{19}F$ Coupling Constants and $^{29}Si-^{19}F$ Coupling Constants (in Hz) and ^{29}Si Chemical Shifts for 1,2-disilacyclobutanes[a,n].

Compound	$^{2}J_{F-F}$(gem)	$^{3}J_{F-F}$(cis)	$^{3}J_{F-F}$(trans)	$^{1}J_{SiF}$	$^{2}J_{SiF}$	δ_{Si}^{b}
	$-^{c}$	-3.0	-13.5	±408	±33.0	+13.8
 d	$+41.9^{e}$, $+41.1^{f}$	-2.0^{g}, -2.1^{h}	-15.8^{i}, -15.3^{j}	±405, $\pm413^{k}$	±32.0, ±30.1	+7.4 +12.0
 d	+42.8	-2.3^{ℓ}	-15.1^{ℓ}	$\pm413^{\ell}$	$\pm31.7^{\ell}$	+4.9
 d	+41.7	-2.1^{ℓ}	-15.2^{ℓ}	±409, ±416	±32.1, ±29.1	+6.0
 d	+37.0	-3.7	-13.8	- not observed[m] -		
 d	$+45.0^{e}$, $+44.0^{f}$	-2.1^{g}, -2.1^{h}	-14.6^{i}, -14.5^{j}	- not observed[m] -		

(continued on facing page)

Footnotes to Table II

[a] ^{19}F spectra analyzed using spectral analysis program LAOCN3 (18).

[b] Chemical shifts in ppm from $^{29}Si(CH_3)_4$. Lowfield shifts are positive.

[c] Spectrum analyzed from ^{29}Si satellite peaks. $^2J_{F-F}$ could not be determined because necessary transitions to determine this coupling were too weak to be observed.

[d] Vertical line indicates methyl group.

[e] Coupling between F_1 and F_2. Geminal couplings assigned positive (see text)

[f] Coupling between F_3 and F_4.

[g] Coupling between F_1 and F_3.

[h] Coupling between F_2 and F_4.

[i] Coupling between F_1 and F_4.

[j] Coupling between F_2 and F_3.

[k] Only two different couplings were observed rather than the expected four. Essentially equal couplings were observed between the two fluorines on the same silicon.

[ℓ] Only one coupling observed rather than the expected two different couplings.

[m] Compounds were obtained in too low yield to give good ^{29}Si spectra.

[n] Fluorine chemical shifts are published elsewhere [2].

TABLE III.

Geminal and Vicinal $^{19}F-^{19}F$ Coupling Constants and $^{29}Si-^{19}F$ Coupling Constants and ^{29}Si Chemical Shifts for 1,2-Disilacyclohexanes.[i]

Compound[h]	$^2J_{F-F}$(gem)[a]	$^3J_{F-F}$(cis)[a]	$^3J_{F-F}$(trans)[a]		$^1J_{SiF}$[b]	$^2J_{SiF}$[b]	δ_{Si}[c]
			a,a[d]	e,e[d]			
ET-c6	+6.8	+2.2	<-14.6>[e]		±348	±39.4	-4.9
PRET-c6	+6,+7	+2,+2	-18	-11	—	—	—[f]
a,a-PR-c6	+7.0	+3.0	-14.5	-11.0	±347	±37.4	-4.4
a,e-PR-c6	<+6.4>[e]	+3.4,+2.9	<-13.8>[e]		±348	±36.6	-2.8
e,e,e-TBPR-c6	+10,+6	+2,+2	-15	-11	—	—	—[f]
a,a,e-TBPR-c6	+8,+7	~0	-18	-8	—	—	—[f]
e,e,e,e-CB-c6	+8	+2.5	-14.0	-12.4	±351	±35	-6.8
a,e,a,e-CB-c6	+10,+3	~0	-17	-10	—	—	—[f]
e(a,e)(a,e)e-MB-c6	+4.0	+4.0	-14.0	-8.5	±350[g]	—	—
a(a,e)(a,e)e-MB-c6	+10,+6	+4,+4	-14	-10	—	—	—[f]
DB-c6	+10.0	+3.5	-17.0	-8.6	±353[g]	—	—

[a] F-F coupling constants for chair conformation at -80°C or lower.

