THE UNIVERSITY OF MANITOBA

NMR STUDIES OF FLUORINE EXCHANGE IN SULPHUR AND PHOSPHORUS FLUORIDES

by

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ABSTRACT

The synthesis of the N,N dialkylaminosulphur trifluorides R_2NSF_3 where R= CH_3, C_2H_5, and $(CH_3)_2CH$ has been reported. The fluorine and proton NMR spectra of these compounds were recorded under anhydrous conditions at -68° and +22°. The spectra were well resolved with no complications from fluorine exchange. The fluorine NMR spectrum of SF_4 was studied over the temperature range -70° to +70° and resolution was obtained at a temperature 30° higher than previously reported.

Evidence which strongly suggests that hydrolysis is the mechanism of fluorine exchange in these compounds has been obtained. The possible implication of this mechanism in a similar exchange in the fluorophosphoranes is discussed and evaluated.

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GENERAL INTRODUCTION

A great deal of interest has been shown during the last 15-20 years in the structures of compounds containing sulphur, carbon and fluorine. In particular many perfluoro-, polyfluoro-, and polyhaloalkyl-sulphur compounds have been prepared and studied [1]. The ease of preparation of such compounds was aided to a large extent by the discovery of sulphur tetrafluoride.

Sulphur tetrafluoride is an extremely useful reagent yet its existence was doubted as late as 1950. In this same year it was synthesized unequivocally by Silver and Cady [2]. They obtained SF_4 from the decomposition of CF_3SF_5 in an electrical discharge.

$$CF_3SF_5 \longrightarrow CF_4 + SF_4$$

Several other methods have since been published; Brown and Robinson [3] obtained sulphur tetrafluoride by reaction of elemental fluorine on thin films of sulphur at -75° C. Action of chlorine monofluoride or iodine pentafluoride on sulphur or sulphur dibromide also yields sulphur tetrafluoride [4,5].

The most convenient and practical laboratory synthesis of sulphur tetrafluoride is that reported by Tullock [4] which involves heating sulphur dichloride in acetonitrile in the presence of sodium fluoride.

$$3\ SCl_2 + 4\ NaF \longrightarrow SF_4 + S_2Cl_2 + 4\ NaCl$$

The above reaction requires no special apparatus for handling of reactive fluorine compounds.

The very facile hydrolysis of sulphur tetrafluoride makes it difficult to handle in glass apparatus unless special precautions are taken. Though this hydrolysis is well known, reports of samples of SF_4 "invariably contaminated with SOF_2" [6] seem to be simply a result of contamination during original preparations and not as a result of "improper" handling. The hydrolysis also yields hydrogen fluoride.

$$SF_4 + H_2O \longrightarrow SOF_2 + 2\ HF$$

The fluorinating reactions of sulphur tetrafluoride are very useful and widely used due to their specificity. Though such reactions have been reviewed in the literature [7], some of the more important ones will be mentioned. A parallel to hydrolysis exists in the reaction of SF_4 with hydroxyl groups and thus carboxylic groups are converted to acid fluorides.

$$RCOOH + SF_4 \xrightarrow{r.t.} RCOF + SOF_2 + HF$$

The reaction with carbonyl groups in aldehydes, ketones, and carboxylic acids replaces oxygen with fluorine.

$$\diagup C{=}O + SF_4 \longrightarrow \diagup CF_2 + SOF_2$$

$$-CHO + SF_4 \longrightarrow -CHF_2 + SOF_2$$

$$-COOH + SF_4 \xrightarrow[temp.]{high} -CF_3 + SOF_2$$

Sulphur tetrafluoride has also found extensive use in inorganic chemistry for production of other inorganic fluorides from corresponding oxides and sulphides [8]. Gaseous thionyl fluoride is the principle by-product in reactions with oxides, while elemental sulphur contaminates reactions with sulphides.

$$I_2O_5 + SF_4 \longrightarrow 2\ IF_5 + SOF_2$$

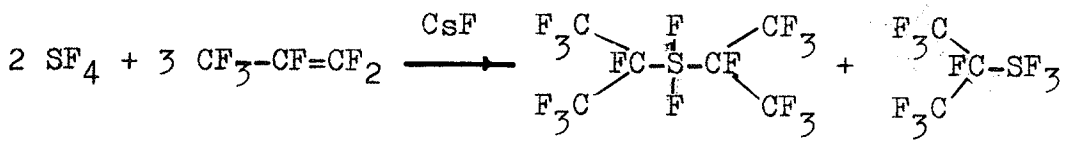
$$SnS_2 + SF_4 \longrightarrow SnF_4 + 3S$$

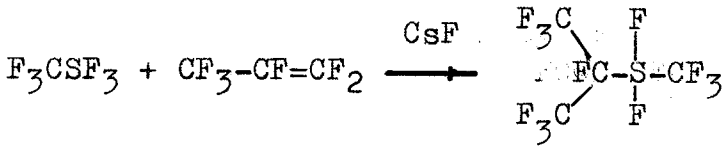
An important group to consider when discussing sulphur tetrafluoride is its derivatives which entail compounds with the functional groups $-SF_3$ or $=SF_2$. There are only limited numbers of each type and these derivatives were relatively unknown before the 1960's, although several preparative attempts were reported [9,10]. Those that were known usually contained perfluoroalkyl groups, viz. CF_3SF_3 [11], $F_3SCF_2SF_3$ [12]. The only arylsulphur trifluoride known before 1960 was 2,4 dinitrophenylsulphur trifluoride prepared by fluorination of the corresponding disulphide in liquid HF with fluorine diluted with nitrogen [13].

The first general preparative route to arylsulphur trifluorides did not appear until 1962. The general reaction, reported by Sheppard [14], involved reaction of aryldisulphides with silver difluoride in 1,1,2 trichloro- 1,2,2 trifluoroethane solvent. Silver difluoride selectively fluorinates the sulphur atom without attacking adjoining hydrocarbon groups in direct contrast to other common metal fluorides (eg. HgF_2, PbF_4). Aliphatic disulphides also reacted with AgF_2 but products were either inseparable from the solvent or, in the case of n-butyl disulphide , the aliphatic chain was fluorinated giving $C_4H_8FSF_3$.

Also in 1962, Rosenberg and Muetterties reported a method for the direct synthesis of perfluoroalkyl sulphur (IV) fluorides from a fluoro-olefin and sulphur tetrafluoride or a mono-substituted sulphur (IV) fluoride [15]. They also reported the first

examples of perfluoroalkyl sulphur (IV) fluorides.





RSF_3 acts as a fluorinating agent much like SF_4.

Though sulphur - nitrogen compounds have been investigated for over 100 years[16,22], it was not until the late 1960's that sulphur tetrafluoride was used as a convenient starting material. Thus the iminosulphur difluorides, $-N=SF_2$, are an interesting new class of compounds. They may be obtained from the reaction of sulphur tetrafluoride with amines or amides [18], cyanides, cyanates, and thiocyanates[17], or from the cleavage of silicon-nitrogen compounds[19] as shown below.

$$3\ RNH_2 + SF_4 \longrightarrow RN=SF_2 + 2\ RNH_3^+\ F^-$$

$$KNCO + 2\ SF_4 \longrightarrow F_3CN=SF_2 + KF + SOF_2$$

$$RNCO + SF_4 \longrightarrow RN=SF_2 + COF_2$$

$$RC\equiv N + SF_4 \longrightarrow RCF_2-N=SF_2$$

$$(R_3Si)_2NR + SF_4 \longrightarrow RN=SF_2 + 2\ R_3SiF$$

Sulphur tetrafluoride also cleaves the silicon - nitrogen bond of silylamines to yield aminosulphur trifluorides with the formula R_2NSF_3. These particular derivatives have only recently been reported.

$$R_2N-Si(CH_3)_3 + SF_4 \longrightarrow R_2NSF_3 + (CH_3)_3SiF$$

$R=CH_3$, C_2H_5 [20,21]

This synthesis goes very smoothly due to the facile Si-N bond cleavage and the high bond energy of the resulting Si-F bond.

The stereochemistry around sulphur in all of the above mentioned compounds is of particular interest since sulphur retains a non-bonding electron pair. As well as the lone pair, the substituents around sulphur are of varying electronegativity and thus may assume different positions in the trigonal bipyramid. The factors influencing the stereochemistry as well as the problems involved in actually determining the structure of sulphur fluorides will be discussed later.

A further class of compounds of relevance to this thesis is that of the "fluorophophoranes". Compounds of this group are those derived from phosphorus pentafluoride by substitution of one or more fluorines with various groups. Although phosphorus pentafluoride has been known since 1876, fluorophosphoranes were not isolated until 1958-59 when Smith reported phenyl- and isooctenyltetrafluorophosphorane [25]. Numerous reports of the synthesis of fluorophosphoranes have appeared since that time. Rather than discussing all aspects of fluorophosphorane chemistry here, the reader is referred to two excellent reviews by Schmutzler [26,27]. Only two subgroups of fluorophosphoranes will be discussed here; those containing hydrocarbon substituents, R_nPF_{5-n}(n=1,2,3), and dialkylaminofluorophosphoranes, $(R_2N)_nPF_{5-n}$ (n=1,2).

The original method of preparing fluorophosphoranes of the type R_nPF_{5-n} was fluorination of the complexes formed between PCl_3, alkyl chlorides, and $AlCl_3$ [28].

$$[R_nPCl_{4-n}][AlCl_4] \xrightarrow[\text{agent}]{\text{fluorinating}} R_nPF_{5-n} \quad (n=1,2)$$

They are also prepared by a reaction involving halogen exchange as well as a concurrent redox reaction. The fluorinating agents are arsenic or antimony trifluorides[29].

$$3\ R_nPCl_{3-n} + (5-n)\ MF_3 \longrightarrow 3\ R_nPF_{5-n} + 2M + (3-n)\ MCl_3$$

M=As,Sb n=1,2

A further synthesis of fluorophosphoranes involves sulphur tetrafluoride as a fluorinating agent with phosphorus-oxygen compounds or tertiary phosphines.

$$RPO(OH)_2 + 3\ SF_4 \longrightarrow RPF_4 + 2HF + 3\ SOF_2$$
$$R_2PO(OH) + 2\ SF_4 \longrightarrow R_2PF_3 + HF + 2\ SOF_2$$
$$2\ R_3P + ,SF_4 \longrightarrow 2\ R_3PF_2 + S$$

Alkyl- or arylaminofluorophosphoranes are conveniently prepared by a method analogous to the preparation of aminosulphur trifluorides. The Lewis acid phosphorus fluorides react with silylamines to cleave the Si-N bond.

$$R_2N\text{-}Si(CH_3)_3 + PF_5 \xrightarrow{-78^\circ} R_2NPF_4 + (CH_3)_3SiF$$
$$R_2N\text{-}Si(CH_3)_3 + R_2NPF_4 \xrightarrow{150^\circ} (R_2N)_2PF_3 + (CH_3)_3SiF$$
$$R = CH_3\ ^{19,20},\ C_2H_5\ ^{31}$$

The initial formation of a 1:1 adduct has been established in the case of R = CH_3 above and decomposition of a similar adduct between secondary amines and phosphorus pentafluoride also leads to dialkylaminofluorophosphoranes[32].

$$PF_5 + R_2NH \longrightarrow R_2\overset{H}{N}\rightarrow PF_5 \xrightarrow{100^\circ\text{-}120^\circ} R_2NPF_4 + R_2\overset{+}{N}H_2PF_6^-$$

R = methyl, ethyl, n-propyl

The dialkylaminofluorophosphoranes form solid adducts with further dialkylamine, but these decompose at room temperature to yield bisdialkylaminofluorophosphoranes, $F_3P(NR_2)_2$ ($R = CH_3, C_2H_5$), which are very inert.

For a complete listing of all known fluorophosphoranes up to 1967, the reader is referred to reference (27). All further comments on fluorophosphoranes include all such compounds and not just those whose synthesis has been described earlier.

All fluorophosphoranes can be handled in glass equipment, but the glass is often attacked if moisture and HF are not rigorously excluded. The hydrolytic stability of fluorophosphoranes with hydrocarbon substituents is as follows:

$$R_3PF_2 > R_2ArPF_2 > Ar_2PF_3 > RArPF_3 > R_2PF_3 > R(Ar)PF_4 (> PF_5)$$

Hydrolysis of these alkylfluorophosphoranes occur in several stages:

$$R_nPF_{5-n} \xrightarrow[-HF]{H_2O} R_nPOF_{3-n} \xrightarrow[-HF]{H_2O} R_nPO(OH)_{3-n} \quad (29)$$

Though little is known about hydrolysis of other fluorophosphoranes, their hydrolytic stability appears to be comparable to that of R_nPF_{5-n}.

As with the sulphur fluorides, fluorophosphoranes provide a complex study in stereochemistry. They provide an excellent example of pentaco-ordination with its two possible geometries of trigonal bipyramid and square pyramid. The problems involved in determing the structures of the fluorophosphoranes is discussed later along with the sulphur fluorides.

ELECTRON PAIR REPULSIONS AND MOLECULAR SHAPE

The modern stereochemical theory most often used is that known as the Valence-Shell-Electron-Pair-Repulsion theory[37]. The theory emphasizes the stereochemical importance of interactions between the electron pairs in the valence shell of a central atom. Interactions between ligands are of lesser importance but may play a role in determing stereochemistry if they are sufficiently bulky. There are few cases where electron pairs in the valence shell do not determine stereochemistry[37].

Even though the rules for VSEPR theory are actually empirical generalizations, they are repeated here because of their great success in correlating molecular structure. The first rule states simply that lone pair electrons (E) repel adjacent electron pairs more strongly than bonding electron pairs (X). The repulsions increase in the order X-X < X-E < E-E. This rule seems intuitively sound since the lone pairs are under the influence of only one positive center and hence would be expected to have a more radial distribution than bonding electrons[38]. This rule explains why lone pairs occupy equatorial positions of the trigonal bipyramid in the electron arrangements of AX_4E (SF_4), AX_3E_2 (ClF_3), and AX_2E_3 (XeF_2). Equatorial groups have two

nearest neighbours at 90° whereas axial groups have three nearest neighbours at 90°.

The second rule states that the repulsions exerted by bond pairs decrease as the electronegativity of the bonded atom increases. Since a bonded atom will draw the σ-bonded electrons away from the central nucleus, it effectively contracts the bonding orbital. The more electronegative atoms will contract the bonding orbital to a greater extent, thereby lowering repulsions to other electron pairs. This is the simple reason why the more electronegative atoms occupy axial positions in trigonal bipyramidal arrangements. Since axial positions have three nearest neighbours at 90° in the trigonal bipyramid, the repulsions are lowered more by axial placement of electronegative atoms than by equatorial placement.

Multiple bonds do not affect the gross stereochemistry of a molecule; however angles involving multiple bonds will be larger than those involving single bonds[39]. This is again intuitively obvious, since multiple bonds occupy the same site as the sigma bond that they accompany. However, since, the multiple bond is larger than the single bond, the angle between double bonds and other bonds will be slightly larger than angles between single bonds alone.

The VSEPR theory has been very useful in predicting the molecular structures of inorganic molecules. Although electron diffraction and microwave studies ultimately confirm the predicted molecular structures, ^{19}F NMR studies have also been very useful in similar studies. The technique has often been

complicated by chemical exchange effects (see below).

EFFECT OF CHEMICAL EXCHANGE ON NMR SIGNALS

High resolution nuclear magnetic resonance has seen a rapid advancement in the last two decades and has developed into one of the most valuable tools for obtaining direct and detailed insight into events at the molecular level. Applications to structural inorganic chemistry are of growing importance[33]. Resonance signal position as well as their fine structure give information about the bonding of magnetic nuclei as well as their spatial relationships. NMR spectra can be completely analyzed by quantum theory in terms of resonance frequencies and intensities. The final parameters obtained, chemical shift δ and coupling constant J_{ij}, completely determine energy levels of nuclear spins in an external magnetic field H_o. It is assumed that the reader is familiar with this material which determines the static information obtainable from the NMR experiment.

In addition to variation in chemical shifts and coupling constants, NMR spectra are influenced by time-dependent phenomena. One such phenomenon is molecular motions such as chemical exchange of nuclei. If a nuclear spin jumps at random from one environment to another, then the multiplet structure is altered in a selective way [34]. Some lines may broaden, others remain sharp, and some groups of lines coalesce to a single peak [35,36]. These processes are due to motions which have frequencies similar to the frequency separation between resonance lines in a multiplet (rate constant $\simeq 10^{-1} - 10^{5}$ sec^{-1}).

Two limiting cases of exchange exist. In the first case the nuclear spin jumps between sites with a frequency ω_e much greater than the frequency separation $\Delta\omega$ of the two spectral lines affected by the motion. Another method of stating this is to say that the average lifetime of the nuclear spin is short in comparison to the NMR time scale. The result is a single line at the average frequency with a width

$$\delta\omega \approx \frac{(\Delta\omega)^2}{\omega_e} \qquad \text{fast exchange}$$

The nuclear spin is jumping so fast in comparison to the difference in resonance frequencies that it effectively never loses phase from site to site and thus sees the average of the two environments.

