

FLUOROSULFANYLIMINATION INCLUDING RELATED REACTIONS
AND STRUCTURAL PROBLEMS
AND
THIAZYL TRIFLUORIDE COMPLEXES OF THE TRANSITION METALS

by

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INTRODUCTION

During World War II, the requirement for materials with unusual properties of chemical inertness and thermal stability generated a program of research in the previously modest field of fluorine chemistry. This new research was stimulated by the discovery that certain fluorinated compounds possess physical, chemical and physiological properties which make their application highly desirable carried on in both academia and industry it has been extensive and remarkably successful. Thousands of fluorinated organic compounds have been synthesized. They represent classes of compounds of outstanding versatility that have a wide spectrum of properties and applications,¹⁻³ in such diversified fields as refrigerants, aerosol propellants, thermally stable and chemically inert polymers and elastomers (Teflon^R, Kel-F^R, and Viton A^R), lubricants, coating materials, drugs, inhalation anesthetics, and many others.⁴

Particular interest was directed to the sulfur fluorine derivatives when an efficient synthesis was developed for sulfur tetrafluoride, SF₄, a highly reactive compound which contrasted sharply with the better known, extremely inert hexafluoride, SF₆. This interest led to the synthesis of SF₆ derivatives having the sulfur atom attached to carbon, oxygen or nitrogen.

Of these newly synthesized fluorinated sulfur compounds, the chemistry of the nitrogen-sulfur-fluorine derivatives, in particular the thiazyl fluorides, has undergone especially extensive development during the past few years. These have been comprehensively reviewed by Cady,⁵ Roberts,⁶ Glemser,⁷⁻¹² Roesky,¹³ Williamson,¹⁴ and many others.¹⁵⁻²³

Sulfur is a remarkably versatile element, and may commonly be found in the di-, tetra-, and hexavalent states. With nitrogen it forms a unique bonding system, the first example known in pure inorganic chemistry, where single, double and triple bonds, as well as localized and delocalized double bonds occur. Such a system gives rise to an enormous variety of novel compounds.

The thiazyl fluorides and their derivatives present a wide spectrum of properties, from the very reactive and easily decomposed thiazyl monofluoride, $N\equiv SF$ to the relatively inert thiazyl trifluoride, $N\equiv SF_3$, and pentafluorosulfanyliminosulfur difluoride, $SF_5N=SF_2$; from the thermodynamically stable (but reactive) SF_5NF_2 to the explosive SF_5NCl_2 ; and from the simple $N\equiv SF$ to the complex $SF_5N=SF_2=NSF_5$ and cyclic $S_4N_4F_4$.

Orientation in this complexity of structures and properties can be partially achieved by classification of the various compounds with respect to the oxidation state of sulfur.

The sulfur(IV) family contains the various classes of basic structure presented in Table 1 and also some classes of fluorine-free derivatives which stem from them. It also demonstrates the versatility of the sulfur(IV)-nitrogen group in forming single and several types of multiple bonds. To a first approximation the chemical properties of these compounds resemble those of the active sulfur tetrafluoride.

Starting from either sulfur tetrafluoride, or thiazyl monofluoride, $N\equiv SF$, all the above classes may be synthesized.

For synthetic applications the most interesting class in the sulfur family is probably that of the iminosulfur difluorides, $-N=SF_2$,

TABLE 1
 TYPES OF COMPOUNDS WITH SULFUR (IV)

Sulfur Nitrogen Bond

| Single | Double | Triple |
|---|--|----------------------|
| $\diagup \text{N-SF}_3$ | $-\text{N}=\text{SF}_2$ | $\text{N}=\text{SF}$ |
| $\diagup \text{N-SF}_2-\overset{\text{I}}{\text{C}}-$ | $-\text{N}=\text{SCL}_2$ | |
| | $-\text{N}=\text{S} \begin{array}{l} \text{F} \\ \diagdown \text{N} \end{array}$ | |
| | $-\text{N}=\text{S}=\text{N}-$ | |
| $\diagup \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{SF} \end{array}$ | $-\text{N}=\text{S}=\text{O}$ | |
| $\diagup \text{N} \begin{array}{c} \text{O} \\ \parallel \\ \text{S-N} \end{array}$ | | |

TABLE 2
 TYPES OF COMPOUNDS WITH SULFUR (VI)

Sulfur Nitrogen Bond

| Single | Double | Triple |
|---|-----------------------------|----------------------|
| \diagup -N-SF ₅ | -N=SF ₄ | N≡SF ₃ |
| \diagup -N-SF ₄ -R | -N=SF ₂ =N- | N≡SF ₂ -N |
| \diagup -N-SF ₃ O | -N=S-F O F | |
| \diagup -N-S-F O | | |

although recently attention has also been focused on reactive >N-SF_3 derivatives as well.^{24,25}

The sulfur(VI) family contains the classes generally represented in Table 2, which may be considered formally as derivatives of the highly inert sulfur hexafluoride.

As with the sulfur(IV)-nitrogen family, interest in the sulfur(VI)-nitrogen family is focused on the different types of bonding: single bonds, various types of double bonds (terminal, internal and adjacent) and triple bonds.

Among these classes of sulfur(VI) derivatives, thiazyl trifluoride $\text{N}\equiv\text{SF}_3$, the iminosulfur tetrafluorides, $\text{R-N}=\text{SF}_4$, and the pentafluoro-sulfanylimino, $\text{SF}_5\text{-N}=\text{}$, derivatives are of particular synthetic importance.

The rapid expansion of knowledge in the field of nitrogen-sulfur-fluorine compounds in the last 10 years or so has been mainly within its own boundaries. With only a few exceptions, there have been no serious attempts to broaden the base of this field and to expand the accumulated achievements into other areas of synthetic chemistry.

Conspicuously lacking in this respect is a common ground with organic chemistry. The gap between the organic and inorganic chemists, resulting from the paucity of materials at the borderline between their fields, may be spanned by development of compounds capable of:

- a. incorporation of inorganic moieties into organic structures to form novel classes of organo-nonmetal compounds.
- b. utilization of inorganic sulfur fluorides as reactive agents in modifying organic functional groups.

Our project addresses itself to the problem of synthesizing novel nitrogen-sulfur-fluorine derivatives capable of linking the organic and inorganic fields. Emphasis is placed specifically on those compounds that bear the potential of serving as useful chemical agents and intermediates.

The pentafluorosulfanyl-nitrogen derivatives sought in this work would be expected not only to function as powerful pentafluorosulfanyl-elimination reagents for incorporation of the SF_5N group into a variety of structures, but also to provide valuable new insights into the remarkable properties of the perfluorosulfanylimino moiety.

Unique Properties of Pentafluorosulfanyl Group

Compounds which contain the SF_5 group tend to have chemical and thermal characteristics similar to those of SF_6 , but with the added bonus of more desirable physical properties, such as higher molecular weight, higher boiling and freezing points and greater viscosity than SF_6 has.

Furthermore, incorporation of pentafluorosulfanyl, SF_5 , groups into molecular structures often results in greater stability, inertness, and dielectric strength than does incorporation of the similar fluorocarbon groups. Successful generation of such materials would constitute a major breakthrough in efforts to develop new classes of thermally stable fluids, polymers and drugs based on "perfluorosulfur" rather than "perfluorocarbon" substituted molecular structures.

Chemically, the SF_5 group with five fluorine atoms surrounding the hexavalent sulfur is a potent electron-withdrawing group, which creates an entirely different electronic environment for functional groups.

Consequently, new compounds become available with reactions and properties quite different from those usually encountered for similar functional groups in organic chemistry.

While other electron-withdrawing groups such as F and CF_3 replace hydrogen without much distortion of the original geometry of the system, the rather bulky SF_5 group should be expected to impose significant steric effects. In systems where such effects are known to be of importance, moderation of activity, the lack of it altogether or a new mode of reaction should be anticipated.

In addition the SF_5 group is stable to chemical attack and it has not been possible to carry out reactions substituting the SF_5 fluorine atoms except under conditions resulting in complete destruction of the group.

The observation that the sulfur atom in the SF_5 group is in its highest oxidation state implies great resistance to oxidation. The high fluorine content also increases both hydrophobic and oleophobic characteristics and thus improves stability toward hydrolysis.

The SF_5 group is also well suited to serve as a useful probe because of its nuclear characteristics. The fluorine-19 nucleus possesses a spin quantum number of $1/2$ and is suitable for high resolution nuclear magnetic resonance studies. In the environment of the SF_5 group the fluorine absorption appears at low field with respect to Freon-11 and is split into an easily recognizable AB_4 pattern.

Even under intense radiation, both sulfur and fluorine atoms will produce only short-lived radioactive isotopes, F-18 with a half-life of 109 min and S-35 with a half-life of 87 days.

Development of structural materials rich in sulfur and fluorine should be quite adequate for use in a high neutron flux, such as found in nuclear reactors. The short-lived isotopes could be quantitatively monitored directly or with neutron activation analysis. Sulfur-35 can be obtained in isotopically pure form and has good characteristics for tracer studies. It has been used extensively for this purpose, especially in the agricultural and biological fields.^{26,27}

Although the physiological properties of the SF₅ derivatives have not been determined as yet, the similarities in chemical and physical properties between CF₃ and SF₅, and the increased utilization of CF₃ derivatives in useful drugs open new challenging possibilities for those SF₅ derivatives yet to be explored.

Two important classes of SF₅ compounds, SF₅-oxygen derivatives,¹⁸ and SF₅-carbon derivatives have been extensively studied^{28,29} and will not be discussed further. Our emphasis will be devoted to the study of SF₅-nitrogen compounds.

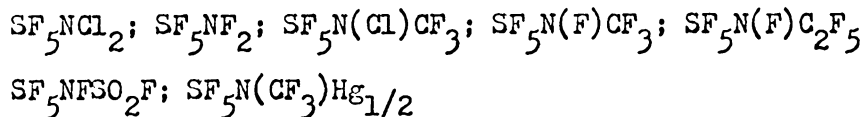
Classification of SF₅-Nitrogen Compounds

Pentafluorosulfanyl-nitrogen, SF₅-N, compounds can be generally divided into three classes:

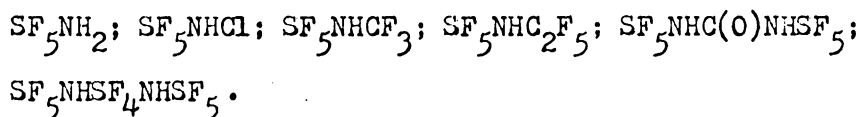
- a. Compounds of general formula SF₅NRR' (R, R' ≠ H)
- b. Compounds of general formula SF₅NHR
- c. Compounds of general formula SF₅N=X

a. SF₅NRR' compounds

This class contains such known compounds as:

b. SF₅NHR compounds

In this class of compounds the following have been synthesized:



Although the reactivity at the nitrogen has been shown to be greatly reduced it is still believed that under suitable conditions indirect substitution and cyclization reactions may be achieved.

c. SF₅N=X compounds

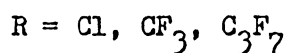
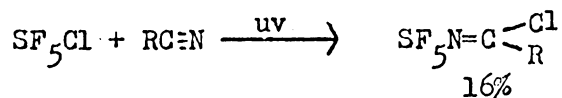
Several compounds in this class are known where X=CO, CS, CF₂, CCl₂, CClCClNSF₅, CClC₃F₇, SCl₂, and SF₂.

This class possesses a unique electronic environment due to the electron withdrawing SF₅ group, and it probably represents the most active class within the sulfur(VI) family. Since much of the synthetic work reported here is devoted to exploring useful reactions involving compounds of this class, a review of general synthetic methods developed for preparation of SF₅-N derivatives prior to the discussion of their reactions is appropriate.

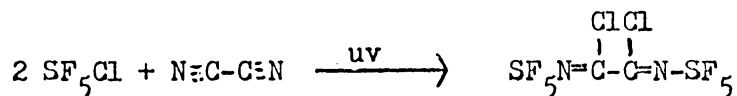
Synthesis of Pentafluorosulfanyl-Nitrogen (SF₅N=) Compounds

Two distinct methods for the preparation of pentafluorosulfanyl nitrogen, SF₅ derivatives have been developed, one based on (a) SF₅Cl,^{30,31} and the other on (b) thiazyl trifluoride, N≡SF₃.³²⁻³⁵

a. Addition of SF₅Cl to the nitrile group

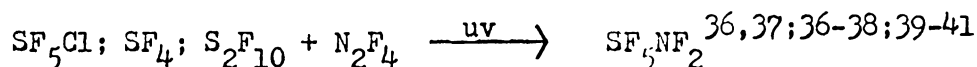


Similarly:



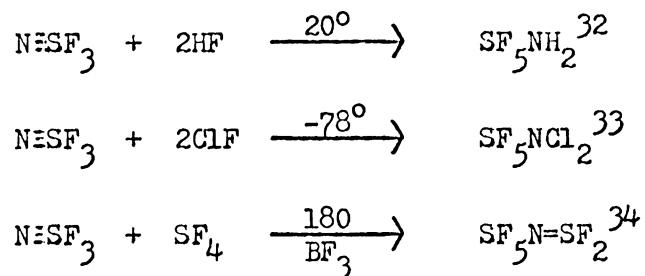
The low yield and the formation of disulfur decafluoride, SF₅-SF₅, and chlorine as byproducts suggest a free radical mechanism in which the uv radiation stimulates the generation of the SF₅ radical.

Combination of SF₅ and NF₂ radicals was also reported³⁶⁻⁴¹ in the formation of pentafluorosulfanyl difluoroamine, SF₅NF₂.



b. Polar Addition to Thiazyl Trifluoride, N≡SF₃

One of the most characteristic reactions of thiazyl trifluoride, N≡SF₃, is its addition of anhydrous hydrogen fluoride, to form pentafluorosulfanylamine, SF₅NH₂. This reaction, first reported by Clifford and Duncan³² has been an important step in the synthesis of SF₅N-containing derivatives, and has been extended to other polar additions including ClF and SF₄.



No monoaddition products were isolated at the first two reactions, although there was infrared evidence for the formation of $\text{SF}_4=\text{NCl}$ in the second. The yields were generally high and product formation was sensitive to reaction conditions.

Once the SF_5 moiety has been introduced it can be used further for the preparation of a wide range of pentafluorosulfanyl-nitrogen derivatives.

Figure 1 shows such transformations derived from pentafluoro-sulfanyliminocarbon dichloride (also referred to as pentafluorosulfanyl-ozomethine), and Figure 2 shows similar transformations derived from thiazyl trifluoride.

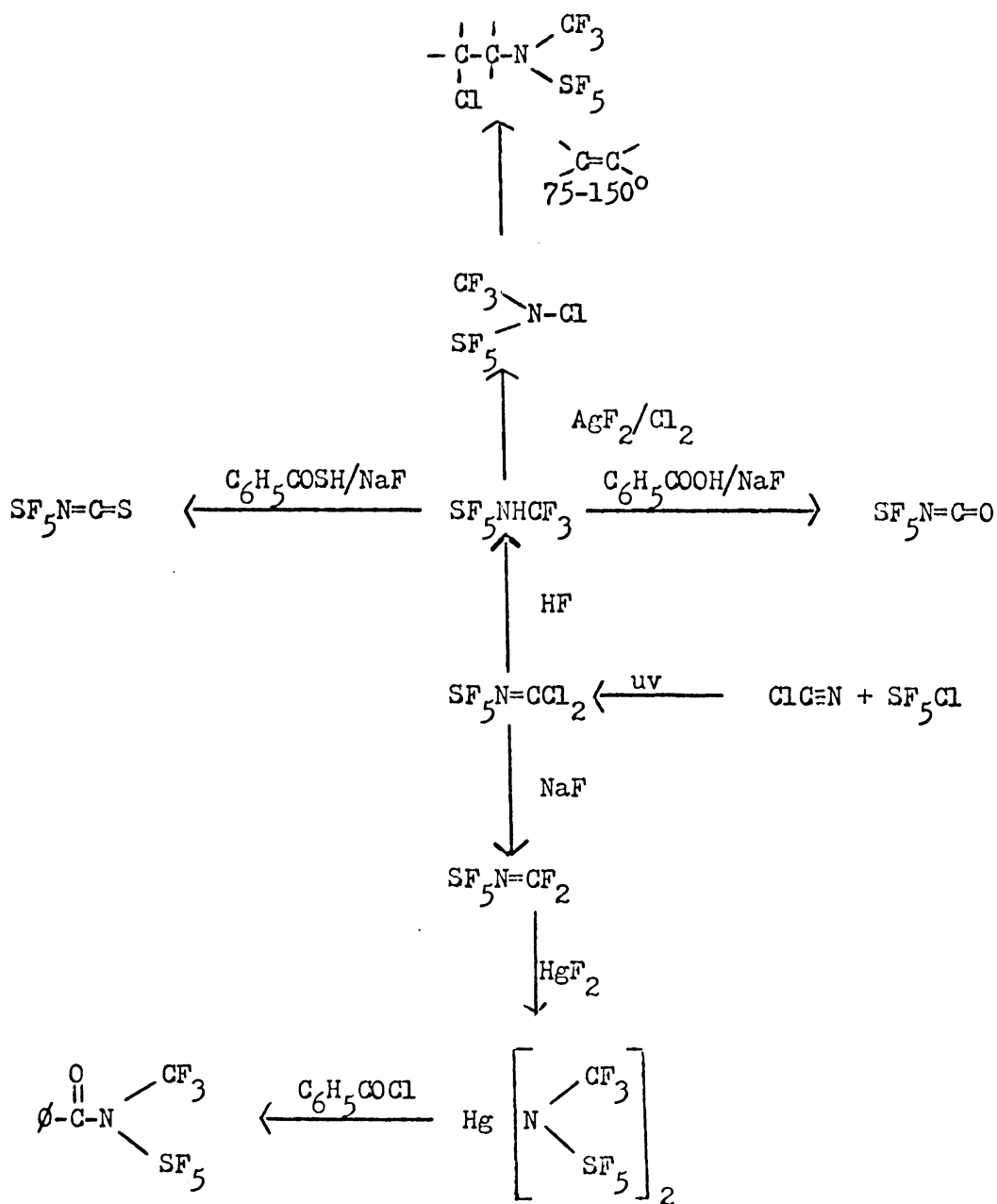


Figure 1. Pentafluorosulfanyl-nitrogen, $\text{SF}_5\text{-N}$, compounds derived from pentafluorosulfanylazomethine.

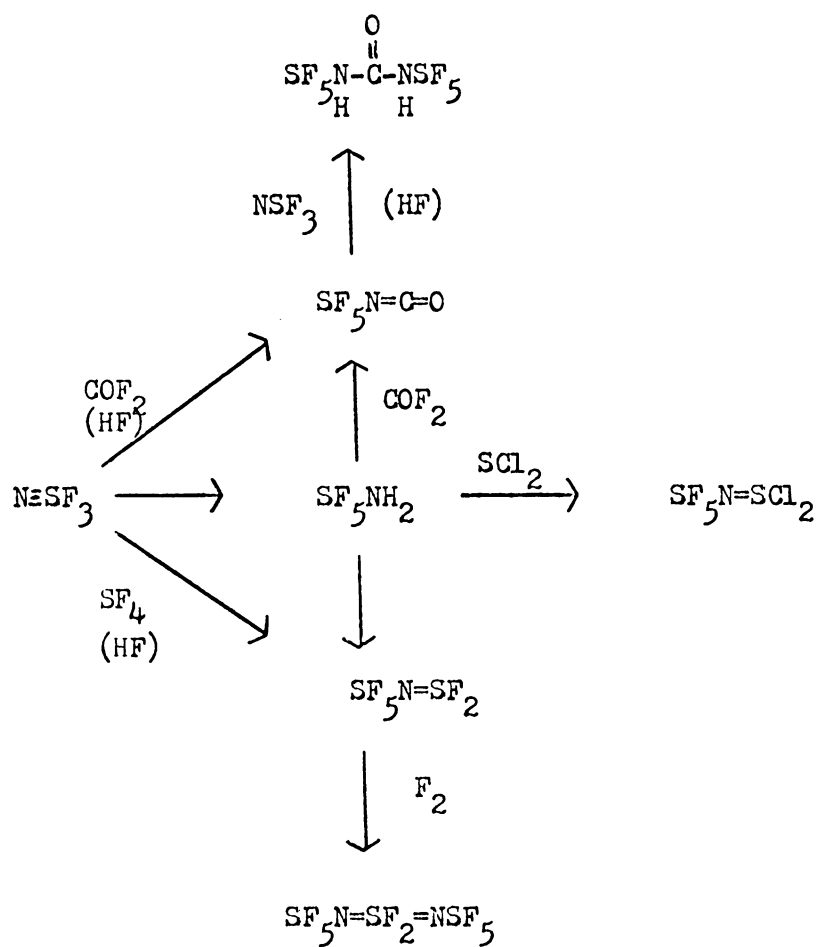


Figure 2. Pentafluorosulfanyl-nitrogen, $\text{SF}_5\text{-N}$, compounds derived from thiazyl trifluoride.

PART I. FLUOROSULFANYLIMINATION INCLUDING RELATED
REACTIONS AND STRUCTURAL PROBLEMS

Basic Principles and Selection of Systems

The pentafluorosulfanyl group has been shown to have a strong inductive effect. The effect of such groups on the nature of organic compounds is therefore of considerable interest. Since the SF_5 group in particular, is very bulky, it might be expected that, in addition to the strong inductive effect steric factors would have great influence on the reactions of compounds containing it. It has indeed been found, for example, that in the case of the di-substituted urea $(\text{SF}_5\text{NH})_2\text{CO}$ the attempted cyclization reactions with $\text{CH}_2(\text{COC}_2\text{H}_5)_2$, $\text{CH}_2(\text{COCl})_2$ and even C_3O_2 have failed to give the expected barbiturates.⁴²

However, if the distance between the SF_5 group and the site of reactivity could be increased while maintaining an unsaturated system linking them, the inductive effect of the SF_5 group could be felt with less complication from the steric effect. The $\text{SF}_5\text{N}=\text{C}$ group should be capable of performing this function, thus providing new synthetic routes for the preparation of SF_5 -nitrogen derivatives.

This generalized approach is the heart of the synthetic work and may be further clarified by a specific example. Pentafluorosulfanyl isocyanate, $\text{SF}_5\text{N}=\text{C}=\text{O}$, will be used for this purpose with the understanding that other $\text{SF}_5\text{N}=\text{C}$ compounds represent systems of similar properties.

Organic isocyanates have been extensively studied; the reactivity of the functional group depends strongly on the nature of the organic

moiety. The stronger its electron-withdrawing character the greater the reactivity of the isocyanate group. The potent electron withdrawing SF_5 group transfers its inductive effect to the carbon atom via the multiple bonded nitrogen. This transfer imparts a charge to the carbon atom and creates a new active site removed from the SF_5 group and the sterically hindered environment it generates.

From the previously reported compounds containing the SF_5 group (see p. 10), two complementary systems, SF_5NCO , and $\text{SF}_5\text{N}=\text{SF}_2$, have been selected as starting materials for the introduction of SF_5 -nitrogen into a variety of structures. In addition, the pentafluorosulfanyl isocyanate system is suitable for determining the extent to which the SF_5 group alters the functional group's susceptibility to some basic type reactions.

The reactions to be studied were selected from those capable of retaining the $\text{SF}_5\text{N}=\text{}$ group in the product, thus forming new substrates suitable for further synthetic utilization as starting materials.

Research Outline

To accomplish these objectives two pentafluorosulfanylimino derivatives, SF_5NCO and $\text{SF}_5\text{N}=\text{SF}_2$ have been systematically studied. These studies include development of new and improved methods for their preparation, and participation in basic reactions of several types such as:

- A. addition
- B. nucleophilic displacement
- C. exchange
- D. coupling

Once new pentafluorosulfanylimino derivatives were synthesized, cross interactions were examined for the preparation of bis-(pentafluoro-sulfanyl)carbodiimide, $\text{SF}_5\text{N}=\text{C}=\text{NSF}_5$, as the first step in a synthesis aimed at preparing novel pyrimidines and assessing their utility as useful drugs.

The anomalous behavior of the iminosulfur difluoride functional group with respect to addition reactions prompted structural investigations supported by molecular orbital calculations and low temperature F-19 nmr studies leading to some exciting insights into the nature of the sulfur(IV) nitrogen multiple bond system.

CHAPTER 1. PREPARATION OF AND REACTIONS WITH PENTAFLUORO-
SULFANYL ISOCYANATE SF_5NCO .

A New Method for the Preparation of Pentafluorosulfanyl
Isocyanate, SF_5NCO .

Pentafluorosulfanyl isocyanate, SF_5NCO , was first synthesized by Tullock, et al.^{30,31} by the reaction of benzoic acid, sodium fluoride, and pentafluorosulfanyltrifluoromethylamine, SF_5NHCF_3 . Subsequently, Clifford and Rhyne⁴³ succeeded in preparing the compound by addition of carbonyl fluoride to thiazyl trifluoride in anhydrous hydrogen fluoride.

The high solubility of thiazyl trifluoride and other gaseous byproducts in SF_5NCO present a difficult separation problem in the preparation of pure samples of this compound. To overcome this difficulty, a new synthetic method that would produce SF_5NCO as the sole volatile product was needed.

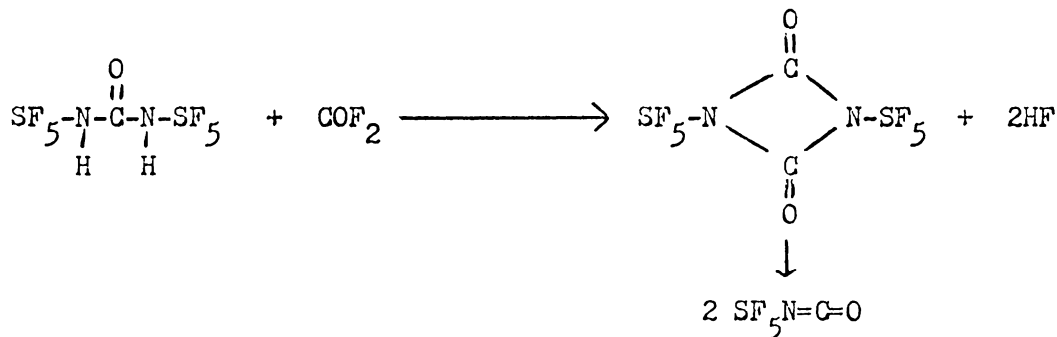
N,N' -Bis(pentafluorosulfanyl)urea,⁴⁴ $\text{SF}_5\text{NHCONHSF}_5$, a solid compound that can be purified by sublimation and stored for prolonged periods without decomposition, offered a potential starting material. It was found that the reaction of urea with a slight excess of carbonyl fluoride, COF_2 , (12 hr. at 100°) produced SF_5NCO essentially pure except for a small amount of COF_2 which could easily be separated by trap-to-trap distillation.

When COCl_2 was used instead of COF_2 , the reaction proceeded much less neatly, resulting in a complex mixture we had hoped initially to

avoid. However, when the reaction with COCl_2 was carried out at lower temperatures the infrared spectrum of the product mixture in addition to indicating the presence of HCl , COCl_2 , COClF , NSF_3 and SF_5NCO , had peaks about 1390 and 1595 cm^{-1} , strongly suggesting a four-membered C-N-C-N ring and urea-type carbonyl groups, respectively. This is in good agreement with similar compounds reported by Hass.⁴⁵

Mechanism

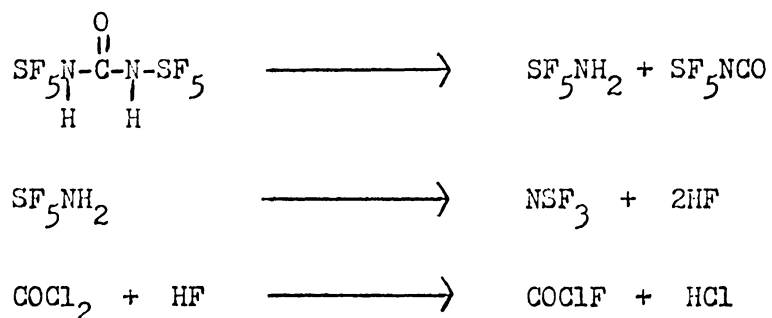
A possible mechanism to account for the experimental observations suggests a cyclic condensation between the urea and carbonyl fluoride with the elimination of two molecules of hydrogen fluoride to form a uretidine-dione* intermediately followed by thermal decomposition to yield pure SF_5NCO .



