

Figure 4.  $^{19}\text{F}$  nmr spectrum of  $\text{Sn}(\text{CF}_3)_4$ .

stitution, the partially substituted iodides are obtained. If  $\text{SnI}_4$  is positioned in the reactor to promote partial reaction, the new compounds  $\text{Sn}(\text{CF}_3)_3\text{I}$  ( $-19.8$  ppm vs. external  $\text{CF}_3\text{C}_6\text{H}_5$ ,  $J_{119\text{Sn}-\text{F}} = 582$ ,  $J_{117\text{Sn}-\text{F}} = 553$  Hz) and  $\text{Sn}(\text{CF}_3)_2\text{I}_2$  ( $-16.4$  ppm vs. external  $\text{CF}_3\text{C}_6\text{H}_5$ ,  $J_{119\text{Sn}-\text{F}} = 615$ ,  $J_{117\text{Sn}-\text{F}} = 587$  Hz) are produced. The new compound  $\text{Ge}(\text{CF}_3)_3\text{Br}$  (chemical shift of the neat compound =  $-23.1$  vs. external TFA; mass spectrum containing (P), (P - F), and (P -  $\text{CF}_3$ ) ions) is formed from  $\text{GeBr}_4$  in a similar fashion.

One of the advantages of this synthetic procedure, aside

from providing a novel route to certain compounds, is that the reaction proceeds virtually unattended. Other preparations of bis(trifluoromethyl)mercury, for example, require considerably more time and effort. Although the yields based on the metal halide are excellent, the conversion in many cases is very low. A second disadvantage is the sometimes difficult separation of the desired products from perfluorocarbons of similar volatility which are produced along with hexafluoroethane from the recombination of trifluoromethyl radicals.

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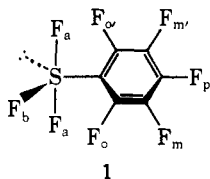
## (Pentafluorophenyl)sulfur Fluorides. A Detailed Analysis of Their $^{19}\text{F}$ Nuclear Magnetic Resonance Spectra

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**Abstract:** A complete nmr line shape analysis has been carried out for the temperature-dependent  $^{19}\text{F}$  nmr spectrum assigned to  $\text{C}_6\text{F}_5\text{SF}_3$ . Rate data correspond to the activation parameters  $\Delta H^\ddagger = 10.5 \pm 0.4$  kcal mol $^{-1}$ ,  $\Delta S^\ddagger = -7.7 \pm 1.3$  cal mol $^{-1}$  deg $^{-1}$ . The dynamic effects are ascribed to restricted internal rotation about the C-S bond, and no indication of loss of stereochemistry about sulfur was found. Dynamic effects were not observed for  $\text{C}_6\text{F}_5\text{SOF}$  or  $\text{C}_6\text{F}_5\text{SO}_2\text{F}$ ; internal rotation about the C-S bond must be fast in these molecules at all temperatures investigated. The room temperature spectra for  $\text{C}_6\text{F}_5\text{SOF}$  and  $\text{C}_6\text{F}_5\text{SO}_2\text{F}$  were analyzed using AA'BB'CX models. The results are in agreement with the linear relationship between the meta F-F coupling constants and the chemical shift of the para fluorine discussed by other workers. The substituent parameters  $\sigma_1$  and  $\sigma_R$  were calculated for the  $\text{SF}_3$ , SOF, and  $\text{SO}_2\text{F}$  groups and compared to values determined from the *m*- and *p*-fluorophenyl system.

In a preliminary report,<sup>1</sup> the low-temperature  $^{19}\text{F}$  nmr spectra of (pentafluorophenyl)sulfur trifluoride were explained by the trigonal bipyramidal structure (**1**) with the



pentafluorophenyl ring in the basal plane and a relatively high barrier to rotation about the C-S bond. In the presence of a hydrogen fluoride scavenger, a high barrier to intramolecular rearrangement of the sulfur fluorines about the sulfur atom was found. The single basal fluorine couples strongly with one ortho fluorine and weakly with the other,

but the two apical fluorines couple equally with both ortho fluorines. A six-bond coupling between S-F and *p*-F was found in (pentafluorophenyl)sulfur trifluoride and in (pentafluorophenyl)sulfinyl fluoride. The six-bond coupling was not observed for (pentafluorophenyl)sulfonyl fluoride in the preliminary studies, but a small 0.6-Hz coupling was noted in the more detailed work.

In the present work, the temperature-dependent  $^{19}\text{F}$  spectra of (pentafluorophenyl)sulfur trifluoride have been measured and fitted by computer simulations. The  $^{19}\text{F}$  spectra of (pentafluorophenyl)sulfinyl fluoride and (pentafluorophenyl)sulfonyl fluoride were measured as a function of temperature, but no changes indicative of the slowing down of internal motion were detected. A complete analysis has been made of the room temperature spectra of these molecules.

## Experimental Section

The compounds used in this study were prepared by procedures reported earlier from this laboratory.<sup>2</sup>

The <sup>19</sup>F nmr spectra were recorded at 84.67 MHz using a Bruker HFX-90 spectrometer and at 94.08 MHz using a Varian HA-100 spectrometer. Freon-11 (CFCl<sub>3</sub>) and hexafluorobenzene were used as <sup>19</sup>F lock materials.