The other extreme exists when the average lifetime is above an upper limit, or, in other words, when the motion is very slow with $\omega_e \ll \Delta\omega$. Both lines are resolved but somewhat broadened with a width

$$\delta\omega \approx \omega_e \qquad \text{slow exchange}$$

The collapse of signals arising from nuclei in different chemical positions (ie. collapse of chemical shift) is only one aspect of the effect of chemical exchange on NMR spectra. It is also found that components of a spin multiplet may be partly or completely collapsed by similar mechanisms. In place of expected multiplets, such as triplets or quartets, one often observes a single broad peak which can sometimes be very close to the signal/noise limit.

From the discussion above it should be obvious that the determination of stereochemistry by NMR is seriously hindered by chemical exchange effects. Expected non-equivalence of magnetic nuclei may not be observed leading the investigator to incorrect structures. Even if non-equivalence is observed, multiplet fine structure may be smeared by exchange, leaving absolute structure confirmation to another spectroscopic method such as Raman or infrared spectroscopy.

An estimate of the activation energy for chemical exchange may also be obtained from the NMR spectra. The pseudo first order rate constant "k" for an exchange reaction is given by

$$k_1 = 1/\tau \quad [40]$$

and the activation energy "E_a" is obtained from the Arrhenius equation

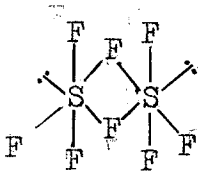
$$k = A \exp^{(-E_a/RT)}$$

where "A" is the frequency factor. "E_a" is therefore obtainable from a plot of log k_1 versus 1/T. The slope of the line is $-E_a/2.303$ R and the intercept is log A. Other thermodynamic data may be obtained from the usual equations[41] once the rate constant k_1 is determined from the NMR spectrum by such techniques as line shape analysis[34,36,42], spin echo, fast passage, and double resonance methods[42,43].

GENERAL SCOPE OF THIS WORK

A variety of mechanisms have been suggested to explain NMR studies of fluorine exchange in compounds such as SF_4[6,44], PF_5[45a&b], RPF_4[26,27,46], R_2SeF_2[47], $RSiF_4^-$ and $R_2SiF_3^-$[48]. The mechanism of the exchange process has been indicated clearly in relatively few instances.

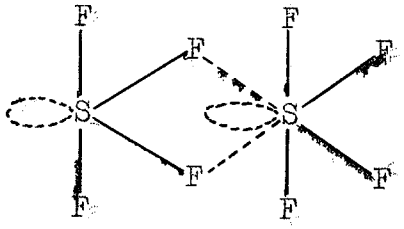
The ^{19}F NMR of SF_4 [6](-85°) reveals separate peaks due to axial and equatorial fluorines. The coalescence temperature was found to be concentration dependent and thus it was suggested that the exchange process was second order or higher. Such a process would involve a dimer or ionic intermediate. No correlation was found between dielectric constant of the medium and the observed exchange rate however this does not rule out the ionization mechanism since nothing was known about solvation effects for possible ionic species. A fluorine bridged intermediate as shown below was proposed for SF_4 simply on the basis that a similar mechanism had been proposed for SbF_5.



These studies did not rule out the possibility of a first or higher than second order process. Similar concentration dependence was noted for RSF_3 compounds[14]. It was concluded that the exchange process in these compounds proceeded by a bimolecular process which could be explained by a dimer inter-

mediate similar to that shown above for SF_4.

As well as the above intermolecular mechanism postulated for SF_4 an intramolecular mechanism was proposed by Redington and Berney in 1965 [51]. Infrared studies of SF_4 and SOF_2 at low temperatures showed that weak bonding appeared to exist between the equatorial pair of fluorine atoms on one SF_4 molecule and the sulphur lone pair of electrons on an adjacent SF_4 molecule. The spectrum of SOF_2, present as an impurity, showed changes suggestive of the formation of an SF_4-SOF_2 complex. The model proposed by them is shown below.



The critical assumption made by these authors is that in SF_4 and SOF_2 the lability of fluorine atoms toward intermolecular exchange is not signifigantly different and that fluorine exchange between these species should be observed but, in fact, is not. Thus their observation of distinct intermolecular association between SF_4 and SOF_2 (in an argon matrix at cryoscopic temperatures) suggested to them that axial-equatorial fluorine exchange in SF_4 could be explained without intermolecular fluorine exchange.

Muetterties and Phillips, who proposed the intermolecular mechanism, critisized the model of Redington and Berney in 1967, drawing particular attention to the improbability of such a structure [52].

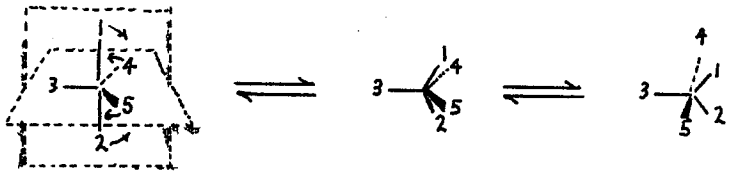
They presented more evidence for their mechanism but also raised the possibility that the exchange observed by NMR reflected an exchange catalyzed by impurities. They pointed out that intramolecular fluorine exchange (similar to Berry pseudorotation as discussed below for P(V) compounds) probably occurred in SF_4 at a reasonably high rate but that the barrier must be greater than the 4.5 kcal/mole barrier determined for fluorine exchange by NMR studies.

Redington and Berney followed the above paper with a criticism of the criticism [53]. They finally concluded that they did not believe the question of fluorine exchange in SF_4 had been conclusively settled in favor of either an intramolecular or an intermolecular mechanism. Since this paper in 1967, no further studies have been reported.

Pentacoordinate phosphorus derivatives and, in particular, the fluorophosphoranes have been investigated extensively. The ^{19}F NMR spectrum of PF_5 has been reported by several authors [54-55]. In each case a simple doublet was observed which arises from coupling of five equivalent fluorines with the central phosphorus atom. This is despite the fact that PF_5 has been shown to be a trigonal bipyramidal molecule by infrared and Raman [56,57], and electron diffraction studies [58].

Muetterties and Mahler suggest that further splitting is not observed due to a very small chemical shift between axial and equatorial fluorines [55]. The more widely held view is that intramolecular exchange of axial and equatorial fluorines takes

place via a process called Berry pseudorotation[49]. This process interconverts two equatorial ligands with the two axial ligands by a bending process as outlined below.



The transition state has square pyramidal geometry and the bending motion is a genuine vibration for an ML_5 species. Evidence to support the Berry process of simultaneous exchange of the two axial with the two equatorial ligands has been obtained for $(CH_3)_2NPF_4$ [50]. Though such a process is widely accepted, the matter is far from being closed.

Studies done by Brownstein on phosphorus pentafluoride led him to the conclusion that there was an intermolecular mechanism for the intramolecular exchange[45b]. Thus a collision with another molecule of PF_5 and formation of some loose complex or transition state would be required to effect the axial-equatorial exchange in the given molecule. The question of fluorine exchange in phosphorus pentafluoride is thus still not settled.

Though Berry pseudorotation has been used to explain NMR equivalence of fluorines in fluorophosphoranes, there are some exceptions. The observation that the P-C-H coupling is maintained while F-P-C-H coupling is lost at higher temperatures and concentrations suggests that P-F bonds are broken in the exchange process for $(CH_3)_3PF_2$. Loss of P-F coupling immediately

rules out a "Berry process" for this compound. Cowley has suggested a dimer intermediate [59] similar to that proposed for SF_4 by Muetterties and Phillips [6].

One other process has been envisioned to explain NMR equivalence of fluorine in pentacoordinate structures. This process first appeared in the literature in 1970. The process has been termed "turnstile rotation" by Ugi and Ramirez [61]. The process is described as a "permutation of ligands among skeletal positions of the trigonal bipyramid". Four equivalent turnstile processes effect the same isomerization as Berry pseudorotation. The reader is referred to the above mentioned review since the process is much too complex to discuss here.

The purpose of this work then was to reinvestigate the stereochemistry of sulphur fluorides via ^{19}F NMR as well as to gain some definite proof of the mechanism of fluorine exchange in such compounds. In particular, the dialkylaminosulphur trifluorides have never been investigated by methods other than NMR and their structures were never proved definitely. It was then attempted to extend the progress made in the study of the sulphur fluorides to that of the fluorophosphoranes.

GENERAL PROCEDURE, APPARATUS AND REAGENTS

TOXICITY AND HAZARDS

Sulphur tetrafluoride is of the same order of toxicity as phosgene. This toxicity and the ease with which it hydrolyzes to give hydrogen fluoride on contact with moisture make extreme care a prerequisite when working with this fluoride. As stated in the introduction, fluorinating reactions of RSF_3 compounds parallel those of SF_4 and thus they warrant the same precautions.

Phosphorus pentafluoride should be handled very carefully as well. Besides the fact that it hydrolyzes with the evolution of HF, it is a more reactive fluorinating agent than sulphur tetrafluoride.

GENERAL

Due to the air and moisture sensitivity of most compounds, either starting materials or products, conventional vacuum techniques were used to handle them at all times. Sulphur tetrafluoride was handled in a metal vacuum system as was phosphorus pentafluoride. Reactions were carried out in a glass U-tube with a directly attached standard NMR tube. The whole U-tube was pre-dried, pre-silylated with hexamethyldisilazane and trimethylchlorosilane, flamed out, and evacuated at 10^{-4} torr. After reaction solvent was distilled over and the NMR tubes sealed under dynamic vacuum.

INSTRUMENTAL

All infrared spectra were recorded on a Perkin-Elmer, Model 337 grating spectrophotometer using KBr windows for liquids. A metal infrared cell with AgCl windows was used for gas samples.

Nuclear magnetic resonance spectra were recorded on a Varian A56/60A NMR spectrometer using 56.4 and 60 MHz for fluorine and proton respectively. The spectrometer was equipped with a variable temperature probe.

All mass spectra were recorded using a Finnigan 1015 mass spectrometer.

CHEMICALS

Trimethylchlorosilane (Penninsular Chemresearch Inc.) was used without further purification.

Hexamethyldisilazane (Alfa Inorganics) and N,N diethyl-aminotrimethylsilane (Penninsular Chemresearch Inc.) were checked by NMR and used without further purification.

Sulphur tetrafluoride (Matheson Co.) was distilled from a dry/ice acetone bath to remove traces of HF.

Phosphorus pentachloride (Allied Chemical) was pumped on to remove traces of HCl and $POCl_3$.

Arsenic trifluoride (Alfa Inorganics) was used without further purification.

Dimethylamine (Matheson Co.) was used without further purification.

Di-isopropylamine (Matheson, Coleman and Bell) was dried over sodium metal and distilled twice before use.

Trimethylfluorosilane and hexamethyldisiloxane (Penninsular Chemresearch) were obtained for comparison purposes.

Diphenylchloroarsine (Penninsular Chemresearch) was used without further purification.

Succinimide (Aldrich Chemicals) was heated and pumped on for several hours to remove water.

EXPERIMENTAL

PREPARATION OF N,N DIMETHYLAMINOTRIMETHYLSILANE

Dimethylamine (9g.,0.2mole) was condensed onto trimethylchlorosilane (11g.,0.1 mole) in a reaction bulb connected to the vacuum rack. The 2:1 ratio is absolutely essential. Reaction occurred while warming to room temperature and the product was purified by conventional techniques. An uncharacterized white solid was found to form after distillation of product. This eventually disappeared and it was found that one could be assured of product purity if this solid were present.

The purity of product was checked by proton NMR and samples showing any amount of dimethylamine were not used.

PREPARATION OF N,N DIISOPROPYLAMINOTRIMETHYLSILANE

Diisopropylamine (6g.,0.06 mole)was purified by storage over fresh sodium metal for one-half day followed by distillation. The amine was then distilled onto trimethylchlorosilane (2.5g.,0.025 mole) and reaction occurred on warming to room temperature. Once again the 2:1 molar ratio is essential.

The purity of product was checked by proton NMR and a white solid similar to that found in the above reaction was noted in "pure" samples. The amount of solid was probably never more than 0.01g however it was hard to judge the amount since it was gelatinous.

PART I

SULPHUR FLUORIDES

REACTION OF SULPHUR TETRAFLUORIDE WITH N,N DIMETHYLAMINO-TRIMETHYLSILANE

i.) Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto N,N dimethylaminotrimethylsilane (0.28g, 2.4 mmole) in a U-tube which had been treated as previously mentioned in the general procedure. Reaction occurred while warming to room temperature. The contents of the U-tube were then re-frozen and allowed to warm to room temperature again. This was repeated several times to ensure complete mixing of reactants.

The contents of the U-tube were distilled into the attached NMR tube along with trichlorofluoromethane (freon 11). The NMR tube was then sealed under dynamic vacuum and transferred to the NMR spectrometer with the probe maintained at -68°.

The ^{19}F NMR spectrum showed a doublet at -59.2 ppm and a triplet at -20.3 ppm with J=58 Hz. (All chemical shifts are relative to internal freon 11). In addition, each component of the doublet showed septet fine structure with a coupling constant J=5.0 Hz. The components of the triplet also showed septet fine structure with J= 8.2 Hz. The proton NMR spectrum at -68 showed a doublet (J= 8.2 Hz) of triplets (J= 5.0 Hz) at -3.06 ppm relative to internal TMS. (Trimethylfluorosilane was used as internal standard for proton NMR spectra

but chemical shifts are reported relative to internal TMS using the formula ppm($(CH_3)_3SiF$ internal) - 0.179 ppm = ppm (TMS internal).NMR spectra are shown in Figures 1 & 2. Coupling constants and chemical shifts are summarized in Table I.

Trimethylfluorosilane was always present as the second product. The ^{19}F NMR spectrum of this product consisted of a dectet centered on +157.2ppm (relative to internal freon 11) with J =7.5 Hz. The ^{1}H NMR spectrum of trimethylfluorosilane consisted of a doublet at 0.179 ppm (relative internal TMS) with J =7.5 Hz. Parts of the NMR spectra corresponding to this product are not reproduced here.

The mass spectrum was recorded at an ionizing voltage of 70.0 V and at an ionizing current of 50 a. A molecular ion peak of mass number 133 was visible. Other peaks corresponding to expected molecular fragments were present. Some of the major fragments are assigned as follows: $C_2H_4N^+$(m/e 42), $C_2H_5N^+$(m/e 43), $C_2H_6N^+$(m/e 44), $^+SF_3$ (m/e 89), $(CH_3)_2NSF_2^+$ (m/e 114). Since no attempt was made to separate the $(CH_3)_2NSF_3$ from $(CH_3)_3SiF$ or any remaining silylamine, it is pointless to try and determine relative intensities. The spectrum is, however, in close agreement with the spectrum obtained by Demitras and MacDiarmid [20].

ii.) Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto N,N dimethylaminotrimethylsilane (0.56g, 4.8 mmole) in a U-tube in a manner similar to that described above. ^{19}F

NMR showed no signals characteristic of the second addition product. Standing overnight at room temperature did not produce further reaction. Numerous attempts to synthesize the second addition product, $[(C_2H_6)_2N]_2SF_2$, met with similar results.

REACTION OF SULPHUR TETRAFLUORIDE WITH N,N DIETHYLAMINO-TRIMETHYLSILANE

i.) Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto N,N diethylaminotrimethylsilane (0.36g, 2.4 mmole) in a U-tube in a manner similar to that described above. The sealed NMR tube was transferred to the spectrometer with the probe maintained at -68°.

The fluorine NMR spectrum of $(CH_3CH_2)_2NSF_3$ shows a doublet (J= 62 Hz) at -54.0 ppm relative to internal freon 11. Additional fine structure is apparent and an approximate value for the coupling constant is 3 Hz. A triplet (J= 62 Hz) of quintuplets (J= 6.1 Hz) is also present at -34.4 ppm.

The ^1H NMR spectrum shows a multiplet at 3.49 ppm relative to internal TMS. This multiplet may be analyzed as a first order spectrum consisting of a quartet (J= 7 Hz) of doublets (J= 6.1 Hz) of triplets (J= 3 Hz). Another multiplet at 1.25 ppm relative to internal TMS is simply analyzed as a triplet with J= 7 Hz. No further splitting is observed.

The ^{19}F and ^1H NMR spectra are shown in Figures 3 & 4. and,although the characteristic resonances of $(CH_3)_3SiF$ were also present, they are not shown.