[b] Si-F coupling constants obtained at 31°C from spectra corresponding to rapid chain to chair conversion.

[c] Chemical shifts relative to $^{29}Si(CH_3)_4$. Lowfield shifts positive.

[d] a,a refers to diaxial fluorine pairs while e,e refers to diequatorial fluorines (see VIII).

[e] Averaged value at 31°C. Chair to chair conversion was still rapid at -95°C.

[f] ^{29}Si peaks obscured by peaks due to other compounds.

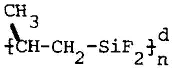
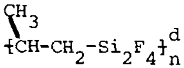
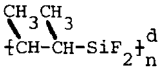
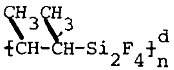
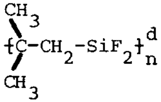
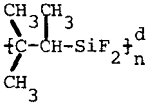
[g] Determined from ^{29}Si satellites in ^{19}F spectra.

[h] See reference 2c for description of symbolism.

[i] Fluorine chemical shifts are published elsewhere [2].

TABLE IV.

$^{19}F-^{19}F$ and $^{29}Si-^{19}F$ Coupling Constants (in Hz) and ^{29}Si Chemical Shifts for $R-SiF_2-SiF_2-R'$ and $R-SiF_2-F'$ Derivatives.[j]

Compound	$^2J_{FF}$(gem)	$^3J_{FF}$	$^1J_{SiF}$	$^2J_{SiF}$	δ_{SiF}
V	+14.8[a]	-17.1,-9.2[b]	—— not observed ——		
VI	+10[a]	-21,-6[b]	—— not observed ——		
VII	+5,+7[a]	-19,-19,-6.5,-6.5[c]	—— not observed ——		
 $\left[\overset{CH_3}{CH}-CH_2-SiF_2\right]_n$[d]	+21[a]	——	+314.0	——	-3.8
 $\left[\overset{CH_3}{CH}-CH_2-Si_2F_4\right]_n$[d]	—— e		—— f		-8.3
 $\left[\overset{CH_3}{CH}-\overset{CH_3}{CH}-SiF_2\right]_n$[d]	—— e		+324.5[g]	——	-4.9[g]
 $\left[\overset{CH_3}{CH}-\overset{CH_3}{CH}-Si_2F_4\right]_n$[d]	—— e		±353.2[h],±354.9[i]	±42.2[h],±48.5[i]	-7.6[h],-7.6[i]
 $\left[\overset{CH_3}{\underset{CH_3}{C}}-CH_2-SiF_2\right]_n$[d]	—— e		+323.7	——	-4.4
 $\left[\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-SiF_2\right]_n$[d]	—— e		±332.9	——	-5.5

[a] Assumed positive by analogy with 1,2-disilacyclobutanes.

[b] Both of same sign, assigned negative. Larger coupling assigned as a coupling between *anti* fluorines and smaller coupling between gauche couplings.

[c] Couplings assumed negative. Assignments as in footnote b.

[d] Polymer from reaction of SiF_2 with olefin (1,2,6).

[e] Complex ^{19}F spectrum obtained with very broad peaks.

[f] Only central peak of triplet observed. Therefore coupling constants cannot be determined.

[g] Identical coupling constants and chemical shifts found for *cis*-butene and *trans*-butene polymers.

[h] Data for *cis*-butene polymer.

[i] Data for *trans*-butene polymer.

[j] Fluorine chemical shifts are published elsewhere [2].