The temperature-dependent <sup>19</sup>F nmr spectra of C<sub>6</sub>F<sub>5</sub>SF<sub>3</sub> were recorded on the Bruker spectrometer; 5-mm quartz tubes were employed because of the reactivity of the compound toward glass. The solvent used was toluene with triphenylphosphineimine added as a scavenger for hydrogen fluoride to prevent fluoride catalyzed intermolecular exchange.<sup>1</sup> Temperatures for the samples run on the HFX-90 were measured with a copper-constantan thermocouple located just below the sample tube and were calibrated using a similar thermocouple held coaxially in the spinning nmr tube partially filled with solvent.

The simulations of the temperature-dependent nmr spectra were carried out using the density matrix approach of Kaplan<sup>3</sup> and Alexander.<sup>4</sup> The details of such line shape calculations have been presented in a recent paper.<sup>5</sup> The nmr spectra are first order so that considerable simplifications are possible in the calculations. We have written general computer programs for both mutual and nonmutual intramolecular exchange processes in first-order systems. Exchange rates are obtained by a visual comparison of calculated and observed spectra.

The observed changes in the nmr line shapes on warming the sample were exactly reproduced on cooling the sample from room temperature. If the sample was heated much above room temperature, partial decomposition, probably by reaction with the glass tube, was observed.

## Results

**A. (Pentafluorophenyl)sulfur Trifluoride.** In this section an analysis of the low-temperature limit <sup>19</sup>F nmr spectrum assigned to this molecule is carried out. The nmr parameters are used in the calculation of the temperature-dependent nmr line shape effects resulting from restricted internal rotation about the S-C bond.<sup>1</sup>

**Resonances Associated with the Apical Fluorines.** The temperature-dependent <sup>19</sup>F nmr spectra associated with the apical fluorines are shown on the left-hand side of Figure 1. The low-temperature limit spectrum indicates that the apical fluorines are unequally coupled to four of the six other <sup>19</sup>F nuclei in the molecule with the coupling to the other two nuclei being too small to resolve. The simulated spectrum at the bottom of Figure 1 was calculated using the nmr parameters  $J_{ab} = 69.75$ ,  $J_{ao} = 15.55$ ,  $J_{ao'} = 10.0$ ,  $J_{ap} = 3.35$ , and  $J_{am} \sim J_{am'} \sim 0$  Hz.

In calculating the line shapes shown on the right-hand side of Figure 1, a first-order mutual exchange model was used in which  $J_{ao}$  and  $J_{ao'}$  were exchanged. The coupling constants did not vary significantly within the rather limited temperature range over which line shape effects can be observed.

The temperature dependence of the exchange rate determined from the line shape analysis is given by the Eyring equation

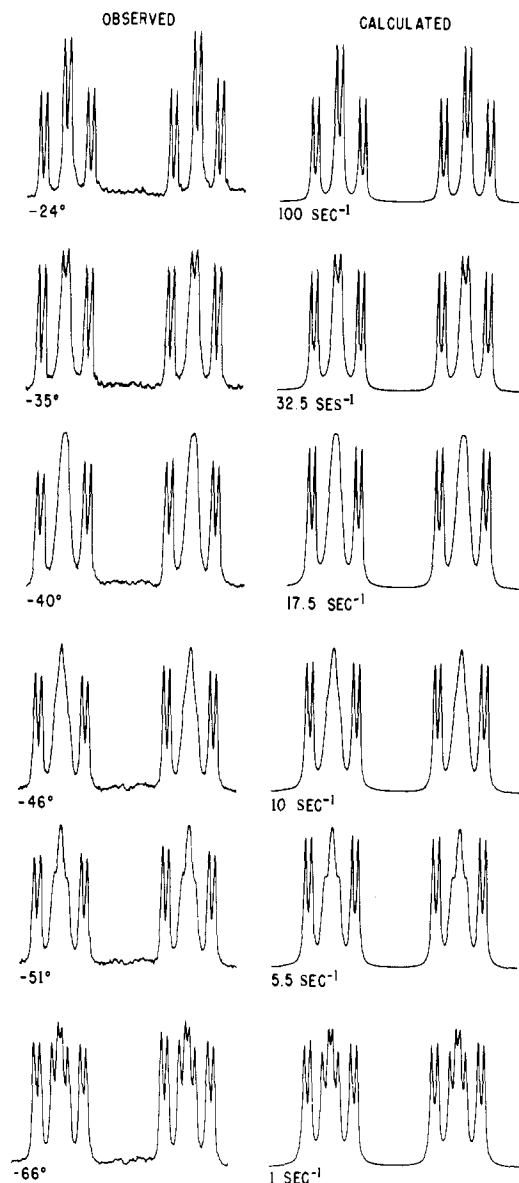
$$R(T) = K(kT/h)e^{-\Delta G^*/RT} \text{ sec}^{-1}$$

with the activation parameters (assuming  $K = 1$ ):  $\Delta H^* = 10.8 \pm 0.2$  kcal mol<sup>-1</sup>,  $\Delta S^* = -5.8 \pm 0.9$  cal mol<sup>-1</sup> deg<sup>-1</sup>,  $\Delta G^*_{298} = 12.6 \pm 0.1$  kcal mol<sup>-1</sup>, assuming  $\Delta H^*$  and  $\Delta S^*$  are temperature independent.<sup>6</sup> The corresponding Arrhenius expression is

$$R(T) = Ae^{-E_a/RT} \text{ sec}^{-1}$$

with  $\log(A)_{298} = 11.9 \pm 0.2$  and  $E_{a298} = 11.4 \pm 0.2$  kcal mol<sup>-1</sup>.