When COCl_2 was used instead of COF_2 (80° , 6 hr) it was possible to identify peaks in the infrared spectrum indicating the presence of the isocyanate dimer in addition to those due to NSF_3 , COCl_2 , COClF , HCl and SF_5NCO .

*In 1939 Chemical Abstracts⁴⁶ indexed isocyanate dimers as uretidiones. Subsequently this was changed to uretidine dione, a term which is currently in use. The compounds are still commonly referred to as simply as isocyanate dimers.

It is suggested that in the presence of COCl_2 the condensation reaction which forms the cyclic intermediate and hydrogen chloride is followed by the HCl-catalysed decomposition of the urea to its starting materials, SF_5NH_2 and SF_5NCO . Pentafluorosulfanylamine is unstable under the reaction conditions and decomposes further by loss of HF and formation of thiazyl trifluoride.



The hydrogen fluoride reacts with the phosgene to form the carbonyl chlorofluoride byproduct.

The absence of thiazyl trifluoride in the product mixture resulting from the reaction between the urea and carbonyl fluoride, in contrast to the reaction with phosgene, COCl_2 , suggests that hydrogen fluoride is a much less efficient catalyst than HCl for the decomposition of the urea. This observation finds further support in a report⁴² indicating that the urea is insoluble in hydrogen fluoride and reverts only slowly to starting material.

Previous attempts⁴⁴ to obtain a barbiturate by the reactions of the substituted urea with malonyl chloride failed to produce the desired compounds, the compound $(\text{SF}_5\text{NHCO})_2\text{CH}_2$ being formed instead. These results suggest that the use of diacyl fluorides instead of the chlorides may provide an alternative method for preparing those interesting cyclic derivatives.

A. Nucleophilic Substitution Reactions.

The activity exhibited by the isocyanate functional group toward nucleophilic reagent may be subdivided into two distinct types.

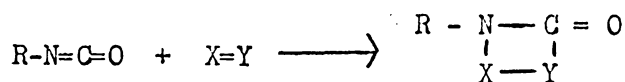
1. Nucleophilic Addition
2. Nucleophilic Displacement

1. Nucleophilic Addition.

One of the most useful reactions of organic isocyanates is with nucleophiles containing active hydrogens such as alcohols, phenols, amines, acids and amides. These reactions result in the addition of the nucleophilic agent across the azomethine linkage (of the isocyanate) to form urethanes and substituted ureas.

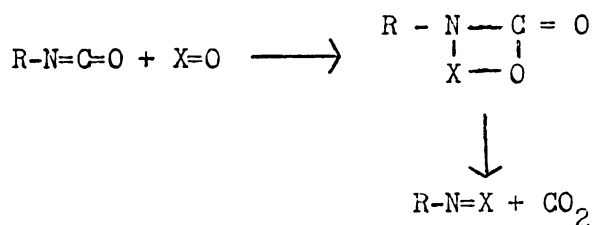
Previous studies of the chemical properties of the SF_5NCO system have devoted attention to this type of reaction. Tullock described^{30,31} the reaction between SF_5NCO and benzyl alcohol to form the corresponding urethane and Clifford^{44,42} reported two reactions with amines: one with pentafluorosulfanyl amine, SF_5NH_2 and the other with aniline to form symmetrical and unsymmetrical substituted ureas respectively.

When the nucleophilic agent does not possess active hydrogens other functional groups such as carbon-carbon multiple bonds may be added across the azomethine linkage to form four-membered cyclic compounds according to the general formula:



2. Nucleophilic Displacement.

A special case in the latter category arises when oxygen nucleophiles such as carbonyls and sulfoxides are allowed to react with highly reactive isocyanates. In such cases the cyclic adduct formed eliminates carbon dioxide and a nucleophilic displacement reaction takes place.



Reactions of this type are extremely rare and have been observed⁴⁷⁻⁵⁰ to occur only with highly polarized isocyanates, resulting from direct attachment of the isocyanate group to strongly electron-attracting substituents.

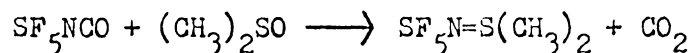
The potent electron withdrawing character of the perfluoro-sulfur group would make pentafluorosulfanyl isocyanate highly reactive and a prime candidate to be examined for its susceptibility to undergo nucleophilic displacement reactions.

Two oxygen containing compounds, dimethyl sulfoxide and benzaldehyde, have been reported in previous works⁴⁷⁻⁴⁹ to participate in reactions of this type with both organic and inorganic activated isocyanates; and since they have distinctly different nucleophilic properties, they have been selected as suitable agents for this study.

a. Reaction of SF₅NCO and (CH₃)₂SO.

The reaction between pentafluorosulfanyl isocyanate, SF₅NCO and dimethylsulfoxide results in replacing the sulfoxide oxygen with the SF₅N= group and thus provides the means of obtaining organic derivatives of tetravalent sulfur in high yields (85%).

Pentafluorosulfanyl isocyanate dissolved in dimethyl sulfoxide reacted with the solvent at room temperature producing a crystalline product after several hours. The only volatile product identified was CO₂. The crystalline product was identified by its H-1 and F-19 nmr and ir spectra as SF₅N=S(CH₃)₂.



The F-19 nmr spectrum, obtained at room temperature on the saturated (CH₃)₂SO product solution (Figure 3), displayed a normal SF₅ spectrum characterized by an AB₄ spin pattern. The spectrum consisted of two main fluorine groupings: one of 9 lines and the other of a broad doublet with relative intensities of 1:4. The fluorine multiplets were assigned to the apical and basal fluorines in the SF₅ group respectively.

The center for the apical fluorine appears at -113.3 ppm and for the basal fluorine at -92.4 ppm relative to external Freon-11, with a coupling constant of 154 cps.

The proton nmr spectrum had, in addition to a very broad peak for the hydrogens of the (CH₃)₂SO centered at 2.5 ppm relative to external T M S a peak at 2.98 ppm corresponding to the methyl groups of the -N=S(CH₃)₂ moiety, in agreement with the methyl chemical shifts observed

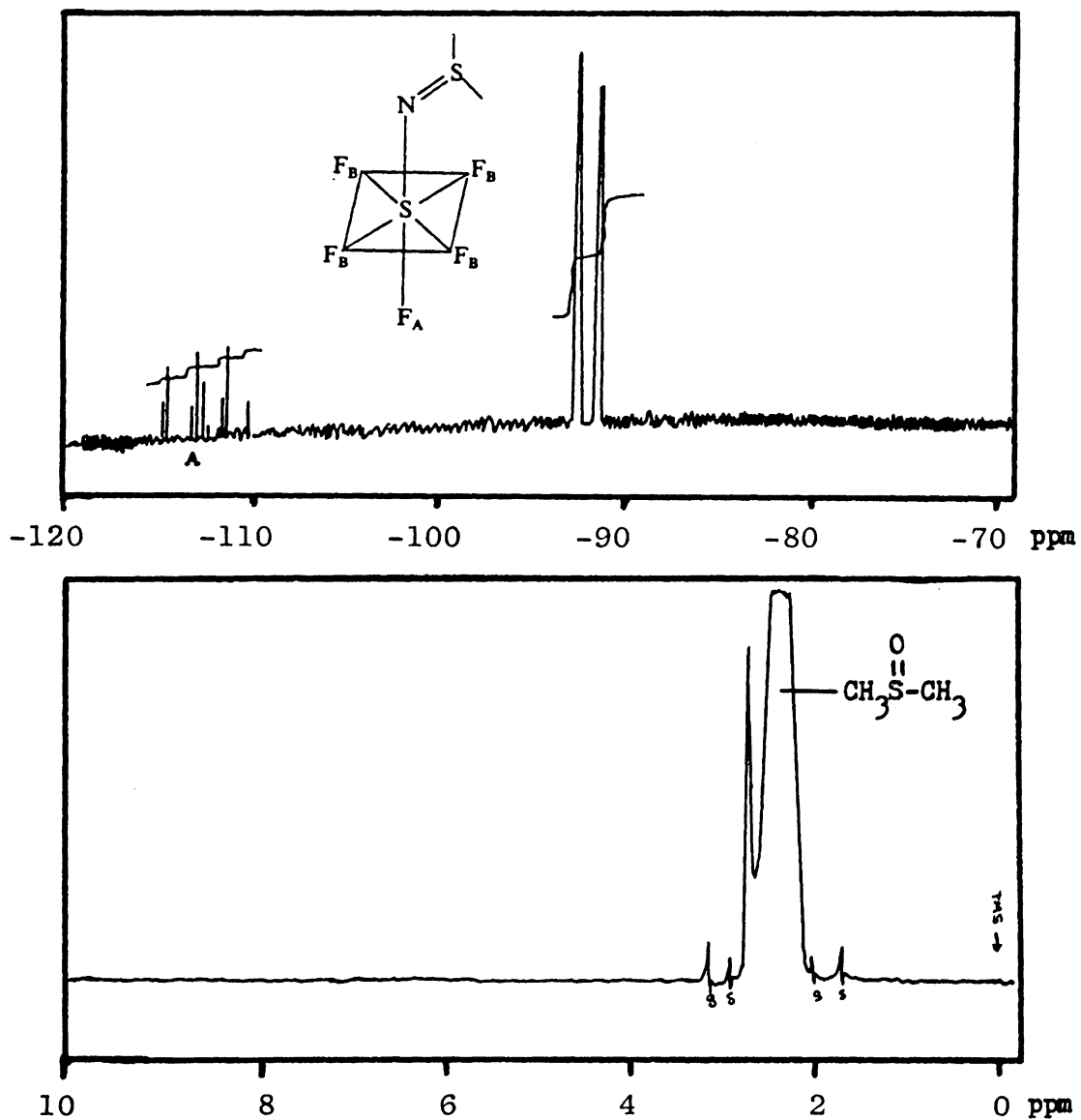


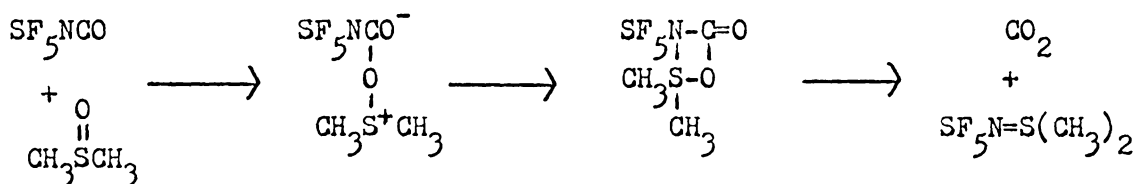
Figure 3. Fluorine-19 and hydrogen-1 nmr spectra of $\text{SF}_5\text{N}=\text{C}(\text{CH}_3)_2$.

by Roesky, et al.⁴⁷ and by Appel, et al.⁴⁸ for other $\text{N}=\text{S}(\text{CH}_3)_2^-$ containing compounds.

The infrared spectrum of the isolated product showed a broad band at 1250 cm^{-1} assigned to the S(IV)-N stretching vibration and peaks at 3250 , 3050 , 2950 , and 1360 cm^{-1} assigned to the C-H bonds of the methyl groups and at 905 , 860 , and 602 cm^{-1} assigned to stretching vibrations of the SF_5 group. A weak band observed at 1400 cm^{-1} is probably attributable to some residual $(\text{CH}_3)_2\text{SO}$.

Mechanism

As a mechanism for this reaction we propose the first step to involve an attack of sulfoxide oxygen on the electrophilic carbon in pentafluorosulfanyl isocyanate. The 4-membered cyclic intermediate subsequently formed rearranges with the elimination of carbon dioxide to yield the observed products.



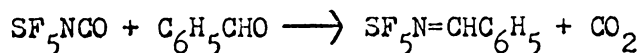
Similar reactions of electron deficient isocyanates with dimethyl sulfoxide have been reported by King,⁴⁹ Roesky,⁴⁷ and Appel.⁴⁸

b. Reaction of $\text{SF}_5\text{N}=\text{C}=\text{O}$ with benzaldehyde.

The reaction between pentafluorosulfanyl isocyanate, SF_5NCO , and benzaldehyde resulted in replacing carbonyl oxygen with the $\text{SF}_5\text{N}=\text{C}$ group.

Pentafluorosulfanyl isocyanate and freshly distilled benzaldehyde reacted after a few hours at room temperature producing a yellow solution

and carbon dioxide. The solution was determined by nmr, ir and mass spectra to contain $\text{SF}_5\text{N}=\text{CHC}_6\text{H}_5$, a novel, electron-deficient Schiff base.



The F-19 nuclear magnetic resonance spectrum of the saturated benzaldehyde solution showed (see Figure 4) the usual AB_4 pattern for the SF_5 group: apical F at -80.4 ppm, basal at -58.8 ppm, coupling constant, 157 cps.

The infrared spectrum (Nujol) exhibited a $\text{C}=\text{N}$ resonance at 1630 cm^{-1} , higher than for the usual organic $\text{C}=\text{N}$ frequency, presumably because of the great electron-withdrawing power of the SF_5 group. Characteristic SF_5 bands occurred at 915, 860 and 600 cm^{-1} .

The mass spectrum, which also served to confirm the identity of the compound, follows. The molecule ion peak was observed at m/e 231 (relative intensity 8.5%) with an isotopic distribution consistent with one sulfur atom in the molecule. The largest peak was that of SF_5^+ , m/e 127, with the second largest at m/e 230 assigned to $\text{SF}_5\text{NCC}_6\text{H}_5^+$. Peaks at m/e 211 (12.4%) $\text{SF}_4\text{NC}_7\text{H}_5^+$, m/e 153 (17%) SF_5NC^+ , m/e 141 (11.2%) SF_5N^+ , m/e 103 (18.4%) $\text{C}_6\text{H}_5\text{CN}^+$, m/e 70 (42.6%) SF_2 were also identified.

Mechanism

A nucleophilic attack of carbonyl oxygen at the electrophilic carbon of SF_5NCO is proposed to be the first step, followed by formation of a 4-membered cyclic intermediate which eliminates carbon dioxide to form the products.

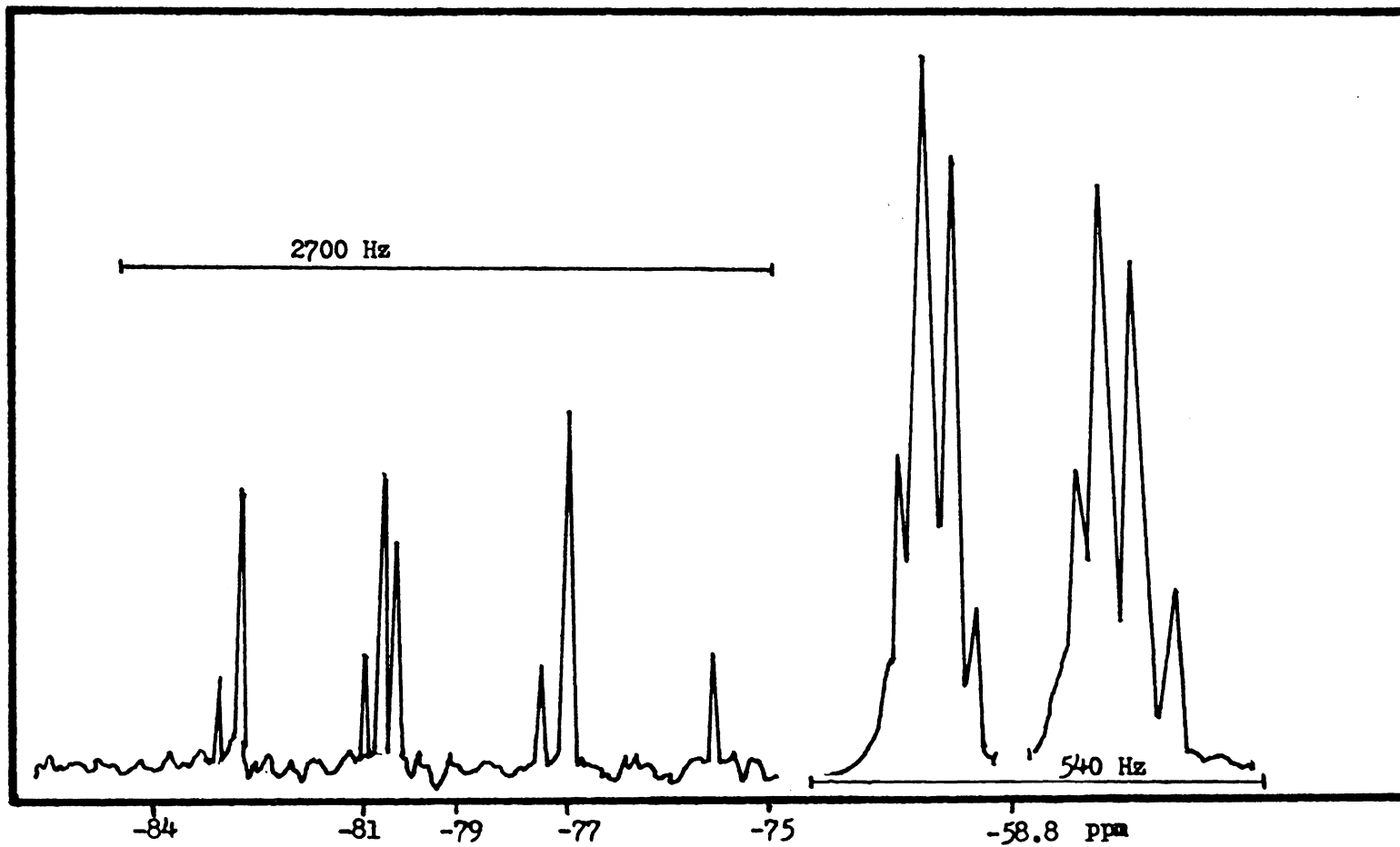
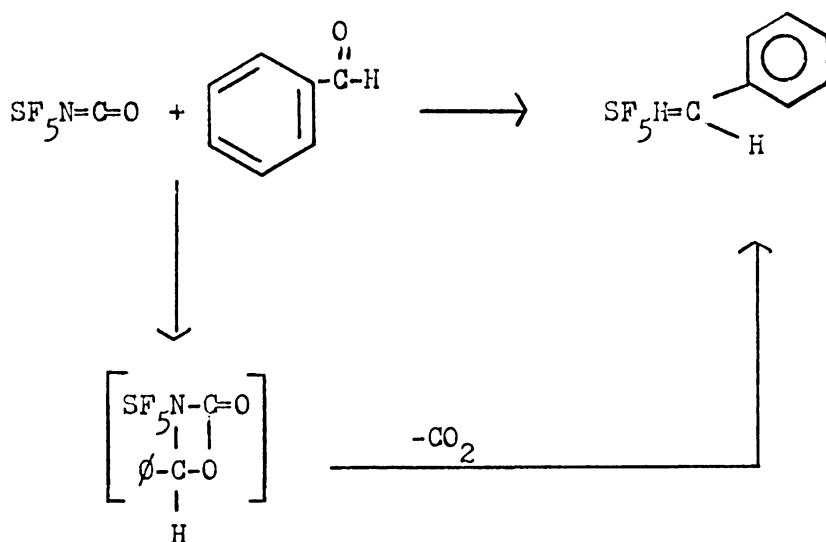


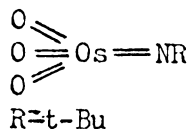
Figure 4. Fluorine-19 nmr spectrum of $\text{SF}_5\text{N}=\text{CHC}_6\text{H}_5$.



3. Transition Metal-Nitrogen Multiple Bonds

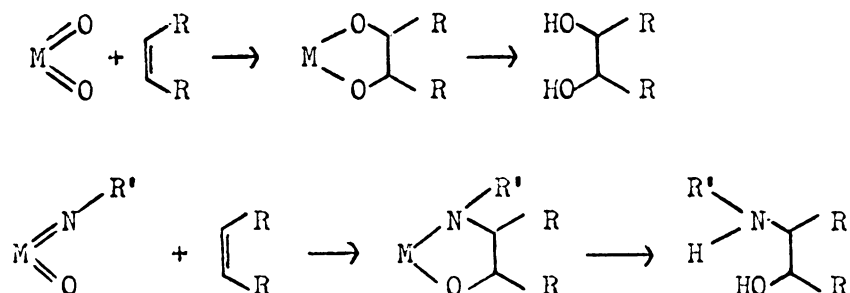
An additional aspect associated with the ability of pentafluoro-sulfanyl isocyanate in replacing oxygen with the $\text{SF}_5\text{N}=\text{C}=\text{O}$ group was to examine whether this tendency could be extended to inorganic oxygen-containing compounds. Of particular interest in this regard are the transition metal oxides. Should a reaction with metal oxide take place to a manner analogous to that with organic oxygen compounds, then transition metal-nitrogen multiple bonds would be formed.

In 1956, Clifford and Kobayashi⁵¹ reported the novel compound N-tert-butylosmiumate, which they prepared by the reaction between osmium tetroxide and t-butylamine.



Recently⁵¹ this compound attracted particular attention when it was found to extend the long known hydroxylation of olefins with OsO_4 to

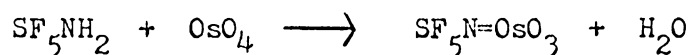
cis vicinal diols also to yield cis amino alcohols analogs of this transformation.⁵²



Attempts have been made to synthesize osmium compounds and also uranium compounds containing metal-nitrogen multiple bonds according to the equation;



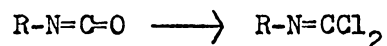
Preliminary experiments have been performed with osmium and uranium oxides. Neither of these reactions, however, has given so far the desired product. A previous attempt to synthesize $\text{SF}_5\text{N}=\text{OsO}_3$ by the reaction



had also failed.

B. Exchange Reactions.

Organic isocyanates have been shown to possess two active reaction sites, the azomethine linkage and the carbonyl linkage. While nucleophilic additions take place at the azomethine linkage exchange reactions have only recently^{53,54} been carried out on the carbonyl site to form the transformation:

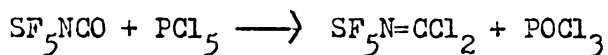


The dichloroazomethine* formed presents an extremely active class of compounds exhibiting a close relationship to isocyanates, isothiocyanates, and carbodiimides, as well as to phosgene and thiophosgene.

To extend this reaction to inorganic isocyanates, specifically to pentafluorosulfanyl isocyanate, $\text{SF}_5\text{N=C=O}$, would not only result in development of a new method for the synthesis of $\text{SF}_5\text{N=CCl}_2$ but also provide a link between the two independent general synthetic methods by which $\text{SF}_5\text{N=}$ compounds may be prepared (p. 10).

1. Reaction of SF_5NCO with PCl_5 .

Pentafluorosulfanyl isocyanate, SF_5NCO , and PCl_5 react very slowly at room temperature but readily at 60-80° producing $\text{SF}_5\text{N=CCl}_2$ in good yield (64%). The products were identified by nmr and ir spectra. This compound was previously prepared in low yield (16%) by Tullock, et al.^{30,31} from the ultraviolet irradiation of a mixture of SF_5Cl and cyanogen chloride.



The infrared spectrum had a peak at 1655 cm^{-1} assigned to C=N absorption, a doublet at 885 and 915 cm^{-1} , and a singlet at 603 cm^{-1} characteristic of the SF_5 group. The peaks at 800 cm^{-1} and 948 cm^{-1} were

*The dichloroazomethines are sometimes also referred to as isocyanide dichlorides, isonitrile dichlorides, carbylamine dichlorides, dichloromethyleneamides, carbonyl dichlorideimide, iminophosgene, or imidoyl chloride.

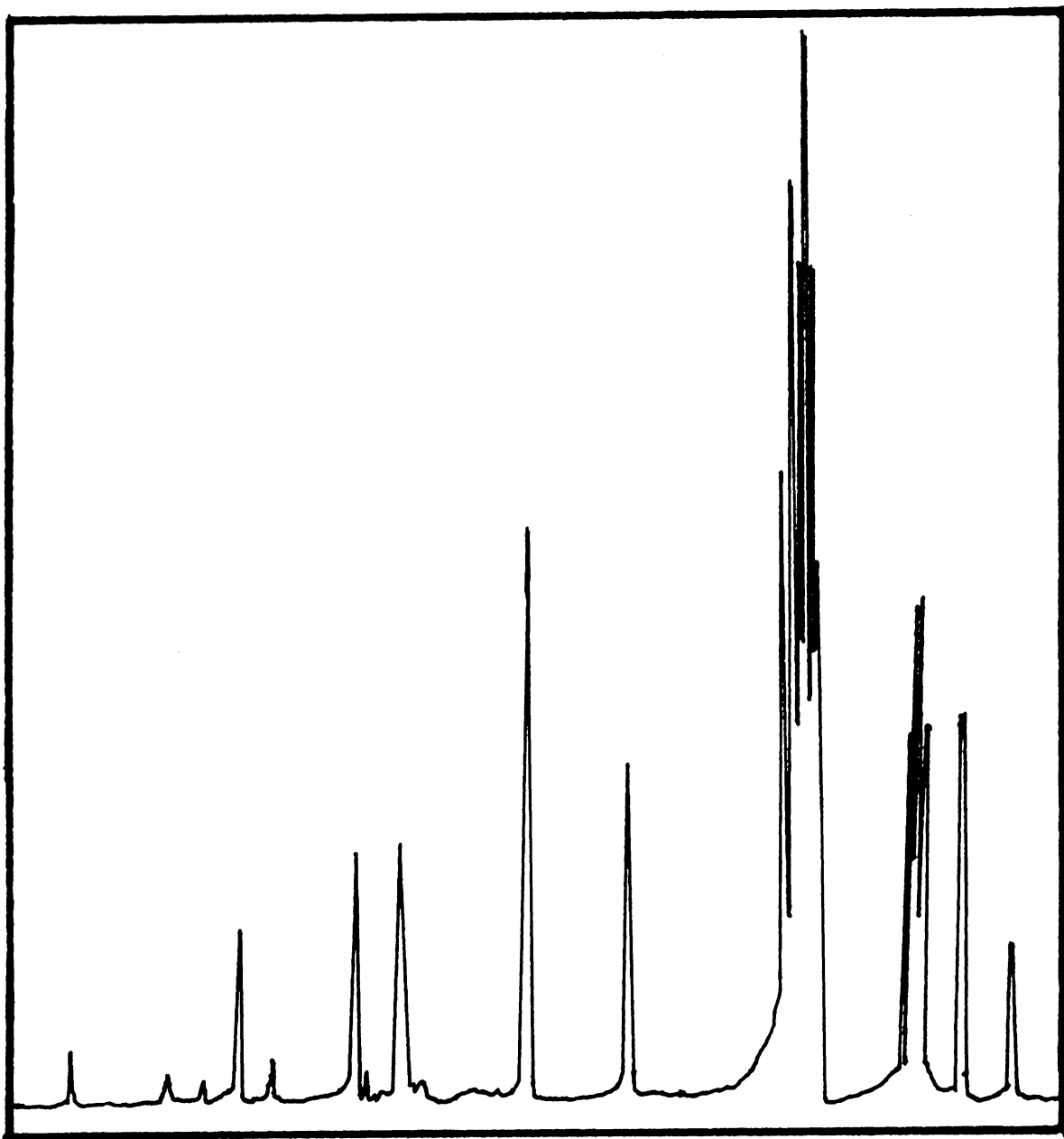


Figure 5. Fluorine-19 nmr spectrum of SF₅N=CCl₂.

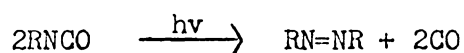
assigned to symmetrical and asymmetrical $=\text{CCl}_2$ stretchings, respectively. This was in good agreement with the reported values for $\text{FSO}_2\text{N}=\text{CCl}_2$ and $\text{ClSO}_2\text{N}=\text{CCl}_2$ given by Roesky and Biermann.⁵⁵

The F-19 nmr spectrum (Figure 5) exhibited a multiplet for the basal fluorine atoms, centered at -62.6 ppm relative to internal Freon-11, and the apical multiplet, centered at -67.2 ppm with a coupling constant of 156 c p s. The spectroscopic results correlated well with those reported by Tullock et al.^{30,31}

Once prepared and identified, $\text{SF}_5\text{N}=\text{CCl}_2$ was used further in reactions aimed at the preparation of bis-(pentafluorosulfanyl)carbodiimide. This will be described in Chapter 3.