The mass spectrum was recorded at an ionizing voltage of 70.0 V and at an ionizing current of 50μa. A molecular ion peak of mass number 161 was visible. Other peaks corresponding to expected molecular fragments were present. Some of the major fragments are assigned as follows: $C_3H_7NSF_3^+$ (m/e 146), $C_4H_{10}NSF_2^+$ (m/e 142), $C_4H_{10}NSF^+$ (m/e 123), $C_4H_7NSF^+$ (m/e 120) $C_4H_{10}NS^+$ (m/e 104), and $CNSF^+$ (m/e 77). Since no attempt was made to remove $(CH_3)_3SiF$ or any remaining silylamine from the trifluoride, it is pointless to try and determine relative intensities.

ii.) Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto N,N diethylaminotrimethylsilane (0.72g, 4.8 mmole) in a U-tube in a manner similar to that described previously. The ^{19}F NMR spectrum showed no signals characteristic of the product $[(C_2H_5)_2N]_2SF_2$. Standing at room temperature overnight did not produce further reaction.

REACTION OF SULPHUR TETRAFLUORIDE WITH N,N DI-ISOPROPYLAMINO-TRIMETHYLSILANE

Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto N,N di-isopropylaminotrimethylsilane (0.42g, 2.4 mmole) in a U-tube in a manner similar to that described above. The sealed NMR tube was transferred to the spectrometer with the probe maintained at -68°.

The fluorine NMR spectrum of the product shows a doublet

(J= 53 Hz) at -61.9 ppm relative to internal freon 11. Additional fine structure is not apparent. Also present in the ^{19}F NMR spectrum is a triplet (J= 53 Hz) at -18.3 ppm. Although additional fine structure is not readily apparent in the triplet, one would expect triplet fine structure if the compound were $[(CH_3)_2CH]_2NSF_3$. Assuming this is indeed the compound, the coupling constant may be estimated from the linewidth at half-peak height to be 4.3 Hz (linewidth at half-peak height/3). The ^{19}F NMR spectra are shown in Figure 5.

The proton NMR spectrum shows a multiplet at 2.60 ppm relative to internal TMS. This multiplet is simply a septet with J= 7Hz. A doublet (J= 7Hz) is also present at 0.97 ppm. Expected fine stucture in the septet is not readily apparent, however this may be attributed to the extremely weak signal.

ADDITION OF WATER TO ANHYDROUS N,N DIETHYLAMINOSULPHUR TRIFLUORIDE

A sealed NMR tube containing an anhydrous sample of $(C_2H_5)_2NSF_3$ was broken open after immersion in liquid nitrogen. The tube was then capped with a rubber septum which in turn was wrapped with teflon tape. Addition of water (5.6×10^{-4}g, 0.031 mmole) with a syringe to anhydrous $(C_2H_5)_2NSF_3$ (1.0 mmole in 0.5 ml $CFCl_3$) resulted in loss of fine structure and only two broad peaks were observed in the fluorine NMR spectrum. On adding $(CH_3)_3SiN(C_2H_5)_2$ (8.4×10^{-2}g, 0.58 mmole), a well resolved spectrum reappeared, identical to the anhydrous spectrum of $(C_2H_5)_2NSF_3$. In a separate experiment it was shown that $(C_2H_5)_2NSi(CH_3)_3$ did not react with $(C_2H_5)_2NSF_3$ under the same conditions.

The anhydrous spectra of $(C_2H_5)_2NSF_3$, before and after addition of water, are shown in Figures 6 and 7 respectively and the result of adding $(C_2H_5)_2NSi(CH_3)_3$ is shown in Figure 8.

REACTION OF SULPHUR TETRAFLUORIDE WITH HEXAMETHYLDISILAZANE

Sulphur tetrafluoride (0.26g, 2.4 mmole) was condensed onto hexamethyldisilazane (0.19g, 1.2 mmole) in a U-tube in a manner similar to that described previously. Vigorous reaction occurred on warming to room temperature. Freon 11 was distilled into the attached NMR tube along with the volatile components of the reaction mixture. The ^{19}F NMR spectrum was

studied over the temperature range -70° to +70°.

At -70° the ^{19}F NMR spectrum showed two triplets at -89.2 ppm and -34.0 ppm relative to internal freon 11, each with doublet fine structure with J = 2 Hz. The spectrum was similar to that reported by Gillespie[63] for sulphur tetrafluoride and its presence was confirmed in our case by infrared and mass spectra.

The triplets retained their 2 Hz splitting up to -60° and the triplets themselves were resolved up to -30°. At -20°, only two broad peaks were observed which remained until complete collapse occurred at 0°. A single broad peak centered between the ex-triplet positions did not begin to appear until +30°. This peak then sharpened as the temperature was raised to +70°. These spectra are shown in Figures 9 - 12.

As well as the dectet characteristic of $(CH_3)_3SiF$ (+ 157.2 ppm, J =7.5 Hz) a very uncommon peak was found at ±136.5ppm. This peak is shown in Figure 13, page 45. Though the peak remained for several days, it gradually disappeared until nothing but baseline noise remained.

Temperatures studies on this peak showed nothing but a gradual sharpening as the temperature was lowered from -40° to -80°. This small change is probably indicative of a gaseous product which dissolves in solution as the temperature is lowered.

PART II

FLUOROPHOSPHORANES

PREPARATION OF PHOSPHORUS PENTAFLUORIDE

Arsenic trifluoride (4.4g, 0.033 moles) was added via a dropping funnel to phosphorus pentachloride (8g, 0.04 mole) which had been pumped on to remove traces of HCl and $POCl_3$. The reaction flask was immersed in a salt/ice water bath to reduce the volatility of arsenic trifluoride. The PF_5 which evolved was trapped in the metal vacuum system with a liquid nitrogen trap. Product purity was checked by ^{19}F NMR and found to be 98 %. The small amount of impurity was POF_3.

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH N,N DIETHYLAMINO-TRIMETHYLSILANE

Phosphorus pentafluoride (0.30g, 2.4 mmole) was condensed onto N,N diethylaminotrimethylsilane (0.31g, 2.4 mmole) in a U-tube in a manner similar to that described previously for the reactions with SF_4. The reaction mixture was left at room temperature for forty minutes and then all volatile contents were condensed into the attached NMR tube. The NMR tube was sealed and its contents checked by ^{19}F NMR.

At room temperature, the ^{19}F NMR spectrum consisted of a 1:1 doublet. On cooling the sample, the doublets gradually broadened and at -85° the spectrum consisted of a doublet of

doublets ($J_{P-F}a$ = 790 Hz and $J_{P-F}e$ = 920 Hz), each of whose components had triplet fine structure ($J_{F}a_{-F}e$ = 70 Hz).

REACTION OF PHOSPHORUS PENTAFLUORIDE WITH HEXAMETHYLDISILAZANE

Phosphorus pentafluoride (0.30g, 2.4 mmole) was condensed onto hexamethyldisilazane (0.19g, 1.2 mmole) in a manner similar to that given previously. Reaction, which occurred on warming to room temperature, was vigorous and exothermic. The ^{19}F NMR spectrum did not reveal any resonances.

Several attempts using milder conditions were tried but the results were the same. The reaction was not pursued further.

PART III

PREPARATION OF N-(DIPHENYLARSINO) SUCCINIMIDE

REACTION OF POTASSIUM METAL WITH SUCCINIMIDE

Potassium metal(1g, 10 mmole) was cut into small pieces under dry cyclohexane and added to succinimide(1.75g, 10 mmole) in 35 ml of dry tetrahydrofuran. This mixture was refluxed under a dry nitrogen atmosphere for approximately two(2) hours during which time a thick white precipitate formed.

REACTION OF POTASSIUM SUCCINIMIDE WITH DIPHENYLCHLOROARSINE

Diphenylchloroarsine(5.01g, 10 mmole) was added slowly to a stirred mixture of potassium succinimide in THF at 0° under a dry nitrogen atmosphere. A fine white precipitate formed which was identified as a chloride by the silver nitrate test. The solid was filtered off through a sintered glass tube, while a stream of dry nitrogen was passed through at all times. THF and unreacted arsine were pumped off on a vacuum line and spectrograde chloroform added. Samples of the resulting solution were checked by ^{1}H NMR spectroscopy. (Succinimide is not soluble in chloroform.)

The spectrum consisted of two singlets, one at 2.41 ppm and the other at 2.45 ppm relative to external TMS. The former singlet is assigned to the methylene protons in succinimide and the latter singlet is assigned to the methylene protons in the

succinimide grouping of N-(diphenylarsino)succinimide. The multiplets due to the phenyl groups were centered on 7.27 ppm. The singlet proton assignments were made by adding H_2O and observing the increase in the supposed succinimide peak and the concomittant decrease of the supposed product peak.

Low temperature studies showed no change in the singlet of the product other than gradual broadening due to solvent freezing.

The mass spectrum was recorded at an ionizing voltage of 80 V and at an ionizing current of 500 μa. Some of the more important peaks are assigned as follows:

m/e	% Relative Abundance	Assignment
399	10	$(M^+ + C_4H_8O)^+$
327	100	M^+
250	40	$(M^+ - C_6H_5)^+$
173	26	$(M^+ - C_{12}H_{10})^+$
229	41	$^+As(C_6H_5)_2$
98	15	$C_4H_4NO_2^+$