**Resonances Associated with the Basal Fluorine.** The low-temperature limit (-66°) <sup>19</sup>F nmr spectrum associated



**Figure 1.** Observed and calculated temperature-dependent (84.67 MHz) <sup>19</sup>F nmr spectra assigned to the apical fluorines of (pentafluorophenyl)sulfur trifluoride.

with the basal fluorine (top row of Figure 2) consists of an essentially first-order doublet of doublets of triplets. The large triplet splitting is assigned to the F<sub>a</sub>-F<sub>b</sub> coupling  $|J_{ab}| = 69.75$  Hz. This coupling constant is temperature dependent and its value increases to 71 Hz at +40°. The two doublet separations are assigned to coupling to the ortho fluorines with  $J_{bo} = \pm 31.2$  and  $J_{bo'} = \mp 6.8$  Hz. The line shape effects prevent measurement of the temperature dependence of these two coupling constants individually. However, the inner two lines of the doublet of doublets remain sharp at all temperatures (Figure 2). The separation between these two lines, which are invariant to the exchange process, corresponds to the sum of  $J_{bo}$  and  $J_{bo'}$ , showing that the two coupling constants have opposite signs.  $|J_{bo} + J_{bo'}|$  varies from 24.4 Hz at -66° to 27.6 Hz at +40°.

The nmr line shape simulation shown on the right-hand side of Figure 2 was carried out using a first-order mutual exchange model. Since the temperature dependence of  $J_{bo'}$  and  $J_{bo}$  cannot be determined separately, they were varied equally from their low-temperature limit values to fit the observed value of  $|J_{bo'} + J_{bo}|$ . The rate data obtained from a

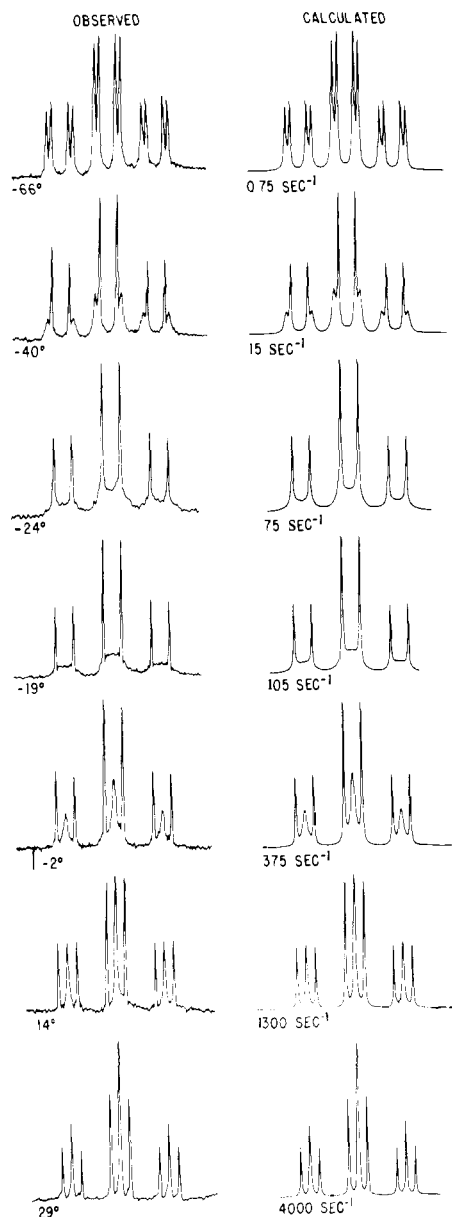


Figure 2. Temperature-dependent (84.67 MHz)  $^{19}\text{F}$  spectrum associated with the basal fluorine of (pentafluorophenyl)sulfur trifluoride. The spectra on the right are simulated using a first-order density matrix calculation.

visual fitting of the temperature-dependent nmr spectra for the basal fluorine are shown in Figure 3 in the form of an Arrhenius plot corresponding to the rate expression

$$R(T) = 10^{11.7} e^{-11,260/RT}$$

The activation parameters obtained from a least-squares fit<sup>6</sup> using the Eyring equation are  $\Delta H^* = 10.67 \pm 0.07$  kcal mol<sup>-1</sup>,  $\Delta S^* = -7.0 \pm 0.3$  cal mol<sup>-1</sup> deg<sup>-1</sup>,  $\Delta G^*_{298} = 12.75 \pm 0.02$  kcal mol<sup>-1</sup>,  $\log(A)_{298} = 11.70 \pm 0.06$ , and  $E^{\ddagger}_{298} = 11.26 \pm 0.07$  kcal mol<sup>-1</sup>.