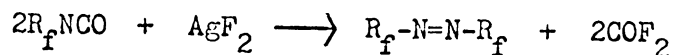
C. Coupling Reactions

The ability of organic isocyanates to undergo coupling reactions to form azoalkanes is of great interest.

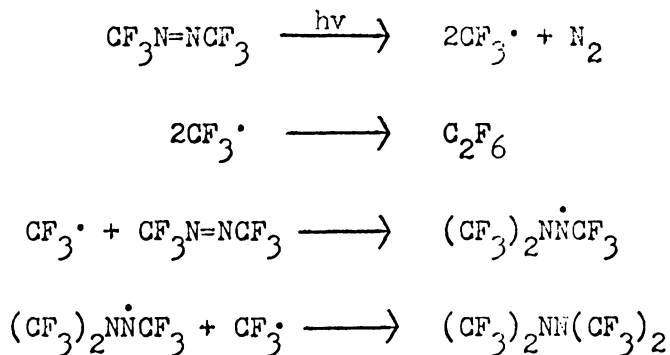


It is a widely employed method for generation of nitrenes, believed today to play a central role as key intermediates in organic chemistry. At the same time the principle product, azoalkanes, are outstanding sources for "clean" free radicals.

Recently the work has been extended to perfluoroorganic isocyanates. Dresdner et al.⁵⁶ who studied the indirect fluorination of perfluoroorganic isocyanate with silver difluoride showed that the main reaction products were carbonyl fluoride and perfluoroazoalkanes.



Like the hydrocarbon analogs, highly fluorinated azo compounds decompose on photolysis and pyrolysis to give nitrogen and the corresponding organic radicals.⁵⁷ In the photolysis of hexafluoroazomethane, the trifluoromethyl radicals produced combine with each other and add to the N=N bond.⁵⁸



It was our intention to extend these reactions to the field of inorganic isocyanates, in particular pentafluorosulfanyl isocyanate, hoping not only that a successful synthesis would produce a new member of the $\text{SF}_5\text{N}=\text{N}$ family but that such a member would be a useful source for SF_5 radicals.

1. Fluorination of SF_5NCO with AgF_2 .

Pentafluorosulfanyl isocyanate, SF_5NCO , was found to be remarkably resistant to fluorination (cf. $\text{SF}_5\text{N}=\text{SF}_2$ ³⁵), having been recovered largely unchanged after being in contact with AgF_2 at 80° for 12 hr.

At room temperature a slow reaction between SF_5NCO and excess AgF_2 took place in which COF_2 , SF_6 , and a new compound was formed possessing two distinct peaks in the infrared spectrum (Figure 6A) at 1380 cm^{-1} and 600 cm^{-1} . The major peaks in the infrared spectrum at 2275, 917, and 875 cm^{-1} were due to unreacted SF_5NCO .

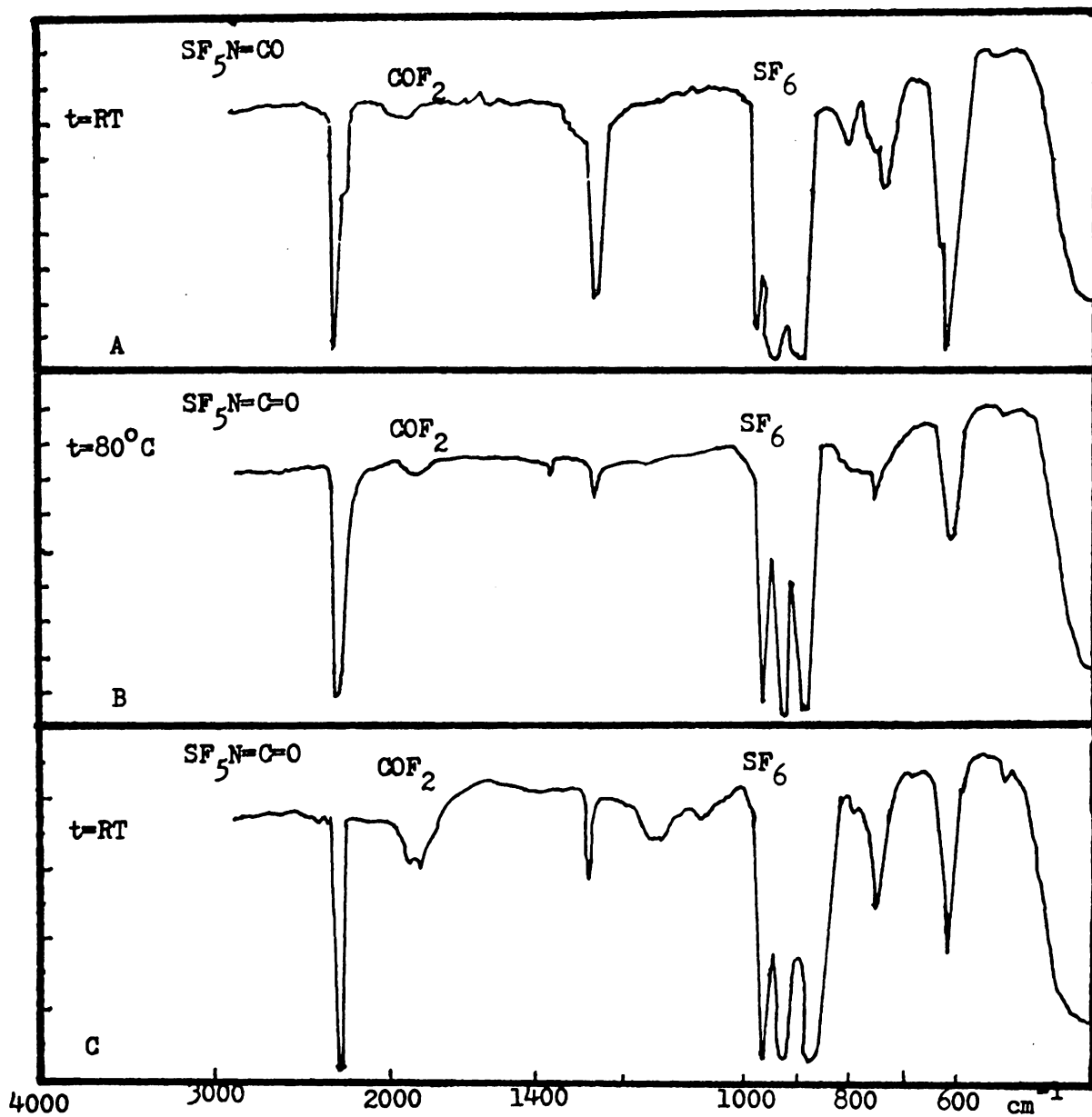


Figure 6. Temperature effects on the fluorination of SF_5N with AgF_2 .

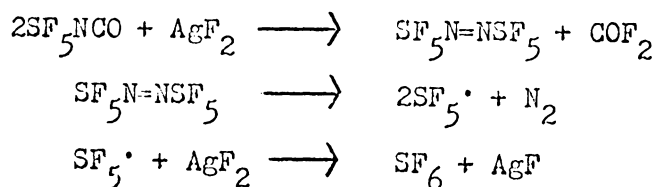
While the bond at 600 cm^{-1} is characteristic of all compounds containing the SF_5 group, the intensity of the absorption is subjected to large variation. The intense absorption of this band with respect to that of pure SF_5NCO suggests that the new compound also contains the SF_5 group.

The infrared spectrum also indicates (Figure 6B) that this new compound was sensitive to decomposition or further reaction with AgF_2 at higher temperatures (80° , 12 hr) resulting in the formation of additional SF_6 . (Note the decrease in the intensities of the bands at 1380 and 600 cm^{-1} .)

Further reaction with additional silver difluoride took place at room temperature producing products whose infrared spectrum (Figure 6C) showed increased intensity of the 1380 and 600 cm^{-1} bands and also of those due to COF_2 .

The absence of a band about 1600 cm^{-1} by analogy with $-\text{C}=\text{N}-$ and $\text{C}=\text{C}$ groups probably to indicate a symmetrical structure.

A possible reaction that accounts for the experimental and spectroscopic results involves the formation of an azo derivative, $\text{SF}_5\text{N}=\text{NSF}_5$, at low temperatures, which decomposed at elevated temperatures in a manner similar to that reported by Dresdner⁵⁶ for $\text{CF}_3\text{N}=\text{NCF}_3$.



The infrared absorption band at 1380 cm^{-1} is slightly lower than those for organic azo compounds, which have been reported to have absorptions at $1406 \pm 14\text{ cm}^{-1}$.⁵⁹

CHAPTER 2. PREPARATION OF AND REACTIONS WITH
PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE, $\text{SF}_5\text{N}=\text{SF}_2$.

A. Introduction

The enhanced reactivity of pentafluorosulfanylisocyanate, SF_5NCO , is believed to be a result of both the strong inductive effect of the SF_5 group and the ability of the doubly bonded nitrogen to transfer this effect across the multiple bond. To state it in a different manner, the $\text{SF}_5\text{N}=\text{}$ group governs the activity of the pentafluorosulfanylisocyanate. Therefore, other compounds containing the $\text{SF}_5\text{N}=\text{}$ should exhibit chemical properties similar to those of SF_5NCO .

To examine this hypothesis, studies of the ability of pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$, to participate in reactions similar to those observed for the isocyanate were undertaken.

It has been reported that $\text{SF}_5\text{N}=\text{SF}_2$, like all other known iminosulfur difluorides resists polar additions across the sulfur(IV)-nitrogen bond. Also like the isocyanate is its remarkable resistance to fluorination. Under extreme conditions (elemental fluorine) the formation of $\text{SF}_5\text{N}=\text{SF}_2=\text{NSF}_5$ results, in which a type of coupling reaction occurs (similar to the formation of $\text{SF}_5\text{N}=\text{NSF}_5$ from SF_5NCO).³⁵

Since no systematic work concerning exchange reactions has been reported, we decided to examine reactions of this type, starting with a study of the photolysis of NSF_3 . This resulted in discovery of a new method for the preparation of $\text{SF}_5\text{N}=\text{SF}_2$.

B. New Method For The Preparation of $\text{SF}_5\text{N}=\text{SF}_2$.

1. Photolysis of Thiazyl Trifluoride.

The preparation of pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$, has been described several times. One method of preparation involved the reaction of N SF_3 and SF_4 using BF_3 as catalyst, but resulted in yields of only 3%.³⁴ The fluorination of S_4N_4 with elemental fluorine reported earlier by Glemser et al.¹², also yielded $\text{SF}_5\text{N}=\text{SF}_2$, along with SF_6 , SF_4 , NF_3 , N_2F_2 , and $\text{N}=\text{SF}$. Subsequently, the method based on thiazyl trifluoride was refined by replacing the BF_3 catalyst with anhydrous hydrogen fluoride, either in a two step reaction in which SF_5NH_2 is prepared and purified prior to the reaction with SF_4 , or by a direct combination of $\text{N}=\text{SF}_3$ and SF_4 in anhydrous hydrogen fluoride.

In the course of studies aimed at developing methods to enhance the reactivity of thiazyl trifluoride at the triple bond, it was found that ultra violet irradiation of thiazyl trifluoride yielded an easily separated mixture of two volatile components, unreacted N SF_3 and pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$ in 34% yield (identified by ir, nmr and mass spectrometry) along with an unidentified solid yellow component left in the reactor. The F-19 nmr spectrum of the yellow residue (in acetonitrile) showed a broad singlet at -236 ppm downfield from Freon-11 and a negligible amount of thiazyl monofluoride.

A more powerful uv source (Hanovia medium pressure mercury resonance arc, 450 watt) required only 3 minutes to give similar results.

While the yields of $\text{SF}_5\text{N}=\text{SF}_2$ obtained from the direct irradiation of thiazyl trifluoride, $\text{N}=\text{SF}_3$, are somewhat lower than those obtained by other methods, the new preparation offers several distinct advantages, such as the elimination of expensive reagents (SF_4), and the need for special handling techniques associated with the use of anhydrous hydrogen fluoride. In addition, the new method is well suited to continuous preparation of $\text{SF}_5\text{N}=\text{SF}_2$ with little loss of starting material and a relatively easy separation of the reaction mixture.

Mechanism

The mechanism for the reaction is not fully understood. At present, we tend to favor a free radical mechanism in which free radical generation is stimulated by uv radiation.

To examine this possibility, photolysis of thiazyl trifluoride was carried out in the presence of an equimolar quantity of nitric oxide, NO, for 30 minutes. The reactor was powered by a medium pressure Hanovia mercury arc light source with the total intensity output of 450 watts.

The infrared spectrum of the volatile products indicated the formation of nitrous oxide, N_2O . Unreacted nitric oxide, NO, and thiazyl trifluoride were also present. Separation of the reaction mixture showed practically no loss of thiazyl trifluoride.

Since the reaction of pure thiazyl trifluoride in the absence of nitric oxide proceeded to form $\text{SF}_5\text{N}=\text{SF}_2$ after short periods of irradiation (3 minutes), and such reaction was not observed in the presence of nitric oxide, some question as to the validity of a free radical mechanism has been raised. It has, therefore been suggested that thiazyl trifluoride

may serve as a free radical transfer agent in a role similar to that of benzoquinone in many organic photochemical reactions (photosensitizer). More kinetic studies are needed to fully understand the mechanism of this reaction.

C. Exchange Reactions of $SF_5N=SF_2$

1. Reaction between $SF_5N=SF_2$ and PCl_5

Pentafluorosulfanyliminosulfur difluoride, $SF_5N=SF_2$, was found to react at room temperature with PCl_5 to produce in good yield (65%) a pale yellow volatile liquid subsequently identified by ir, nmr and mass spectra as pentafluorosulfanyliminosulfur dichloride, $SF_5N=SCl_2$.

Pentafluorosulfanyliminosulfur dichloride, $SF_5N=SCl_2$, was previously synthesized by Clifford and Goel⁶¹ by the reaction between SF_5NH_2 and SCl_2 at room temperature.

The infrared spectrum (Figure 7) agreed with that reported earlier: 1235 cm^{-1} (s), N=S stretch (cf. Glemser and Biermann⁶³); $910, 855\text{ cm}^{-1}$ and 600 cm^{-1} , SF_5 ; $475, 415\text{ cm}^{-1}$, attributed to $=SCl_2$ group, very close to those observed by Lustig⁶⁴ for the compound $CF_3N=SCl_2$, and Roesky⁶⁵ for the compound $FSO_2N=SCl_2$.

The distillate, dissolved in Freon-11 (1 part to 5) gave a F-19 nmr spectrum (Figure 8) with the apical nonuplet of the SF_5 group centered at -73.5 ppm and the basal doublet at -76.6 ppm . The coupling constant was 153.4 cps .

Mass spectral peaks at m/e 210 and 208, in an approximate ratio of 3:1, which were attributed to $S_2F_5NCl^+$, support the assignment of the formula as $S_2F_5NCl_2$.

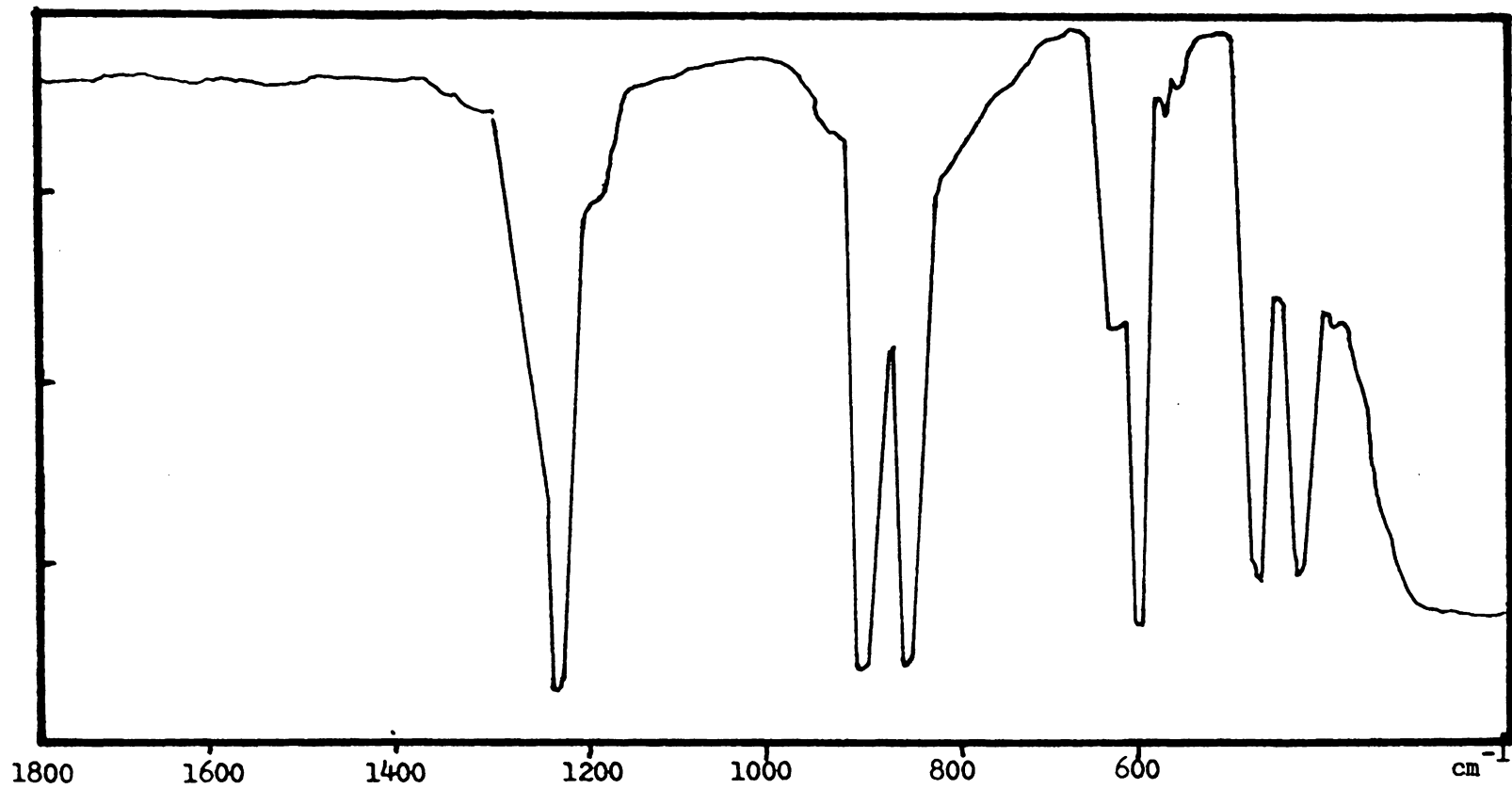


Figure 7. Infrared spectrum of SF₅N=SCl₂

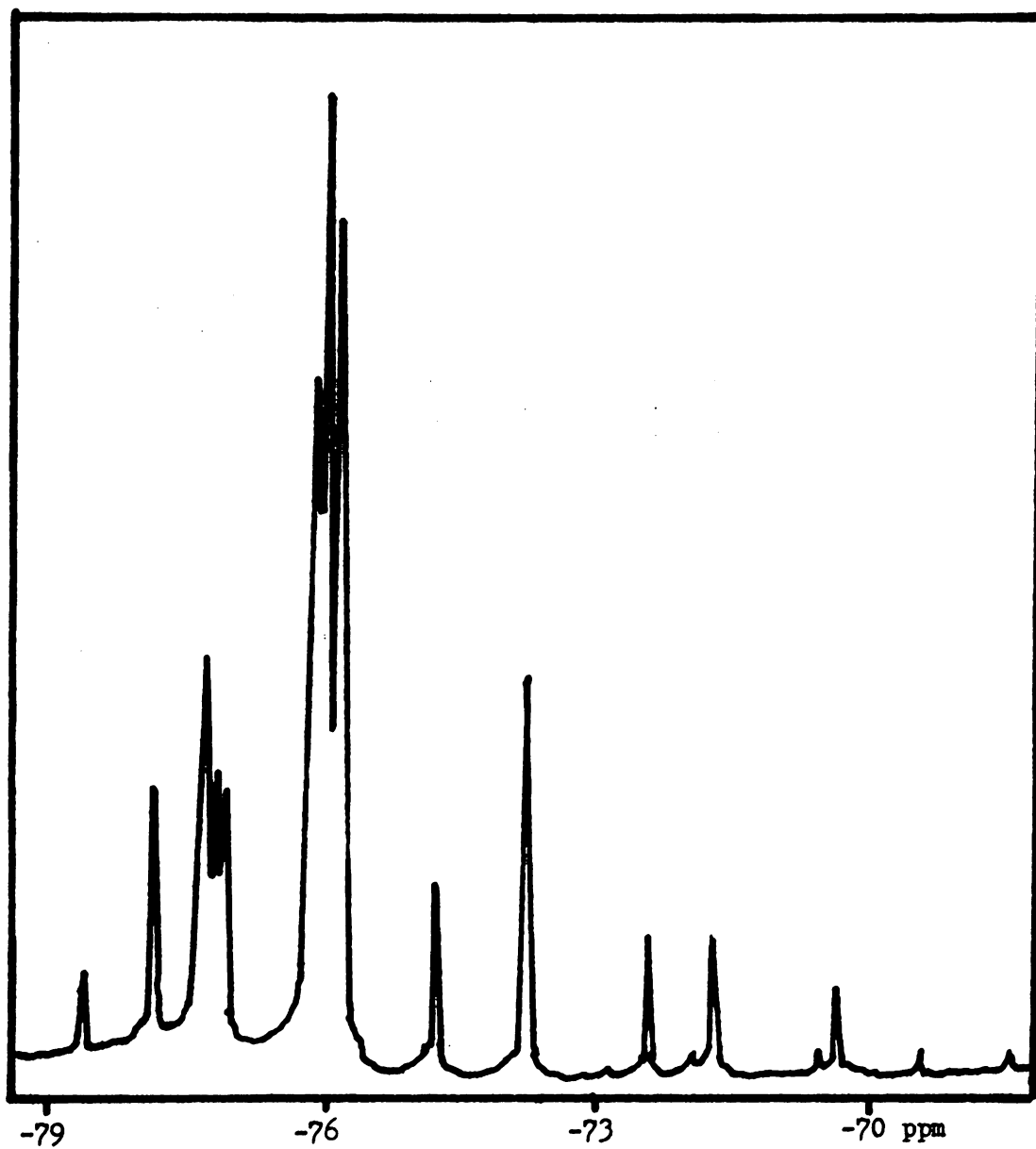
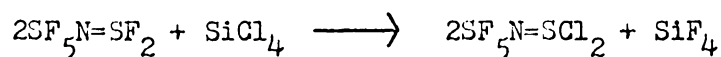


Figure 8. Fluorine-19 nmr spectrum of SF₅N=SCl₂.

In an attempt to improve the yield and reduce the need for tedious separations, exchange reactions with other chlorinating agents were examined.

2. Reaction between $\text{SF}_5\text{N}=\text{SF}_2$ and SiCl_4 .

It was hoped that the volatile SiF_4 formed as a byproduct from the exchange reaction between $\text{SF}_5\text{N}=\text{SF}_2$ and SiCl_4 would be easily separated



from the reaction mixture (SiF_4 may be trapped only at liquid nitrogen temperatures), thus providing a simplified method for the preparation of pure $\text{SF}_5\text{N}=\text{SCL}_2$. However, the reaction proceeded with somewhat more difficulty than with PCl_5 , requiring more vigorous conditions (100° , 6 hr) and only partial conversion was achieved as indicated by the ir spectrum. Peaks due to $\text{SF}_5\text{N}=\text{SF}_2$ were still evident even in the product from reaction at 150° for 6 hr. The purified product was shown by ir, nmr and mass spectra to be identical to that from the PCl_5 reaction.

3. Reaction between $\text{SF}_5\text{N}=\text{SF}_2$ and AlCl_3 .

Attempts to develop a synthetic method that would produce $\text{SF}_5\text{N}=\text{SCL}_2$ as the sole volatile product were made using AlCl_3 as the chlorinating agent. The non-volatile AlF_3 expected to be formed in the chlorination with AlCl_3 should be left in the reaction bomb allowing the transfer of only volatile products to the vacuum line. Aluminum trichloride was indeed found to react with $\text{SF}_5\text{N}=\text{SF}_2$, but only at elevated temperatures (150° ; 6 hr). The pale yellow volatile liquid obtained did not resemble $\text{SF}_5\text{N}=\text{SCL}_2$, however, and was shown by its nmr spectrum to contain

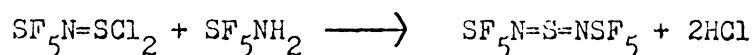
no fluorine atoms. The ir and mass spectra of the volatile product formed are reported in the experimental section.

D. Reactions with $\text{SF}_5\text{N}=\text{SCl}_2$.

Pentafluorosulfanyliminosulfur dichloride, $\text{SF}_5\text{N}=\text{SCl}_2$, is a reactive compound which rapidly attacks mercury. As previously reported it reacted with AgF_2 to produce $\text{SF}_5\text{N}=\text{SF}_2$ in excellent yield (96%). It was also found to react with SF_5NH_2 producing a novel sulfadiimide $\text{SF}_5\text{N}=\text{S}=\text{NSF}_5$.

1. Reaction of $\text{SF}_5\text{N}=\text{SCl}_2$ with SF_5NH_2 .

Pentafluorosulfanyliminosulfur dichloride, $\text{SF}_5\text{N}=\text{SCl}_2$, reacts with excess pentafluorosulfanylamine, SF_5NH_2 , at room temperature producing in addition to HCl , $\text{N}=\text{SF}_3$, and SiF_4 a deep yellow liquid subsequently identified by ir, and nmr spectroscopy as $\text{SF}_5\text{N}=\text{S}=\text{NSF}_5$. The yield based on $\text{SF}_5\text{N}=\text{SCl}_2$ was 46%.



The infrared spectrum exhibited the following bands: 1445 (vs), 1265 (vs), 1068 (vs) cm^{-1} assigned to N=S=N group vibrations by comparison with related compounds.⁶⁶ These bands were also similar to those of SO_2 at 1361 cm^{-1} and 1151 cm^{-1} .⁶⁷ The doublet at 915 and 865 cm^{-1} and the strong absorption at 602 are characteristics of the SF_5 group.

The F-19 nmr (external Freon-11) showed a normal AB_4 spin system with the basal fluorines centered at -61.4 ppm and the apical fluorine at -65.0 ppm in a 4:1 ratio, respectively.

E. Summary.

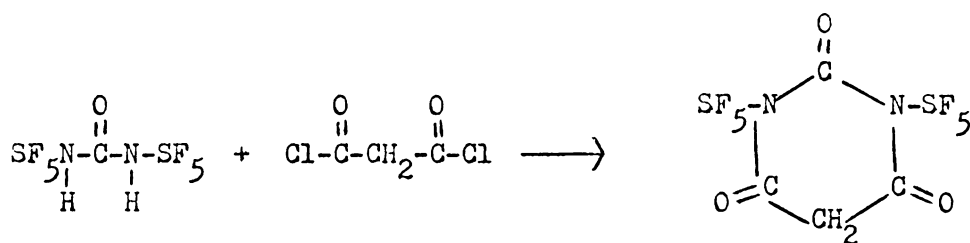
The successful syntheses of highly reactive compounds derived from SF_5NCO , $\text{SF}_5\text{N}=\text{SF}_2$, and SF_5NH_2 prompted interest in the utilization of these compounds as intermediates in the synthesis of sulfur-fluorinated derivatives of potential importance.

From these potential applications, the most interesting is the production of sulfur-fluorinated drugs in analogy with the carbon-fluorinated drugs which have already found extensive use.

CHAPTER 3. ATTEMPTS TO PREPARE BIS-(PENTAFLUOROSULFANYL)-
 CARBODIIMIDS, $\text{SF}_5\text{N}=\text{C}=\text{NSF}_5$.