Trends in $^{19}F-^{19}F$ and $^{29}Si-^{19}F$ coupling constants

Average values and ranges of geminal and vicinal $^{19}F-^{19}F$ coupling constants and of $^{29}Si-^{19}F$ coupling constants for various types of compounds are summarized in Table V.

(a) Geminal $^{19}F-Si-^{19}F$ coupling constants

Geminal $^{19}F-Si-^{19}F$ coupling constants show a wide range of values from +61 Hz for the isolated SiF_2 group in II to near zero in 1,2-disilacyclohexanes and some of the open chain derivatives. Two main trends can be noted. First, isolated SiF_2 units show larger geminal coupling constants than for Si_2F_4 units. For example, compare the geminal coupling constant for the isolated SiF_2 unit in II (+61 Hz) with the Si_2F_4 unit in the same molecule (+33 Hz) and in 1,2-disilacyclobutanes (ca. +42 Hz). Similarly the isolated SiF_2 unit in the propene reaction polymer shows a larger geminal coupling (+21 Hz) than exhibited by the Si_2F_4 units in straight chain $RSiF_2SiF_2R'$ derivatives (see Table IV). A second trend is that the couplings appear to be larger in strained rings (e.g., ca. +42 Hz in 1,2-disilacyclobutanes) than in relatively unstrained rings (e.g., ca. +7 Hz in 1,2-disilacyclohexanes) and straight chain derivatives (ca. +6 Hz).

(b) Vicinal $^{19}F-Si-Si-^{19}F$ coupling constants

The ring compounds containing Si_2F_4 units show quite clear trends in vicinal coupling constants which are very useful for stereochemical assignments. For example, the trans-vicinal coupling constants in II, IV and the disilacyclobutanes are all of the order of -15 Hz while the corresponding cis-vicinal coupling constants fall in the range 0 to -3 Hz. In each system, the dihedral angles for trans-vicinal and cis-vicinal fluorines should be respectively ca. 120° and 0°.

The 1,2-disilacyclohexanes exist in distorted chair conformations with fluorines in axial (a) or equatorial (e) positions [1,2]. The cis-vicinal (a,e) $^{19}F-^{19}F$ coupling is ca. +3 Hz while there are two trans-vicinal couplings. The (a,a) coupling is ca. -16 Hz while the (e,e) coupling is ca. -10 Hz. Molecular models of 1,2-disilacyclohexane show considerable ring flattening about Si due to ring strain by the long Si-Si bond [2c]. This ring flattening has been confirmed by both a microwave investigation of silacyclohexanes [11] and an X-ray crystal determination for a 1,2-disilacyclohexane [12]. As a result of this distortion, the dihedral angles for the various F-F orientations are respectively ca. 20° for (a,e), 100° for (e,e) and 140° for (a,a) fluorine pairs.

TABLE V.

Average Coupling Constants for Various Types of Derivatives Containing SiF_2 and Si_2F_4 Units.

Compound(s)	$^2J_{F-F}$(gem)	$^3J_{F-F}$(cis)	$^3J_{F-F}$(trans)	$^1J_{SiF}$	$^2J_{SiF}$
II	+61[a],+33[b]	~0	-15.3	±350	±45
IV	+2.5	-1.5	-13.5	-[c]	-[c]
disilacyclobutanes	+41	-2.4	-14.9	±410	±31
disilacyclohexanes	+7.2	+2.5[d]	-15.5[e],-10.0[f]	±350	±37
$R-SiF_2-R'$	+21	-	-	±324	-
$R-SiF_2-SiF_2-R'$	+7	-6.5[g]	-19[h]	+354	±48

[a] Bridge SiF_2 unit.

[b] Si_2F_4 unit.

[c] ^{29}Si spectrum not measured.

[d] Coupling between axial and equatorial fluorines in distorted chair conformations.

[e] Coupling between two axial fluorines in distorted chair conformation.

[f] Coupling between two equatorial fluorines in distorted chair conformation.