**The Meta Fluorines.** The low-temperature limit ( $-66^\circ$ )  $^{19}\text{F}$  nmr spectrum associated with the meta fluorines has the appearance of two doublets of triplets. The "triplet" splittings arise from almost equal couplings of the meta fluorines to the adjacent para and ortho fluorines. The small doublet splittings arise from couplings to the ortho fluorines on the opposite side of the  $\text{C}_6$  ring. The apparent line width difference between the two parts of the spectrum (lower line of Figure 4) is due to the inequality of the cou-

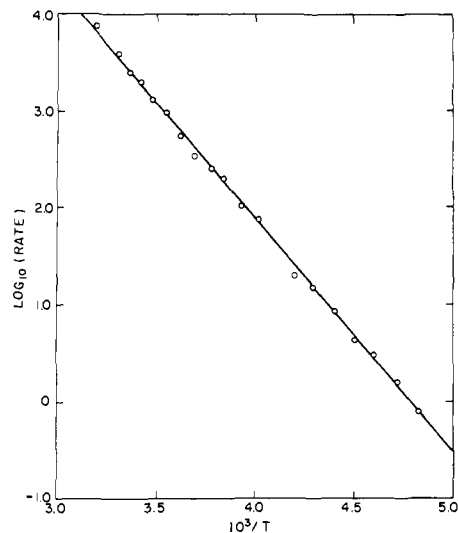


Figure 3. Arrhenius plot for the rate data obtained from the line shape analysis for the temperature-dependent spectra of the basal fluorine of (pentafluorophenyl)sulfur trifluoride. Similar plots were obtained for the spectra assigned to the apical and meta fluorines.

plings to the adjacent fluorines. The simulated spectrum (bottom row of Figure 4) was obtained with the nmr parameters  $J_{m'o'} = 4.9$ ,  $J_{mp} = 22.85$ ,  $J_{mo} = 22.75$ ,  $J_{m'o} = 7.1$ ,  $J_{m'p} = 22.9$ , and  $J_{m'o'} = 24.1$  Hz. The other coupling constants are too small to determine. The chemical shift separation between the two types of meta fluorines is 1.55 ppm at  $-66^\circ$ .

The observed temperature-dependent  $^{19}\text{F}$  nmr spectra associated with this part of the spectrum are shown on the left-hand side of Figure 4. They are overlapped by an impurity spectrum of low intensity which does not interfere with the line shape analysis. Since  $J_{mm'}$  is very small, a first-order nonmutual intramolecular exchange model can be used to simulate the temperature dependence of the spectra; *i.e.*, the calculation employs a two-site approximation. Unfortunately, the nmr spectra cannot be measured over a sufficiently wide temperature range near the slow exchange limit to determine the temperature dependence of the nmr parameters. They were, therefore, held constant at the values given above, in the line shape calculations. The temperature dependence of the exchange rate determined from this analysis is given by the activation parameters  $\Delta H^* = 10.0 \pm 0.1$  kcal mol<sup>-1</sup>,  $\Delta S^* = -9.3 \pm 0.5$  cal mol<sup>-1</sup> deg<sup>-1</sup>,  $\Delta G^*_{298} = 12.77 \pm 0.03$  kcal mol<sup>-1</sup>,  $\log(A)_{298} = 11.2 \pm 0.1$ , and  $E^{\ddagger}_{298} = 10.6 \pm 0.1$  kcal mol<sup>-1</sup>. A comparison between the observed and calculated spectra used to obtain these data is shown in Figure 4.

**The  $^{19}\text{F}$  Nmr Spectra Associated with the Para Fluorines.** The  $^{19}\text{F}$  nmr spectrum associated with the para fluorines is poorly resolved at  $-66^\circ$  and only the large para-meta coupling constants can be measured. On raising the temperature, a well-resolved fast exchange limit spectrum is reached at about  $-46^\circ$  (corresponding to an exchange rate of only  $\sim 10$  sec<sup>-1</sup>, see Figures 1-4). The observation that the high-temperature limit is reached at such a slow exchange rate implies that  $J_{pm} \sim J_{pm'}$ , and  $J_{po} \sim J_{po'}$ . The fast exchange limit spectrum is an apparent triplet of nonbinomial septets (Figure 5). The septet structure results from an overlapping triplet of triplets with an approximately 2:1 ratio of coupling constants. In Figure 5, the observed spectrum at  $-24^\circ$  is compared with a spectrum simulated using the nmr parameters  $J_{pm} = J_{pm'} = 22.65$ ,  $J_{po} = J_{po'} = 6.5$ , and  $J_{pb} = 3.3$  Hz.