A. Introduction

The attempts to prepare useful organic-inorganic hybrid compounds, and to demonstrate their unique properties led to undertaking of a project aimed at the formation of a new family of potential drugs or drug intermediates. The most convenient approach seemed to be to follow the route developed with the synthesis of N,N' -bis(pentafluoro-sulfanyl)urea and to use it as a starting material for the synthesis of members of the pyrimidine family - inorganic barbiturates and uracils.



The direct approach did not lead to the formation of the desired product, probably as a result of the active site being sterically crowded by the SF_5 group.

An indirect approach designed to overcome the steric restrictions was to synthesize a new pentafluorosulfanylimino derivative, bis(pentafluorosulfanyl)carbodiimide, $\text{SF}_5\text{N}=\text{C}=\text{NSF}_5$, in which the steric influence of the SF_5 group on reactions with organic acids, acid chlorides, and the like should be much reduced. Such sequence is shown in Figure 9.

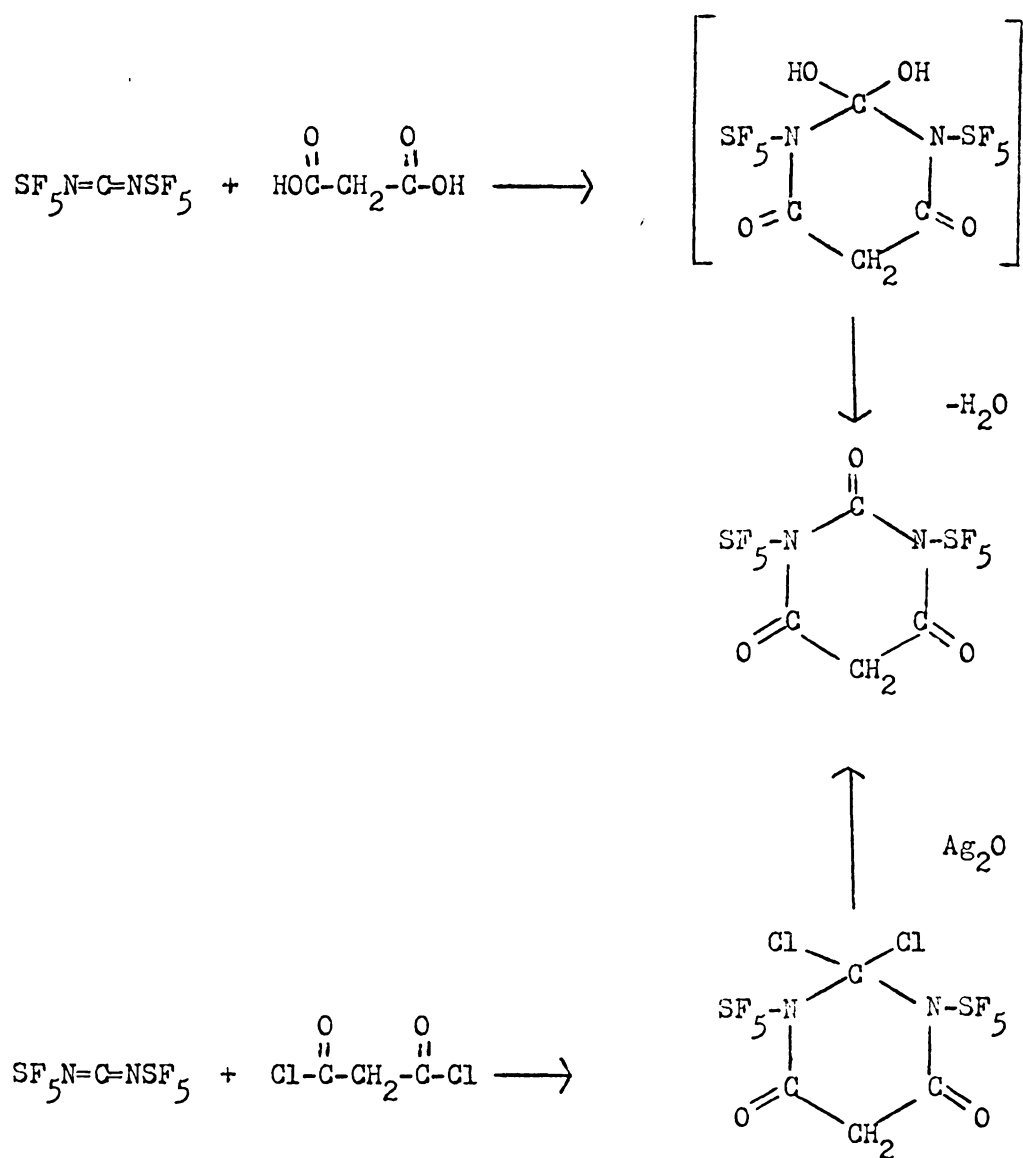


Figure 9 . Reaction sequences for the attempted preparation of N,N'-bis(pentafluorosulfanyl)barbiturate.

B. Preparations and Properties of SF₅N=PX₃ Derivatives

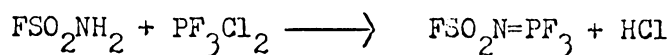
The observation that pentafluorosulfanyl isocyanate, SF₅NCO, can replace carbonyl and sulfoxide oxygen with a SF₅N= group stimulated further attempts to prepare new members of this series with improved chemical properties and greater reactivity.

The requirement for such a reactive member included high affinity for oxygen, and the ability to form unstable four-membered rings which upon rearrangement decompose with the transfer of oxygen.

Phosphazene derivatives of the general formula R-N=PCl₃ represent a class of compounds that has long been known to possess a satisfactory combination of such properties. It was, therefore, of great interest to synthesize SF₅N=PX₃ derivatives and to examine their ability to transfer the SF₅N= group to various oxygen-containing compounds. Of particular interest was their ability to react with SF₅NCO to form the pentafluoro-sulfanyl carbodiimide, SF₅N=C=N-SF₅.

Previous attempts to prepare members of this class have been undertaken. Clifford and Zeilenga³⁵ reported that recombination of SF₅NH₂ and PF₅ did not lead to the formation of SF₅N=PF₃ but rather is a 1:1 adduct, in contrast with the reaction between SF₅NH₂ and SF₄ which yields SF₅N=SF₂.

Several reactions have been reported in which amines reacted with PF₃Cl₂ to eliminate two molecules of HCl, for example⁶⁸



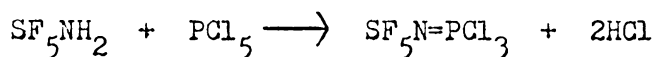
Clifford and Harman⁶⁹ attempted a similar reaction with SF₅NH₂ in a slight excess of PF₃Cl₂ with the hope of producing the phosphazene deriva-

tives. Instead, fluorination of PF_3Cl_2 with HF, probably from the decomposition of SF_5NH_2 to thiazyl trifluoride and HF, took place.

1. Reaction Between SF_5NH_2 and PCl_5

Pentafluorosulfanyl amine, SF_5NH_2 , and excess PCl_5 reacted at room temperature producing HCl and a new pentafluorosulfanylimino derivative, $\text{SF}_5\text{N}=\text{PCl}_3$, in good yield (86% based on SF_5NH_2). The products were identified by ir, nmr and mass spectra.

The new pentafluorosulfanylimino derivative, presumably containing a multiple bond between nitrogen and phosphorus, was a pale yellow



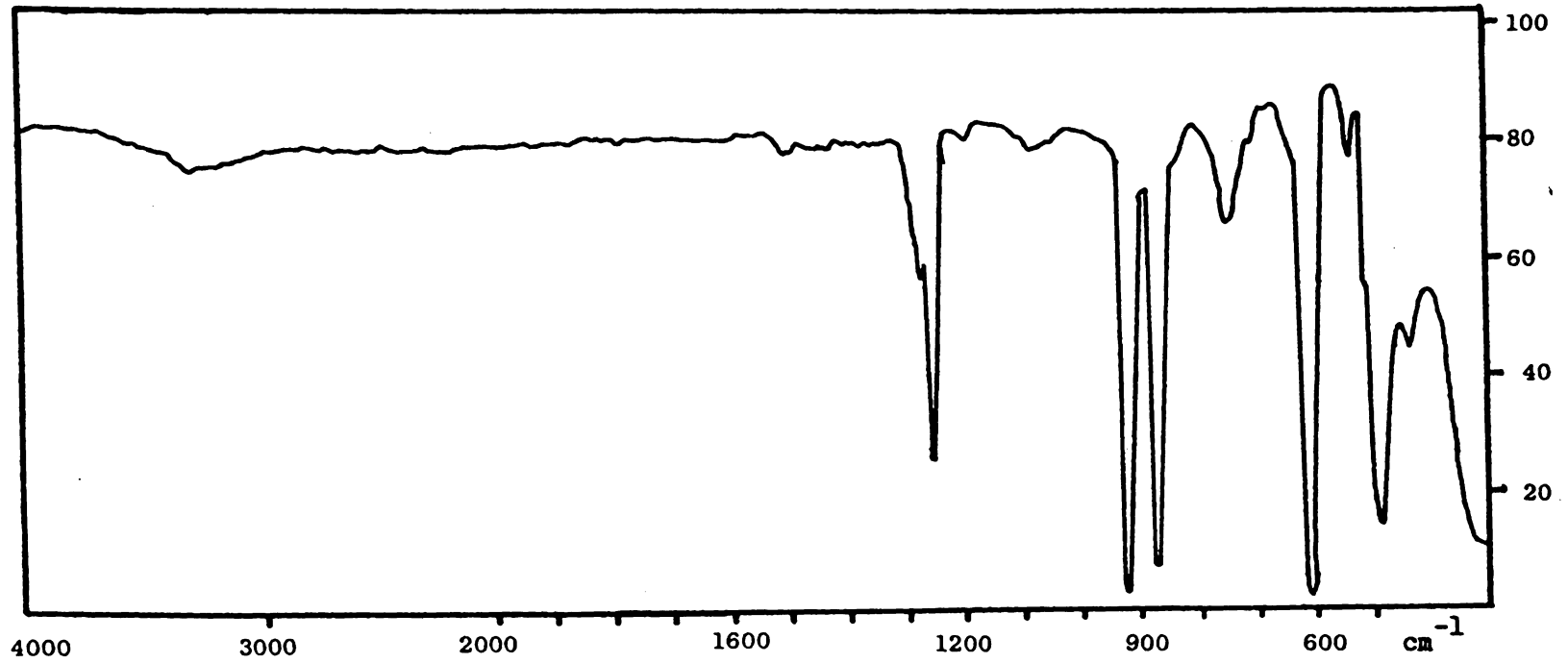
liquid which reacted rapidly with mercury.

The infrared spectrum of the vapor (Figure 10) had a shouldered peak at $1230 (\text{m}) \text{ cm}^{-1}$ assigned to the P=N stretch and a peak at $470 (\text{m}) \text{ cm}^{-1}$ for the P-Cl stretch, in good agreement with other $-\text{N}=\text{PCl}_3$ compounds.⁷⁰ The characteristic bands for the SF_5 group appeared at $915 (\text{s})$, $860 (\text{s})$ and $600 (\text{s}) \text{ cm}^{-1}$.

The F-19 nmr spectrum (Figure 11) showed the apical nonuplet centered at -71.8 ppm and the basal doublet at -69.0 ppm . The coupling constant was 154.7 cps .

Mass spectrometric analysis did not detect the parent peak. However, peaks corresponding to the parent minus a chlorine or fluorine atom were present supporting the assignment of the formula as $\text{SF}_5\text{N}=\text{PCl}_3$.

Once prepared and identified, $\text{SF}_5\text{N}=\text{PCl}_3$ was used further in reactions with SF_5NCO , aimed at the preparation of bis-(pentafluorosulfanyl)carbodiimide.



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Figure 10. Infrared spectrum of SF₅N=PCl₃.

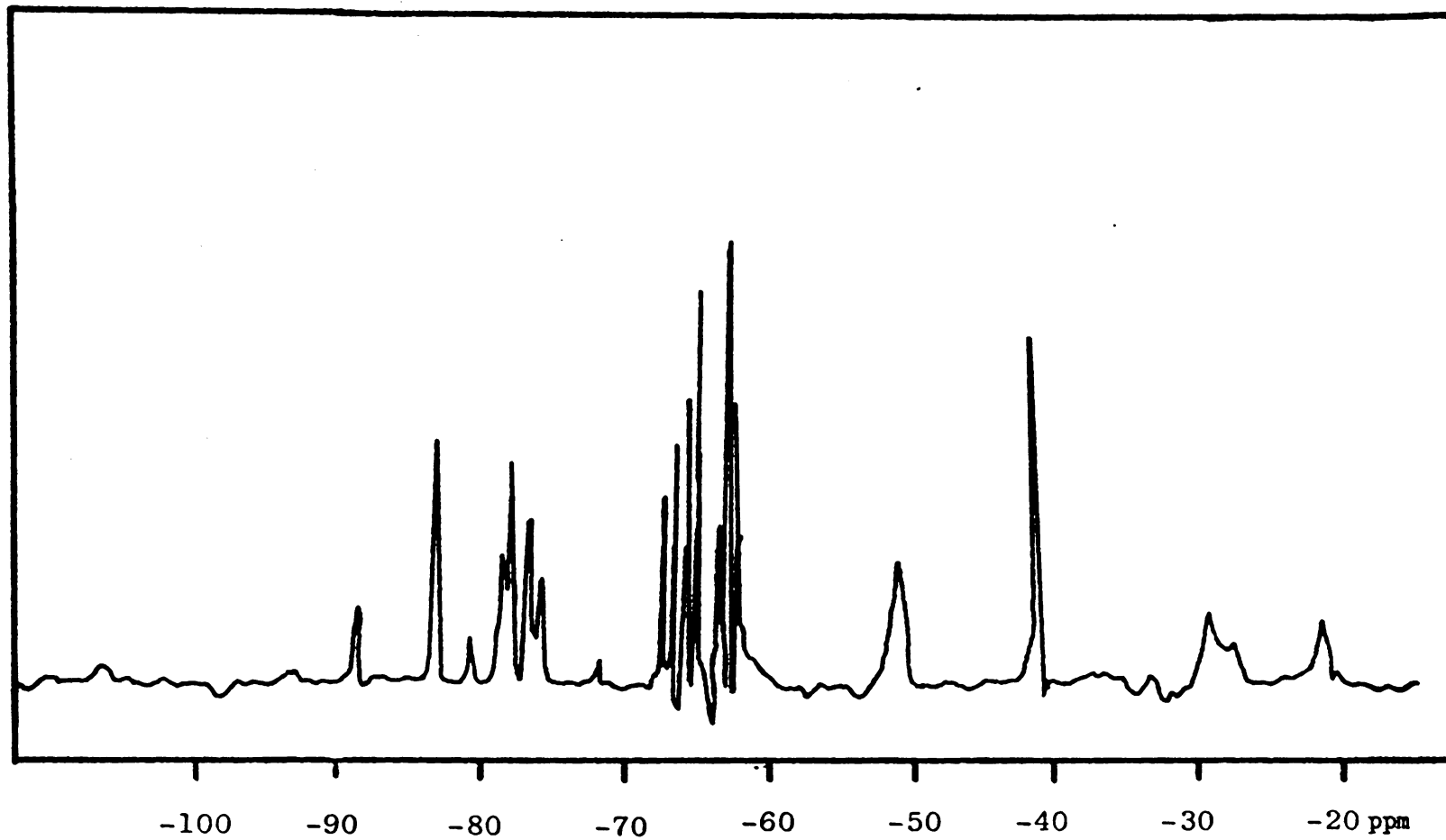
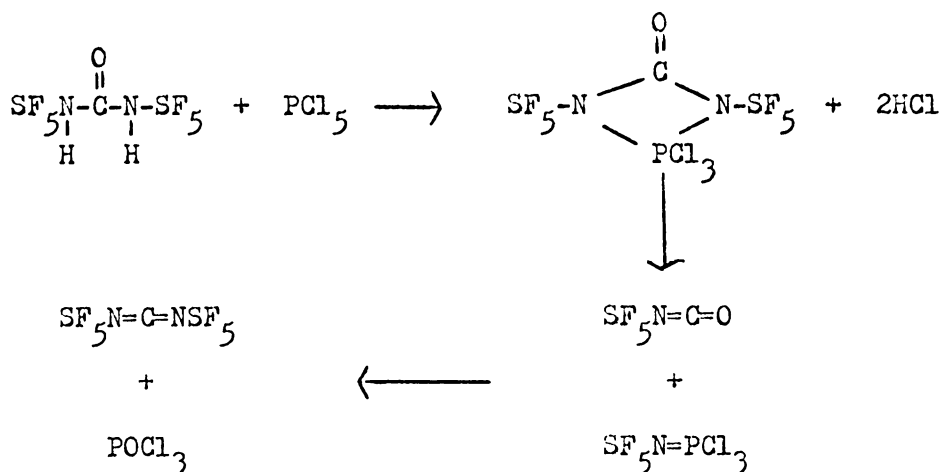


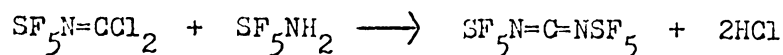
Figure 11. Fluorine-19 nmr spectrum of SF₅N=PCl₃.



Product analysis by infrared spectroscopy showed the presence of HCl, NSF_3 , SF_5NCO and SiF_4 but, no evidence was found for the formation of the carbodiimide.

3. Reaction of $\text{SF}_5\text{N}=\text{CCl}_2$ with SF_5NH_2 .

In contrast to the reaction of $\text{SF}_5\text{N}=\text{SCl}_2$ with SF_5NH_2 (see p. 42), the reaction of $\text{SF}_5\text{N}=\text{CCl}_2$, carried out under the same conditions as with $\text{SF}_5\text{N}=\text{SCl}_2$, was found to proceed with great reluctance and under conditions so far tried has not produced isolable quantities of the expected $\text{SF}_5\text{N}=\text{C}=\text{NSF}_5$. Claim for the preparation is based on spectral evidence.



The infrared spectrum of the product mixture obtained from the reaction carried out at room temperature for 18 hr showed in addition to the presence of HCl, $\text{N}\equiv\text{SF}_3$ and unreacted starting materials also peaks at 2154 cm^{-1} attributable to the $\text{N}=\text{C}=\text{N}$ group (cf. 2150 cm^{-1} for

organic carbodiimides found by Khorana⁶⁰ and 2152-2128 cm^{-1} found by Meakins and Moss).⁶²

The nmr spectrum exhibited peaks as follows: -60.3 ppm for the basal fluorines and -63.7 ppm for the apical fluorine in a 4:1 ratio respectively and a coupling constant of 152.3 cps. It, therefore, appears highly probable that $(\text{SF}_5\text{N}=\text{C})_2$ was formed.

D. Summary.

The introduction of novel functional groups into organic molecules has great interest in terms of the effects of such introduction upon the physical and biological properties thus obtained. This paper reports the preparation of a number of new pentafluorosulfanyl-imino $(\text{SF}_5\text{N}=\text{C})$ derivatives, both organic and inorganic which have been synthesized from pentafluorosulfanyl isocyanate, SF_5NCO , pentafluorosulfanylamine, SF_5NH_2 and pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$.

Reaction of SF_5NCO , $\text{SF}_5\text{N}=\text{SF}_2$, and SF_5NH_2 with appropriate substrates in several basic reaction systems including nucleophilic substitution, addition, exchange reaction, and coupling reactions produced the following products: $\text{SF}_5\text{N}=\text{S}(\text{CH}_3)_2$, $\text{SF}_5\text{N}=\text{CHC}_6\text{H}_5$, $\text{SF}_5\text{N}=\text{CCl}_2$, $\text{SF}_5\text{N}=\text{SCl}_2$, $(\text{SF}_5\text{N}=\text{C})_2$, $(\text{SF}_5\text{N}=\text{C})_2\text{S}$ and $\text{SF}_5\text{N}=\text{PCL}_3$.

Some of these reactions led to new compounds and some represent improved routes to compounds previously reported.

The chemical similarities between SF_5NCO and $\text{SF}_5\text{N}=\text{SF}_2$ with respect to nucleophilic substitution, exchange reactions, and coupling reactions reflect the similarity in bonding expected in these two

systems. However, there is no report of the successful addition of polar reagents like HF to $\text{SF}_5\text{N}=\text{SF}_2$ or any compound containing the $-\text{N}=\text{SF}_2$ group. This failure to undergo addition reactions indicates some gross discrepancy from the usual behavior of multiply bonded systems.

This unexpected behavior of the $-\text{N}=\text{SF}_2$ system is believed to originate in the nature of the sulfur orbitals involved in the bonding. The ability of the sulfur atom to utilize d-orbitals in π -bonding deserves further exploration in light of the behavior of the $-\text{N}=\text{SF}_2$ system.

Thus, a theoretical study of the $-\text{N}=\text{SF}_2$ system was undertaken to clarify the role and magnitude of d-orbitals in the bonding of $-\text{N}=\text{SF}_2$ compounds. This theoretical study is discussed in the next chapter.

CHAPTER 4. THE QUESTION OF ROTATION ABOUT THE

$p\pi$ - $d\pi$ DOUBLE BOND IN $RN=SF_2$ COMPOUNDS.

A. Introduction

The role of d-orbitals is important in inorganic chemistry, especially in the higher oxidation states of both main group and transition elements, where multiple bonding is a common phenomenon.

For the last decade or two, there has been a controversy among chemists over the role and magnitude of d-orbital involvement in π -bonding.

The marked chemical and physical differences between ketones and sulfoxides, and between carboxylic acids and sulfonic acids, for example, did not find a satisfactory explanation within the framework of the $p\pi$ - $p\pi$ bonding concept.

Theoretical studies by Kimball,⁷¹ Coulson,⁷² Sutton⁷³ and Moffit⁷⁴ on the nature of π -bonding that originates by overlap of p- and d-orbitals, weakened the controversy and today the potential utilization of d-orbital in π -bonding is generally recognized.⁷⁵

Recently, S(IV)-N multiple-bonded compounds have been subjected to detailed studies which revealed some chemical and physical anomalies that suggest the possibility of rotation about the S(IV)-N multiple bond in contrast to the geometrical restriction of the $p\pi$ - $p\pi$ bond.

X-ray studies of sulphimides ($R'R'S=NSO_2R''$)⁷⁶⁻⁷⁹ indicate that in the crystalline state a racemic mixture of two enantiomers exists, which, however, cannot be resolved into optical antipodes,⁸⁰ nor can the chiral conformers be detected in solution by nmr methods.⁸¹

The nmr spectrum shows only one singlet for the methyl groups even though these groups are symmetrically nonequivalent in the conformation observed by x-ray diffraction.

In an attempt to explain this anomalous behavior Mezey and Kucsman⁸² studied the system theoretically, using extended Hückel calculations, and demonstrated that internal rotation about the S(IV)-N multiple bond is a possible explanation for the experimental observations.

Their findings that rotation about a double-bonded system is possible, may conclusively resolve the long standing controversy concerning d-orbital involvement in π -bonding, since it is in contrast to the geometrical rigidity observed in $p\pi$ - $p\pi$ systems.

The possibility of rotation about the S(IV)-N double bond is of such a fundamental nature that a critical examination would be required. One method of validation consists of developing a model system that maximizes the bond strength of the S(IV)-N bond and examining the new system for the extent of rotation. The theory of d-orbital involvement in π -bonding helps in developing the basis for such system.

Three factors, namely proper symmetry, similarity in size and similarity in energy are necessary conditions for significant mixing and bond formation between orbitals. d-Orbitals are no exception, since their proper symmetry for π -bonding evolves from group theory.

d-Orbitals in neutral atoms are too diffuse⁸³⁻⁸⁵ to form useful bonds; however, it has been shown⁸⁶ that the presence of strongly electronegative groups on an atom, such as oxygen or fluorinated substituents, contracts the d-orbitals to such an extent that efficient bond formation to that atom, using the d-orbitals becomes favorable. In addition the groups withdraw

electron density from the central atom, increasing the atom's effective nuclear charge, and lowering the orbital energies.

A satisfactory model system for maximum $d\pi$ -bonding should contain a strongly electronegative group attached to the central atom rather than an electron donating group as in the case of sulphimide.

In the field of thiazyl fluoride chemistry, members of the imino-sulfur difluoride series, $R-N=SF_2$, have been synthesized and appear to be eminently suited to serve as model systems.

In addition, fluorine substitution results in increased volatility and thermal stability, and provides a nucleus suitable for nmr studies.

Chemically the S(IV)-N multiple bond of iminosulfur difluorides possesses properties that differentiate it from the usual behavior of a double bond. For example, there is no available evidence for addition reactions of HF or other polar reagents to $FC(O)N=SF_2$; $CF_3N=SF_2$; $SF_5N=SF_2$, or other iminosulfur difluorides, furthermore, experiments involving the S(IV)-N multiple bond in Diels-Alder Type reactions, using both $SF_5N=SF_2$ and $FC(O)N=SF_2$ as dienophiles have so far been unsuccessful.⁸⁷

An understanding of the nature of the S(IV)-N multiple bond, including the question of rotation, is therefore of considerable interest from both a theoretical and a synthetic point of view.

B. Molecular Orbital Calculations of Iminosulfur Difluorides.

Molecular orbital calculations (CNDO) of the total energy of the $R-N=SF_2$ system as a function of rotation of the SF_2 group about the double bond were performed for the following compounds $ClN=SF_2$, $FN=SF_2$, $CF_3N=SF_2$, $SF_5N=SF_2$, $FC(O)N=SF_2$, $CF_3C(O)N=SF_2$ and $C_2H_5N=SF_2$, by Professor J. C. Schug and Danna Brewer.

Whenever the R group could assume several geometrical configurations with respect to the SF₂ fluorines, resulting from rotation about the RN bond, separate calculations were performed for the extreme configurations.

Separate sets of calculations were also performed, one including and one omitting d-orbital participation in bond formation. Total energies obtained were compared and generally found to be lower for those calculated with d-orbital participation.

C. Result and Discussion.

The iminosulfur difluorides used in this study showed similar total energy curves. Each point on a typical curve (see for example Figure 12) corresponds to a specific geometrical rotamer resulting from rotation of the SF₂ group about the sulfur(IV)-nitrogen multiple bond. The minimum points on the energy curve represent configurations of low energy and therefore stable geometrical forms.

Two minima of equal energy separated by a low lying maximum represent the most stable geometrical arrangement. The energy curve is surprisingly broad and flat in the neighborhood of the lower minima.

With only slight excitation any derived rotamer within an interval of about 120° may occur resulting in a flexible type of double bond in direct contrast to the usual rigid geometrical requirement for a ππ-ππ multiple bond.

The calculated bond orders of the various orbital overlaps were graphed with respect to rotation about the sulfur(IV)-nitrogen multiple bond. Two distinct systems evolved. The first case, exemplified by SF₂=N-C≡N, Figure 13, graphically depicts the bond order to be essentially independent of the angle of rotation.