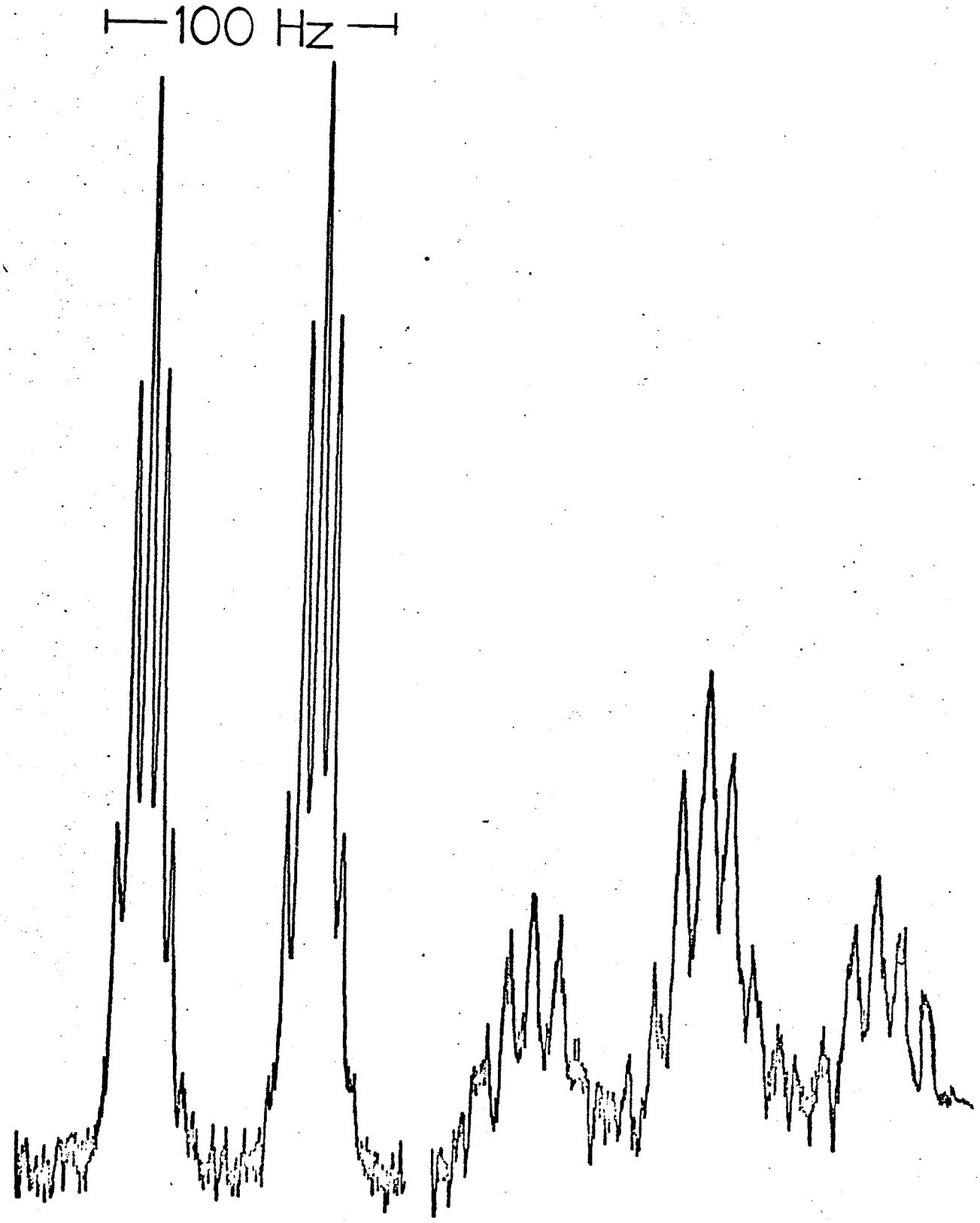


Figure 1. ^{19}F NMR Spectrum of $(CH_3)_2NSF_3$ at -68°

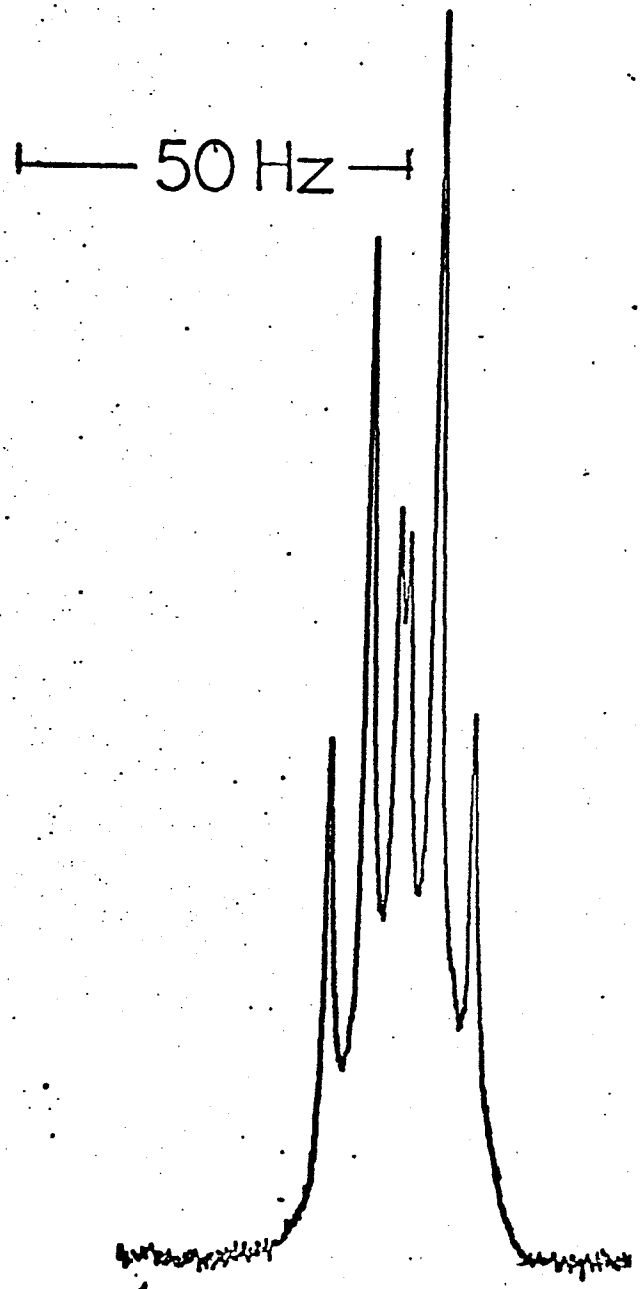


Figure 2. ^{1}H NMR Spectrum of $(CH_3)_2NSF_3$ at -68°

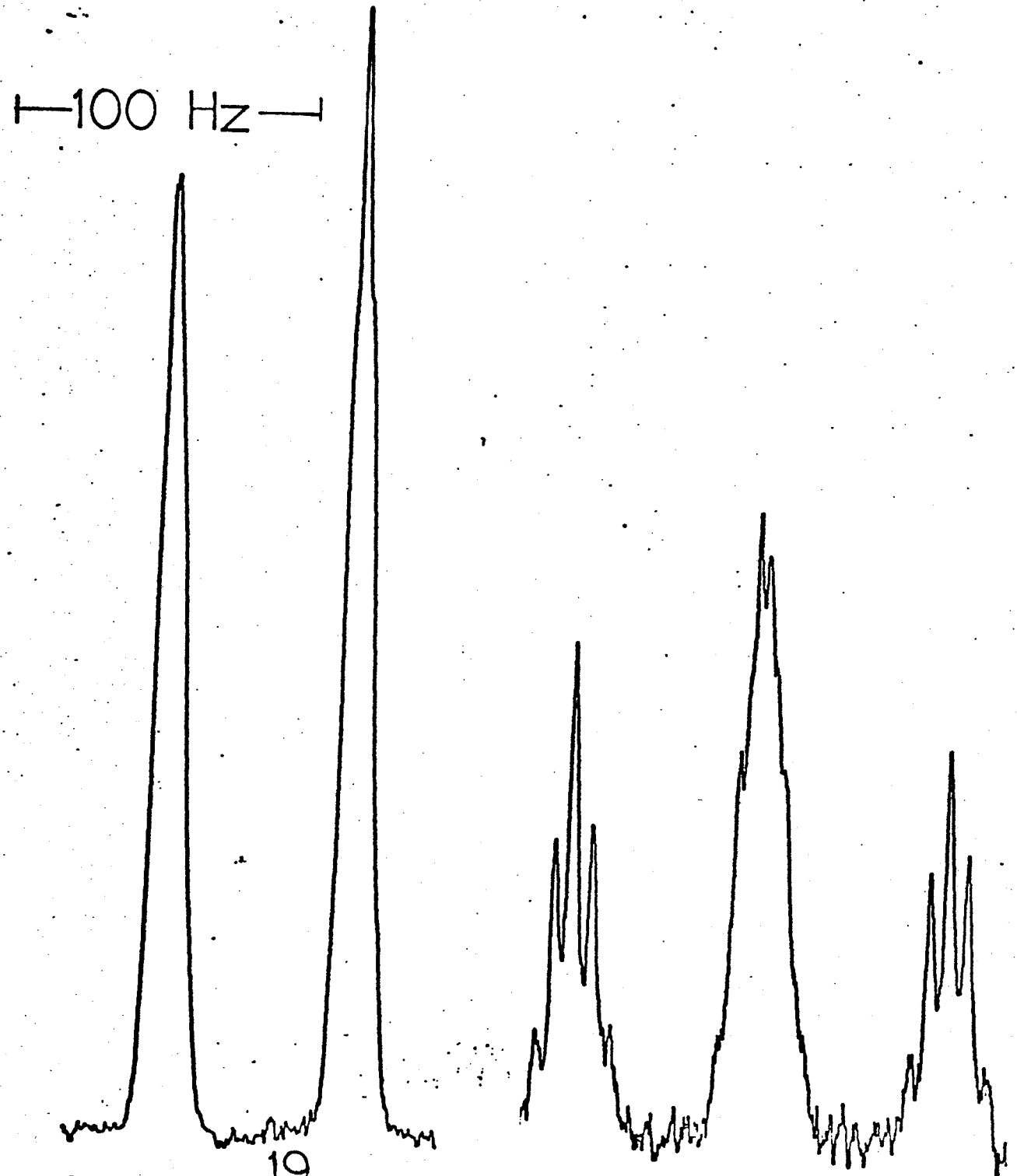


Figure 3. ^{19}F NMR Spectrum of $(CH_3CH_2)NSF_3$ at -68°

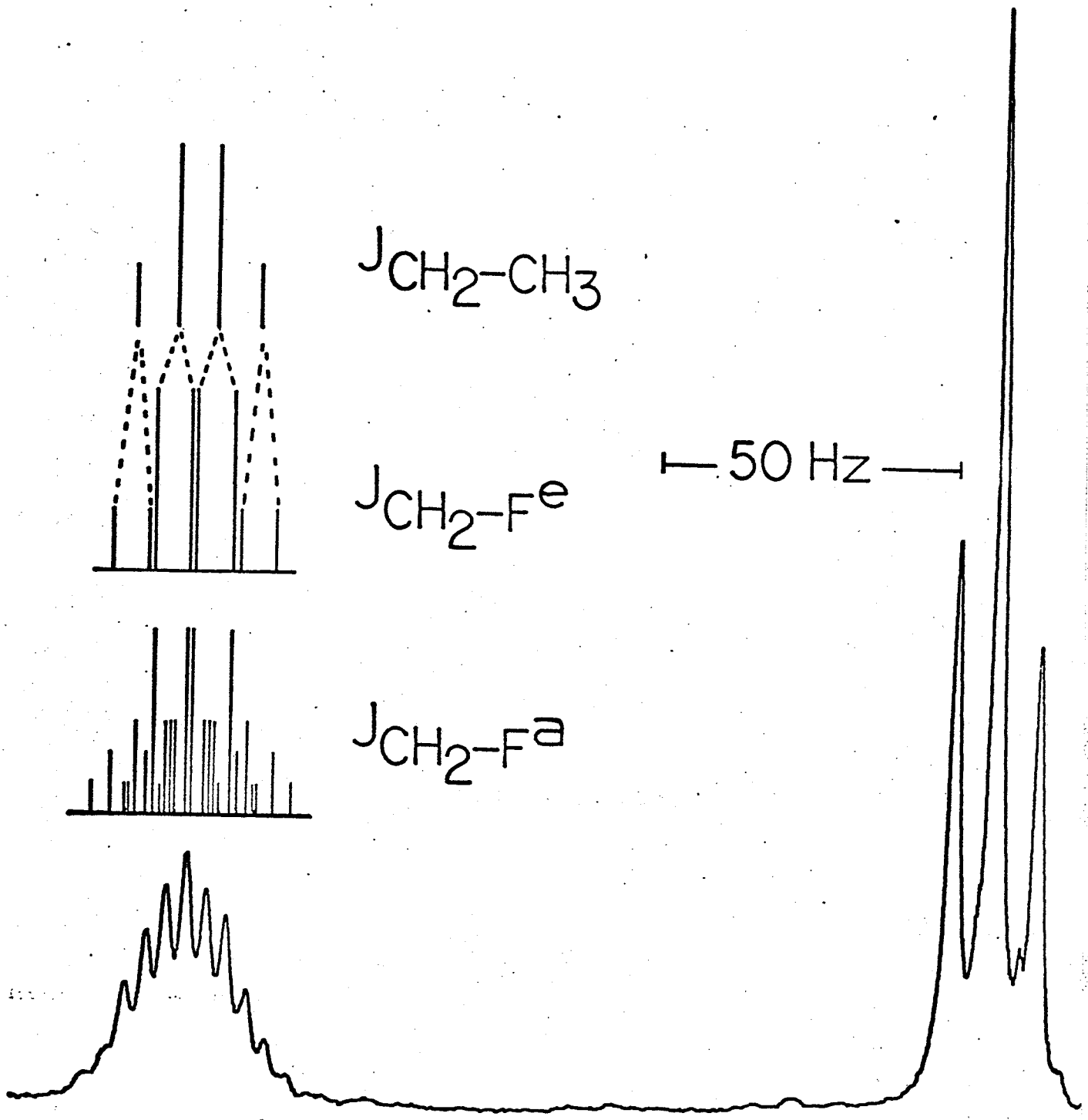


Figure 4. ^1H NMR Spectrum of $(CH_3CH_2)_2NSF_3$ at -68°