**The  $^{19}\text{F}$  Nmr Spectrum of the Ortho Fluorines.** The low-temperature limit spectrum of the ortho fluorines has a

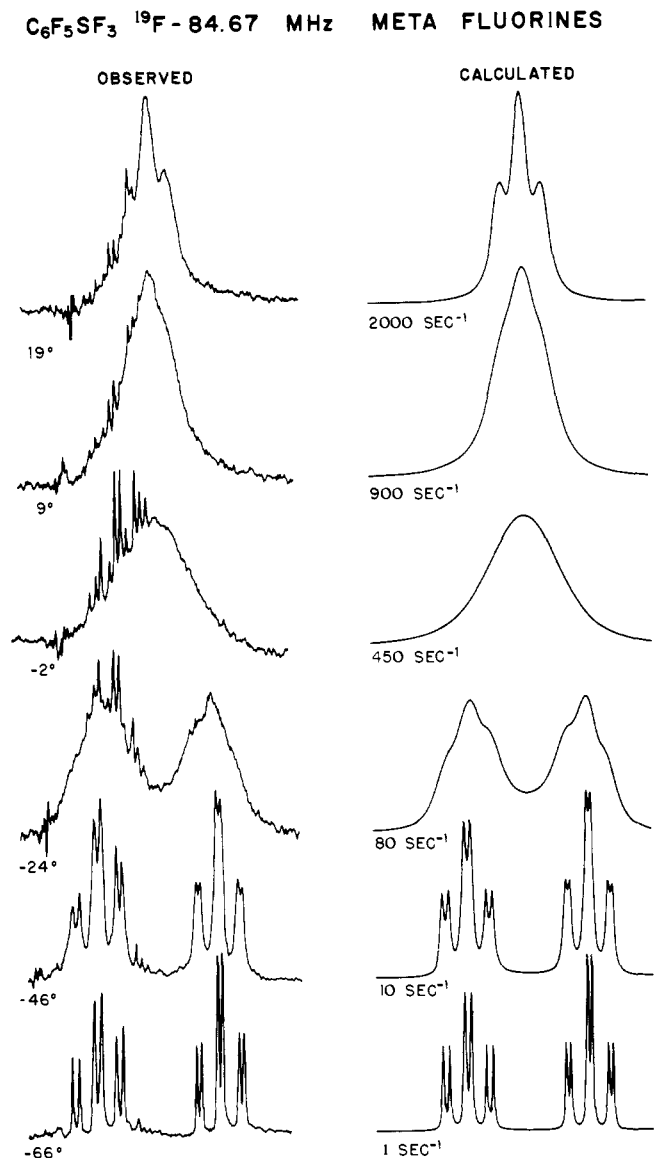


Figure 4. Observed and calculated temperature-dependent  $^{19}F$  nmr spectra assigned to the meta fluorines of (perfluorophenyl)sulfur trifluoride. In this case, both chemical shifts and coupling constants are averaged in the exchange process and there are no lines which remain sharp at all temperatures (*i.e.*, no lines invariant to the exchange process).

quite complex appearance (upper row of Figure 6). The spectrum shown in the lower part of Figure 6 was calculated by holding constant all the nmr parameters previously determined and varying only  $J_{oo'}$ ,  $J_{op}$ , and  $J_{o'p}$  (keeping the average value of  $J_{op}$  and  $J_{o'p}$  fixed at 6.5 Hz as required by the spectrum associated with the para fluorines). The nmr parameters determined in this fashion are  $J_{oo'} = 9.5$ ,  $J_{o'p} = 5.75$ ,  $J_{op} = 7.25$  Hz. The chemical shift separation is 2.14 ppm, and the parameters give a good fit to the observed spectrum. As the temperature is raised, the spectrum broadens and then coalesces into a spectrum which can be crudely described as a quintet of doublets at about  $60^\circ$ . The spectrum is not well resolved and the fast exchange limit has not been reached. Above  $60^\circ$  the sample decomposes rapidly. Since the line shape calculation cannot be carried out using a first-order two-site model (due to the fairly large ortho-ortho coupling), a line shape analysis of the temperature dependence of this multiplet was not carried out. A complete line shape analysis in a case such as this should be quite tractable due to the extensive "X fac-

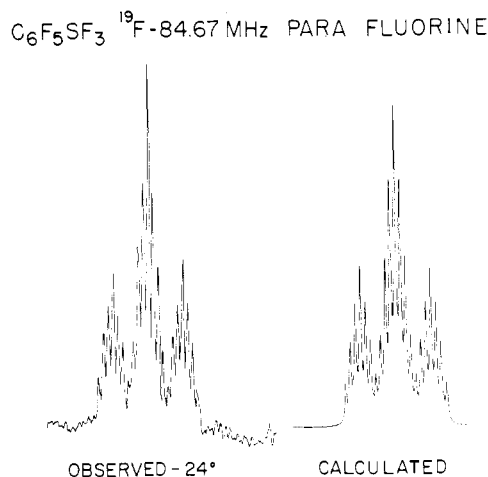


Figure 5. Observed and calculated high-temperature ( $24^\circ$ )  $^{19}F$  nmr spectrum associated with the para fluorine of (perfluorophenyl)sulfur trifluoride.