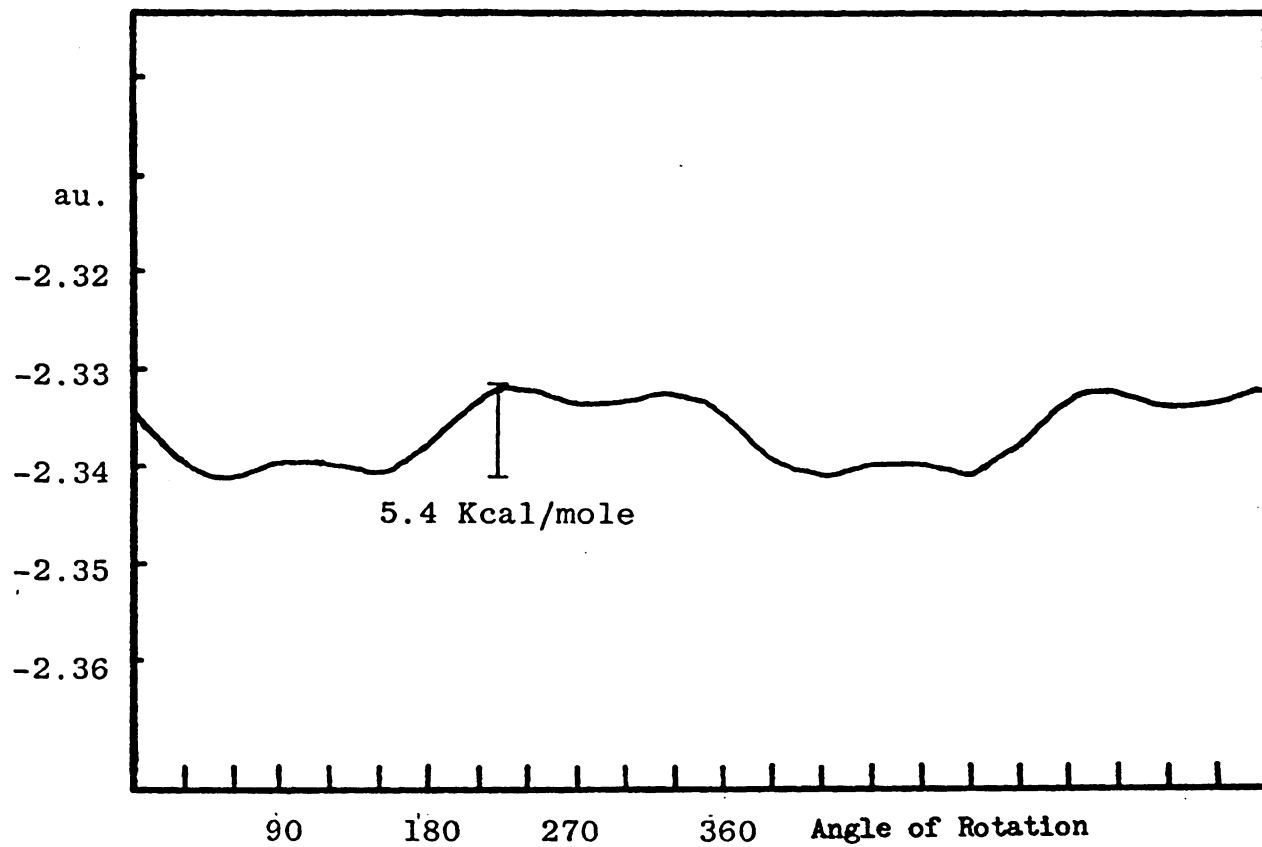


Figure 12. Total energy of $\text{SF}_2=\text{N}-\text{C}\equiv\text{N}$ as, a function of rotation about the $\text{S}=\text{N}$ bond.

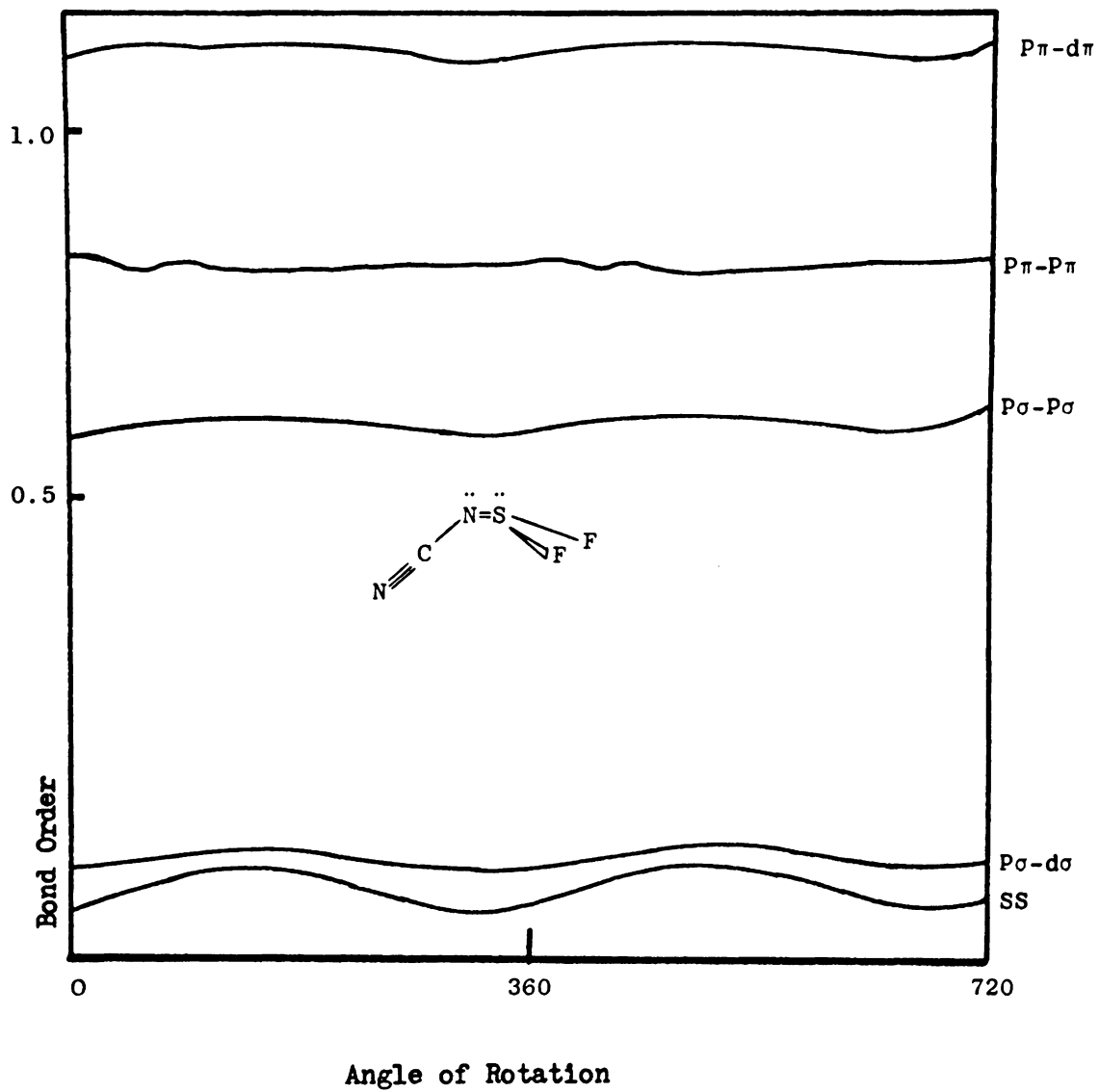


Figure 13. Bond order in $\text{SF}_2=\text{N}-\text{C}\equiv\text{N}$.

The second case, exemplified by $\text{SF}_2=\text{N}-\text{F}$, Figure 14 shows orbital overlap with respect to rotation to vary in the following manner: Every change in $p\pi-p\pi$ bond order is balanced by a similar change of opposite sign in the $p\pi-p\pi$ bond order - thus, the net result that the total bond order is approximately independent of rotation.

The magnitude of d-orbital involvement in π -bonding and the energy barrier to free rotation for a set of compounds studied is given in Table 3. It demonstrates that d-orbital contribution accounts for close to 50% of the total π -bonding and is practically independent of the nature of the nitrogen substituents.

The substituents do, however, affect greatly, to a first approximation, the energy barrier to free rotation. The larger the substituent the larger the barrier to free rotation it imposes.

Pentafluorosulfanylimino sulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$, seems to be slightly out of order. This result may be due to the calculations themselves, since this case has been calculated with some uncertainty as to the S(VI)-N bond length.

In summary, while a substituent apparently does not affect the bonding characteristics of d-orbitals, steric hindrance is apparently the governing factor in free rotation.

An additional aspect in the bonding of $\text{SF}_2=\text{N}-\text{R}$ system involves the question of whether the unique system in these compounds exhibits tendencies similar to those associated with the usual π system, such as involvement in conjugation and aromaticity.

The usual π -system associates conjugation with a requirement of coplanarity. Should the same criterion hold for the π -system constructed

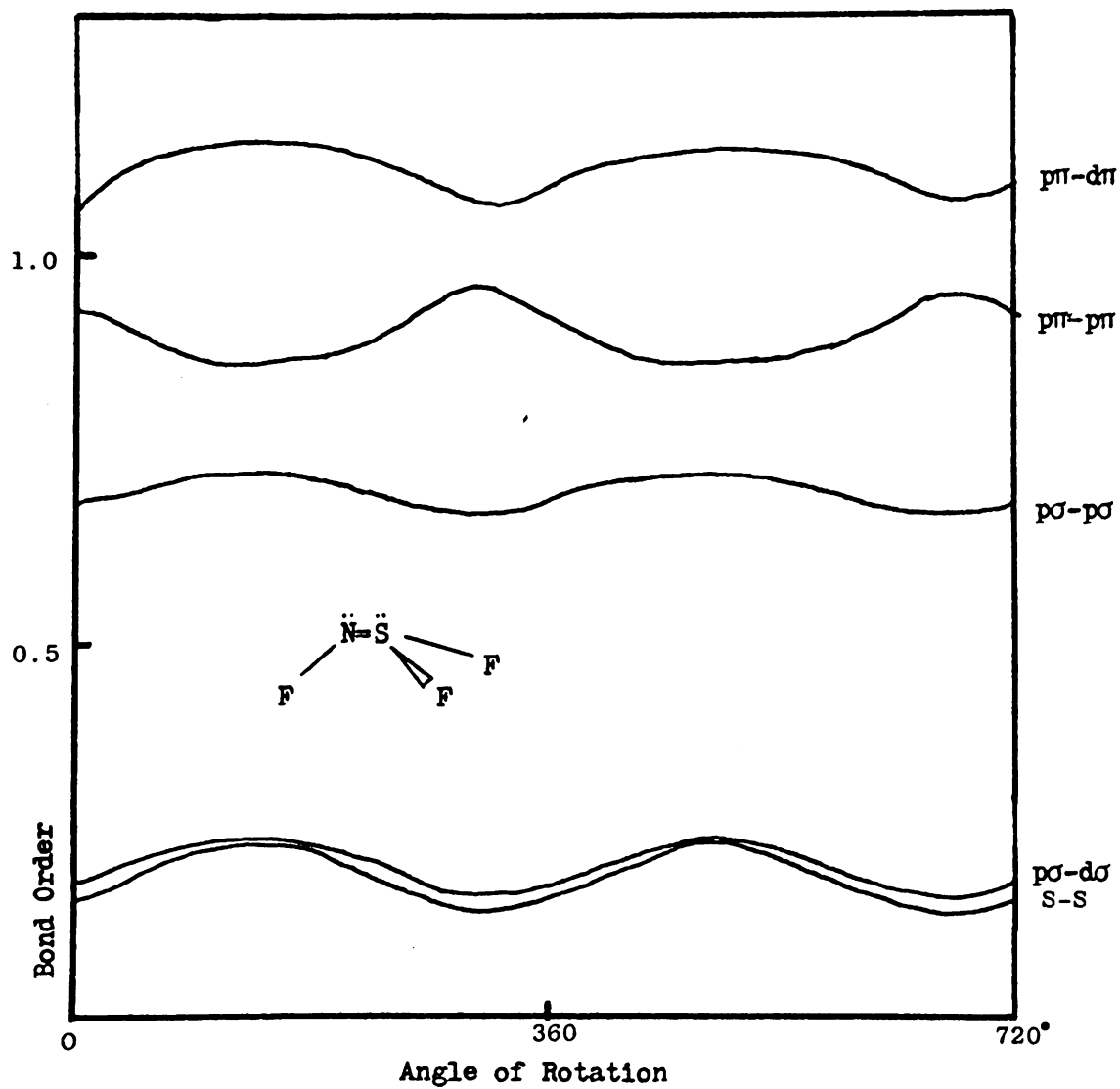


Figure 14. Bond order in $\text{SF}_2=\text{NF}$

Table 3

Substituent Effect on the Barrier to Free Rotation

| Compound | Total pd % | Barrier Kcal/mole |
|---|---------------|----------------------|
| $\text{SF}_2=\text{NF}$ | 42.6 | 5.02 |
| $\text{SF}_2=\text{N}-\text{C N}$ | 47.1 | 5.46 |
| $\text{SF}_2=\text{N}-\text{CF}_3$ | 43.4 | 6.74 |
| $\text{SF}_2=\text{N}-\text{SF}_5$ | 43.9 | 13.31 |
| 0 | | |
| $\text{SF}_2=\text{N}-\text{C}-\text{F}$ | 43.6 | 13.57 |
| 0 | | |
| $\text{SF}_2=\text{N}-\text{CCH}_3$ | 42.7 | 27.29 |
| $\text{SF}_2=\text{N}-\text{C}_6\text{H}_5$ | 42.75 | 55.18 |

from d-orbital participation, it would require coplanarity with the sulfur(IV)-nitrogen multiple bond. If a system in which the inverse relationship between coplanarity and steric hindrance is selected and the total energy compared, the system that would show the lowest total energy would directly point to the dominating effects.

The system selected to shed light on this problem was $\text{SF}_2=\text{N}-\text{C}_5\text{H}_6$. If conjugation is indeed the dominating factor, then an orientation would be adopted which would make the phenyl ring coplanar with the S(IV)-N bond and consequently place an orthohydrogen in a position that would increase steric hindrance. This should nevertheless show lower total energy.

If the geometrical requirements, on the other hand, are the dominating factors, then the ring would adopt a perpendicular orientation to the sulfur(IV)-nitrogen bond and minimize these effects.

The study on this system clearly demonstrates that the geometrical form in which a coplanar arrangement is adopted also represents the system of lowest energy.

Thus, the $\text{p}\pi\text{-d}\pi$ bond system shows, at least in this respect, similarities to the $\text{p}\pi\text{-p}\pi$ system.

D. Nuclear Magnetic Resonance Studies.

The possibility that partial rotation may take place in the imino-sulfur difluorides implies that the multiple bond between sulfur(IV) and nitrogen cannot be represented by the $\text{p}\pi\text{-p}\pi$ bonding model, and must be of a different nature, probably $\text{p}\pi\text{-d}\pi$.

Demonstration of these findings experimentally is a great challenge, since it would resolve a long controversy by showing that d-orbitals are of great importance in the formation of systems having properties fundamentally distinct from those of $\pi\pi$ - $\pi\pi$ bonding systems.

Since different geometrical requirements have to be satisfied, it was hoped that partial rotation would exhibit a F-19 nmr spectrum different from that of one with fixed configuration expected at sufficiently low temperatures. Therefore, F-19 nmr spectra of several substances were obtained at various temperatures.

The selection of compounds to be studied was dictated by the method used. Only compounds that contain fluorine atoms in the R group in addition to the SF_2 fluorines could supply useful nmr data, including chemical shifts and coupling constants.

In addition, simple molecules of high symmetry had to be selected to simplify the spectral analysis.

On this basis $SF_5-N=SF_2$, $CF_3N=SF_2$, $C_2F_5N=SF_2$ and $FCO-N=SF_2$ were selected.

1. Low temperatures nmr studies of pentafluorosulfanyliminosulfur difluoride.

Preliminary low temperature F-19 nmr studies of $SF_5N=SF_2$ have been carried out. They indicated unsymmetrical shifts occurring in the position of the fluorine groupings and that a standard for reference is needed. It also indicated that a solvent with a very low freezing temperature would be advantageous in increasing the available range of the study. A satisfactory standard would require an unreactive compound

with a F-19 nmr spectrum at the vicinity of the SF_5 fluorines, and with a nmr spectrum independent of temperature variations.

Experimentation with several compounds failed to uncover a compound which could serve both as the standard and as the solvent. The combination selected consisted of a mixture of SF_6 as standard and propane as solvent.

The F-19 nmr spectrum of $SF_5N=SF_2$ dissolved in propane (SF_6 standard) was obtained at various temperatures as shown in Figure 15.

At -90° the spectrum was found to consist of a complex doublet and a complex quintet characteristic of the planar SF_4 and the apical SF (of the SF_5 group) and a quintet of the SF_2 group resulting from splitting by the planar fluorine. The areas under these peaks, in the order given, were in the ratio 4:1:2.

At -100° a second quintet in the SF_2 region had appeared up field from the first and the intensity of the first had diminished proportionately so that the total under these two quintets remained the same as that under the first at -90° .

At -110° the second SF_2 signal had increased again at the expense of the first, but again without changing the original ratio.

A possible interpretation of these spectral changes is that at -90° or above, the SF_2 group undergoes partial rotation resulting in an average SF_2 multiplet. At a lower temperature some of the SF_2 groups become immobilized in a more thermodynamically favored position.

At still lower temperatures the more stable configuration which is responsible for the second SF_2 quintet becomes predominant.

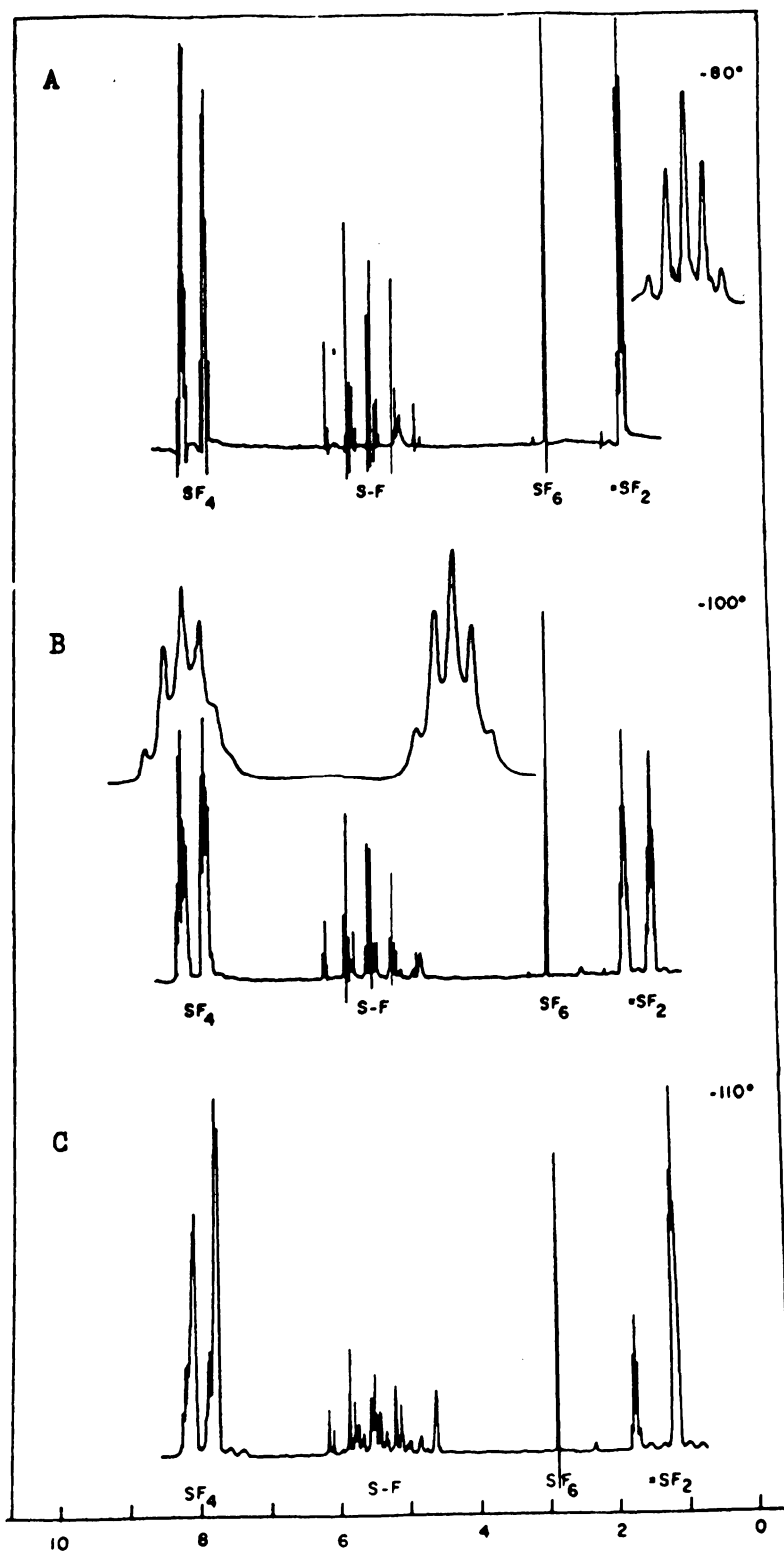


Figure 15. Fluorine-19 nmr spectra of $\text{SF}_5\text{N}=\text{SF}_2$ at different temperatures.

An alternative explanation for the observed spectral changes is also possible. Instead of freezing the partial rotation of the SF₂ group about the S(IV)-N multiple bond, a rotation of the SF₅ group about the nitrogen single bond may occur which is frozen out at lower temperatures.

To distinguish between these possibilities spectra of SF₅NCO at various temperatures were compared with those of SF₅N=SF₂ in the same solution. Should the spectral changes originate from internal rotation of the SF₅ group, the spectrum of SF₅NCO at room temperature would exhibit an AB₄ relationship, but if rotation is slowed, an AB₂C₂ spectrum should be observed. In the case of SF₅N=SF₂ in addition to such changes in the SF₅ region a change in the SF₂ region is also to be anticipated, since upon cessation of rotation of the SF₅ group the basal fluorines are no longer equivalent and the quintet they cause at room temperature should change to a triplet.

This study was therefore aimed at assigning the temperature in which the rotation of the SF₅ group in both SF₅NCO and SF₅N=SF₂ is stopped and comparing the results with those of the pure SF₅N=SF₂.

As can be seen, at -95° where the lower temperature quintet for the SF₂ group (in SF₅N=SF₂) begins to appear, the SF₅ spectra in both SF₅N=SF₂ and SF₅NCO remain unchanged. At -112°, however, where the low temperature quintet for SF₂ has become predominant, the AB₂C₂ pattern for the SF₅ group is much in evidence. In addition the "quintet" for the SF₂ group changed to a symmetrical triplet.

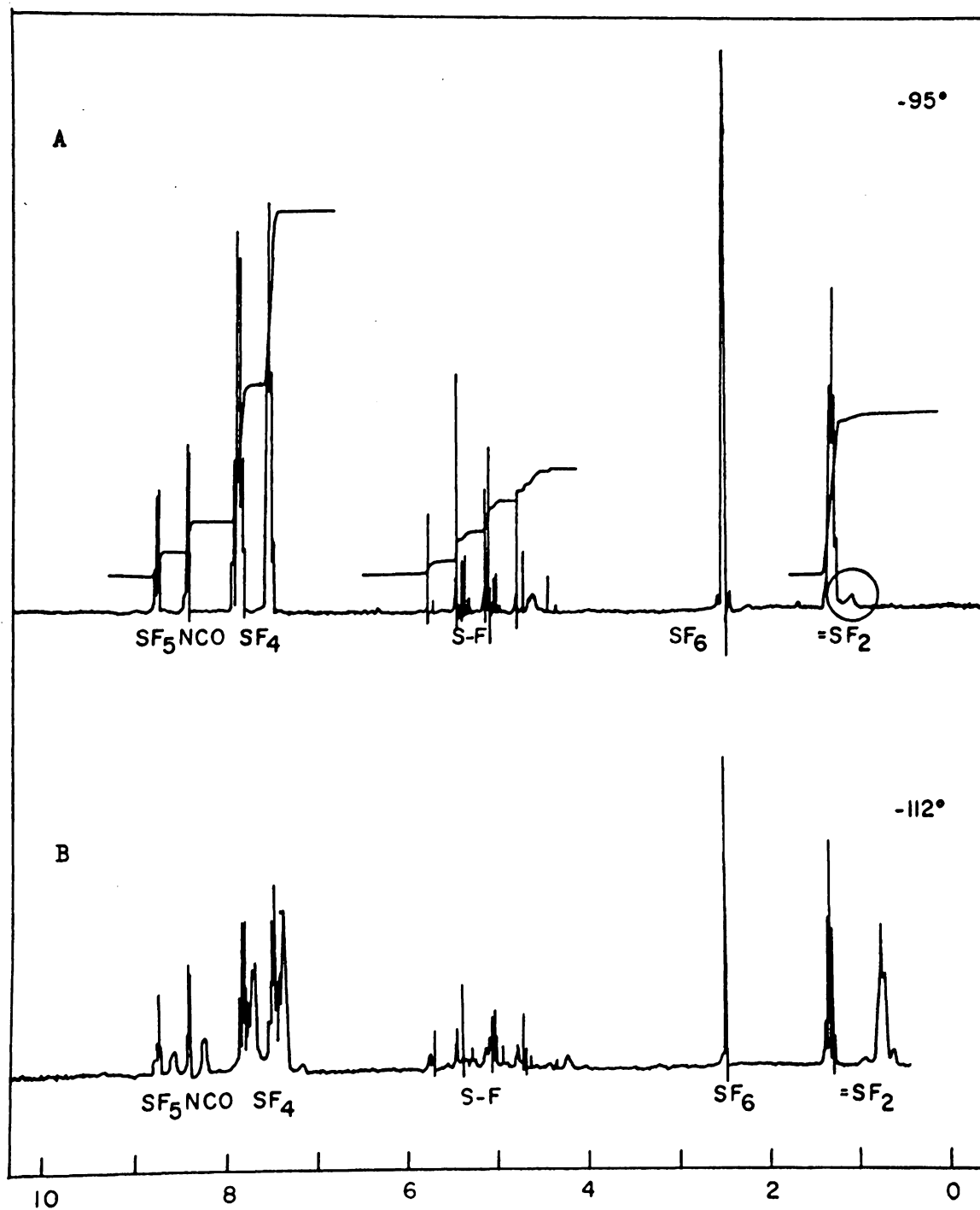


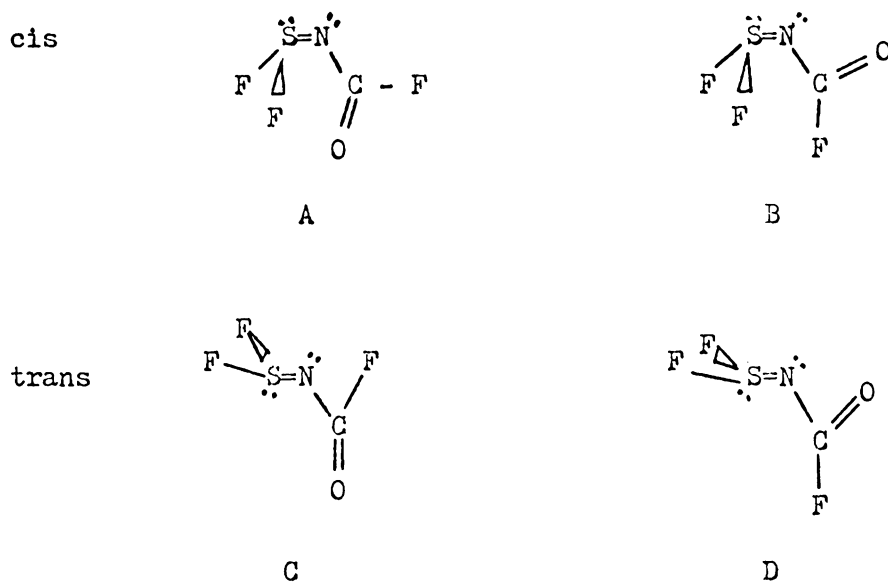
Figure 16. Fluorine-19 nmr spectra of a mixture of $\text{SF}_5\text{N}=\text{SF}_2$ and SF_5NCO .

It is believed, therefore, that the evidence clearly indicates (1) that at temperatures above -90° free rotation of the SF_5 group and oscillation of the SF_2 group occur in $\text{SF}_5\text{N}=\text{SF}_2$; (2) that the replacement of the " SF_2 " quintet by another at lower temperature is due to the cessation of free rotation about the N-S double bond and (3) that at lower temperature yet (below about -105°) free rotation about the N-S single bond ceases because of the steric interference of the cis SF_2 group with the SF_5 basal fluorines. In this regard, it should be noted that if the SF_2 were frozen in the trans configuration, there would be essentially no interference with the rotation of the SF_5 group.

2. Low Temperature nmr Studies of Fluoroformyliminosulfur Difluoride.

The question arises whether conjugation would "tie down" one end of the $\text{p}\pi\text{-d}\pi$ double bond and cause a restriction of rotation of the SF_2 group.