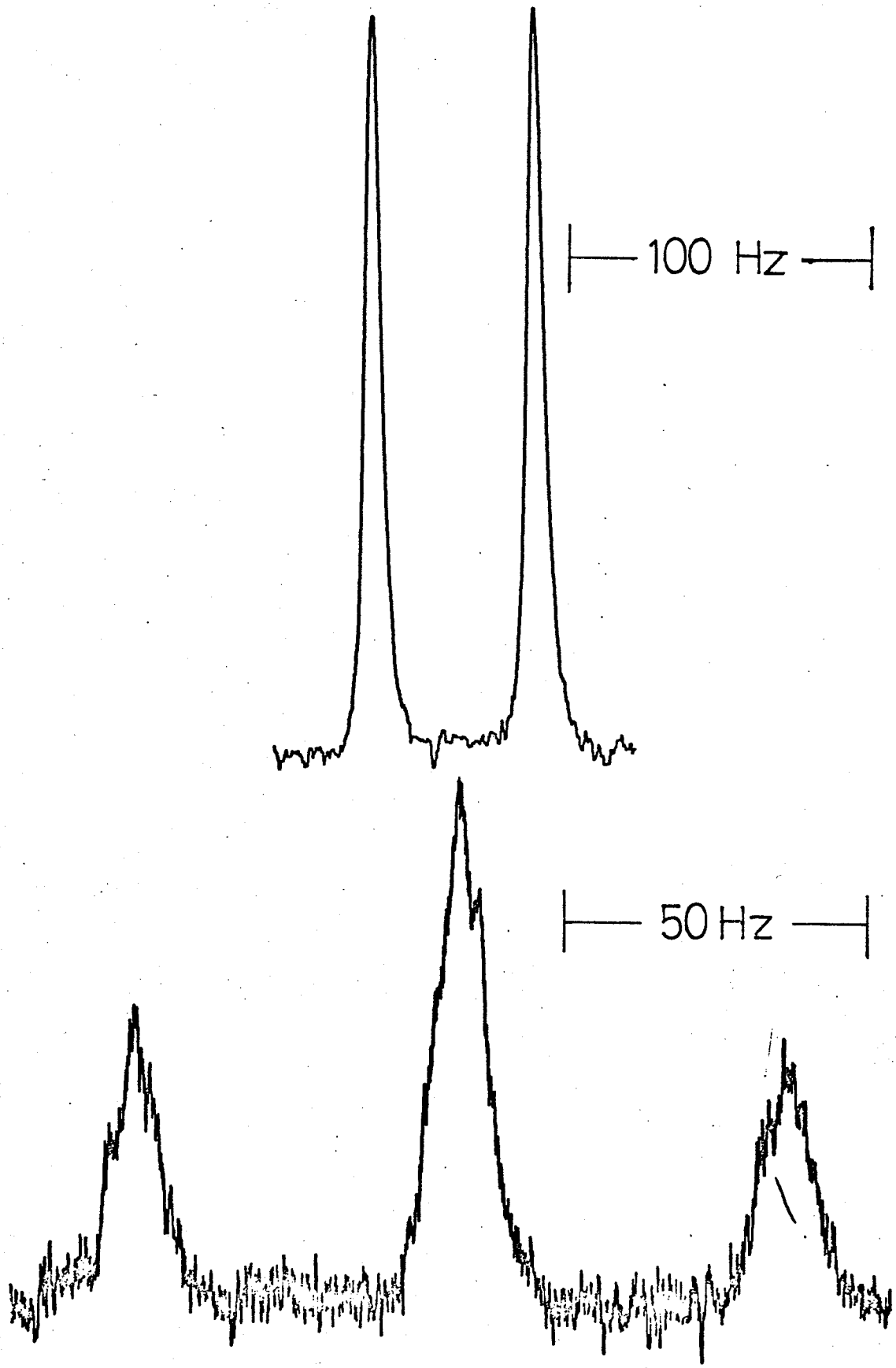


Figure 5. ^{19}F NMR Spectrum of $[(CH_3)_2CH]_2NSF_3$ at -68°

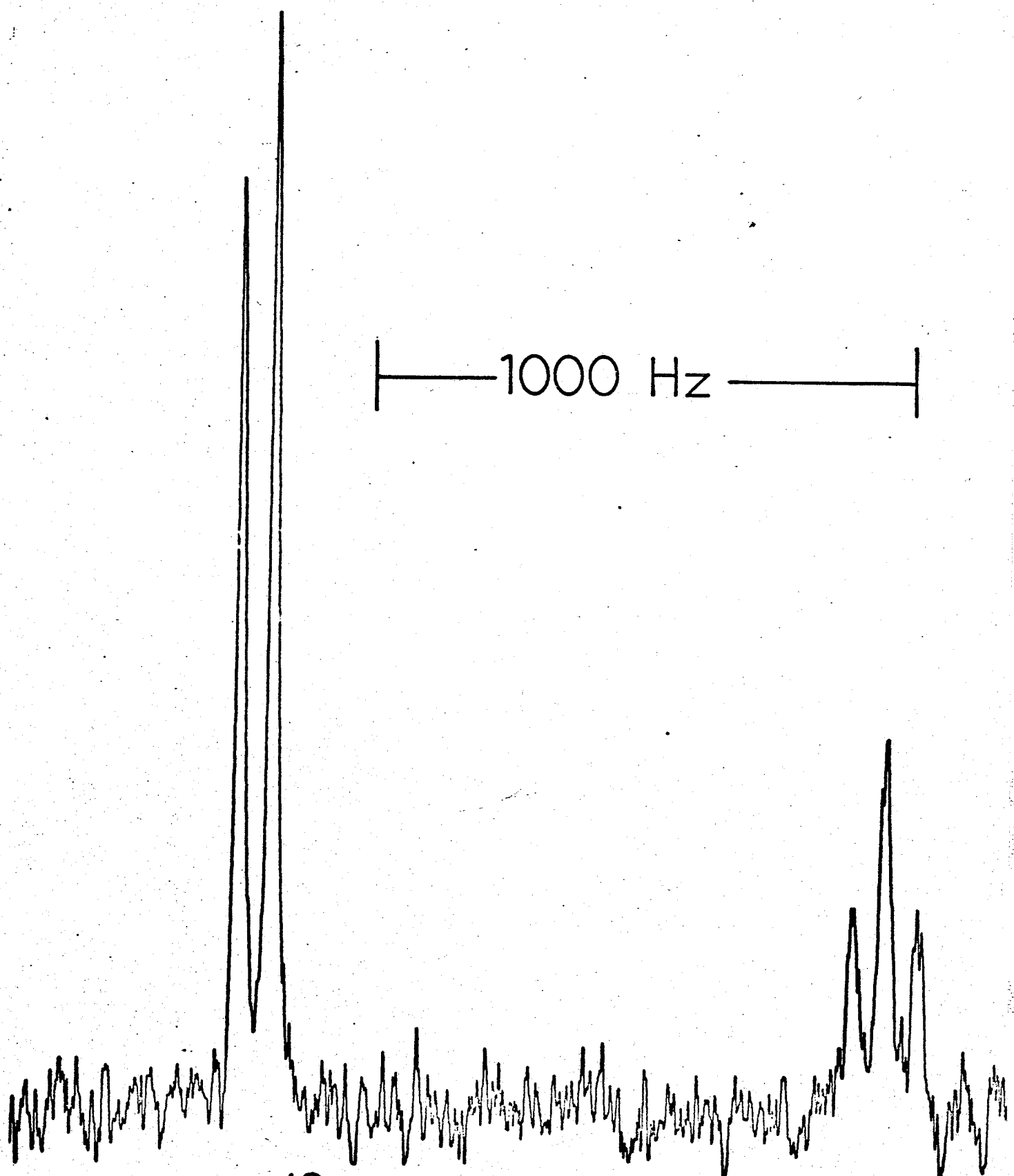


Figure 6. ^{19}F NMR Spectrum of $(C_6H_5)_2NSF_3$

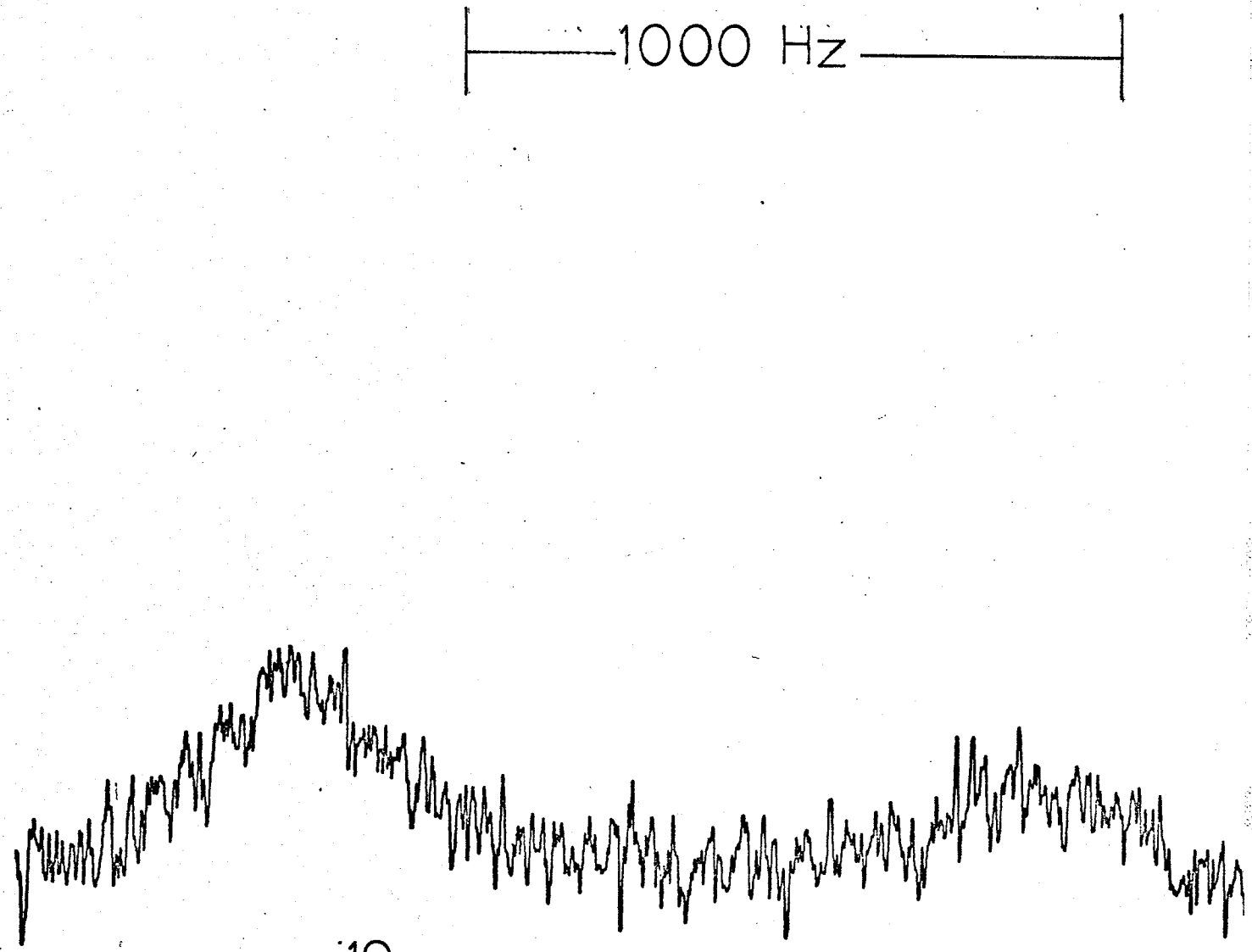


Figure 7. ^{19}F NMR Spectrum of $(C_2H_5)_2NSF_3 + H_2O$

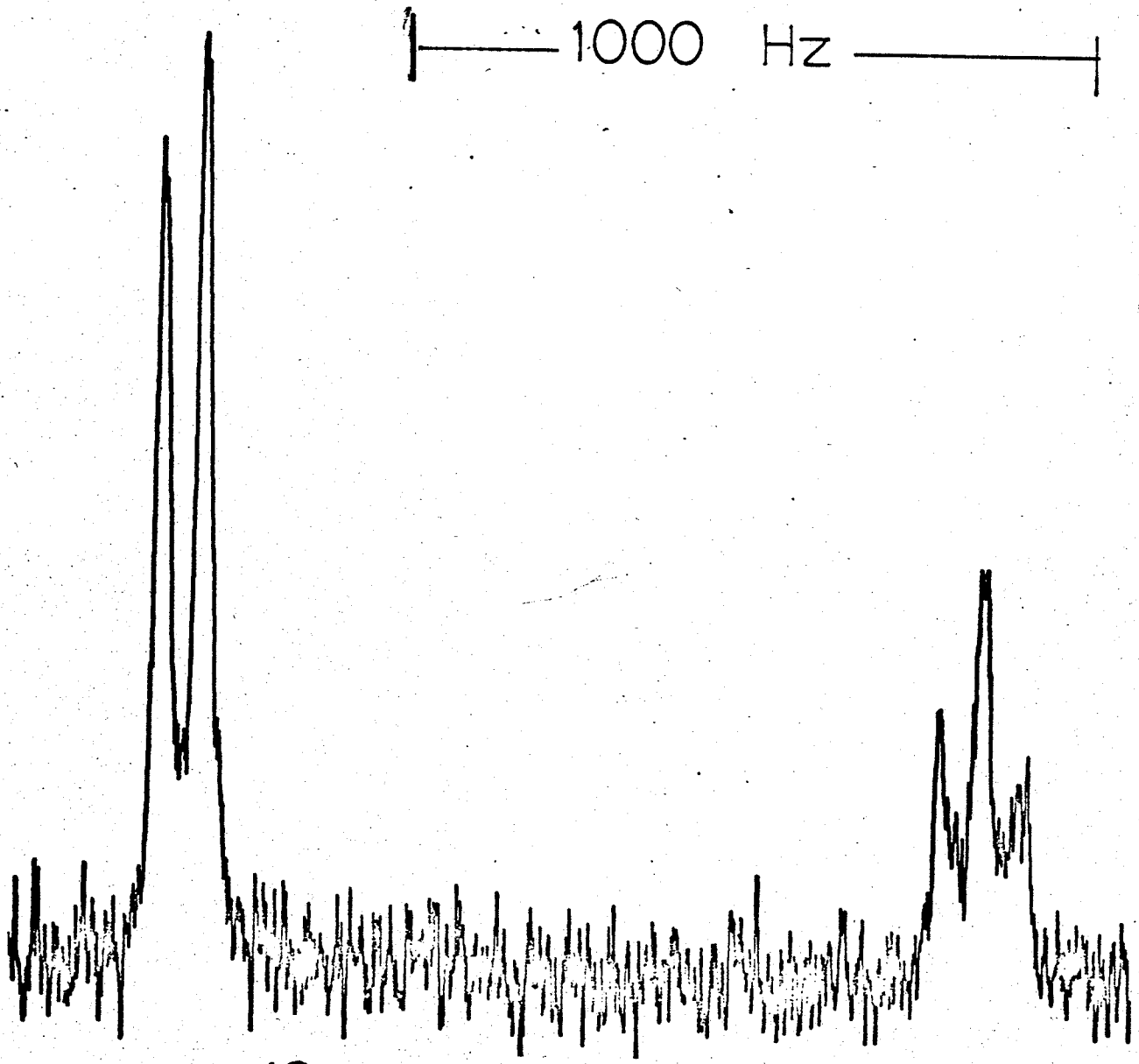


Figure 8. ^{19}F NMR Spectrum of $[(C_2H_5)_2NSF_3 + H_2O] + (CH_3)_3SiN(C_2H_5)_2$