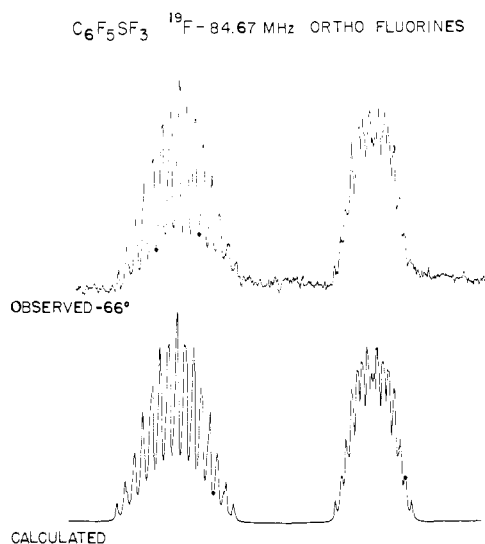


Figure 6. Observed and calculated low-temperature ( $-66^\circ$ )  $^{19}F$  nmr spectrum associated with the ortho fluorines of  $C_6F_5SF_3$ . This spectrum shows strong temperature-dependent line shape effects due to the internal rotation about the C-S bond.

toring."<sup>15</sup> However, due to the large number of spins involved, a new computer program would have to be written. In view of the rather complete rate data obtained from the analysis of the resonances associated with the apical, basal, and meta fluorines, we did not feel that this additional effort would be warranted.

**The Low-Temperature Limit Spectrum.** The coupling constants and chemical shift data obtained from the analysis of the  $-66^\circ$  spectra are shown in Figure 7. The shifts are given in parts per million from internal  $CFCl_3$ . This does not represent the low-temperature limit since the process responsible for the observed line shape effects is still occurring at a rate of  $\sim 1 \text{ sec}^{-1}$ . Lowering the temperature further results in spectra which are quite broad presumably due to increased viscosity of the solvent. The association between the fluorines, ( $F_o, F_m'$ ) and ( $F_o, F_m$ ), and the configuration of the molecule implied by Figure 7 is, of course, ambiguous.

**B. (Pentafluorophenyl)sulfinyl Fluoride and (Pentafluorophenyl)sulfonyl Fluoride.** These compounds were examined in solution in fluorotrichloromethane from  $30$  to  $-55^\circ$  and in chlorodifluoromethane from  $-50$  to  $-130^\circ$  using the



**Table IV.** Comparison of Observed and Calculated Meta Coupling Constants (Hz) for (Pentafluorophenyl)sulfur Fluorides

	C <sub>6</sub> F <sub>5</sub> SF <sub>3</sub>		C <sub>6</sub> F <sub>5</sub> SOF		C <sub>6</sub> F <sub>5</sub> SO <sub>2</sub> F	
	Obsd	Calcd <sup>a</sup>	Obsd	Calcd <sup>a</sup>	Obsd	Calcd <sup>a</sup>
J <sub>op</sub>	7.25	6.6	5.8	6.3	8.7	8.0
J <sub>o'p</sub>	5.75					
J <sub>mm'</sub>	~0	-0.6	-0.18	-0.6	0.1	-0.3
J <sub>oo'</sub>	-9.5	-8.5	-6.63	-8.3	-11.0	-9.7

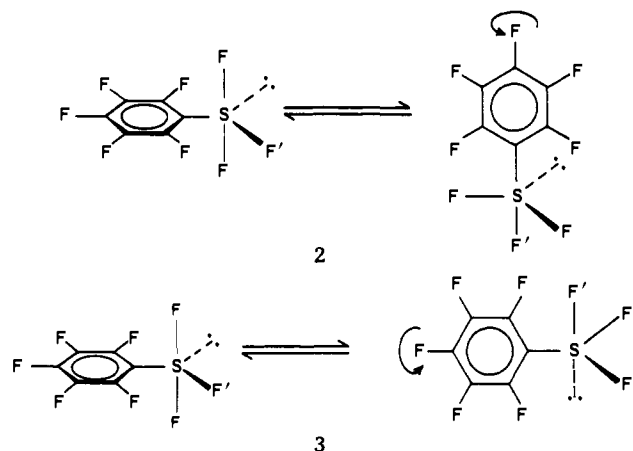
<sup>a</sup> Calculated values from parafluorine atom chemical shifts and eq 5, 9, and 13 of Pushkina, *et al.*, ref 13.

Ortho fluorine-fluorine coupling constants are usually close to -20 Hz. The negative sign has been determined for a few compounds by double resonance methods<sup>15</sup> and by studies on partially oriented molecules.<sup>16</sup> It appears to hold for all pentafluorophenyl derivatives;<sup>13</sup> Pushkina, *et al.*,<sup>13</sup> give ortho coupling from -18.7 to -26.5 Hz for the 65 compounds they list. The para fluorine-fluorine coupling constants listed by Pushkina, *et al.*, vary from +4.1 to +9.1 Hz. Our values for the ortho and para coupling constants in C<sub>6</sub>F<sub>5</sub>SF<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>SOF, and C<sub>6</sub>F<sub>5</sub>SO<sub>2</sub>F fall within these ranges.