In the case of $\text{FC}(\text{O})\text{N}=\text{SF}_2$ construction of the molecular model indicates that there should be little steric restriction to rotation around either the N=S or the N-C bond. If rotation of the COF and SF_2 groups occurs, splitting of the F-19 peak of one group by the other, while expected, perhaps would not be enough to be observed. On the other hand, if the two double bonds are conjugated, splitting would be expected to be greater, as has been observed for the similar compound $\text{F}_2\text{C}=\text{CFC}(\text{O})\text{F}$, if form B, as shown below, is the favored conformer.



To test this hypothesis, the F-19 nmr spectrum of $\text{SF}_2=\text{NC}(\text{O})\text{F}$ dissolved in $\text{CF}_3\text{CF}=\text{CF}_2$, propane, or diethyl ether was obtained at various temperatures, as shown in Figure 17A.

The fluorine-19 nuclear magnetic resonance spectrum of $\text{SF}_2\text{N}-\text{C}(\text{O})\text{F}$ obtained at 25° consisted of two fluorine resonances (singlets) of relative intensity 2:1 assigned to SF_2 and $\text{N}-\text{C}(\text{O})\text{F}$ fluorine atoms respectively. The former occurring at -118.2 ppm and the latter at -96.7 ppm. The spectrum at room temperature was devoid of any fine structure.

Lowering the temperature caused a splitting of the nmr singlets - the S-F peak into a doublet and the C-F peak into a triplet (Figure 17B). At still lower temperature (-90°) the pattern became highly symmetrical (Figure 17C).

Since splitting of the fluorine nmr peaks was not observed at room temperature but only at and below -80° , it would be reasonable

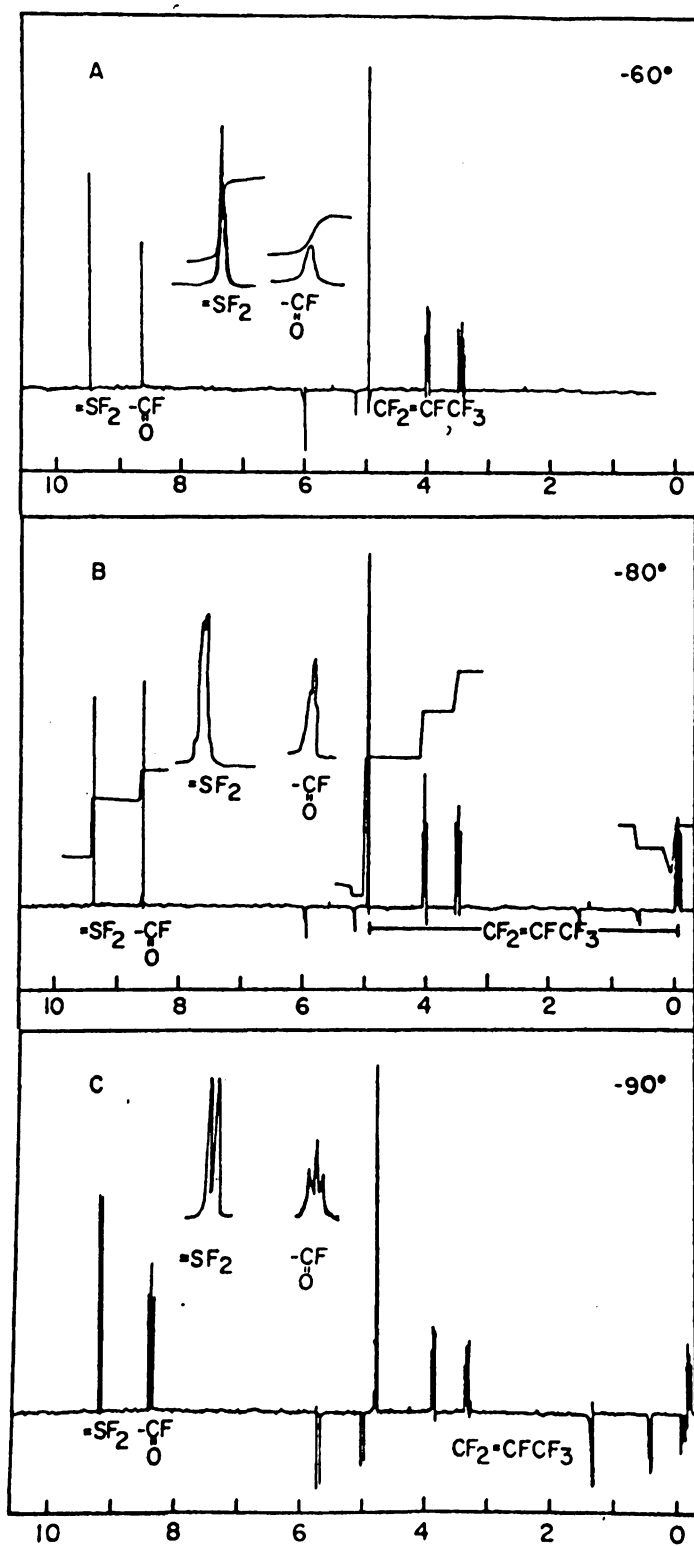


Figure 17. Fluorine-19 nmr spectra of $\text{SF}_2=\text{NC}(\text{O})\text{F}$

to assume that the molecule exists in different structural forms at different temperatures.

Highly symmetrical nmr patterns (such as those observed at -90°) are generally associated with symmetrical structures. Thus $\text{SF}_2=\text{N}-\text{C}(\text{O})\text{F}$ favors a symmetrical structure at low temperature. That this structure is not the result of steric influences is strongly indicated by the fact that the change to symmetrical structure occurs at a higher temperature for $\text{SF}_2=\text{NCOF}$ than for the sterically much more hindered $\text{SF}_5\text{N}=\text{SF}_2$. Since all such symmetrical structures possible for $\text{SF}_2=\text{N}(\text{O})\text{F}$ possess a plane element of symmetry for both the C=O and the S=N multiple bonds, the requirement for conjugation has been satisfied and very probably occurs.

Summary

The role of d- orbitals is fundamental in inorganic chemistry, and is of special importance in the higher oxidation states of elements like sulfur, where multiple bonding is a common phenomenon. For many years there has been debate concerning the possibility of free rotation around such multiple bonds. The present study addresses itself to this problem and has evolved a dual theoretical and experimental approach.

The compounds used for this study ($\text{SF}_5\text{N}=\text{SF}_2$, $\text{CF}_3\text{N}=\text{SF}_2$, $\text{C}_2\text{F}_5\text{N}=\text{SF}_2$ and $\text{FCO}=\text{SF}_2$) were treated theoretically by extended Hückel calculations and experimentally by low temperature F-19 nmr studies.

The calculation of total energy of the molecule as a function of rotation about the N-S(IV) multiple bond showed that the total energy curve possesses a broad and flat minimum. Thus any rotomers derived

with only slight excitation would possess equal energy. Therefore, this multiple bond is non-rigid, in contrast to the usual concept of $p\pi-p\pi$ bonding.

The d-orbital contribution accounts for approximately 50% of the total π -bonding and is practically independent of the nature of the substituents on the nitrogen atom.

CHAPTER 5. EXPERIMENTAL

A. Equipment

Reactions were carried out in reactors of three general types: Metal (stainless steel and Monel), Kel-F, and glass (Pyrex, Quartz).

Metal cylinders of two types were used, stainless steel 316 (30 ml and 75 ml capacity) and Monel (90 ml capacity) both from Hoke (Hoke, Inc., Creskill, N.J.) they were equipped with Whitey D.K. series valves (Crawford Fitting Co., Cleveland, Ohio). In some instances Hoke's 300 series needle valves were also employed.

Teflon tape (Crawford Fitting Co., Cleveland, Ohio) was applied to the threads on the fittings to provide lead-tight seals.

The reactor assembly was completed by connecting a ball-and-socket Kovar-Pyrex tubing to the valve using Swagelok unions and ferrules. The reactor could then be attached directly to a glass vacuum system.

Kel-F reactors were assembled from Kel-F reaction tubes, (Argonne National Laboratory) fitted brass female flare nuts, and Kel-F tapered plugs drilled and threaded to provide vacuum-tight seals when the Kel-F plugs were screwed into the brass nuts.

Pyrex reaction vessels, equipped with Teflon high vacuum stopcocks (Montes, Vineland, N.J.) were used for many of the reactions where hydrofluoric acid was not a problem. Quartz reaction vessels, with breakable seals, 12 in. long and 1 in. O.D. were used for u.v.-catalyzed reactions.

Storage vessels. Reaction materials were stored in the Hoke stainless steel cylinders. More inert materials were stored in glass

bulbs. For low temperature storage, long tubes fitted with vacuum stopcocks were utilized. When placed in Dewar flasks which contained Dry Ice or liquid nitrogen, the stopcocks were far enough removed to remain warm, thus reducing channeling.

Vacuum System. An all Pyrex glass vacuum system equipped with Teflon high vacuum stopcocks (Kontes, Vineland, N.J.) was used for measurements, handling and purification of volatile reactants and products. Materials were added to and removed from the line by using containers attached to the lower manifold through ball-and-socket joints.

All vacuum stopcocks and ground glass joints were lubricated with Halocarbon wax or grease (Halocarbon Products Corps., Hackensack, N.J.).

High vacuum measurements were made using a Hastings VT-GS gauge and gauge tube (Hastings-Raydist, Hampton, Va.).

An auxiliary system constructed of copper tubing and Whitey IKS4 (brass) valves with an open ended manometer of Kel-F tubing was used for handling anhydrous HF. A coil of Kel-F tubing was used for measurement of liquid HF volume.

Infrared spectra. In the range of 4000-250 cm^{-1} spectra were recorded using a Beckman IR-20 AX infrared spectrometer. The spectra were used routinely to determine the purity of materials and efficiency of separations.

Spectra of gas samples were taken using 10 cm gas cells fitted with sodium chloride or potassium bromide windows. The windows were attached to the cell body using either Plibond adhesive or by means of 15 mm I.D. glass connectors, with type M "O" ring and held in place with cover-plates, equipped with springs.

Nuclear Magnetic Resonance Spectra

The proton and fluorine nuclear magnetic resonance spectra were obtained on a JEOL PS-100 at 100 MHz and 94 MHz, respectively. All fluorine spectra are referred to Freon 11.

Volatile compounds were condensed into nmr tubes on the vacuum line and whenever possible Freon 11 was added as internal standard. The tubes were sealed on the vacuum system and allowed to warm up to room temperature before being subjected to nmr studies.

Elemental Analysis

Carbon, hydrogen and nitrogen analysis was performed by the Department analysts on a Perkin-Elmer 240 elemental analyzer.

B. Starting Materials

Sulfur tetrafluoride (Matheson) was used directly from the cylinder. Considerable thionyl fluoride was present as an impurity, but this should not have affected the reactions.

Anhydrous hydrogen fluoride, furnished by Blockson Chemical Division of Olin Matheson Corp., was used without further treatment.

Fluorine (General Chemical Division of Allied Chemical) was passed over sodium fluoride pellets before use to remove HF. Other impurities such as OF_2 , were not removed.

Phosphorus pentafluoride (Matheson) was used directly from the cylinder.

Boron trifluoride (Matheson) was used without further purification.

Sodium fluoride pellets (Harshaw) were heated at 180° for several hr before use.

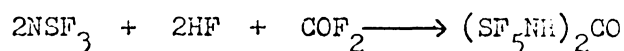
Silver(II) fluoride, technical grade, was purchased from Ozark Mahoning Corporation. Later on we prepared AgF_2 by fluorination of AgF with elemental fluorine.

Cesium fluoride, powder, (Ozark Mahoning Corp.) was dried at 200° in a vacuum for 18 hr, crushed and redried for additional 6 hr, before use.

Fluoroformyliminosulfur difluoride, FC(O)N=SF_2 , was prepared by heating SF_4 with Si(NCO)_4 . An increased yield has been obtained by running the reaction at room temperature.

Thiazyl trifluoride, NSF_3 , was prepared by fluorination of fluoro-sufanyliminosulfur difluoride, FC(O)N=SF_2 , with silver(II) fluoride according to Clifford and Stanton. An increased yield has been obtained using a 75-ml stainless steel (Hoke) cylinder and keeping the reactor at room temperature for 8 hr.

N,N'-Bis(pentafluorosulfanyl)urea, $(\text{SF}_5\text{NH})_2\text{CO}$, was prepared according to the method of Clifford and Shaddix⁴⁴ using the exact ratio of reactants required by the equation



Quantities of 50 mmol of NSF_3 , 25 mmol of COF_2 and 50 mmol of HF were condensed into a Kel-F reactor. The vessel was allowed to warm to room temperature and remain for seven days. Crystals were observed to form after only a few hours, but substantial amounts of liquid remained for several days. After seven days the volatiles were transferred to a cylinder containing NaF pellets to absorb the HF . After most of the volatiles were condensed into the NaF trap, the Kel-F reactor was warmed

to 35° to help remove any residual HF or SF_5NH_2 from the urea. This was necessary because of the tendency of SF_5NH_2 to coprecipitate with the urea. After the NaF trap containing the volatiles had been allowed to warm to room temperature, the volatiles were transferred to the vacuum line and separated by trap-to-trap distillation. The -78° trap (Dry Ice slush) contained SF_5NH_2 while the -131° trap (n-pentane slush) contained NSF_3 and SF_5NCO . No unreacted COF_2 was found. The Kel-F reactor was opened and found to contain 6.5 g (83% yield) of white crystals of the urea. Changing the ratios of reactants only decreased the yield. Any impurities in the urea were removed by sublimation at 90° under high vacuum.

Pentafluorosulfanylamine, SF_5NH_2 , was prepared by the addition of HF to thiazyl trifluoride as described by Clifford and Duncan.³²

C. Experiments

1. Preparation of Pentafluorosulfanyl Isocyanate, SF_5NCO .

a. N,N'-Bis(pentafluorosulfanyl)urea with $COCl_2$.

A slight molar excess of phosgene, $COCl_2$, was introduced into a 75 ml stainless steel Hoke cylinder containing 0.31 g of the urea, $SF_5NHCONHSF_5$, and left at room temperature over night. The pressure was found to be unchanged and infrared spectrum showed peaks belonging only to phosgene.

The phosgene was recondensed into the reactor and the mixture heated at 120° for 12 hr. The reactor was allowed to cool to room temperature and the gaseous product was transferred to the vacuum line. The pressure was found to have increased and the infrared spectrum indicated the

presence of HCl, unreacted phosgene, carbonyl chlorofluoride, COClF , thiazyl trifluoride and pentafluorosulfanyl isocyanate $\text{SF}_5\text{N}=\text{C}=\text{O}$.

The infrared spectra obtained from an independent reaction between $\text{N,N}'$ -bis(pentafluorosulfanyl)urea and phosgene under milder reaction conditions (80° , 6 hr.) was found to be similar to those obtained for the reaction at 120° , 12 hr. but in addition peaks at 1390 and 1595 cm^{-1} were observed.

b. $\text{N,N}'$ -Bis(pentafluorosulfanyl)urea with COF_2 .

Carbonyl fluoride (3.1 mmol) was condensed into a 75 ml stainless steel Hoke cylinder containing 0.96 g (3 mmol) of substituted urea, $\text{SF}_5\text{NHCONHSF}_5$, and left at room temperature overnight. The products were placed over NaF pellets for 4 hr. to remove HF and then transferred into the vacuum line. The pressure was found to be unchanged, and the infrared spectrum showed peaks belonging only to COF_2 .

Carbonyl fluoride was recondensed into the reactor and heated to 100° for 12 hrs. The cylinder was removed from the oven and allowed to cool to room temperature. It was then placed over NaF pellets for 3 hrs. A definite increase in pressure was observed and the infrared spectrum showed that the mixture consisted of only two compounds, mainly SF_5NCO and a small amount of unreacted carbonyl fluoride.

The mixture was separated by passing the gases through two traps cooled to -119° (ethyl bromide) and -196° (liquid N_2) respectively. The contents of the -119° trap was pure SF_5NCO , identified by both infrared and F-19 nuclear magnetic resonance. This represents a 74% yield of pentafluorosulfanyl isocyanate.

2. Nucleophilic Substitution Reaction

a. Reaction of SF₅NCO with (CH₃)₂SO

Pentafluorosulfanyl isocyanate, 4.2 mmol, was condensed into a Kel-F reactor equipped with a magnetic stirrer and containing 1.1 ml of freshly distilled (CH₃)₂SO. The mixture was allowed to warm to room temperature and maintained for 5 days with continuous stirring. Crystals were observed to have formed after several hours. After 5 days the reactor was cooled to -45° and the volatile compounds were transferred to an evacuated glass vessel. The volatile components were found by infrared spectrum to consist mainly of carbon dioxide (3.5 μ m) and traces of SF₅NCO. The reactor was opened in a drybox for examination of the products. This procedure was adopted to avoid getting dimethyl sulfoxide into the vacuum system.

The F-19 nmr spectrum, obtained at room temperature (Figure 3A) on the saturated (CH₃)₂SO product solution, showed a characteristic AB₄ pattern for the SF₅ group. The broad doublet for the basal fluorine atoms, centered at -92.4 ppm relative to external Freon-11, and the 9-line multiplet for the apical fluorine, centered at -113.3 ppm, had the expected intensity ratio of 4 to 1 and a coupling constant of 154 cps.

The H-1 nmr spectrum (Figure 3B) had in addition to a very broad peak for the hydrogens of the (CH₃)₂SO, centered at 2.5 ppm relative to external tetramethylsilane (TMS), a peak at 2.98 ppm corresponding to the methyl groups of the -N=S(CH₃)₂ moiety, in agreement with the methyl chemical shifts observed by Roesky et al.⁴⁷ and by Appel et al.⁴⁸ for other N=S(CH₃)₂ containing compounds.

The infrared spectrum of the isolated product showed a broad band at 1250 cm^{-1} assigned to the S(IV)-N stretching vibration and peaks at 3250, 3050, 2950, and 1360 cm^{-1} assigned to the C-H bonds of the methyl groups and at 905, 860, and 602 cm^{-1} assigned to stretching vibrations of the SF_5 group. A weak band observed at 1400 cm^{-1} is probably attributable to some residual $(\text{CH}_3)_2\text{SO}$.

The crystalline product was very hygroscopic. It melted over a range of several degrees in the vicinity of 72° .

b. Reaction of SF_5NCO with $\text{C}_6\text{H}_5\text{CHO}$

Pentafluorosulfanyl isocyanate 2.7 mmol was condensed into a Kel-F reactor equipped with a magnetic stirrer and contained 1.0 ml of freshly distilled benzaldehyde. The reactor was allowed to warm up progressively to room temperature and maintained at this temperature for 2 days with continuous stirring. No crystals were formed but the solution turned yellow after several hours. At the end of 2 days the reactor was cooled to -45° (chlorobenzene) and the volatile products were transferred to an evacuated glass vessel. The products were worked up as before. Carbon dioxide was identified by its infrared spectrum.

The F-19 nuclear magnetic resonance spectrum (Figure) of the saturated benzaldehyde solution showed the usual AB_4 pattern for the SF_5 group: apical F at -80.4 ppm, basal at -58.8 ppm, coupling constant, 157 cps.

The infrared spectrum (Nujol) exhibited a C=N resonance at 1630 cm^{-1} , higher than for the usual organic C=N frequency, presumably because of the great electron-withdrawing power of the SF_5 group. Characteristic SF_5 bands occurred at 915, 860 and 600 cm^{-1} .

The mass spectrum, which also served to confirm the identity of the compound, follows. The molecule ion peak was observed at m/e 231 (relative intensity 8.5%) with an isotopic distribution consistent with one sulfur atom in the molecule. The largest peak was that of SF_5^+ , m/e 127, with the second largest at m/e 230 assigned to $SF_5NCC_6H_5^+$. Peaks at m/e 211 (12.4%) $SF_4NC_7H_5^+$, m/e 153 (17%) SF_5NC^+ , m/e 141 (11.2%) SF_5N^+ , m/e 103 (18.4%) $C_6H_5CN^+$, m/e 70 (42.6%) SF_2 were also identified.

The melting point was carried out in a wax sealed capillary and was found to be 131-134°C.

c. Attempted Reaction Between SF_5NCO with OsO_4 .

Pentafluorosulfanyl isocyanate, 1.2 mmol, was condensed into a Kel-F reactor containing 0.2 g osmium tetroxide in 5-ml of dry and degassed pentane. The reactor was allowed to warm up to -78° (Dry Ice-acetone slush) where it was left for 6 hr. Volatile products were removed from the reactor, the pressure was found to be unchanged, and the infrared spectrum showed only bands not due to SF_5NCO .

Pentafluorosulfanyl isocyanate was recondensed into the reactor and the temperature was raised to -63° (chloroform slush) for 6 hr. Again there was no evidence for reaction.

d. Attempted Reaction Between SF_5NCO with UO_3 .

Pentafluorosulfanyl isocyanate, 1.4 mmol, was condensed into a Kel-F reactor containing 3.0 g of UO_3 . The reactor was allowed to warm up to -78° (Dry Ice-acetone slush) for 6 hr. and then to -63° (chloroform slush) for additional 6 hr. The volatile products showed only peaks but those assigned to SF_5NCO . SF_5NCO was recondensed and the

mixture allowed to warm to 0° for 6 hr. and finally to room temperature. Again no reaction was observed to take place.

e. Attempted Reaction Between ClSO_2NCO with UO_3 .

Chlorosulfonyl isocyanate, 1.2-ml, was added to 0.3 g of uranium oxide, UO_3 , and the mixture was allowed to remain at room temperature in a dry box with continuous stirring.

After 6 days the solution was filtered and the liquid analyzed by infrared spectroscopy. No reaction took place and the infrared spectrum showed bands due only to the starting material.

3. Exchange Reaction

a. Reaction of SF_5NCO and PCl_5

Pentafluorosulfanyl isocyanate 3.6 mmol was condensed into a 75-ml Hoke stainless steel cylinder containing excess of PCl_5 (2.6 g) and allowed to react overnight at room temperature. The infrared spectrum showed several new peaks of low intensity in addition to those assigned to SF_5NCO .

The material was condensed back into the reactor and the mixture heated to 60° for 6 hours and 80° for 3 hours. The cylinder was allowed to cool to room temperature and the volatile products were transferred to the vacuum line and distilled. The -45° trap (chlorobenzene) contained a colorless liquid identified as POCl_3 by means of infrared spectroscopy. The content of the -78° trap (Dry Ice-acetone) was redistilled several times before samples were submitted to spectroscopic analysis.

The infrared spectrum had a peak at 1655 cm^{-1} which were assigned to C=N absorption, a doublet at 885 and 915 cm^{-1} , and a strong absorption at 603 cm^{-1} characteristic of the SF_5 group. The peaks at 800 cm^{-1} and 948 cm^{-1} were assigned to symmetrical and asymmetrical $=\text{CCl}_2$ stretchings, respectively. This was in good agreement with the reported values for $\text{FSO}_2\text{N}=\text{CCl}_2$ and $\text{ClSO}_2\text{N}=\text{CCl}_2$ given by Roesky and Biermann.⁵⁵

The F-19 nmr spectrum (Figure 5) exhibited a multiplet for the basal fluorine atoms, centered at -62.6 ppm relative to internal Freon-11, and the apical multiplet, centered at -67.2 ppm with a coupling constant of 156 cps. The spectroscopic results correlated well with those reported by Tullock, et al.^{30,31}

Further reactions with $\text{SF}_5\text{N}=\text{CCl}_2$ will be described on p. 93.

4. Coupling Reaction

a. Fluorination of SF_5NCO with AgF_2

Pentafluorosulfanyl isocyanate, 4.2 mmol, was condensed into a 75 -ml Hoke stainless steel cylinder containing an excess of silver difluoride. The cylinder was allowed to warm to room temperature and was left in this condition for 12 hr. The infrared spectrum of the volatile products (Figure 6A) showed the presence of a new peak at 1380 cm^{-1} and an intense peak at 600 cm^{-1} together with a small quantity of SF_6 and COF_2 . Major bands were due to unreacted SF_5NCO . The volatile products were recondensed into the reactor and heated to 80° for 12 hr. The infrared spectrum (Figure 6B) obtained under similar

conditions indicated that the absorption bands at 1380 cm^{-1} and 600 cm^{-1} largely decreased, the SF_6 content increased but no change was observed in the intensity of the band corresponding to COF_2 . The major infrared peaks were due to unreacted SF_5NCO .

The volatile compound was condensed back into the cylinder loaded with an additional 2 g of silver difluoride and allowed to stay at room temperature an additional 6 hr. The infrared spectrum of the reaction products (Figure 6C) showed an increase in the 1380 cm^{-1} band, 600 cm^{-1} band and in the extent of COF_2 . The major peak was due to unreacted SF_5NCO .

The fluorine-19 nmr spectrum of the reaction mixture in Freon 11 (1:5) and the mass spectrum showed only peaks due to SF_5NCO and SF_6 .

5. New Method for the Preparation of $\text{SF}_5\text{N}=\text{SF}_2$

a. Photolysis of Thiazyl Trifluoride

The photolysis reaction was carried out in an ultraviolet photochemical reactor model RPR-204 (Southern New England Ultraviolet Company, Middletown, Connecticut) consisting of four low pressure mercury resonance arcs arranged in a square, air cooled with a maximum intensity output of 60 watts at 2537Å .

A pure sample of thiazyl trifluoride (3.06 mmol) in a sealed quartz tube (12"X1") was irradiated for 12 hr. at room temperature.

The reactor walls were found to be covered with a yellow solid. The reactor was connected to the vacuum line and the volatile products separated by trap-to-trap distillation using a set of traps cooled to -78° , -119° , -131° , and -196° , respectively.

The -78° trap contained a yellow material that could not be removed from the trap by pumping (probably polymerized material). The content of the -119° trap (ethyl bromide) was pure $\text{SF}_5\text{N}=\text{SF}_2$ amounting to 34% yield and the -131° trap (n-pentane) contained unreacted thiazyl trifluoride.

The yellow solid remaining in the reaction vessel was dissolved in acetonitrile and its F-19 nmr spectrum recorded. The spectrum indicated that in addition to a small quantity of a thiazyl monofluoride the main fluorine absorption was a broad singlet at -236 ppm (relative to external Freon 11) a bare region of reported fluorine resonance.

The photolysis reaction has been carried out several times for shorter periods of irradiation. Infrared spectra showed that even after 1 hr. of irradiation separable quantities of $\text{SF}_5\text{N}=\text{SF}_2$ were produced. More powerful uv sources (Hanovia M. pressure mercury resonance arc, 450 watt) required only 3-15 minutes to obtain the same results.

6. Exchange Reactions of $\text{SF}_5\text{N}=\text{SF}_2$

a. Reaction of $\text{SF}_5\text{N}=\text{SF}_2$ with PCl_5

Pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$, 4.2 mmol, was condensed into a 75-ml stainless steel Hoke cylinder containing 3 g of PCl_5 and allowed to warm up to room temperature, where it was left for 48 hrs. The volatile products were separated on the vacuum line by means of trap-to-trap distillation using a set of traps cooled to -45° , -78° , -131° and -196° , respectively. The -78° trap (Dry Ice-acetone) contained a minute amount of yellow-red compound shown by

F-19 nmr not to possess an SF_5 group. No further work was done on this compound. The fraction which was retained in the -45° trap (chlorobenzene), a pale yellow liquid, was further fractionated until no changes in color or infrared spectrum were observed. Yield of product about 2.7 mmol (65%), was subsequently identified by ir, nmr and mass spectra as pentafluorosulfanyliminosulfur dichloride, $\text{SF}_5\text{N}=\text{SCl}_2$.

Elemental analysis was difficult because of the great susceptibility of the compound to hydrolysis but yielded the following results: Anal. Calcd. for SF_5NSCl_2 : S, 26.2; N, 5.73; Cl, 29.1. Found: S, 27.9; N, 7.01; Cl, 28.8.

The strong peak in the infrared spectrum, Figure 7, at 1235 cm^{-1} was assigned to N=S stretching vibration and is in good agreement with the frequencies tabulated for N=S derivatives by Glemser and Biermann.⁶³ The doublet at 910, 855 cm^{-1} and the intense absorption at 600 cm^{-1} are highly characteristic of the SF_5 group. The band at 475 cm^{-1} and 415 cm^{-1} was attributed to $=\text{SCl}_2$ group in agreement with similar compounds.^{64,65} With some variations these peaks were reported for this compound by Clifford and Goel⁶¹ and are in general agreement.