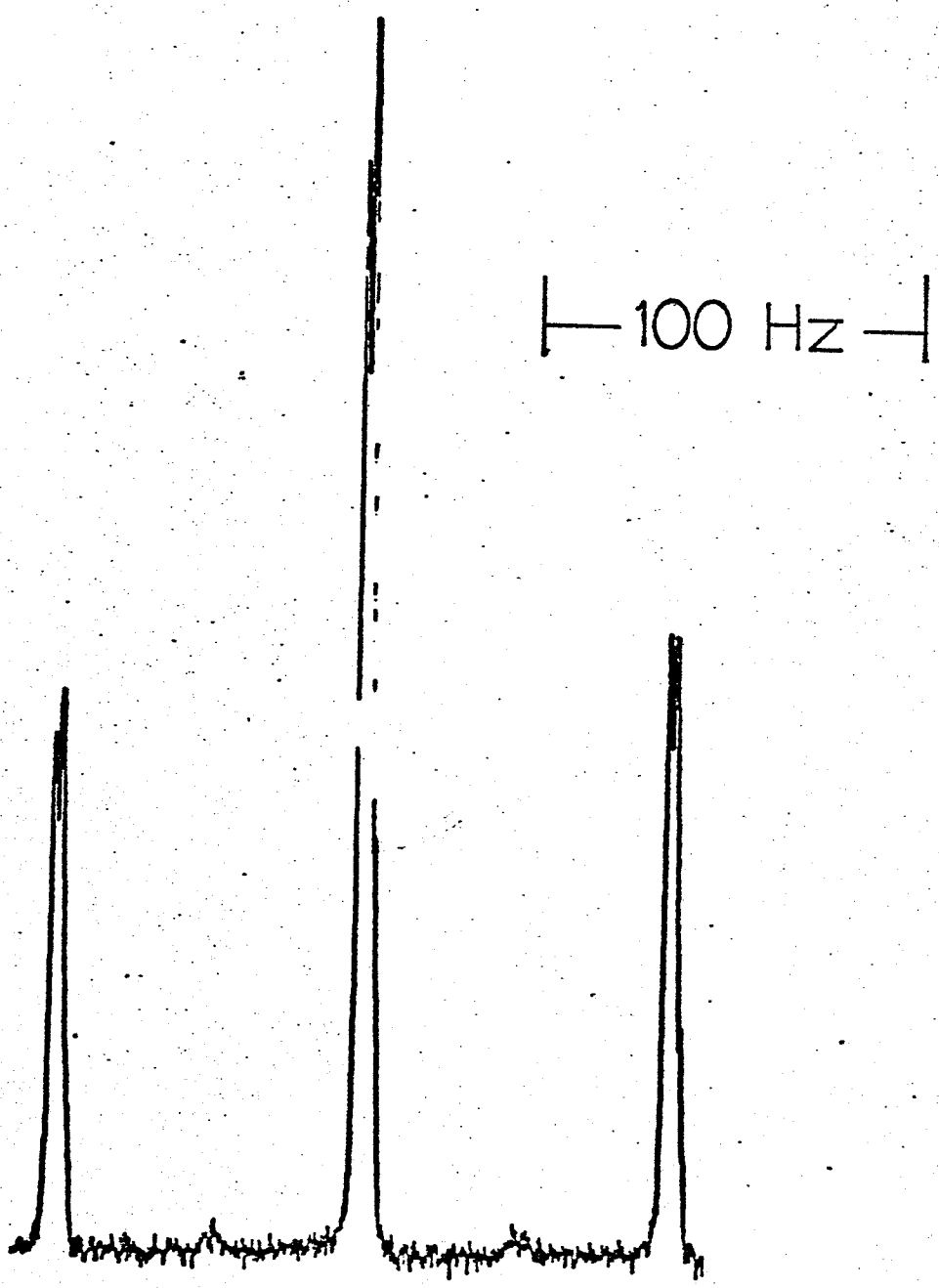


Figure 9. ^{19}F NMR Spectrum of Axial Fluorines In SF_4 at -60°

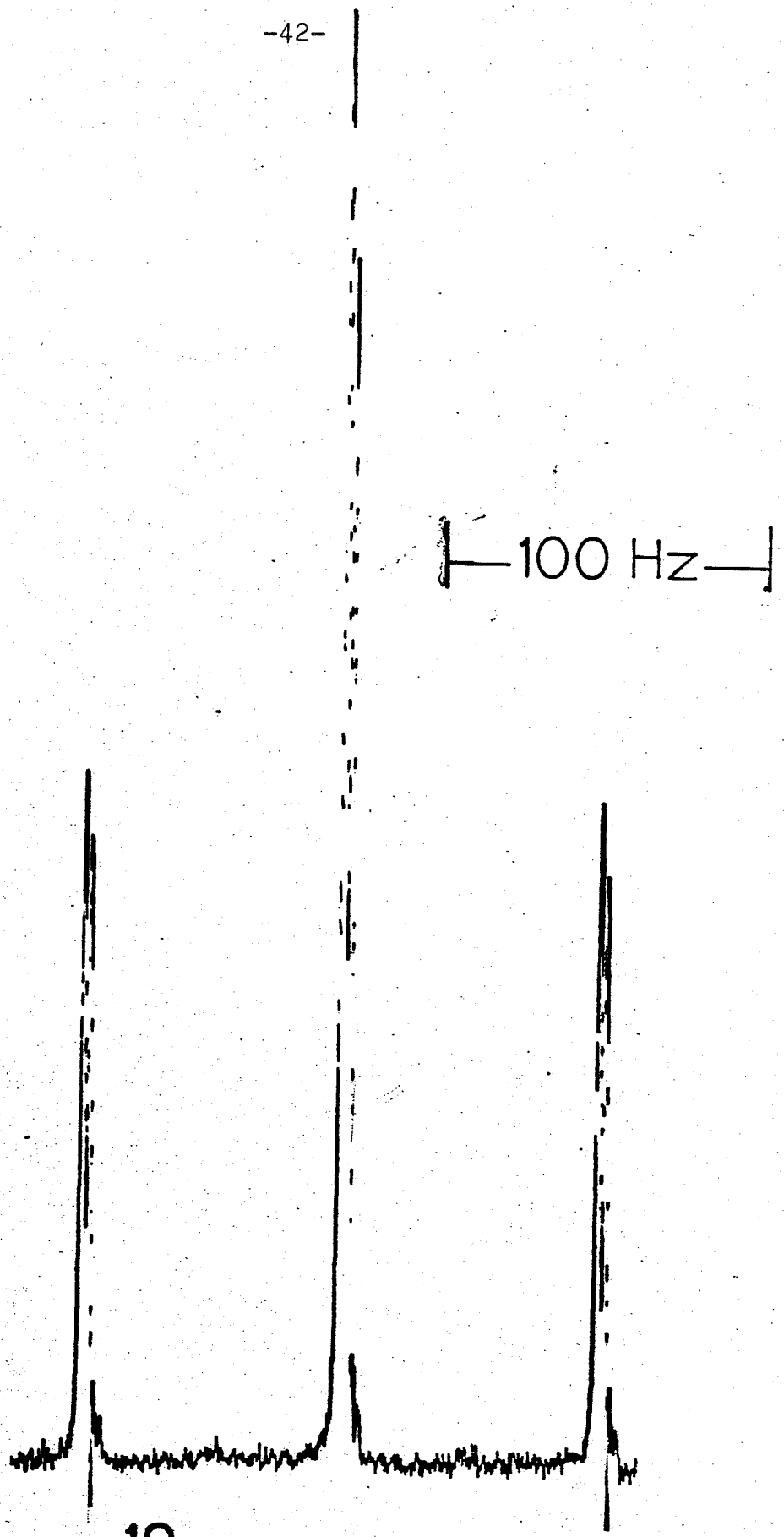


Figure 10. ^{19}F NMR Spectrum of Equatorial Fluorines in SF_4 (-60°

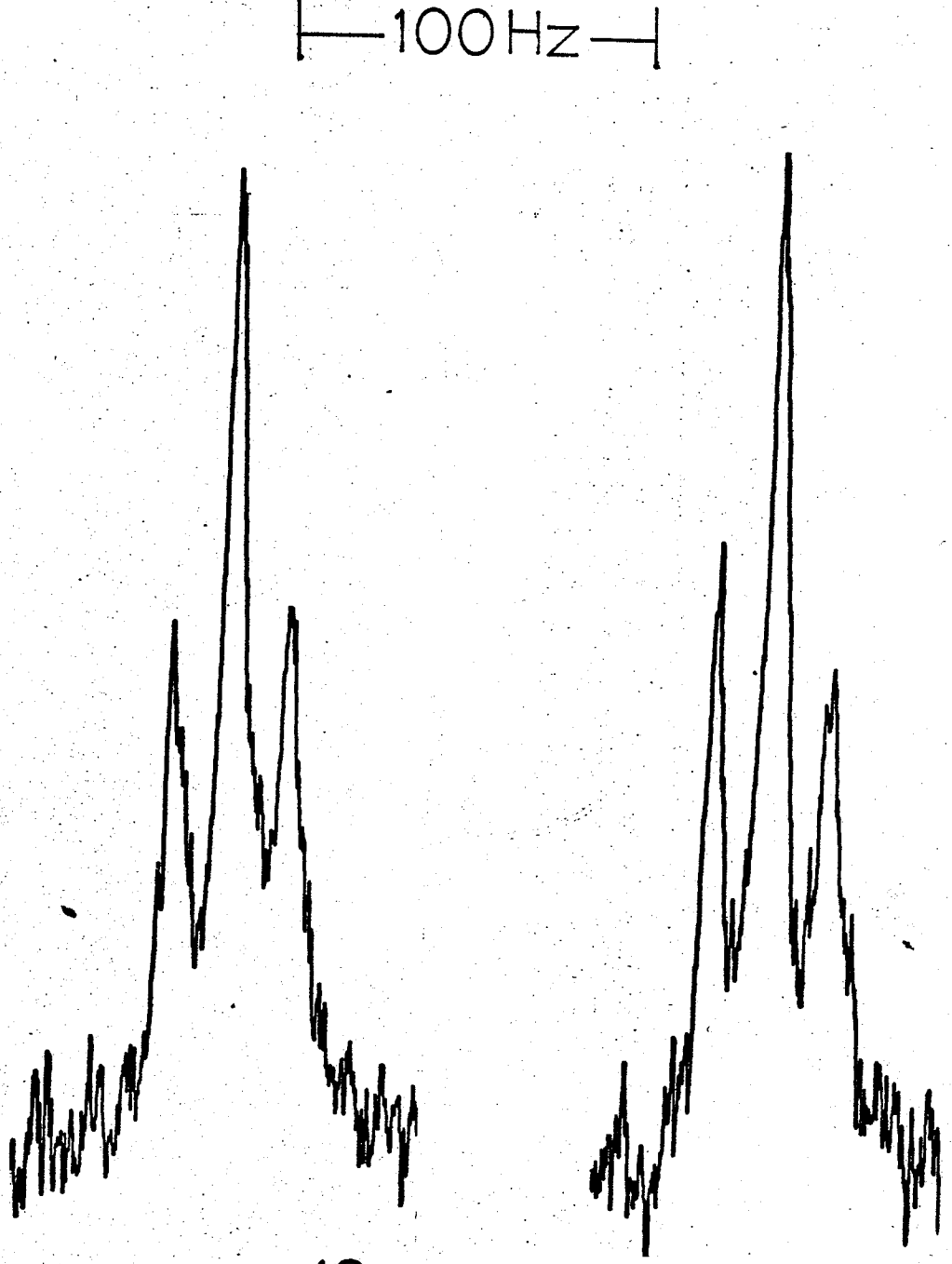


Figure 11. ^{19}F NMR Spectrum of SF_4 at -30°

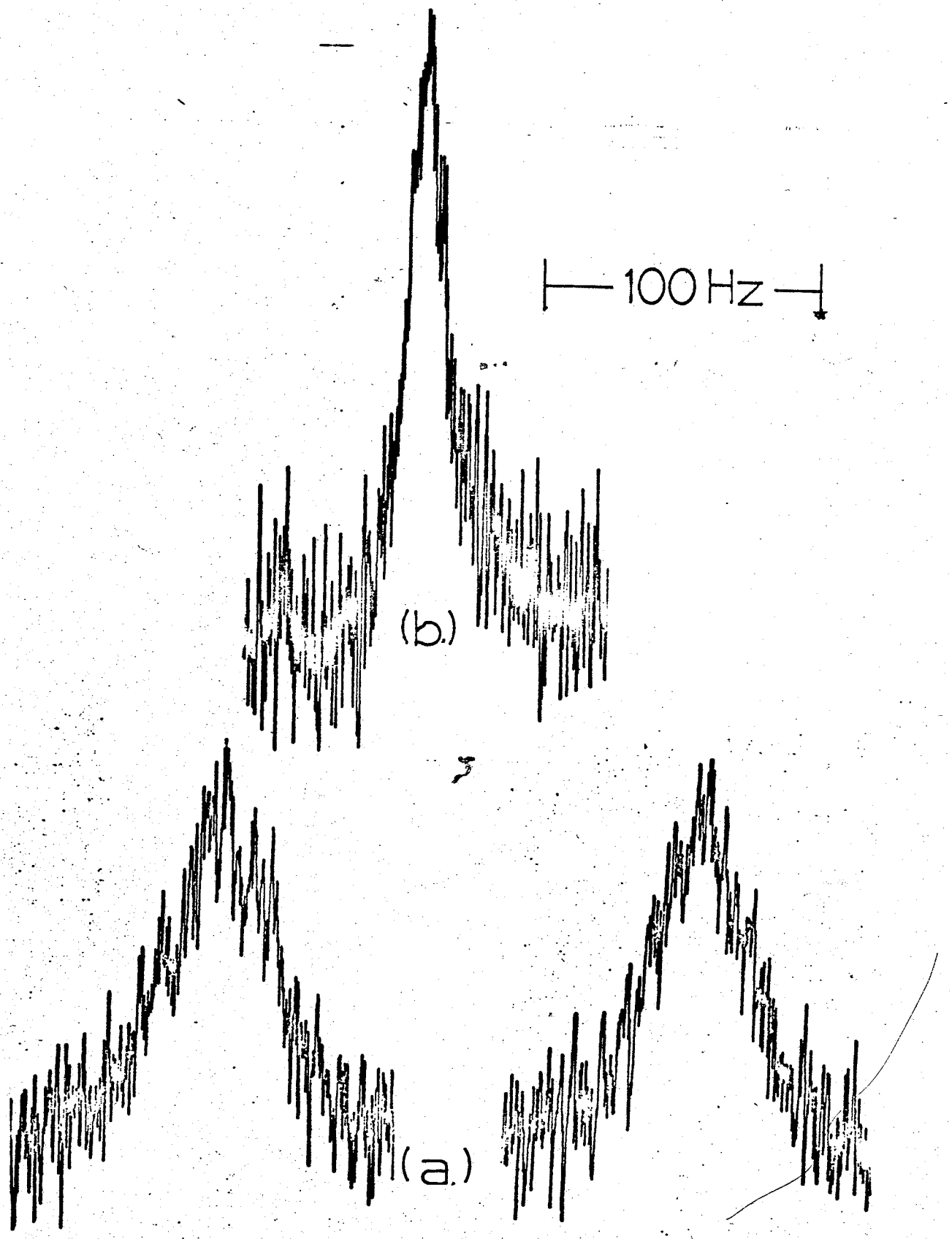


Figure 12. ^{19}F NMR Spectrum of SF_4 a.) at -10° b.) +70°

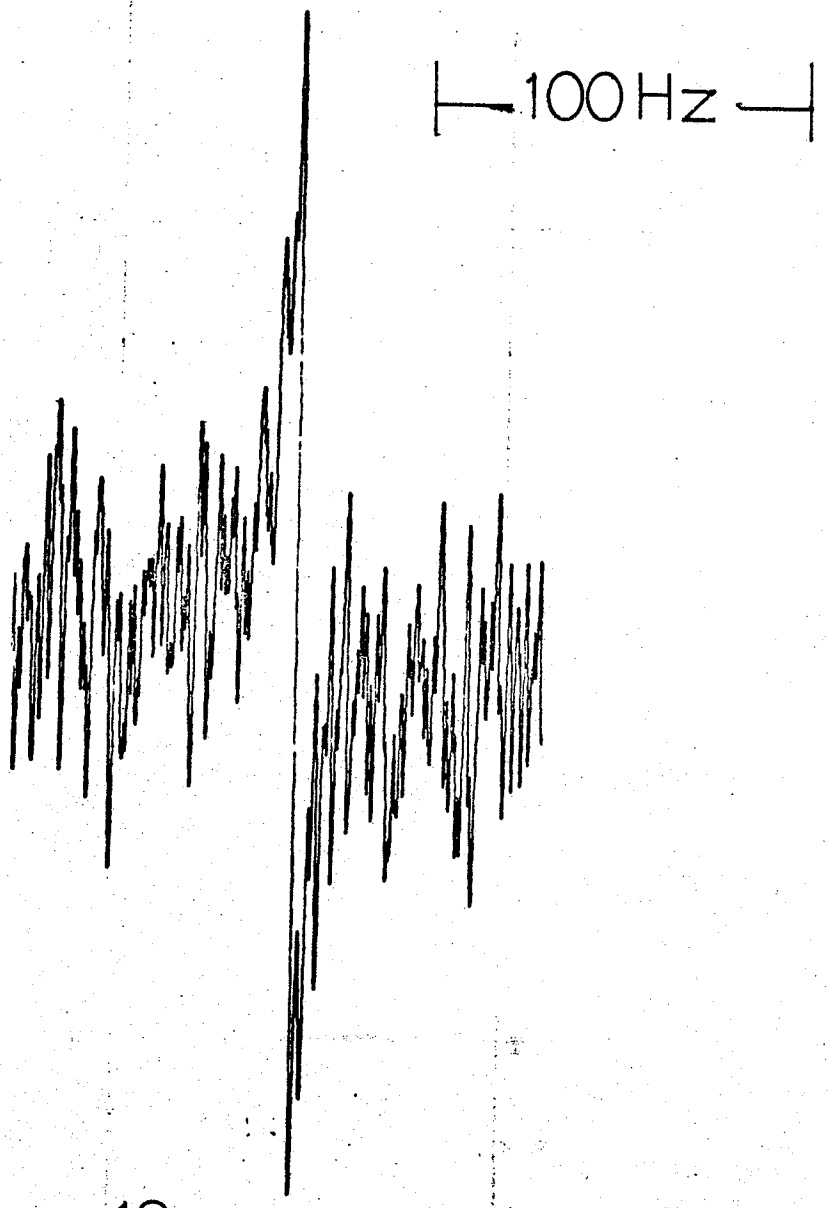


Figure 13. ^{19}F NMR Signal Characteristic of the Phenomenon of CIDNP

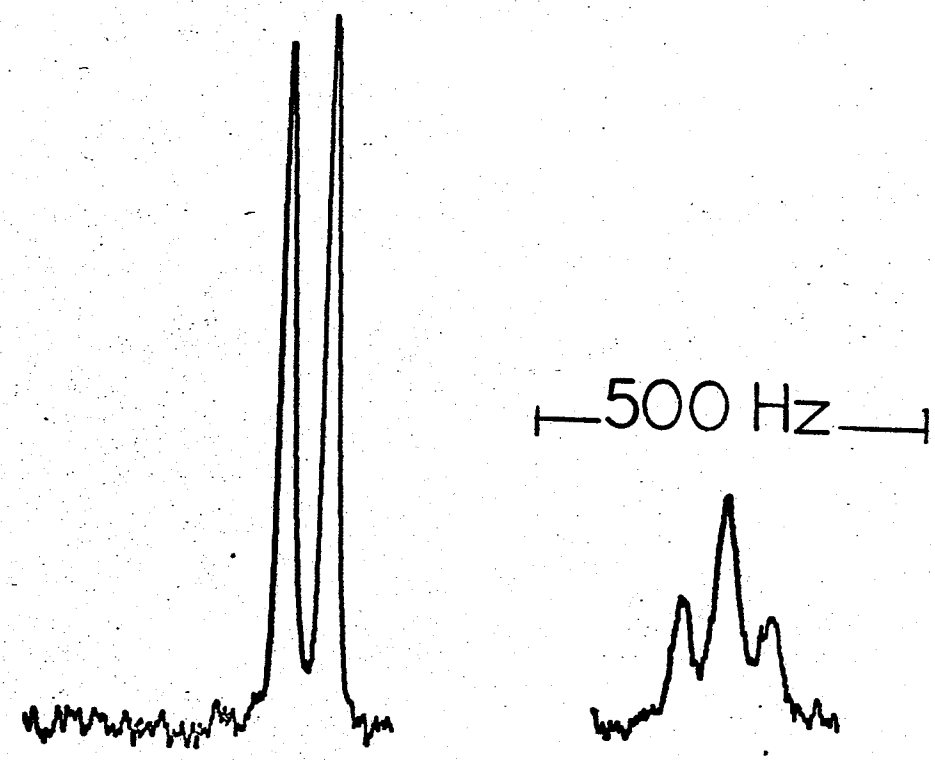
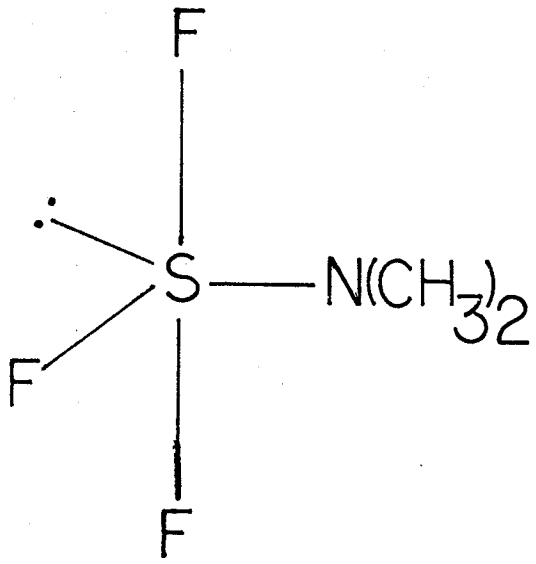


Figure 14 ^{19}F NMR Spectrum of $(C_2H_5)_2NSF_3$ at +22°



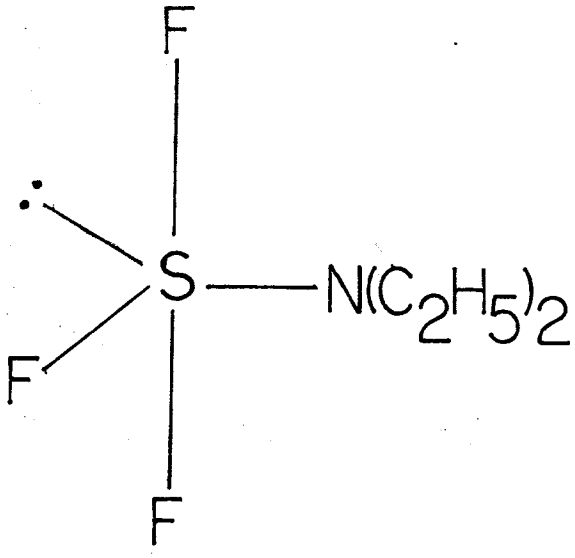


Figure 15. Proposed Structures

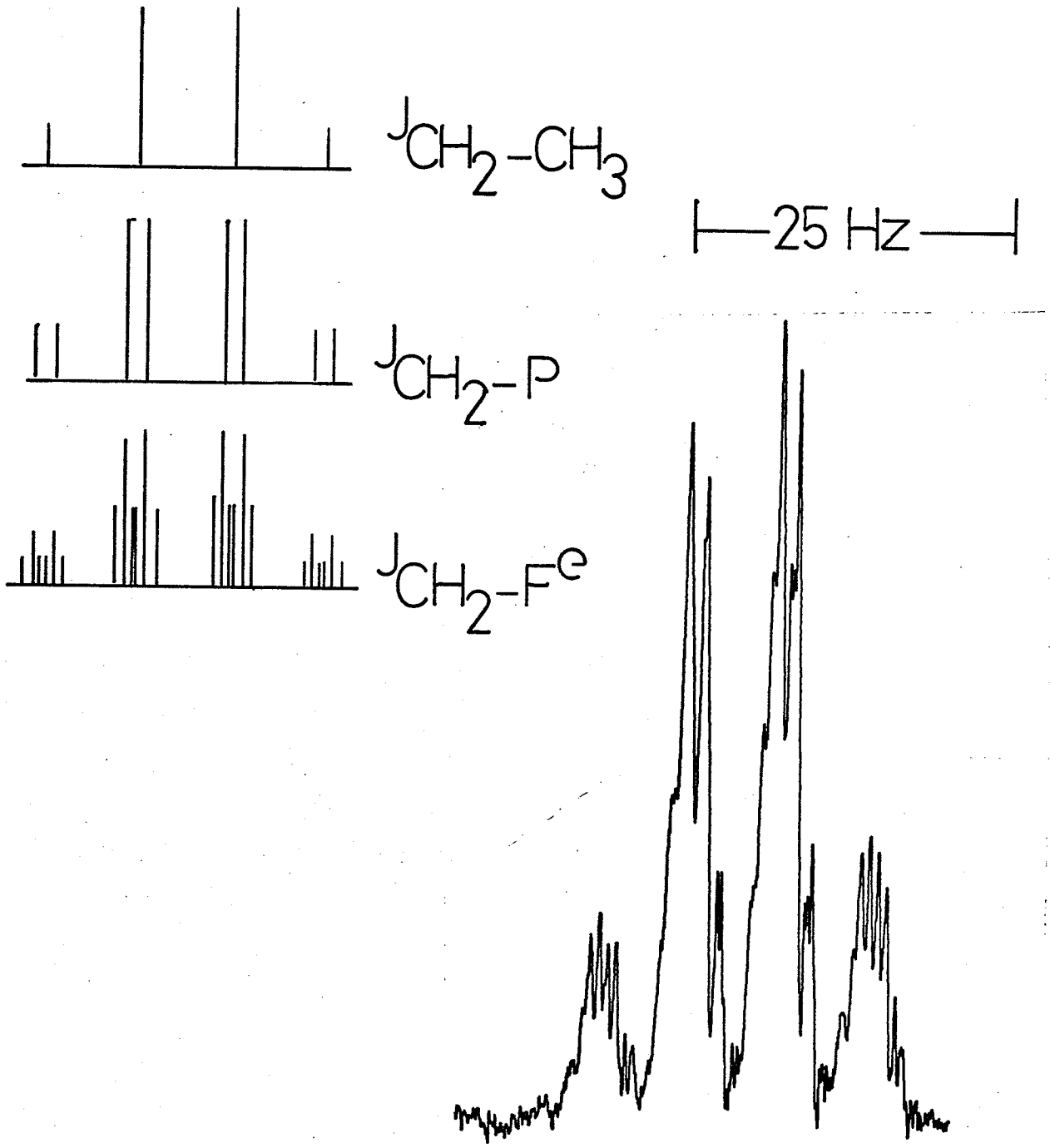


Figure 16 Portion of ^1H NMR Spectrum of $(C_2H_5)_2NPF_4$ at -40°

RESULTS AND DISCUSSION

PART I

SULPHUR FLUORIDES

Molecules with five electron pairs in their valence shell present a clear example of the success of Gillespie's electron - pair repulsion theory[37]. Axial and equatorial positions are not equivalent in the trigonal bipyramidal arrangement of five points on the surface of a sphere. For n=4, the forces acting on the equatorial positions are less than those on the axial positions and hence this is not an equilibrium arrangement. Equilibrium is reached only if the axial electron pairs are at a greater distance from the electron core than the equitorial pairs. The total interactions on the equatorial pairs are less than those on the axial pairs, thus there is more space in the equatorial positions and the lone pairs are predicted to occupy equatorial positions. The covalent radius of the central atom in the axial direction must be greater than in the equatorial direction. This has been the case for the molecules of this type which have been studied (av. r_{ax}/r_{eq}=1.1-1.2). Since the lone pairs take up more space than the bonding pairs, bond angles in AX_4E and AX_3E_2 should in general be less than the ideal values of 180 120, and 90. This has also been borne out by experiment. Gillespie also predicts that the electronegative ligand will

occupy the axial positions as stated previously in the introduction.