**Molecular Motion in (Pentafluorophenyl)sulfur Trifluoride.** In the case of C<sub>6</sub>F<sub>5</sub>SF<sub>3</sub>, the process responsible for the observed line shape effects must be intramolecular since <sup>19</sup>F-<sup>19</sup>F coupling constants are averaged in the process but not lost. The model used to obtain the calculated line shapes is one in which the environments of F<sub>o</sub> and F<sub>o'</sub> are averaged and the environments of F<sub>m</sub> and F<sub>m'</sub> are averaged. Since there is no evidence for exchange of the axial and equatorial fluorines up to +50°, the barrier to intramolecular exchange of the fluorine substituents on the sulfur atom must be at least 15-16 kcal mol<sup>-1</sup>. The observed line shape effects can be accounted for in two ways.

A. The simplest physically reasonable process which is consistent with the observed nmr line shape effects is internal rotation about the C-S bond.

B. The internal rotation process could occur in combination with an intramolecular rearrangement of the coordination at the sulfur atom in which the fluorine F<sub>b</sub> is not exchanged with the fluorines F<sub>a</sub>. This could be achieved by means of a Berry type process<sup>17</sup> with the lone electron pair (2) or C<sub>6</sub>F<sub>5</sub> (3) acting as the pivotal ligand. The intermedi-



ate with an apical lone pair is probably quite energetically unfavorable. This type of intermediate could also be involved in an exchange process, with F' as the pivotal ligand, in a Berry process which would exchange the two types of fluorine ligands F<sub>a</sub> and F<sub>b</sub>. The observation that the barrier to this exchange process is high (see above) can also be rationalized in terms of the unfavorable energy requirement for an apical lone pair.

**Table V.** Substituent Parameters Calculated from Chemical Shifts

Substituent	Conditions	Calcd		Lit. values	
		—from C <sub>6</sub> F <sub>5</sub> X <sup>a</sup> —	σ <sub>R</sub> <sup>o</sup>	—from FC <sub>6</sub> H <sub>4</sub> X <sup>b</sup> —	σ <sub>R</sub>
SOF	25°, CFCl <sub>3</sub>	0.56	0.18	0.66	0.17
SO <sub>2</sub> F	25°, CFCl <sub>3</sub>	0.64	0.27	0.75	0.26
SO <sub>2</sub> Cl	<i>a</i>	0.72	0.28	0.80	0.24
SF <sub>3</sub>	25°, Toluene	0.70	0.12	0.60	0.20
	-66°, Toluene	0.63	0.18	0.56 <sup>c</sup>	0.22 <sup>c</sup>
		1.08	0.05		

<sup>a</sup> Reference 13. <sup>b</sup> Reference 18. <sup>c</sup> Unpublished results from W.A.S. Calculated from chemical shifts at -80°.

Process 2 (with the lone pair as the pivotal ligand) cannot be eliminated. It is an attractive alternative to the simple internal rotation process.

Since line shape effects can be observed over only a limited temperature range for the part of the spectrum assigned to the apical fluorines, and since the analysis of the line associated with the meta fluorines assumed a constant chemical shift separation, the most accurate activation parameters are probably those obtained from the analysis of the F<sub>b</sub> resonances.

The errors given for the activation parameters in the experimental section are those obtained from a statistical analysis.<sup>6</sup> Unfortunately, systematic errors are far more serious than random errors in this type of experiment. Consequently, a statistical error analysis can be quite misleading. This is demonstrated by the observation that the differences in the activation parameters obtained from line shape analysis for the meta fluorines and those obtained for the apical and basal fluorines are considerably larger than the statistical errors obtained for one set of resonances. The systematic error responsible for this discrepancy is probably a result of the assumption of a temperature-independent chemical shift separation for the meta fluorines. We believe that the major contribution to the systematic errors for the apical and basal fluorines comes from errors in the temperature measurement which increases with increasing deviation from room temperature. Assuming that the temperature error may be as large as 2% of the difference from room temperature and including the contributions from statistical errors, an error analysis using the data obtained from the line shape analysis for the apical and basal fluorines gives the following results: ΔH\* = 10.5 ± 0.4 kcal mol<sup>-1</sup>, ΔS\* = -7.7 ± 1.3 cal mol<sup>-1</sup> deg<sup>-1</sup>, ΔG\*<sub>298</sub> = 12.75 ± 0.02 kcal mol<sup>-1</sup>, log (A)<sub>298</sub> = 11.6 ± 0.3, E<sub>a298</sub> = 11.1 ± 0.4 kcal mol<sup>-1</sup>.

The small entropy of activation, ΔS\* = -8.0 cal mol<sup>-1</sup> deg<sup>-1</sup>, is consistent with a simple intramolecular process such as internal rotation. The activation enthalpy of 10.4 kcal mol<sup>-1</sup> is large for internal rotation about a single bond suggesting either partial double bond character for the S-C bond or fairly strong steric interactions between the ortho fluorines and the fluorines on the sulfur atom.