[g] Assigned as coupling between gauche fluorines.

[h] Assigned as coupling between anti fluorines.

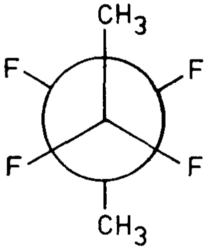
Considering the estimated dihedral angles, ϕ, the vicinal coupling constants for the various disilacycloalkane and disilacycloalkene derivatives, it appears that the vicinal ^{19}F-Si-Si-^{19}F coupling constants in these derivatives can be predicted with reasonable accuracy by a surprisingly simple relationship:

$$^{3}J_{F-F} \approx -0.1\ \phi° \qquad (1)$$

This is most unusual since in other cases where vicinal coupling constants between two nuclei show a dihedral angle dependence, the coupling constant is usually approximately proportional to $\cos^{2}\phi$ with large values for $\phi = 0°$ and 180° and minimal values near $\phi = 90°$ [13]. Furthermore, the corresponding ^{19}F-C-C-^{19}F coupling constants vary dramatically with ring size [9,14] and appear to be quite unreliable for determining stereochemistry [9].

One possible explanation for the form of equation (1) is that there are opposing through bond and direct (or through space) contributions to the vicinal couplings between the spatially proximate fluorines. While the importance of through space contributions to ^{19}F-^{19}F coupling constants has been the subject of considerable controversy, available evidence indicates a positive contribution to the coupling constant between spatially proximate fluorines due to a through space mechanism [15]. This could result in a near zero coupling for cis ^{19}F-Si-Si-^{19}F couplings due to near cancellation of the (positive) through space contribution and the (presumed negative by analogy with trans couplings) through bond contribution. If so, then the precise magnitude of the cis couplings would be sensitive to the fluorine-fluorine separation and consequently to ring size and strain, etc. This could account for the change in sign for the cis couplings in disilacyclobutanes and disilacyclohexanes and for the larger deviations from predicted values shown by the cis couplings.

The data for several open chain R-SiF_2SiF_2-R' derivatives appear to be consistent with equation (1). For example, Servis and Sharp analyzed the ^{29}Si satellites of the ^{19}F spectrum of 1,2-dimethyl-1,1,2,2-tetrafluorodisilane (AA'XX' spectrum) [16]. The two vicinal coupling constants had magnitudes of 17.1 Hz and 9.2 Hz and both had the same sign. Assuming a preferred anti conformation of methyl groups, XI,



XI

one gauche ($\phi = 60°$) and one anti ($\phi = 180°$) would be expected which can be assigned respectively as -9 Hz and -17 Hz. Similarly, analysis of the AA'XX' spectrum of XII [1]

$(CH_3)_2CH\text{-}C(CH_3)_2\text{-}SiF_2\text{-}C(CH_3)_2\text{-}C(CH_3){=}CH_2$ XII

gave vicinal couplings of 6 Hz and 21 Hz (both of the same sign and again assigned negative). Finally, the ^{19}F spectrum of XIII [1]

$(CH_3)_2CH\text{-}CH(CH_3)\text{-}SiF_2\text{-}SiF_2\text{-}CH(CH_3)\text{-}C(CH_3){=}CH_2$ XIII

showed four non-equivalent fluorines (note that it contains two chiral carbons). Although there is some ambiguity in the assignment of individual coupling constants due to partial spectral overlap, the most reasonable assignment gives two vicinal couplings of 19 Hz and two of 6.5 Hz (no sign information). Again assuming anti conformations of alkyl groups for XI and XII, the three derivatives given above are consistent with an anti coupling of -19 ± 2 Hz and a gauche coupling of -6.5 ± 1 Hz. In turn these are consistent with equation (1).