The geometry of tetracoordinate group VI compounds is predicted therefore to be trigonal bipyramidal with an electron pair occupying one of the equatorial sites. In the case of N,N dialkylaminosulphur trifluorides, $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$, Demitras and MacDiarmid[20] and von Halasz and Glemser [21] have postulated a trigonal bipyramidal structure in which the dialkylamino group also occupies an equatorial site.

Fluorine NMR studies of these compounds have been complicated by fluorine exchange effects and thus Demitras and MacDiarmid observed only a broad signal for $(CH_3)_2NSF_3$ at room temperature and two broad signals at -100°. Von Halasz and Glemser observed a broad signal at room temperature and two broad signals at -84° for $(C_2H_5)_2NSF_3$. Additional fluorine-fluorine or fluorine-hydrogen spin-spin splitting was apparently not observed in either case. This obviously is not the case in the studies presented in this work.

Figure 1 on page 33 shows the ^{19}F NMR spectrum of N,N dimethylaminosulphur trifluoride at -68°. The broad signals observed by Demitras and MacDiarmid are clearly identifiable as a doublet and triplet. The doublet is assigned to the axial fluorines and the triplet is assigned to the equatorial fluorines. Axial fluorines resonate at -54.2 ppm while the equatorial fluorines resonate at -20.3 ppm and the two types

of fluorine interact with a coupling constant J = 58 Hz. The axial fluorines are coupled to the methyl protons as evidenced by the septet fine structure in the doublet. The magnitude of the coupling constant is 5 Hz. The equatorial fluorines are more strongly coupled to the methyl protons with J = 8.2 Hz. In all cases above the multiplet fine structure is readily discernable and the magnitude of the coupling constants are easily obtained by direct measurement. As mentioned in the experimental section, all chemical shifts in the ^{19}F NMR spectra are relative to internal freon 11.

The ^{1}H NMR spectrum showed a multiplet centered at 3.06 ppm relative internal TMS (as explained in the experimental). This is assigned as a doublet ($J_{H-C-N-S-F^e}$ = 8.2 Hz) of triplets ($J_{H-C-N-S-F^a}$ =5.0 Hz) due to coupling of the methyl protons to the equatorial and then axial fluorines. This multiplet is shown in Figure 2 and, as in the ^{19}F NMR, the fine structure and coupling constants are readily discernable. The ^{19}F and ^{1}H NMR spectra of $(CH_3)_2NSF_3$ are thus consistent with a trigonal bipyramidal structure with the lone pair and the dialkylamino group occupying equatorial positions(Fig.1).

The fluorine NMR spectrum of $(CH_3CH_2)_2NSF_3$ at -68° is shown in Figure 3 . Two multiplets were evident; one at -54.0 ppm and the other at -34.3 ppm relative to internal freon 11. The low field multiplet was a doublet while that to higher field was a triplet. The former arises from the axial fluorines coupled to the equatorial fluorines while the latter arises

from the equatorial fluorines coupled to the axial fluorines. The magnitude of the coupling constant $J_{F^e-F^a}$ or $J_{F^a-F^e}$ is 62.0 Hz. Additional fine structure is apparent in the doublet and an approximate value for the coupling constant $J_{F^a-S-N-C-H}$ is 3 Hz. The quintuplet fine structure in the triplet is due to coupling of the equatorial fluorines to the methylene protons of the dialkylamino group. The magnitude of the coupling constant $J_{F^e-S-N-C-H}$ is 6.1 Hz.

The multiplet in the ^1H NMR spectrum (Figure 4, -68°) at 3.49 ppm relative to internal TMS is assigned to the methylene protons in the diethylamino group. These protons are coupled first to the methyl protons of the diethylamino group, then to the equatorial fluorines, and finally coupled to the axial fluorines. The multiplet may be analyzed as a first order spectrum consisting of a quartet ($J_{H-C-C-H}$ = 7 Hz) of doublets ($J_{H-C-N-S-F^e}$ = 6.1 Hz) of triplets ($J_{H-C-N-S-F^a}$ = 3 Hz). This is simplified by means of a "stick" diagram above the multiplet in Figure 4 . The other multiplet in the ^1H NMR spectrum at 1.25 ppm is analyzed as a triplet and assigned to the methyl protons of the diethylamino group. No further coupling to fluorines is apparent and this is not surprizing since it would be over five bonds. The ^{19}F and ^1H NMR spectra are thus consistent with a trigonal bipyramidal structure with the lone pair and the dialkylamino group occupying equatorial positions (Figure 5).

The fluorine NMR spectrum of $[(CH_3)_2CH]_2NSF_3$ at -68° is shown in Figure 5. Two multiplets were evident; one at -61.9 ppm and the other at -18.3 ppm relative to internal freon 11. The low field multiplet is a simple doublet (J = 53.0 Hz) assigned to the axial fluorines and no fine structure is apparent. The high field multiplet, assigned to the equatorial fluorine is a triplet (J = 53.0 Hz) with no well-defined fine structure. If the compound was indeed $[(CH_3)_2CH]_2NSF_3$, then triplet fine structure would be expected due to coupling with the hydrogen in the di-isopropylamino group. Assuming this triplet fine structure, a coupling constant of J = 4.3 Hz is estimated from the peak width at half-height.

The doublet (J = 7 Hz) at 0.97 ppm relative to internal TMS in the ^1H NMR is assigned to the methyl hydrogens which couple to the hydrogen in the di-isopropylamino group. Similarly the septet at 2.60 ppm is assigned to the hydrogen which couples to the six equivalent methyl protons.

Unfortunately better resolved spectra were not obtained for this compound. Difficulties with the metal vacuum system arose and the compound could not be resynthesized. Consequently an elemental analysis was not available and no better proof for the existence of this compound was obtained. The fluorine resonances are however in the correct radiofrequency region for fluorine bonded to sulphur. The pattern of lower coupling to axial fluorines than to equatorial fluorines is also in accord with

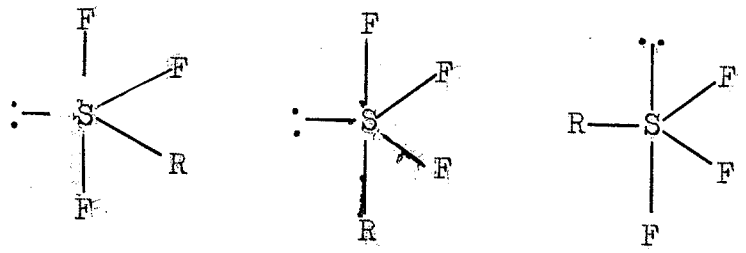
the sulphur trifluorides as will be discussed overleaf.

The chemical shifts and coupling constants of all the sulphur trifluorides in this work are summarized in Table I, page 54 .

	Fluorine					Proton		
	ppm		J Hz			ppm		J Hz
	F^a	F^e	F^a-F^e	F^a-H^1	F^e-H^1	H^1	H^2	H^1-H^2
$(CH_3^1)_2NSF_3$	-59.2	-20.3	58	5.0	8.2	3.06	---	---
$(CH_3^2CH_2^1)_2NSF_3$	-54.0	-34.3	62	2	6.1	3.49	1.25	7.0
$(CH_3^2CH^1)_2NSF_3$	-61.9	-18.3	53	0	4.3	2.60	0.97	7.0

TABLE I

The NMR spectra presented here are considered sufficient proof for the given trigonal bipyramidal structures. The presence of a doublet and a triplet can only be explained on the basis of two different fluorine environments in which one environment is doubly occupied while the other is singly occupied. Three structures consistent with this data are possible and are shown below.



Structure I is the proposed structure for the N,N dialkylaminosulphur trifluorides in this work and is based simply on an empirical rule. Work in the fluorophosphoranes has established that the NMR resonance for axial fluorines occurs at lower fields than the equatorial fluorine resonances. It was also found that the axial fluorines exhibit a much smaller phosphorus-fluorine coupling than the equatorial fluorines [65]. The extention to sulphur fluorides was made in 1964 [66]. Since in all cases reported in this work the low field resonance was a doublet, the arrangement of fluorines around sulphur must have been that shown in structure I. The coupling constants are also in accord with this structure. Analogies to the fluorophosphoranes indicate that the axial fluorines in sulphur

fluorides should couple to the protons of the dialkylamino group to a lesser extent than that of the equatorial fluorines. Reference to Table I shows that the fluorine-hydrogen coupling in the doublet was always ~4 Hz less than the coupling in the triplet, once again suggesting structure I.

These arguments, though based on empirical rules, are considered sufficient evidence for the structural assignment given. Unfortunately ^{19}F NMR analysis of these trigonal bipyramidal compounds will remain on this empirical basis since the theories of ^{19}F chemical shifts are numerous and varied and several discrepancies exist [68].

The most striking feature of the spectra of the sulphur fluorides in this work is the resolution obtained. This is in direct contrast to other workers in the field who have had problems with fluorine exchange in these compounds. In the case of $[(CF_3)_2CF]_2SF_2$ and $(CF_3)_2CFSF_3$, Rosenberg and Muetterties made structural assignments strictly on the basis of relative intensities and Gillespie's theory [15]. This was also the case for $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$ as previously mentioned.

The question of why the samples of $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$ reported here show no exchange complications immediately arose. Even at +22°, two peaks remain which can be readily identified as a doublet and a triplet as shown in Figure 14. There was no doubt as to the authenticity of the samples. The chemical shift data for $(C_2H_5)_2NSF_3$ agreed with that reported

by von Halasz and Glemser. Although the chemical shift difference for MacDiarmid's spectrum of $(CH_3)_2NSF_3$ is less than that reported here, there is no direct contradiction since it is a well known fact that the effect of exchange of nuclei is to decrease the apparent chemical shift difference between the two nuclei. The preparation of $(CH_3)_2NSF_3$ was carried out on at least four different occasions and in each case the results were those reported here. Furthermore, the same sample of sulphur tetrafluoride was used for the preparation of $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$ and the chemical shifts of the latter agree with those reported by von Halasz and Glemser. Mass spectra are consistent with the proposed compounds.

The possibility that R_2NSF_3 reacts with the NMR standards used was also checked. A solution of $(CH_3)_2NSF_3$ and $(C_2H_5)_2NSF_3$ in $CFCl_3$ and $(CH_3)_3SiF$ was allowed to stand for eight days at room temperature in sealed NMR tubes. No change occurred in the NMR signals of any reagent, thereby eliminating the possibility of reaction with NMR standards. The extra precautions to exclude moisture were concluded to be the prime reason for the excellent spectra in this work.

If hydrolysis were the mechanism of fluorine exchange, then addition of water to the previous samples should show multiplet collapse. Since this also would be observed if the only cause of the water was decomposition, it would also be necessary to remove the water and witness the resolved spectra again. The results of such a study are shown in Figures 6 - 8.

Addition of water to anhydrous $(C_2H_5)_2NSF_3$ resulted in loss of fine structure and upon adding $(CH_3)_3SiN(C_2H_5)_2$, a well resolved spectrum reappeared. In a separate experiment it was shown that $(CH_3)_3SiN(C_2H_5)_2$ did not react with $(C_2H_5)_2N$-SF_3 under the same conditions. The N,N diethylaminotrimethylsilane apparently reacted with H_2O and HF to stop hydrolysis and fluorine exchange. This facile cleavage of the Si-N bond was one of the reasons that precautions were taken to remove H_2O from the U-tube at the start of these preparations.

$$(CH_3)_3SiN(C_2H_5)_2 + H_2O \longrightarrow (CH_3)_3SiOH + \underset{H}{N}\text{-}(C_2H_5)_2$$

$$\downarrow$$

$$1/2\ (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + 1/2\ H_2O$$

$$(CH_3)_3SiN(C_2H_5)_2 + HF \longrightarrow (CH_3)_3SiF + \underset{H}{N}\text{-}(C_2H_5)_2$$

These experiments support the hypothesis that hydrolysis is the mechanism of fluorine exchange in N,N dialkylaminosulphur trifluorides.

Since hydrolysis was the apparent mechanism of fluorine exchange in the N,N dialkylaminosulphur trifluorides, it was reasoned that it might also be the fluorine exchange mechanism in sulphur tetrafluoride. As pointed out in the introduction, sulphur tetrafluoride is easily hydrolyzed with liberation of HF and, in fact, this is one of the hazards of handling the gas.

The main drying agent used previously was found to be

unsatisfactory with sulphur tetrafluoride. Hexamethyldisilazane was used in a 1/2:1 molar ratio with sulphur tetrafluoride. Though the reaction was quite vigorous, sulphur tetrafluoride was still present after reaction. A portion of the ^{19}F NMR spectrum at -70° is shown in Figure 9-10. These are the triplets (J =78 Hz) at -89.2 ppm and -34.0 ppm assigned to the axial and equatorial fluorines of sulphur tetrafluoride respectively. Other portions of the ^{19}F NMR spectrum of the reaction mixture will be discussed later.

The presence of sulphur tetrafluoride in the reaction mixture was confirmed by comparison of the infrared spectrum with that of a pure sample. In addition the mass spectrum showed M^+ = 108. The ^{19}F NMR spectral parameters of the two triplets at -70 are also in accord with the best spectra previously reported by Gillespie [63]. As reported by Gillespie, the ^{19}F NMR spectrum of sulphur tetrafluoride is an example of second order splitting for an extremely small value of $J/\Delta\sigma$ (0.026). It is observed for sulphur tetrafluoride because of the large absolute values of J and $\Delta\sigma$.

The temperature studies done in this work, however, indicate that rigorous exclusion of moisture and hydrogen fluoride has had a dramatic effect on the fluorine exchange. Gillespie's paper reports that the SF_4 spectrum is resolved into two triplets at -60° and all the peaks of both triplets were observed to split into doublets at -90° . These temperatures were the highest ever reported. The temperatures in this work are thirty

(30) degrees higher in each case. Fluorine exchange has slowed here such that the second order splitting of 2 Hz is resolved as high as -60°. The two triplets were found to remain until -30° and the two different fluorine environments were apparent as high as 0°. The spectra of SF_4 at -70°, and -30° are shown in Figure 9-12. It thus appears that hydrolysis is the mechanism of fluorine exchange in sulphur tetrafluoride.

Though some might argue that hydrolysis may not involve rapid reversible reactions as implied in an exchange reaction, this has been shown to be the case in the base-catalyzed hydrolysis of trimethylfluorosilane [62]. The authors have shown that hydrolysis and fluorine exchange involves an equilibrium system in the case of $(CH_3)_3SiF$ as shown below.

$$(CH_3)_3SiF + H_2O \underset{CH_3CN}{\overset{(C_2H_5)_2NH}{\rightleftharpoons}} (CH_3)_3SiOH + HF$$

$$\downarrow$$

$$1/2\ (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + 1/2\ H_2O$$

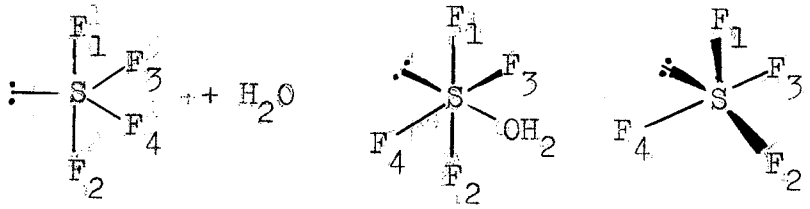
The equilibrium nature of the above hydrolysis suggests that the rate of fluorine exchange is more a function of the equilibrium constant and the absolute values of the forward and reverse rates than the amount of moisture present in solution.

Though no definite evidence for such an equilibrium was obtained for the R_2NSF_3 compounds or for SF_4, it is certainly a possibility. Two mechanisms are possible to explain the role of water in fluorine exchange. These are illustrated for SF_4 in the equations below.

1.) $$SF_4 + H_2O \underset{}{\overset{\text{slow}}{\rightleftharpoons}} SF_3OH + HF$$

$$SF_3OH \xrightarrow{-HF\,(\text{fast})} SOF_2$$

2.) $$SF_4 + H_2O \rightleftharpoons SF_4 \cdot H_2O$$



The studies reported here give no indication as to the more likely mechanism. A fundamental fact which is still not known is whether or not the sulphur-fluorine bonds are broken in the exchange process. As suggested several years ago by Redington and Berney, studies of ^{33}S-enriched sulphur tetrafluoride would provide evidence on this point. Although ^{33}S has a quadrapole moment, it also has a spin of 3/2. Thus sulphur fluorine coupling would perhaps be evident if sulphur fluorine bonds were not broken in the exchange process. Until such studies, mechanism (2) is favoured by this author since

it closely parallels the apparent mechanism for fluorine exchange in phosphorus (V) fluorides as will be discussed later. The fact that water is the cause of fluorine exchange is certainly established, especially for the N,N dialkylamino-sulphur trifluorides.