One part of the -45° fraction dissolved in 5 parts of Freon 11 displayed the F-19 nmr spectrum given in Figure 8. The spectrum showed a similar arrangement to those found previously for $\text{SF}_5\text{NHCONHSF}_5$ where the peaks due to the apical fluorine and basal fluorine lie very close to each other, with the center for the apical fluorine at -73.5 ppm and the basal fluorine at -76.6 ppm (from internal Freon 11). The coupling constant was determined from the spectrum to be cps.

Mass spectral peaks at m/e 210 and 208, in approximate ratio of 3:1 attributable to $S_2F_5NCl^+$ and the largest peak at m/e 127 attributed to SF_5^+ supported the assignment of the formula as $SF_5N=SCl_2$.

b. Reaction of $SF_5N=SF_2$ and $SiCl_4$

The silicon-chlorine bond is highly susceptible to exchange reactions in the presence of fluorinated compounds. This reaction yields the highly volatile SiF_4 . It was hoped, therefore, that an exchange reaction with $SF_5N=SF_2$ would proceed under mild conditions to form easily separable exchange products.

Equimolar quantities of pentafluorosulfanyliminosulfur difluoride and silicon tetrachloride were condensed into a 75-ml stainless steel Hoke cylinder and allowed to warm to room temperature. After 12 hr. the infrared spectrum showed no peaks other than those assigned to the starting materials. The volatile materials were recondensed and heated to 100° for 6 hr. Infrared spectra of the products indicated that $SF_5N=SCl_2$ was produced together with SiF_4 ; however, peaks due to unreacted $SF_5N=SF_2$ were also observed and could not be entirely eliminated even under more vigorous conditions (150° for 6 hr.).

Pentafluorosulfanyliminosulfur dichloride was separated in the usual manner on the vacuum line and showed by means of infrared nmr and mass spectra to be identical to the product isolated from the reaction with phosphorus pentachloride.

c. Reaction of $SF_5N=SF_2$ and $AlCl_3$

In an attempt to develop an exchange procedure that would result in formation of $SF_5N=SCl_2$ as the sole volatile product, 4.2 mmol of

Table 4

Mass Spectra of the Fraction Collected at -42°

| m/e | Intensity | | m/e | Intensity | | m/e | Intensity | |
|-----|-----------|--|-----|-----------|------|-----|-----------|------|
| | 80° | | | 80° | 100° | | 80° | 100° |
| 28 | 78 | | 47 | 8 | - | 148 | - | 20 |
| 29 | 40 | | 49 | 9 | - | 149 | - | 24 |
| 30 | 16 | | 64 | 20 | - | 150 | - | 5 |
| 31 | 8 | | 70 | 100 | - | 162 | - | 24 |
| 32 | 50 | | 72 | 92 | - | 163 | - | 4 |
| 35 | 96 | | 74 | 50 | - | 164 | - | 2 |
| 36 | 96 | | 77 | 49 | - | 169 | - | 9 |
| 37 | 80 | | 105 | 36 | 98 | 180 | - | 13 |
| 38 | 84 | | 106 | 4 | 40 | 217 | - | 6 |
| 39 | 25 | | 112 | 26 | 80 | 228 | - | 8 |
| 40 | 6 | | 113 | 2 | 20 | 240 | - | 4 |
| 41 | 18 | | 114 | 8 | 62 | 251 | - | 22 |
| 42 | 16 | | 119 | - | 16 | | | |
| 43 | 18 | | 120 | 6 | 58 | | | |
| 44 | 24 | | 121 | - | 4 | | | |
| 45 | 4 | | 127 | 5 | 48 | | | |
| 46 | 6 | | 131 | 2 | 25 | | | |

$\text{SF}_5\text{N}=\text{SF}_2$ were condensed into a 75-ml stainless steel Hoke cylinder containing excess anhydrous AlCl_3 (2 g, 45 mmol). The mixture was allowed to warm to room temperature and was then heated to 100° for 6 hr. and 150° for 2 hr. The volatile products were transferred to the vacuum line and separated by trap-to-trap distillation using a set of traps cooled to -78° , -131° , and -196° , respectively.

The -78° trap (Dry Ice-acetone) contained a good yield of a pale yellow liquid which after several distillations was collected at a -45° trap (chlorobenzene). The infrared spectrum of the compound shown in Figure did not contain any peaks belonging to the SF_5 group. Similarly, the F-19 nmr spectrum showed no fluorine peaks at a wide scan.

The mass spectrum taken at 50 ev is given in Table 4. No further work has been devoted to this compound.

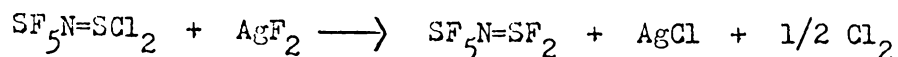
7. Reactions with $\text{SF}_5\text{N}=\text{SCl}_2$

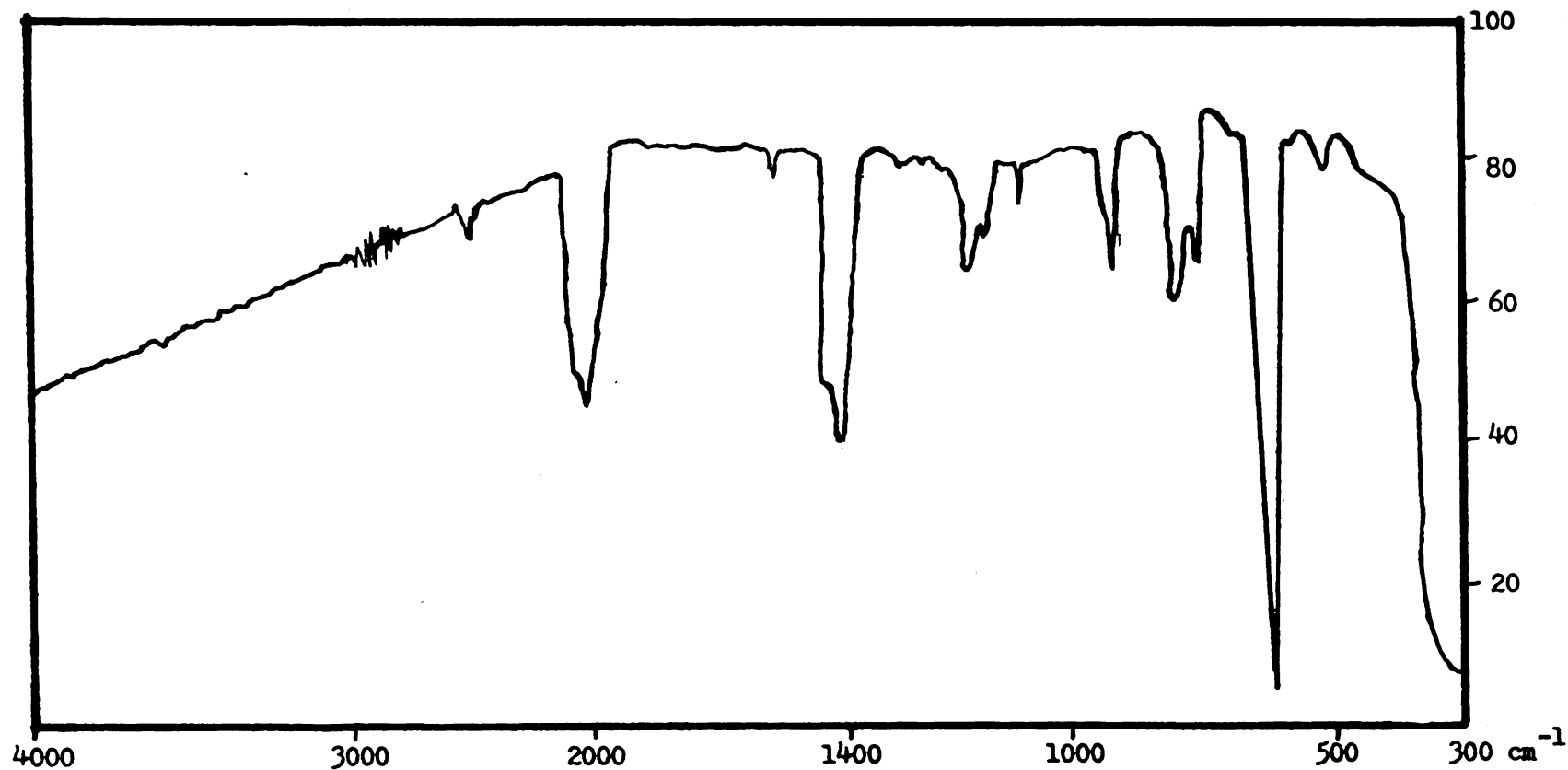
a. Reaction of $\text{SF}_5\text{N}=\text{SCl}_2$ with AgF_2

Pentafluorosulfanyliminosulfur dichloride, $\text{SF}_5\text{N}=\text{SCl}_2$, 2.7 mmol, was condensed into a 10-ml stainless steel Hoke cylinder containing excess of silver difluoride (2 g). The cylinder was left at room temperature for 6 hr. and then heated to 50° for an additional 6 hrs.

The volatile products were separated on the vacuum line. The -119 trap contained 2.5 mmol (92%) pure $\text{SF}_5\text{N}=\text{SF}_2$ identified by its infrared spectrum.

The reaction is presumed to be





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Figure 18. The infrared spectrum of the -42° trap obtained from the reaction between $\text{SF}_5\text{N}=\text{SF}_2$ and AlCl_3 .

b. Reaction of $\text{SF}_5\text{N}=\text{SCL}_2$ and SF_5NH_2

Pentafluorosulfanyliminosulfur dichloride (2.0 mmol) was condensed with a slight excess of SF_5NH_2 for a 1:2 molar ratio into a Kel-F reactor and allowed to react at room temperature for 18 hr. After the usual work up, the -196° trap contained mainly HCl, identified by its characteristic ir spectrum, and SiF_4 . The -131° trap contained thiazyl trifluoride, probably from decomposition of SF_5NH_2 . The -45° trap contained a deep yellow liquid subsequently identified as $\text{SF}_5\text{N}=\text{S}=\text{NSF}_5$. The yellow compound was redistilled several times and when the infrared spectrum remained unchanged, was subjected to spectroscopic analysis. The yield based on $\text{SF}_5\text{N}=\text{SCL}_2$ was 46%.

The infrared spectrum exhibited the following bands: 1445 (vs), 1265 (vs), 1068 (vs) cm^{-1} assigned to N=S=N group vibrations by comparison with related compounds.⁶⁶ These bands were also similar to those of SO_2 at 1361 cm^{-1} and 1151 cm^{-1} .⁶⁷ The doublet at 915 and 865 cm^{-1} and the strong absorption at 602 are characteristic of the SF_5 group.

The F-19 nmr (external Freon-11) showed a normal AB_4 spin system with the basal fluorines centered at -61.4 ppm and the apical fluorine at -65.0 ppm in a 4:1 ratio, respectively. The product was a viscous yellow liquid soluble in pentane, diethyl ether and, to a lesser extent, in CHCl_3 .

8. Preparation of Bis(pentafluorosulfanyl)carbodiimide.

a. Synthesis of $\text{SF}_5\text{N}=\text{PCl}_3$

Pentafluorosulfanylamine (4.2 mmol) and 3 g (14 mmol) PCl_5 were held at room temperature for 24 hr and the products then worked up as

usual. Hydrogen chloride, collected at -196° , was identified by its ir spectrum. The content of the -131° trap (n-pentane) was found to be N SF_3 identified by its ir spectrum. The pale yellow liquid collected at -42° was identified by its infrared spectrum, F-19 nmr spectrum and mass spectrum as $\text{SF}_5\text{N}=\text{PCl}_3$ and was obtained in 84% yield (3.5 mmol). Although it reacted with mercury, it was possible to determine that it had a vapor pressure of approximately 10 mm Hg at room temperature. The infrared spectrum (Figure 10) of the vapor showed a shouldered peak at $1230 (\text{m}) \text{ cm}^{-1}$ assigned to the P=N stretch and a peak at $470 (\text{s}) \text{ cm}^{-1}$ for the P-Cl stretch in good agreement with other $-\text{N}=\text{PCl}_3$ compounds.⁷⁰ The characteristic bands for the SF_5 group appeared at $915 (\text{s})$, $860 (\text{s})$ and 600 cm^{-1} .

The F-19 nmr spectrum (Figure 11) showed the apical nonuplet centered at -71.8 ppm and the basal doublet at -69.0 ppm . The coupling constant was 154.7 cps . In good agreement with other SF_5 , containing compounds.

Mass spectral analysis did not detect a parent peak. However, peaks at m/e 242 (relative intensity 12.4%) 244, and 246 in an approximate ratio 10:6.8:1, consistent with an isotopic distribution of two chlorine atoms in the molecule, were assigned to $\text{SF}_5\text{NPCl}_2^+$. The largest peak was that of SF_5^+ m/e 127 with the second largest at m/e 207 (41.8%) assigned to SF_5NPCl^+ . Peaks at m/e 176 (18%) SF_5NCl^+ , m/e 223 (11.8%) $\text{SF}_4\text{NPCl}_2^+$, m/e 153 (11.2%) SF_4NP^+ (2), m/e 141 (11.2%) SF_5N^+ , m/e 70 (38%) SF_2 were also identified and they support the assignment of the formula as SF_5NPCl_3 .

8. Attempts to Prepare Bis(pentafluorosulfanyl)carbodiimide.a. Attempted Reaction Between $\text{SF}_5\text{N}=\text{PCl}_3$ and SF_5NCO

Equimolar amounts of $\text{SF}_5\text{N}=\text{PCl}_3$ and $\text{SF}_5\text{N}=\text{CO}$ (2.7 mmol) were condensed into a 10-ml Hoke cylinder and allowed to react for 12 hr at room temperature. No change in pressure was observed and the infrared spectrum showed no new peaks. The gaseous compounds were recondensed into the reactor and allowed to react for an additional 12 hr at 80°C ; again no reaction was observed to take place.

b. Reaction Between $\text{SF}_5\text{N}=\text{CCl}_2$ and SF_5NH_2

Pentafluorosulfanyl dichloroazomethine (2.0 mmol) was condensed with a slight excess of SF_5NH_2 to give a 1.2 molar ratio into a Kel-F reactor and allowed to react at room temperature for 18 hr.

The infrared spectrum of the product mixture showed in addition to the presence of HCl , $\text{N}=\text{SF}_3$, SiF_4 , and unreacted starting materials, a peak at 2157 cm^{-1} which was assigned to an $\text{N}=\text{C}=\text{N}$ group (cf. 2150 cm^{-1} for organic carbodiimides)

The nmr spectrum exhibited the following peaks: a doublet with fine structure at -60.3 ppm and a multiplet of 8 lines of low intensity centered at -63.7 ppm assigned to the basal and apical fluorines in the SF_5 group.

Although the product was not isolated it appears highly probable from the spectroscopic evidence that $(\text{SF}_5\text{N}=\text{C})_2$ was indeed prepared.

PART II. THIAZYL TRIFLUORIDE COMPLEXES OF THE TRANSITION METAL

A. Introduction

The molecular orbital calculations on the iminosulfur difluoride group were performed in the hope of obtaining insight into potential synthetic applications. Little direct indication of such nature has been gained. The calculations did, however, indicate the possibility that internal rotation might be responsible for the lack of chemical reactivity, from a kinetic standpoint, by inhibiting the approach of the attacking species to the multiple bond.

If the flexibility and the dynamics of rotation were indeed the inhibiting factors governing reactivity, then it is reasonable to assume that a system capable of restricting such rotation should lead to increased reactivity.

Proceeding along this line of thought, the means of typing up an unsaturated compound in the manner least affecting its chemical characteristics was sought.

Unsaturated systems can be tied up by forming unsaturated-metal complexes. Studies of such complexes have indicated that the unsaturated moiety remains essentially intact and the bonding is presumed to involve interaction of metal atomic orbitals with a π -molecular orbital of the unsaturated system analogous to the π -bonding in ferrocene.

The degree of multiplicity of the unsaturated system, however, is reduced and butadiene-iron-carbonyl complexes, for example, resist hydrogenation, and do not undergo Diels-Alder type reactions. On the other hand, acetylenes and nitriles, which in comparison to olefins

are usually less reactive in the free form, form compounds with an increased degree of reactivity when complexed to metals.

The highly unsaturated thiazyl trifluoride may therefore well be suited to form metal complexes similar to those of acetylenes.

This novel species may play an important role as a chemical intermediate stimulating reactions at the unsaturated part with the metal serving as a template for the reaction and thus offering enhanced reactivity, stereospecificity, and reaction modes reserved to such systems as internal cyclization and carbonylations.

B. Results and Discussion.

Reactions of $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$ and $\text{Mn}(\text{CO})_6$ with thiazyl trifluoride resulted in formation of highly insoluble solids and carbon monoxide.

The reactions of nickel tetracarbonyl and iron pentacarbonyl took place at room temperature, while those of the molybdenum and manganese required higher temperatures and prolonged reaction times.

All compounds were found to be sensitive to atmospheric conditions and were handled in a dry box.

Elemental analysis was difficult and suffered from inconsistencies; nevertheless, N:S:F ratios of 1:1:3 have been observed.

The infrared spectra of the compounds showed bands assigned to N-S vibration at about 100 cm^{-1} lower frequency than in $\text{N}=\text{SF}_3$, but somewhat higher than in $-\text{N}=\text{SF}_2$. In addition, there were also bands assigned to bridging and nonbridging carbonyls.

Under controlled hydrolysis, the molybdenum carbonyl-thiazyl trifluoride complex released NSF_3 , identified by its infrared spectrum.

The mass spectra obtained for these compounds was very complex; no discernable molecular ion peak was observed.

However, in each case, peaks were observed corresponding to mass numbers which were too large to be explained in terms of a single metal atom in the complex.

The iron carbonyl complex was examined by means of Mössbauer spectroscopy (Figure 19). A spectrum similar to other iron carbonyl complexes was obtained, and the spectrum clearly shows that the iron atoms exist in a single oxidation state. This is also good evidence that the sample was not a mixture, but a pure complex.

The insolubility of these metal complexes in common organic solvents, the absence of crystallinity (determined by x-ray methods), and the observation of high mass peaks suggest that these complexes exist in the form of metal clusters.

The infrared absorption of the N-S stretch, the elemental analysis ratio of N:S:F (1:1:3), and the release of free NSF_3 by hydrolysis of the molybdenum carbonyl complexes indicate that thiazyl trifluoride remains as an undecomposed unit in the metal carbonyl cluster. The cluster is possibly in the form of a π -complex similar to the clusters formed between butadiene and the metal carbonyls.

Since the metal carbonyl-thiazyl trifluoride complexes did not have properties which made them amenable to detailed structural analysis (especially in light of their lack of crystallinity), attempts to prepare new types of metal complexes were explored. Ferrocene

appeared to be an attractive choice as a substrate since its physical and spectral properties are well defined, and as a result changes in these properties should be easily detected and give a clue as to the type of chemical transformation created by reaction with NSF_3 .

When the reaction between ferrocene and thiazyl trifluoride was carried out in our laboratory, the resulting product was found to be crystalline, and a member of the monoclinic structural group. Detailed x-ray analysis is currently being carried out by Dr. Fred Ross of the V.P.I. & S.U. Chemistry Department.

C. Experimental.

1. Reaction of Metal Carbonyl and Thiazyl Trifluoride.

a. Reaction of Nickel Tetracarbonyl and Thiazyl Trifluoride.

Nickel tetracarbonyl (0.5 ml; 0.65 g) was dissolved in 5 ml of anhydrous benzene and placed into a glass reaction vessel. Helium gas was passed through the solution to provide an inert atmosphere. After 15 minutes the helium flow was disconnected and replaced with a slow flow of thiazyl trifluoride.

A reaction took place within several minutes, with the precipitation of a dark brown solid from the reaction mixture. The solution was transferred to the dry-box, filtered, and the solid obtained was washed several times with absolute diethyl ether to dissolve unreacted starting material.

Exposure of the nickel carbonyl thiazyltrifluoride complex to air resulted in a rapid change in color from brown to gray. Since color

change did not occur under the nitrogen atmosphere in the dry box the compound is most probably sensitive to moisture, oxygen, or both.

The nickel carbonyl thiazyl trifluoride complex was found to be insoluble in the following solvents: dry carbon tetrachloride, chloroform, ethyl ether, acetonitrile and dimethyl sulfoxide.

The difficulty in handling $\text{Ni}(\text{CO})_4$ in the vacuum system, the sensitivity of the product to atmospheric exposure, and the hazard in working with nickel carbonyl terminated further experiments with this compound. Therefore, our focus was shifted to other carbonyl compounds.

b. Reaction Between Molybdenum Hexacarbonyl and Thiazyl Trifluoride.

Molybdenum hexacarbonyl, (0.2 g) was dissolved in 5 ml of dry benzene and placed in a glass reactor equipped with a magnetic stirrer. The reactor was connected to the vacuum system, the contents were frozen with liquid nitrogen, and the air removed. Thiazyl trifluoride was condensed into the reactor and the tube was sealed.

Reaction was not observed to take place at room temperature and the reactor was warmed to 80° . After 12 hrs., the reactor was opened, volatile product removed, and the brown-yellow solid transferred to the dry box.

The product was very sensitive to atmospheric exposure. Changes in color from light brown-yellow to deep brown took place rapidly when the product was exposed to air.

Elemental analysis of the reaction product was performed for carbon, hydrogen, and nitrogen on the department Perkin-Elmer 240

Elemental Analyzer, and for molybdenum, sulfur, and fluorine by means of Neutron Activation Analysis. The results from independent samples were inconsistent and gave the following percentages: carbon, 10.61-13.99; nitrogen, 2.93-3.14; sulfur, 3.6-4.46; molybdenum, 25.5, fluorine, 14.9.

The mass spectrum of molybdenum carbonyl-thiazyl trifluoride is given in Table 5. No clear parent peak was observed.

The infrared spectrum (Figure 19) had peaks at 1420 cm^{-1} , assigned to S N absorption (cf. 1515 cm^{-1} for N SF_3) 2380 cm^{-1} , 2372 cm^{-1} , and 1650 cm^{-1} , assigned to different types of carbonyl absorptions, and unidentified peaks at 925 cm^{-1} and 955 cm^{-1} of equal intensity.

Hydrolysis of the molybdenum carbonyl-thiazyl trifluoride complex resulted in evolution of thiazyl trifluoride identified by its characteristic infrared spectrum.

• Reaction Between Iron Pentacarbonyl and Thiazyl Trifluoride.

Iron pentacarbonyl, (0.5 ml, 3.7 mmol), was dissolved in 5 ml of dry benzene and placed in a Kel-F reactor equipped with a magnetic stirrer. The reactor was connected to the vacuum system, and the contents were frozen with liquid nitrogen. This process was repeated several times in order to de-gas the solvent. Thiazyl trifluoride (3.8 mmol) was condensed into the reactor and the assembly was allowed to warm up to room temperature.

Reaction took place within approximately 2 hr. with the precipitation of a brown solid. The reactor was chilled to -78° (Dry Ice-acetone) and the volatile products transferred to the vacuum line. The

Table 5. Mass Spectrum of Molybdenum Carbonyl-Thiazyl Trifluoride.

| m/e | Intensity | m/e | Intensity | m/e | Intensity |
|-----|-----------|-----|-----------|-----|-----------|
| 32 | 9.27 | 68 | -- | 110 | 11.7 |
| 33 | 0.7 | 69 | 5.8 | 111 | 5.3 |
| 34 | 1.9 | 71 | 3.0 | 112 | -- |
| 39 | 10.2 | 73 | 0.9 | 120 | 1.02 |
| 40 | 0.7 | 74 | 1.6 | 128 | 5.4 |
| 41 | 1.2 | 75 | 2.3 | | |
| 42 | 2.9 | 76 | 3.6 | 141 | 8.6 |
| 43 | 1.45 | 77 | 41.1 | 142 | 0.8 |
| 44 | 3.78 | 78 | 7.59 | 143 | 1.02 |
| 45 | 5.8 | 79 | -- | 138 | 1.6 |
| 46 | 0.7 | 80 | 1.02 | 250 | 7.2 |
| 47 | 2.4 | 81 | 1.7 | 251 | 1.4 |
| 48 | 1.1 | 82 | 5.9 | 252 | 1.89 |
| 49 | 1.3 | 83 | 6.2 | 256 | 4.6 |
| 50 | 3.2 | 84 | 2.77 | 258 | 1.67 |
| 51 | 11 | 85 | 8.9 | 281 | 0.7 |
| 52 | 1.24 | 86 | 7.3 | | |
| 53 | 0.7 | 92 | 1.6 | | |
| 54 | 1.5 | 93 | 1.89 | | |
| 56 | 2.4 | 96 | 14.9 | | |
| 57 | 1.6 | 97 | 3.6 | | |
| 58 | 30 | 98 | -- | | |
| 63 | 1.6 | 101 | 1.02 | | |
| 64 | 67 | 105 | 2.9 | | |
| 65 | 13.8 | 108 | 10.3 | | |
| 66 | 6.1 | 109 | 100 | | |

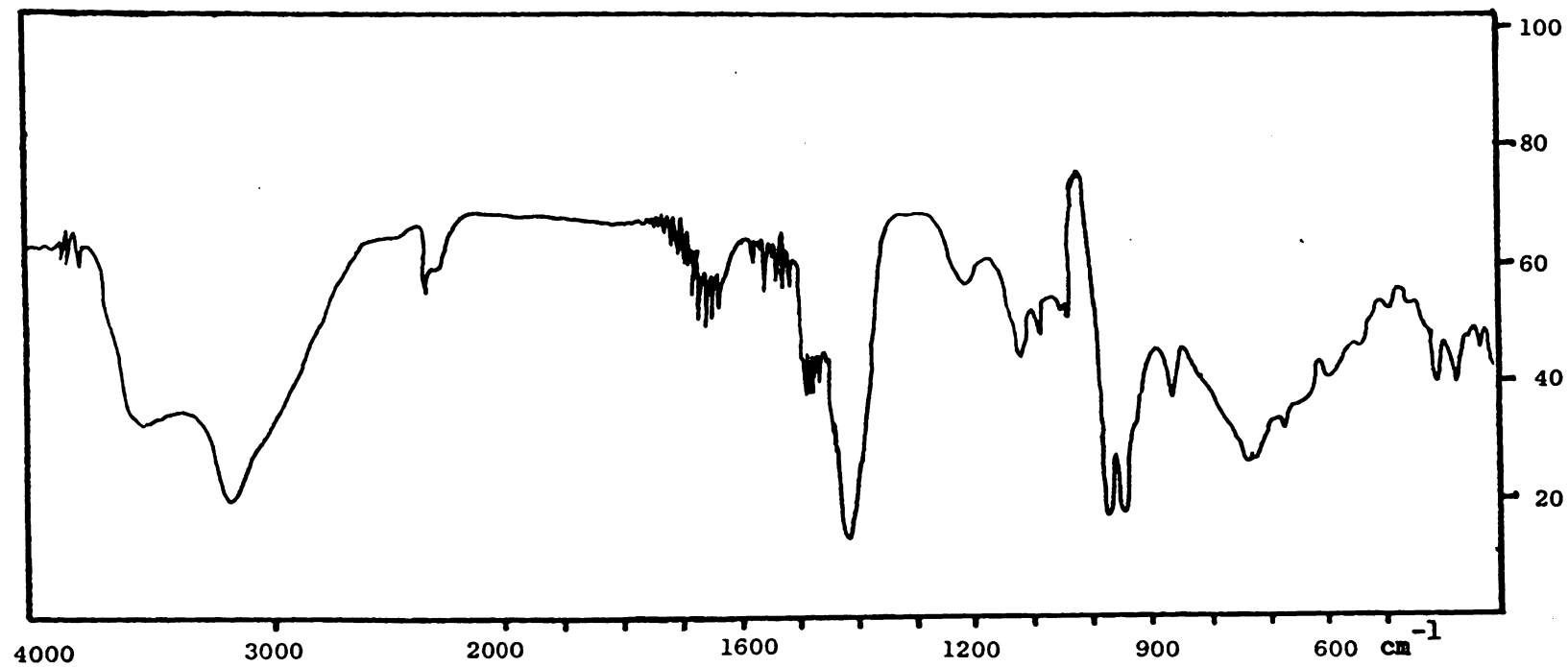


Figure 19. The infrared spectrum of molybdenum carbonyl-thiazyl trifluoride complex.

infrared spectrum indicated a mixture consisting mostly of carbon monoxide with some minor amounts of NSF_3 .