It should be noted that Sharp has assigned the vicinal $^{19}F\text{-}Si\text{-}Si\text{-}^{19}F$ couplings in XI (16) and in other similar compounds (17) as positive, mainly based on electronegativity effects on these couplings (17). It is possible that this assignment is correct, provided that our assignment of the geminal $^{19}F\text{-}Si\text{-}^{19}F$ coupling as positive (2b) is incorrect. In that case, the $^3J_{FF}$ couplings in Table V would all be reversed in sign and equation 1 would also have the opposite sign. However, this does not in any way affect the use of these couplings for stereochemical assignments since this is based on the varying magnitudes of the couplings with dihedral angle.

(c) $^{29}Si\text{-}^{19}F$ Fluorine Coupling Constants

$^{29}Si\text{-}^{19}F$ coupling constants are particularly useful for structure determination in compounds containing SiF_2 units. For example, the different splitting patterns associated with SiF_2 and Si_2F_4 units in SiF_2-olefin copolymers provided the main information for characterization of these polymers [2b,6].

II shows typical values for one bond, two bond and three bond $^{29}Si-^{19}F$ coupling constants (Table 1). The $^{1}J_{SiF}$ values fall in the range 330-370 Hz, the $^{2}J_{SiF}$ values in the range 30 -60 Hz and $^{3}J_{SiF}$ values between 0 and 10 Hz. The different one bond couplings can be assigned by direct observation of the couplings as ^{29}Si satellites in the ^{19}F spectra. In addition, the satellite peaks due to two-bond $^{29}Si-^{19}F$ coupling can be partially observed on fluorine peak A, suggesting that the larger geminal $^{29}Si-^{19}F$ coupling involves the endo fluorine A. The three bond (vicinal) $^{19}F-Si-C-^{29}Si$ couplings cannot be definitely assigned since the satellite peaks in the ^{19}F spectra are buried under the main peaks. However, by analogy with the trends observed for many other types of vicinal coupling [13], it is probable that the larger splittings involve fluorines anti to silicon, i.e., fluorines A and D. No signs of coupling constants could be determined since they were all observed as first order splittings.

The key feature for II is that one, two and three bond $^{29}Si-^{19}F$ coupling constants occur in three distinct, non-overlapping ranges, suggesting that these couplings can be directly assigned from their magnitudes. All of the available data are consistent with this view. The one bond couplings fall in the range 314-416 Hz. However, $^{1}J_{SiF} = 350 \pm 5$ Hz for Si_2F_4 units in polymers (Table IV), straight chain compounds (Table IV) and 1,2-disilacyclohexanes (Table III), suggesting that this is a characteristic value for this coupling in relatively unstrained Si_2F_4 units. $^{1}J_{SiF}$ seems to be smaller for isolated SiF_2 units (e.g., see polymer data in Table IV) and larger for strained rings, e.g., 1,2-disilacyclobutanes (see Table II). The two bond couplings fall in the range 29-55 Hz. This coupling is larger in polymers and other straight chain derivatives (47-50 Hz) than in 1,2-disilacyclobutanes (29-33 Hz) and 1,2-disilacyclohexanes (35-40 Hz).

EXPERIMENTAL

Experimental details of synthesis and isolation of the various products are given elsewhere [1,2a]. The reaction of SiF_2 with 1,3-cyclohexadiene was carried out in a similar manner. ^{19}F spectra were obtained on a Varian XL-100 spectrometer operating in continuous wave mode at a frequency of 94.2 M Hz and a probe temperature of 31°C. ^{29}Si spectra were obtained on a Bruker WP-80 spectrometer operating in Fourier transform mode at a probe temperature of 32°C and a frequency of 15.89 M Hz. Pulse flip angle was 30°, and typical spectra were obtained using a 16,000 data point Fourier transformation and a spectral width of 2,000 Hz. The spectrum in Figure 2 used a 32K Fourier transform and a spectral width of 1,600 Hz, corresponding to 0.1 Hz digital resolution. All ^{29}Si spectra were obtained with ^{1}H random noise decoupling.

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