The explanation for the anhydrous conditions obtained in this work is as follows: The vapours of hexamethyldisilazane or trimethylchlorosilane hydrolyze in contact with water molecules held on the glass surface and a very firmly attached, water-repellent, methylpolysiloxane film forms on the glass [69]. Since this film can only be removed by abrasion or strong acid, it is obvious why removal of HF as well as water is important. Any HF present in the reaction mixtures would remove this film and re-expose the glass surface which is itself attacked by HF to produce H_2O and SiF_4. Any HF or H_2O produced while the SF_4 was reacting would be "mopped up" by the reactive silicon-nitrogen compound.

One point about the ^{19}F NMR spectra of the sulphur fluorides remains to be discussed and that is the uncommon peak found in the tube containing sulphur tetrafluoride and hexamethyl-disilazane. This peak, centered on +136.5 ppm relative to internal freon 11, is pictured in Figure 13, page 45. The peak shape begins as the normal absorption NMR signal but then drops rapidly at the midpoint and resembles an emission peak. This peak remained for several days during which time it gradually disappeared.

The peak is indicative of a phenomenon known as chemically induced dynamic nuclear polarization (CIDNP)[69] which has been assumed to arise from the products of radical reactions. Its presence as such a large peak is not indicative of a large yield of product from a radical reaction since signal enhancement of several orders of magnitude over expected intensities are common with this phenomenon. Indeed this explains why ESR studies were fruitless.

Although this aspect of the SF_4 and hexamethyldisilazane reaction was not pursued further, it is certainly worth a closer examination. It was noted that this peak is very close to the signal position for $(CH_3)_2SiF_2$. If dimethyldifluorosilane is the product from the radical reaction, a very powerful fluorinating radical is present.

PART II

FLUOROPHOSPHORANES

The ^{19}F NMR spectrum of phosphorus pentafluoride consists of a single fluorine resonance split into a doublet by P-F coupling despite the fact that an electron diffraction study by Bartell and Hansen [58] shows the expected non-equivalence of axial and equatorial bonds. An intramolecular exchange mechanism has been postulated by Berry to explain the NMR equivalence of fluorine atoms of PF_5 [49]. This process involves an internal motion as shown in the introduction, page 16. Since the gas phase infrared spectrum and the liquid phase Raman spectrum of PF_5 show normal spectra expected for a trigonal bipyramidal molecule [56,57], the presumed exchange process appears to take place at a rate faster than that detectable by NMR measurements but at a rate slower than that which affects line widths of vibrational bands.

As originally proposed by Muetterties and Mahler [55], accidental magnetic equivalence of fluorine environments could explain the NMR observations. This is improbable since related molecules show huge chemical shift differences for axial and equatorial fluorines. They based their conclusions on studies of CF_3PF_4 in which the apical fluorine was chemically shifted from the three equatorial fluorines by only 0,07 ppm. These spectra could not be reproduced by the same authors three years later [64].

The fluorine NMR spectra of a large number of tetrafluorophosphoranes show equivalence of fluorine atoms at room temperature [27]. In particular all monosubstituted derivatives of phosphorus pentafluoride of the type RPF_4, where R = hydrocarbon group, show positional exchange of fluorine atoms over a wide temperature range. It is particularly interesting to note that non-equivalence of fluorine atoms was not observed for RPF_4 compounds until the compounds $(CH_3)_2NPF_4$ and $(C_2H_5)_2NPF_4$ were synthesized and studied in 1964 [31]. At room temperature the ^{19}F NMR spectrum of $(CH_3)_2NPF_4$ consisted of a 1:1 doublet arising from P-F coupling. The doublet broadened on cooling and below -85 the spectrum consisted of a doublet of doublets, each of whose components had triplet fine structure. The same was observed for $(C_2H_5)_2NPF_4$ and it has been shown that the temperature dependence of this compound is not due to an associative process since coalescence temperatures are identical for pure $(C_2H_5)_2NPF_4$ and its solutions in hydrocarbons [65]. The authors who studied the NMR spectra of the R_2NPF_4 compounds prepared them by reaction of the N,N dialkylaminotrimethylsilanes with phosphorus pentafluoride.

In view of the excellent results obtained with the sulphur trifluorides in this work, it seemed highly possible that the reason R_2NPF_4 compounds were the first to show non-equivalence of fluorine atoms in the RPF_4 series was that the N,N dialkylaminotrimethylsilanes had reacted to remove traces of water and/or HF from the samples. Consequently a study was undertaken

to determine if the hydrolysis hypothesis could be extended to include the fluorophosphoranes as well as phosphorus pentafluoride itself.

The reaction of phosphorus pentafluoride with hexamethyldisilazane was very vigorous and attempts at cooling the reaction mixture were unsuccessful in slowing the reaction. These attempts to obtain anhydrous phosphorus pentafluoride were completely fruitless. The results however are not very surprizing in light of the much greater fluorinating character of phosphorus pentafluoride in comparison to sulphur tetrafluoride.

The attempts to synthesize $(C_2H_5)_2NPF_4$ by reaction of phosphorus pentafluoride with N,N diethylaminotrimethylsilane were successful. The ^{19}F NMR spectrum was compared to that reported by Muetterties et al [66] who saw two doublets (J_{P-F}^a = 793 Hz & J_{P-F}^e = 916 Hz), each component of which had triplet fine structure ($J_{F^a-F^e}$ = 70 Hz). Apparently no hydrogen-fluorine coupling was observed. The spectra reported here showed hydrogen-fluorine coupling and was most apparent in the proton spectra. The evidence of slowed fluorine exchange,however, does not become apparent until the numerous spectra taken are studied.

The preparation of $(C_2H_5)_2NPF_4$ was repeated several times. The majority of the spectra run show the correct fluorine resonances as well as a poorly resolved proton spectrum. However, one particular spectrum shows no detectable fluorine resonances but at the same time shows the best resolved proton spectrum. at -40° . The quartet portion of the proton spectrum is shown

in Figure 16 along with a "stick" diagram using assumed coupling constants of $J_{CH_2-CH_3}$ = 7.5 Hz, J_{CH_2-P} = 1.5 Hz , and $J_{CH_2-F^e}$ = 0.5 Hz.

It is entirely possible that the fluorine exchange was not stopped in the majority of the samples but in this one particular sample it was finally stopped. The fact that no fluorine resonances were observed even though coupling to the protons was resolved is not in direct conflict with no exchange. Since either axial or equatorial fluorine resonances would be split into a doublet by the ^{31}P nuclei, then into a triplet by coupling to the other fluorines, and finally split into a quintet by coupling to the methylene protons, it is possible that the signals are "hidden" in the baseline. This is admittedly scanty evidence but is certainly possible.

The experiments with the fluorophosphoranes went no further than that discussed above. Further supporting facts for the theory that water plays an important role in the fluorine exchange of phosphorus fluorides may be gained by careful perusal of the literature. The main point to remember is that any theory of fluorine exchange in PF_5 or RPF_4 compounds must not involve bond breaking since phosphorus-fluorine coupling is observed in the NMR studies.

Evidence gained by Brownstein in 1967 [45b] suggested that an intermolecular interaction served to lower the barrier to fluorine exchange by allowing weakly held, short-lived solvation complexes to be formed or, alternatively, that a specifically

orientated "collisional complex" might be formed. His studies showed that the width of the PF_5 peaks for a given temperature increased with decreasing concentration and for a given concentration the line width increased with increasing temperature. No evidence was found for line width changes due to viscosity changes or "radiofrequency saturation" effects. The author's reasoning is as follows. There can not be an appreciable rate of intermolecular exchange otherwise a single resonance line would result rather than the doublet observed. The broadening of thePF_5 signals must therefore correspond to a decrease in exchange rate of axial and equatorial fluorines on a given molecule or to an increased intermolecular exchange rate. Since it is improbable that an intermolecular exchange rate is increased by decreasing the PF_5 concentration, it must be that the linewidths are broadening due to a decrease in the rate of intramolecular axial-equatorial fluorine exchange. Although it is suggested that another molecule of PF_5 might form a short-lived intermediate, it is entirely possible that water is the briefly coordinated entity to phosphorus.

Brownstein's paper provides evidence that some species is briefly coordinated to a molecule of PF_5. Other papers in the literature have demonstrated the ability of PF_5 to form addition compounds with organic bases such as amines, ethers, nitriles, and sulphoxides. Physicochemical studies of PF_5-Lewis base systems involving ethers have been reported [66a&b].

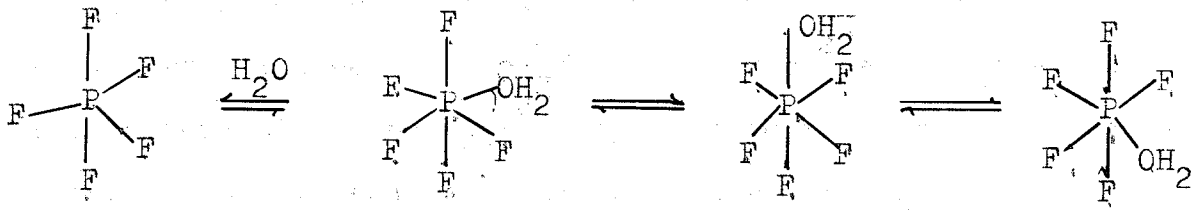
Possible support for the hypothesis of water coordination comes from a paper by Muetterties et al in which the addition compounds of phosphorus pentafluoride with organic bases were studied in view of gaining structural information[67]. Evidence for the structures was obtained from the ^{19}F magnetic resonance spectra. It is interesting to note that the spectra of the amine, sulphoxide, oxime, amide, and thioamide complexes showed two sets of a doublet and quintuplet of relative intensities four and one respectively. This is the predicted pattern for an octahedral structure with four coplanar fluorine atoms and one apical fluorine atom. The doublet-quintuplet structure was <u>not</u> observed for the spectra of PF_5 dissolved in ethers, esters, and nitriles. The loss of fine structure was attributed to a rapid equilibrium

$$PF_5 + \text{base} \rightleftharpoons PF_5 \cdot \text{base}$$

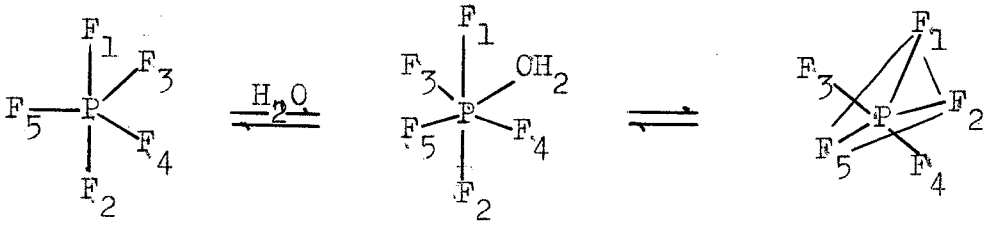
which would yield effective equivalence of fluorine atoms and yet preserve ^{19}F-^{31}P coupling. As stated by Muetterties, a rapid equilibrium such as the above is consistent with the very weak donor properties of the particular bases involved. Certainly it seems plausible that such an equilibrium could be established in the presence of water.

The coordination of water to phosphorus pentafluoride which would equilibrate the fluorines may be envisioned as that pictured overleaf.

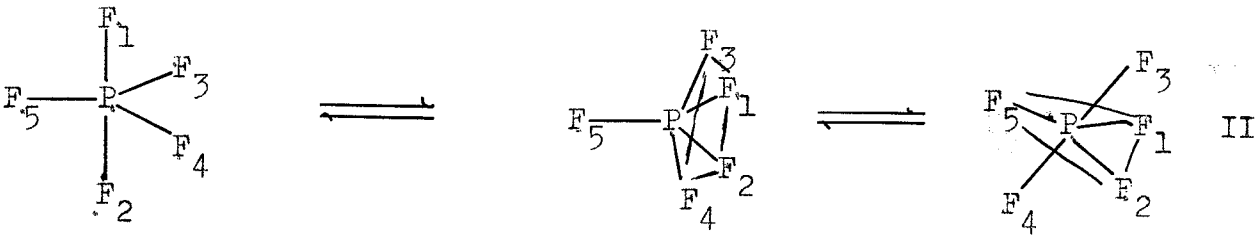
The coordination of water to PF_5 which would equilibrate the fluorines may be envisioned as below.



The symmetry of the octahedral complexes is such that water coordination at any point is equivalent. The experimental fact that simultaneous exchange of axial and equatorial fluorines takes place (proved for $(CH_3)_2NPF_4$) is easily embodied in this hypothesis. Mechanism I below is that proposed in this work while mechanism II below is the Berry pseudorotation presently accepted as the mechanism of fluorine exchange in PF_5.



I



II

In mechanism II the bending motions believed to cause the axial-equatorial fluorine exchange are shown. Similar bending motions in mechanism I are equally plausible. Water coordinates to the phosphorus atom forming the octahedral structure. Axial-equatorial fluorine exchange may take place if, instead of F_3 and F_4 bending back to their original position, F_1 and F_2 bend to become coplanar with F_5.

The bending mechanisms in mechanism one do not appear any more difficult than those proposed for Berry pseudorotation, however this is properly the job for the theoretician. Whether such an equilibrium exists is certainly unknown at this time. The data are certainly consistant with such a proposal. The fact that NMR equivalence of fluorine atoms in RPF_4 was always found until the synthesis of the dialkylamino compounds remains the most puzzling fact. The addition of the R_2N- group should make no obvious difference other than a slight increase in bulk stereochemistry.

SUMMARY AND CONCLUSIONS

This thesis presents what is considered sufficient proof of the structures of the previously synthesized N,N dimethylaminosulphur trifluoride and N,N diethylaminosulphur trifluoride. The synthesis and structure of the new compound N,N di-isopropylaminosulphur trifluoride is also described however definite proof of its existence was not obtained.

Evidence which strongly suggests that hydrolysis is the mechanism of fluorine exchange in these compounds has been obtained. If hydrolysis provides the lowest energy pathway for fluorine exchange in N,N dialkylsulphur trifluorides, then it is obvious that the absence of signifigant exchange at -68 and +22 under anhydrous conditions suggests a much higher energy barrier to fluorine exchange via alternate intra- or intermolecular mechanisms than has previously been suggested(4.5 kcal/mole for SF_4 [6]). This is an important point to note. Though alternate fluorine exchange mechanisms may be possible, they are not directly repudiated here but rather suggested to be much less plausible or facile than previously imagined.

The hypothesis that hydrolysis or at least traces of moisture are responsible for fluorine exchange in phosphorus pentafluoride and fluorophosphoranes was presented. Evidence for this extension of the hydrolysis mechanism to the phosphorus fluorides was presented however no proof was obtained. As pointed out, the fluorine equivalence may be due to formation of octa-

hedral complexes with water.

The question of the validity of other mechanisms is certainly in doubt since it has been shown that as little as 5.6×10^{-4} g of water in 0.5 ml of solution can markedly influence the NMR spectra of the sulphur fluorides. This amount of water is certainly below the detection limit and well within the realm of "anhydrous" conditions, according to the usual definition of that word.

Other workers in the field of fluorine exchange should take note of the method of rigorously excluding moisture both before and during reaction. Although the technique of reducing hydrolysis may not be widely applicable, the glass equipment should certainly be thoroughly dried and pre-silylated. Since it is well known that hydrogen fluoride reacts with glass equipment to generate water, it is important that hydrogen fluoride be removed as well.

Unless the presence of traces of water or hydrogen fluoride has been rigorously excluded, the possibility that hydrolysis provides a low energy pathway for fluorine exchange in other reactive metal fluorides must be considered.

SUGGESTIONS FOR FURTHER WORK

The work suggested here is intended to help clarify and possibly extend the hydrolysis hypothesis.

Further studies on sulphur tetrafluoride would be beneficial. A complete kinetic analysis by ^{19}F NMR should be undertaken similar to that done for $(CH_3)_3SiF$ [62]. The activation energy of 4,5 kcal/mole determined by Muetterties most probably corresponds to the hydrolysis mechanism. The temperature at which fluorine exchange commences in SF_4 could probably be raised even further than the twenty degree temperature obtained in this work since SF_4 is so easily hydrolyzed. Studies with sulphur-33 enriched SF_4 may finally solve the question of whether or not sulphur-fluorine bonds are broken in the exchange process or not.

The author is certain that the hydrolysis hypothesis will someday be extended to include the phosphorus fluorides. The further work involved with phosphorus pentafluoride would simply be a search for the ultimate drying agent. Comtinued work on the N,N dialkylaminofluorophosphoranes may be beneficial since there was some difficulty in preparing the phosphorus pentafluoride needed for their preparation. Trace amounts of AsF_3 were found in some samples.

The best place to start is probably the preparation and study of CF_3PF_4 under anhydrous conditions. As mentioned previously the ^{19}F NMR spectrum of this compound was obtained in

1960 [59]. Fluorine exchange was non-existent even at +25 however these spectra could not be reproduced three years later by the same authors [64]. This inconsistancy hints at an impurity-catalyzed fluorine exchange mechanism and it may be that the "impurity" was water.

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