The solvent was removed from the solid by condensing it into an evacuated glass vessel cooled with liquid nitrogen, and the reactor was transferred to the dry box where it was opened and the brown compound collected.

The reaction product was found to be insoluble in the following solvents: carbon tetrachloride, chloroform, ethyl ether, 1,4-dioxane, methanol, ethanol, acetone, dimethyl sulfoxide, dimethyl formamide, and ethyl acetate.

It did, however, dissolve in HCl to give a deep yellow solution with evolution of gaseous material. The solution was shown by nmr not to contain fluorine.

Elemental analysis of the reaction product has been performed for carbon, hydrogen, and nitrogen on the Department Perkin-Elmer 240 Elemental Analyzer, and for iron, sulfur and fluorine by means of Neutron Activation Analysis. The results for several independent samples were inconsistent and varied appreciably from one analysis to another. Average results gave the following percentages: carbon: 4.48 - 6.46; nitrogen: 6.44 - 7.00; sulfur: 13.92 - 15.52; iron; 38, fluorine: 27.9

The elementary analysis did show that the N:S:F ratio was approximately 1:1:3 as in thiazyl trifluoride.

The infrared spectrum of iron carbonyl-thiazyl trifluoride (Figure 20) showed a band at 1420 cm^{-1} assigned to N S absorption

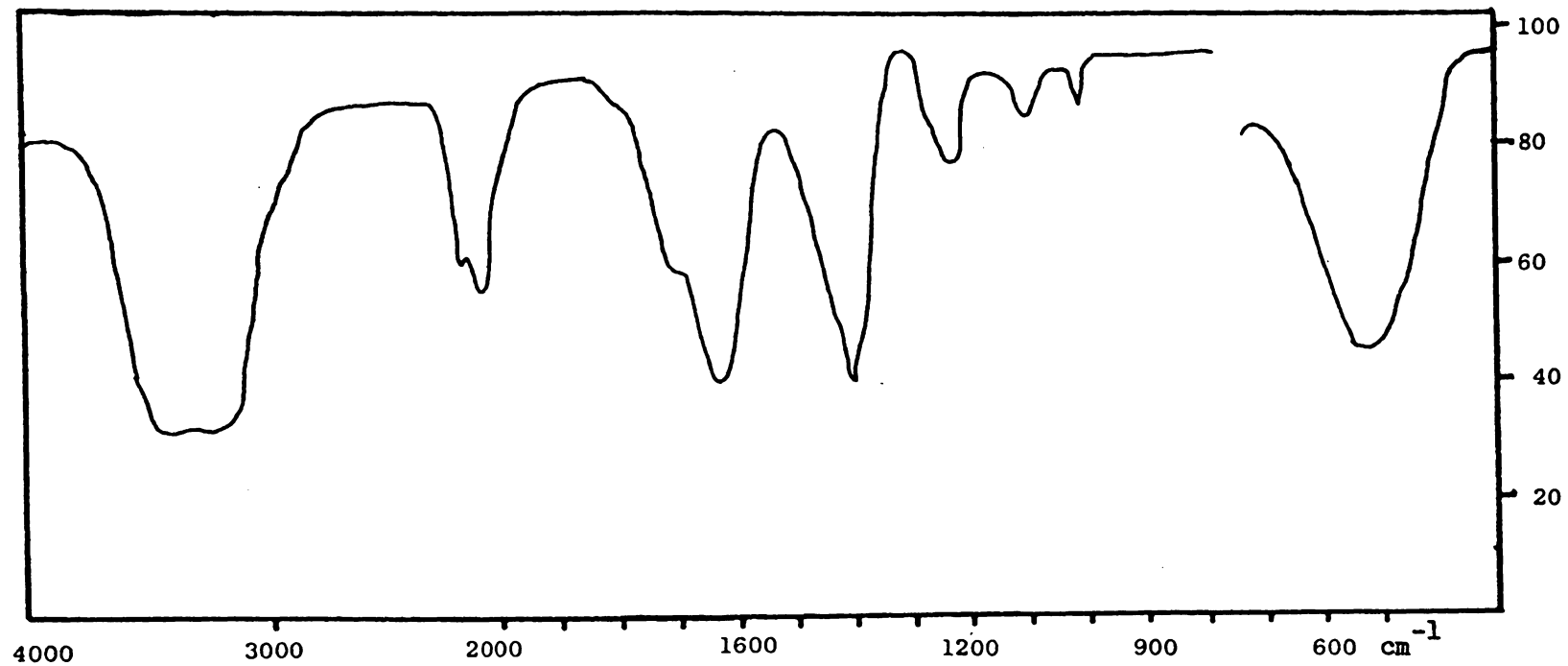


Figure 20. The Infrared Spectrum of Iron Carbonyl-Thiazyl Trifluoride Complex.

(cf. 1515 cm^{-1} for NSF_3). The bands at 2020 cm^{-1} , 2050 cm^{-1} , 1740 cm^{-1} and 1645 cm^{-1} were assigned to different types of carbonyls. A strong, broad absorption at 530 cm^{-1} was unidentified.

A sample of iron carbonyl thiazyl trifluoride was subjected to Mössbauer spectroscopy studies. The source of the gamma radiation was Co^{57} diffused into a platinum matrix, and the spectrum was obtained at room temperature.

The Mössbauer spectrum (Figure 21) showed two distinct bands with an isotopic shift of 0.6319 mm/sec and quadrupole splitting of 0.6352 mm/sec .

The spectrum showed close resemblance to that of iron pentacarbonyl and many other carbonyl derivatives.

X-ray studies were attempted, but the material was found to be amorphous.

2. Reactions of π -Complexes With Thiazyl Trifluoride.

a. Reaction of Ferrocene and Thiazyl Trifluoride.

Freshly sublimed ferrocene (0.77 g, 4.1 mmol) was dissolved in 10 ml of dry benzene and put into a Kel-F reactor equipped with a magnetic stirrer. The reactor was connected to the vacuum system, and the contents were frozen. Thiazyl trifluoride (4.2 mmol) was condensed into the reactor, and then slowly warmed up to room temperature, where it was left for 20 hr. with continuous stirring. The reactor was then chilled to -78° (Dry Ice-acetone and opened to the vacuum system.) The only volatile material was some unreacted thiazyl trifluoride. The solvent was collected into an evacuated

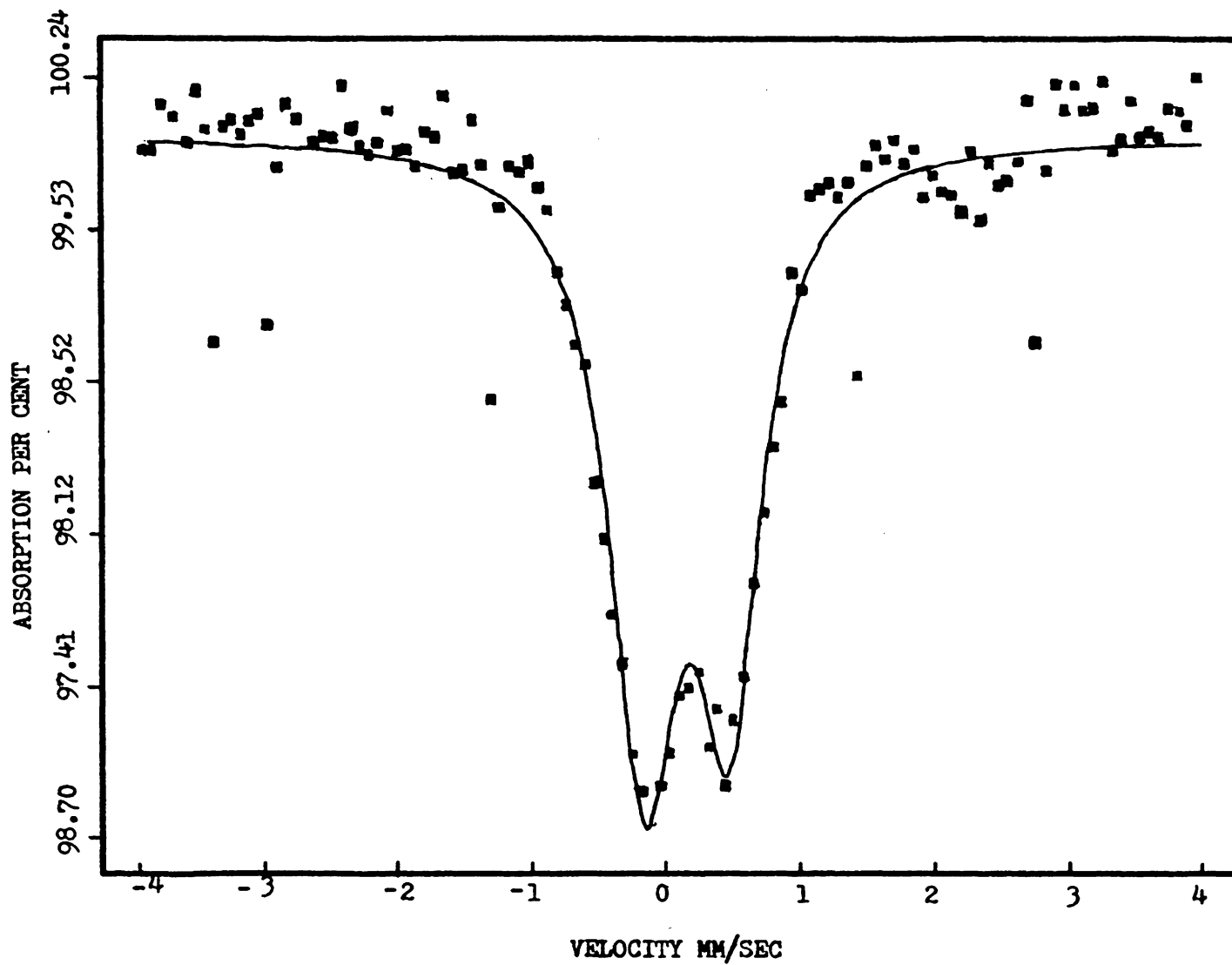


Figure 21. Mössbauer Spectrum of Iron Carbonyl-Thiazyl Trifluoride Complex.

glass reactor chilled with liquid nitrogen. The Kel-F reactor was transferred to the dry box, and a large quantity of yellow-gold crystals was recovered.

Elemental analysis of the reaction product was performed for carbon, hydrogen, and nitrogen on a Perkin-Elmer 240 Elemental Analyzer, and for iron, sulfur and fluorine by means of neutron activation analysis. The results for several independent samples were inconsistent and varied appreciably from one analysis to another. Average results gave the following percentages: carbon: 4.48 - 6.46; nitrogen: 6.44 - 7.00; sulfur: 13.92 - 15.52; iron: 38; fluorine: 27.9.

The elemental analysis did show that the N:S:F ratio was approximately 1:1:3 as in thiazyl trifluoride.

The infrared spectrum of ferrocene-thiazyl-trifluoride (Figure 22) showed an intense peak at 1445 cm^{-1} assigned to S N absorption. Other peaks at 700, 830, 1015 and 1120 cm^{-1} were very sharp and probably belong to an organic moiety in the ferrocene complex.

The Mossbauer Spectrum of the reaction product between ferrocene and thiazyl trifluoride is shown in Figure 23 and the spectrum of pure ferrocene obtained at the same conditions is given for comparison in Figure 24.

The spectra are surprisingly similar, although small differences do exist. The isomeric shift for the ferrocene complex was found to be 0.1126 mm/sec (ferrocene 0.0852 mm/sec) and the quadrupole splitting 2.37 mm/sec (ferrocene 2.37 mm/sec).

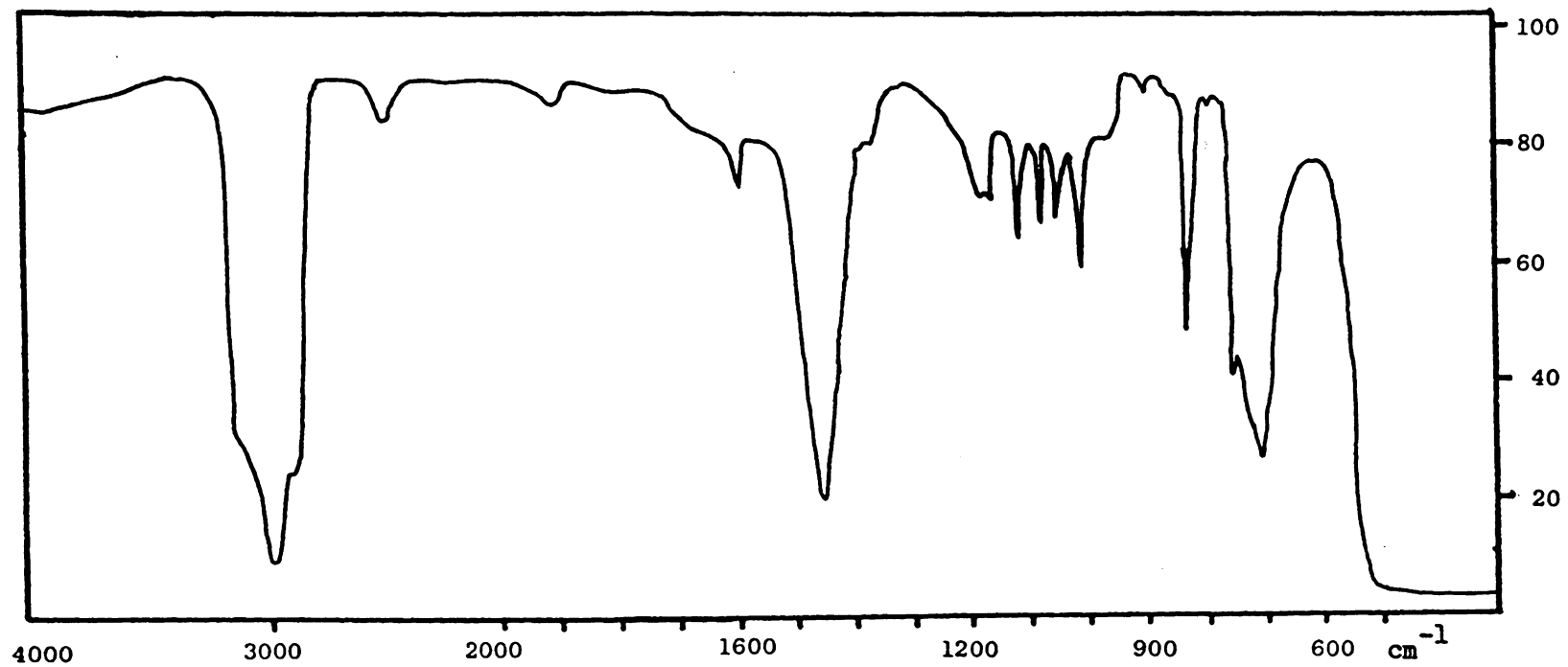


Figure 22. Infrared Spectrum of Ferrocene-Thiazyl Trifluoride Complex.

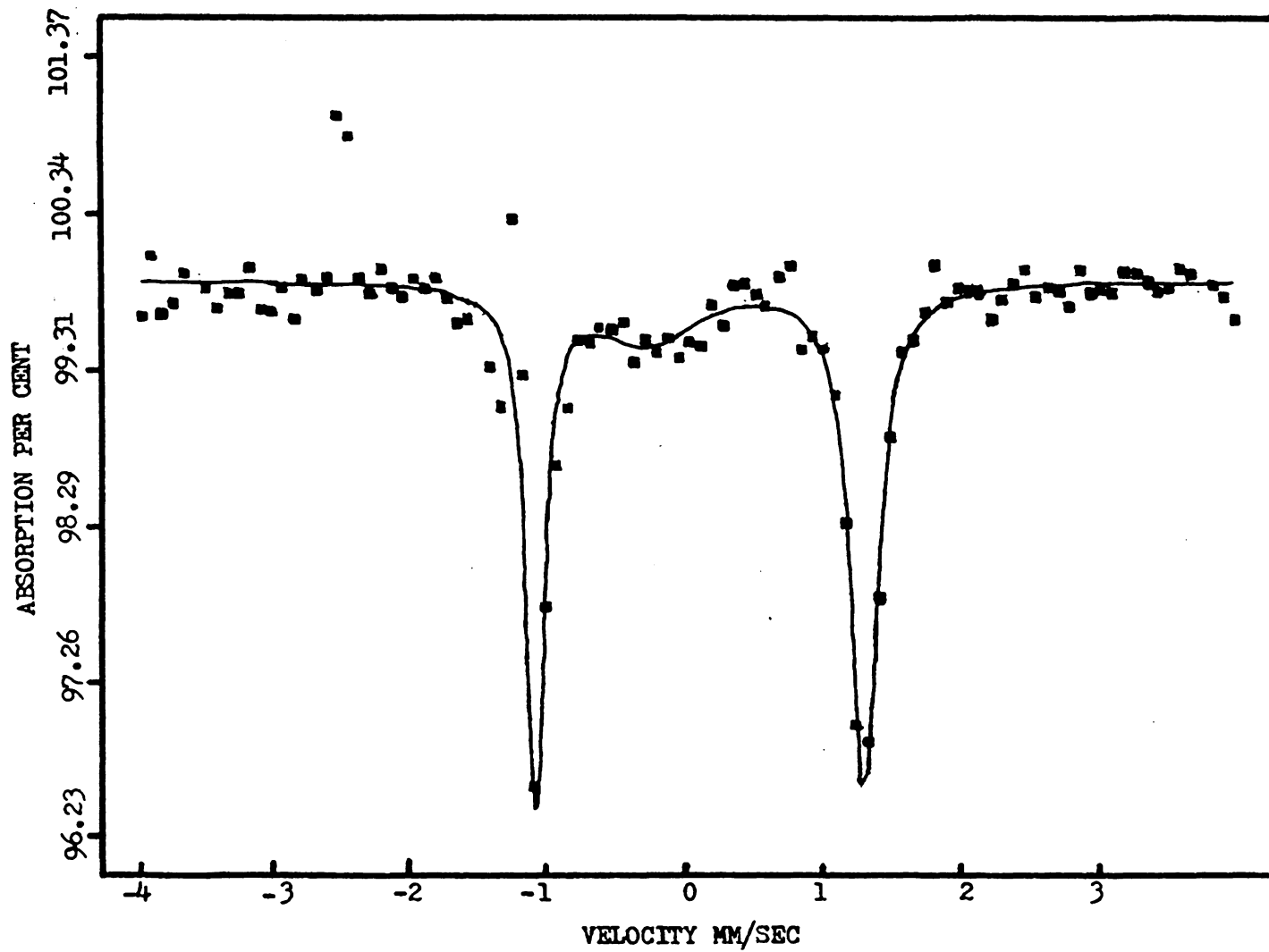


Figure 23. Mössbauer Spectrum of Ferrocene-Thiazyl Trifluorid Complex.

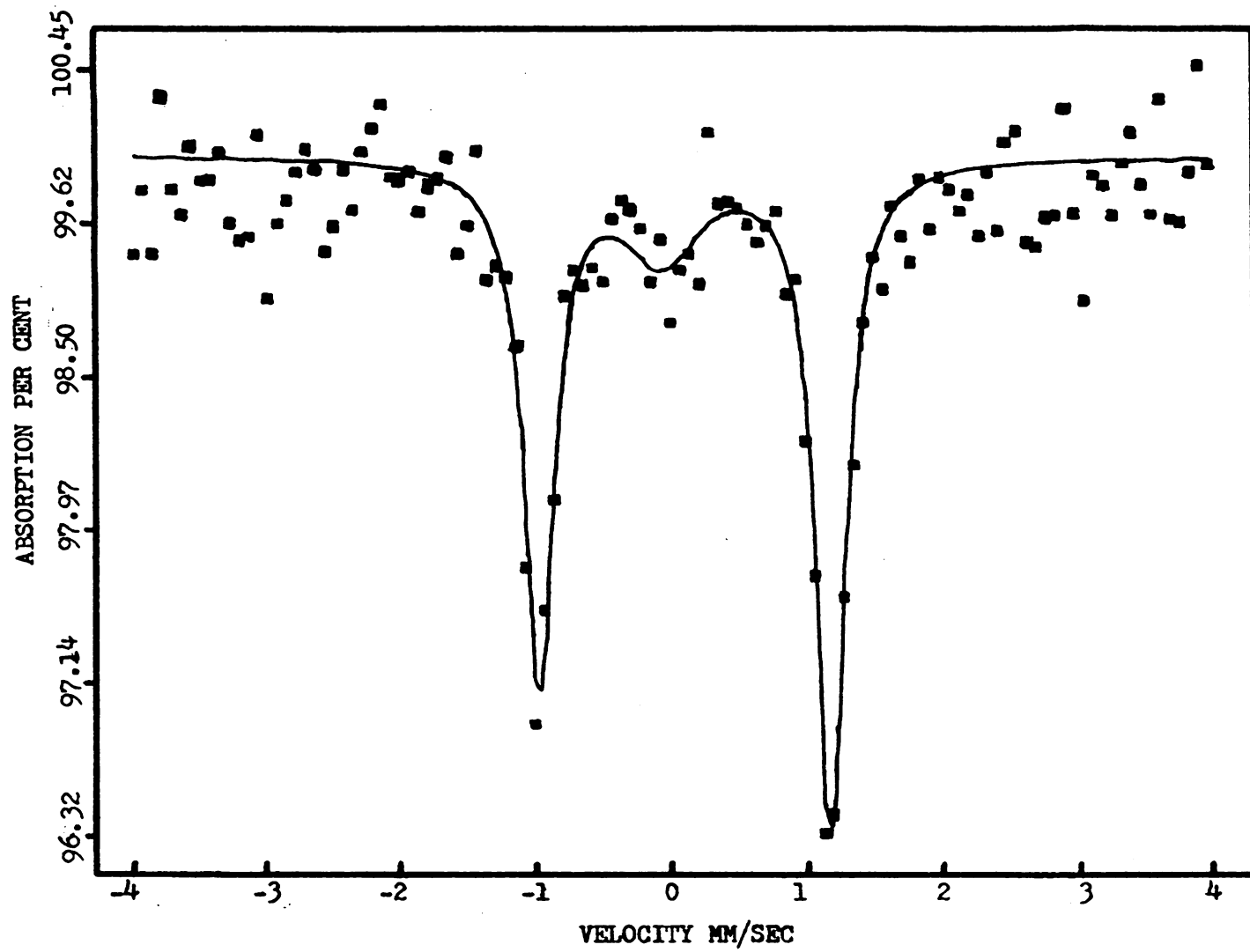


Figure 24. Mössbauer Spectrum of Ferrocene.

Preliminary x-ray analysis is currently being performed by Dr. Fred Ross at V.P.I. & S.U. on a crystal grown from a saturated diethyl ether solution.

D. Summary.

The reaction of metal carbonyls with thiazyl trifluoride has been shown to result in the formation of metal carbonyl cluster compounds. The experimental results, however, are insufficient to provide a detailed structural determination. But the results suggest that thiazyl trifluoride remains as an undecomposed unit in this metal cluster.

The reaction of ferrocene with thiazyl trifluoride was shown to give a crystalline product. Analysis by x-ray diffraction is now being undertaken.

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FLUOROSULFANYLIMINATION INCLUDING RELATED REACTIONS
AND STRUCTURAL PROBLEMS
AND
THIAZYL TRIFLUORIDE COMPLEXES OF THE TRANSITION METALS

by

Abraham Shanzer

(ABSTRACT)

This thesis reports the preparation of new pentafluorosulfanyl-imino ($\text{SF}_5\text{N}=\text{}$) derivatives, which have been synthesized from pentafluorosulfanyl isocyanate, SF_5NCO , pentafluorosulfanylamine, SF_5NH_2 , and pentafluorosulfanyliminosulfur difluoride, $\text{SF}_5\text{N}=\text{SF}_2$.

Reactions of SF_5NCO , $\text{SF}_5\text{N}=\text{SF}_2$, and SF_5NH_2 , with appropriate substrates have produced $\text{SF}_5\text{N}=\text{S}(\text{CH}_3)_2$, $\text{SF}_5\text{N}=\text{CHC}_6\text{H}_5$, $\text{SF}_5\text{N}=\text{SCL}_2$, $(\text{SF}_5\text{N}=\text{})_2\text{C}$, $(\text{SF}_5\text{N}=\text{})_2\text{S}$ and $\text{SF}_5\text{N}=\text{PCl}_3$, some of which are new compounds and some of which represent improved routes to compounds previously reported.

When N,N'-bis(pentafluorosulfanyl)urea, $(\text{SF}_5\text{NH})_2\text{CO}$, reacted with carbonyl fluoride SF_5NCO was formed.

The reactivity of SF_5NCO in several basic reaction types including nucleophilic substitution, addition, exchange and coupling reactions was examined.

Pentafluorosulfanyl isocyanate and dimethyl sulfoxide reacted to produce a crystalline product identified by its H-1 and F-19 nmr and is spectra as $\text{SF}_5\text{N}=\text{S}(\text{CH}_3)_2$.

Pentafluorosulfanyl isocyanate and benzaldehyde reacted to produce a yellow solution and carbon dioxide. The solution was determined by spectroscopic means to contain $\text{SF}_5\text{N}=\text{CHC}_6\text{H}_5$, a novel, electron-deficient Schiff base.

Pentafluorosulfanylisocyanate and PCl_5 reacted readily at $60\text{-}80^\circ$ producing $\text{SF}_5\text{N}=\text{CCl}_2$ and POCl_3 .

A slow reaction between SF_5NCO and excess AgF_2 took place at room temperature. Infrared analysis of the reaction mixture at increasing temperatures gave evidence for formation and subsequent decomposition of $\text{SF}_5\text{N}=\text{NSF}_5$.

Pentafluorosulfanyliminosulfur difluoride (obtained from irradiation of $\text{N}\equiv\text{SF}_3$) reacted at room temperature with PCl_5 to produce $\text{SF}_5\text{N}=\text{SCl}_2$, a pale yellow liquid which rapidly attacked mercury, and reacted with AgF_2 (producing $\text{SF}_5\text{N}=\text{SF}_2$) and with SF_5NH_2 (producing $\text{SF}_5\text{N}=\text{S}=\text{NSF}_5$).

Pentafluorosulfanylamine, SF_5NH_2 , and PCl_5 reacted at room temperature to give $\text{SF}_5\text{N}=\text{PCl}_3$, a pale yellow liquid which reacted rapidly with mercury.

Thiazyl trifluoride reacted with metal carbonyls ($\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$, $\text{Mn}(\text{CO})_6$) and ferrocene to produce thiazyl trifluoride - transition metal complexes.

Chemical similarities between SF_5NCO and $\text{SF}_5\text{N}=\text{SF}_2$ with respect to nucleophilic substitution, exchange and coupling reaction reflect the similarity in bonding expected in these two systems. However, the failure of $\text{SF}_5\text{N}=\text{SF}_2$ and compounds containing the $-\text{N}=\text{SF}_2$ group to undergo additional reactions with polar reagents indicates some gross

discrepancy from the usual behavior of these multiply bonded systems. Thus, a theoretical study of $-N=SF_2$ system was undertaken to clarify the role and magnitude of d-orbitals in the bonding of $-N=SF_2$ compounds.

Theoretical calculations (CNDO) of the total energy of $SF_5N=SF_2$, $CF_3N=SF_2$, $C_2F_5N=SF_2$, and $FCON=SF_2$ as a function of rotation about the N-S(IV) multiple bond showed that each total energy curve possessed a broad, flat minimum.

Rotamers derived with only slight excitation would possess equal energy. Therefore, this multiple bond is nonrigid in contrast to the usual concept of the $p\pi-p\pi$ double bond.

The d-orbital contribution accounts for approximately 50% of the total π -bonding and is practically independent of the nature of the substituents on the nitrogen atom.

Low temperature F-19 nmr studies showed that splittings occurred which can be explained on the basis of the total energy curves derived from the calculations.