**Substituent Parameters from Chemical Shifts.** The substituent parameters, σ<sub>I</sub> and σ<sub>R</sub><sup>o</sup>, were calculated from the chemical shifts of meta and para fluorines for the series (pentafluorophenyl)sulfinyl fluoride, sulfonyl fluoride, and trifluorosulfurane using eq 36 and 37 of Pushkina, *et al.*<sup>13</sup>

$$\delta_m^F = 5.21\sigma_I + 6.26\sigma_{R^o} - 163.11$$

$$\delta_p^F = 8.91\sigma_I + 31.52\sigma_{R^o} - 155.53$$

The calculated values are given in Table V with the comparison to the σ<sub>I</sub> and σ<sub>R</sub><sup>o</sup> values determined by the method of Taft from fmr chemical shifts from the corresponding *m*- and *p*-fluorophenyl derivatives.<sup>18</sup>

For the SOF and SO<sub>2</sub>F substituents the calculated inductive values  $\sigma_I$  are slightly less than the literature values, but the resonance parameters  $\sigma_{R^0}$  agree exceptionally well. These results are comparable to the reported result for SO<sub>2</sub>Cl. The parameters calculated for the SF<sub>3</sub> group at 25° show moderate agreement with the literature values, but in this case the  $\sigma_I$  value is high and the  $\sigma_{R^0}$  value is low. At -66°, the two shifts for the meta fluorine were calculated separately. Now the agreement between  $\sigma_I$  and  $\sigma_{R^0}$  is good from the higher field shift but very poor from the lower field value. A reasonable interpretation is that the lower field shift is for the meta fluorine on the side of the ring remote from the basal fluorine and that *m*-fluorophenylsulfur trifluoride is populated primarily with the configuration where the phenyl ring is oriented so that the meta fluorine is also remote from the basal fluorine. Low-temperature studies on *m*-fluorophenylsulfur trifluoride gave no indication of freezing out of the two ring conformation, but this result could also be interpreted on the basis that only one conformation predominates.

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## Synthetic Analogs of the Active Sites of Iron-Sulfur Proteins. X.<sup>1</sup> Kinetics and Mechanism of the Ligand Substitution Reactions of Arylthiols with the Tetranuclear Clusters [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>]<sup>2-</sup>

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**Abstract:** Previous work in this series has demonstrated that alkylthiolate tetramer dianions [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>]<sup>2-</sup> undergo facile ligand substitution reactions with added thiols R'SH. The rates and mechanism of initial thiolate substitution in reactions of R = Et and *t*-Bu tetramers with arylthiols in acetonitrile solution at 25° have been investigated by stopped-flow spectrophotometry. For the process [Fe<sub>4</sub>S<sub>4</sub>(S-*t*-Bu)<sub>4</sub>]<sup>2-</sup> + R'SH → [Fe<sub>4</sub>S<sub>4</sub>(S-*t*-Bu)<sub>3</sub>(SR')]<sup>2-</sup> + *t*-BuSH, reaction rates are second order, first order in tetramer and in thiol, and the following resolved second-order rate constants (R', M<sup>-1</sup> sec<sup>-1</sup>) were determined: *p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 2.1 ± 0.2; *p*-tolyl, 4.5 ± 0.6; *o*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 110 ± 8; *p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 3600 ± 200. Reaction rates parallel thiol acidities (in aqueous alcohol solutions), and it is proposed that the rate-limiting step is protonation of coordinated alkylthiolate followed by rapid separation of alkylthiol and coordination of arylthiolate. Rate constants for the reactions of the R = *t*-Bu and Et tetramers with *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SH are within experimental error, indicating an absence of tetramer steric effects on reaction rates. Addition of benzoic or acetic acid to the system [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>]<sup>2-</sup>-*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SH produces significant increases in reaction rates but only the rate constant for the benzoic acid assisted process (250 ± 14 M<sup>-1</sup> sec<sup>-1</sup>, R = *t*-Bu) fits the rate-acidity correlation evident in systems containing tetramer and thiol. The relatively rapid rates and apparent mechanistic simplicity of the ligand substitution reactions, together with the previously observed lack of degradation of the Fe<sub>4</sub>S<sub>4</sub> core over the course of full thiolate substitution, further emphasize the synthetic utility of these reactions based on alkylthiolate tetramers.

Recent investigations of the reactivity properties of the alkylthiolate tetramer dianions [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>]<sup>2-</sup>, which are structurally<sup>3-5</sup> and electronically<sup>3,5-8</sup> related to the [Fe<sub>4</sub>S<sub>4</sub>(S-Cys)<sub>4</sub>] active centers in oxidized ferredoxin and reduced high-potential iron-sulfur proteins,<sup>9</sup> have shown that they undergo facile ligand substitution reactions with added thiols R'SH at ambient temperature in nonaqueous or partially aqueous media.<sup>1,5,8,10</sup> These reactions involve substitution of one or more thiolate ligands external to the

Fe<sub>4</sub>S<sub>4</sub> core which, from X-ray diffraction<sup>3-5</sup> and a variety of spectroscopic measurements,<sup>11</sup> is electronically fully delocalized and contains four equivalent metal sites. The typical complexes [Fe<sub>4</sub>S<sub>4</sub>(SCH<sub>2</sub>Ph)<sub>4</sub>]<sup>2-</sup><sup>3,4</sup> and [Fe<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>]<sup>2-</sup><sup>5</sup> have the cubane-type stereochemistry with effective *D*<sub>2d</sub> symmetry and approximately tetrahedral coordination at iron.

Spectrophotometric and pmr studies of equilibrium solutions have shown that the substitution reactions of