TABLE I

	Ppm		
	This work	Cullen and Styan	Δ_1
(a) 1:1 Adduct, $(CH_3)_3SiOCH(CF_3)_2$			
$CH(CF_3)_2$	-4.24	-3.90	-0.34
$(CH_3)_3Si$	-0.21	$+0.16$	-0.37
Δ_2	-4.03	-4.06	
(b) 2:1 Adduct, $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$			
$CH(CF_3)_2$	-4.77	-4.45	-0.32
$(CH_3)_3Si$	-0.30	$+0.08$	-0.38
Δ_2	-4.47	-4.53	

adduct (where there is no dispute on the identity of the compound) is, within experimental error, the same as that found for the 2:1 adduct. On the difference in chemical shift between the two types of proton in the same compound, Δ_2, the agreement between the measurements on both compounds is very good. We are forced to conclude, therefore, that the 2:1 adducts reported by ourselves and Cullen and Styan are in fact the same compound, and we suggest that the claim of the latter workers that their adduct dissociated at 20° is in error.

We must also take issue with the claim of Cullen and Styan that the nmr spectrum of the 2:1 adduct may be seen when the 1:1 adduct is dissolved in excess hexafluoroacetone. We have carefully reexamined the relevant spectra and find no evidence to support this. As an explanation of the observations of Cullen and Styan, we suggest that their sample of hexafluoroisopropoxytrimethylsilane contained unreacted trimethylsilane, which, by reaction with the hexafluoroacetone added in their nmr studies, would have produced detectable quantities of the 2:1 adduct.

In conclusion, therefore, we suggest that the liquid-phase reaction of hexafluoroacetone with trimethylsilane and similar compounds of group IV elements proceeds by an ionic mechanism in which hydride ion abstraction is the first step and the products are exclusively simple four-covalent derivatives incorporating one or two hexafluoroacetone residues. We do not find it necessary to postulate the existence of any product involving higher coordination and we suggest that it is misleading to represent any reactions of this type as examples of the ability of fluorinated ketones to form complexes.

Acknowledgments.—This work was supported in part by the Defense Research Board of Canada through Grant 7583-05. The authors also gratefully acknowledge the award of an Ontario Graduate Fellowship (to A. F. J.).

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY
AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER,
UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Synthesis of Amino Derivatives of Sulfur Tetrafluoride and Phosphorus Pentafluoride by Silicon–Nitrogen Bond Cleavage Reactions[1]

BY GREGORY C. DEMITRAS, F.S.C., AND ALAN G. MACDIARMID

Received October 25, 1966

The compounds N-dimethylaminosulfur trifluoride, $(CH_3)_2NSF_3$, N-dimethylaminotetrafluorophosphorane, $(CH_3)_2NPF_4$, and 1,3,2,4-diazadiphosphetidine, $(CH_3NPF_3)_2$, have been synthesized by the reaction of N-methyl-N-trimethylsilylamines with SF_4 or PF_5, respectively. The structures of these compounds were studied by means of their infrared, mass, and nuclear magnetic resonance spectra.

Although it has been known for several years that the silicon–nitrogen bond may be cleaved by a variety of covalent or semicovalent halides,[2] little attention has been given to exploiting such reactions for the specific purpose of preparing volatile derivatives of the nonmetal fluorides. The synthesis of methylamino derivatives of PF_5 and SF_4 by the reaction of these parent fluorides with appropriate silicon amines was therefore attempted and the present communication describes in greater detail the previously reported[3] preliminary results of this investigation.

It has been found that PF_5 rapidly cleaves the Si–N bond in $(CH_3)_2NSi(CH_3)_3$ at, or below, room temperature to give high yields of $(CH_3)_2NPF_4$, *viz.*

$$PF_5 + (CH_3)_2NSi(CH_3)_3 \longrightarrow (CH_3)_2NPF_4 + (CH_3)_3SiF \quad (1)$$

The reaction proceeds *via* the adduct, $(CH_3)_2NSi(CH_3)_3 \cdot PF_5$, which is stable at $-78°$ and which decomposes to give the products on warming to room temperature. The compound $(C_2H_5)_2NPF_4$ has also been prepared by a similar method[4] and $(CH_3)_2NPF_4$

---

(1) This report is based on portions of a thesis submitted by Gregory C. Demitras, F.S.C., to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

(2) R. Fessenden and J. D. Fessenden, *Chem. Rev.*, **61**, 363 (1961); M. Becke-Goehring and H. Krill, *Chem. Ber.*, **94**, 1059 (1961); H. Nöth, *Z. Naturforsch.*, **16b**, 619 (1961).

(3) G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. Ind.* (London), 1712 (1964).

(4) R. Schmutzler, *Angew. Chem.*, **76**, 893 (1964).

has been synthesized by the reaction of PF_5 with $(CH_3)_2NH$.[5] Although $(CH_3NPF_3)_2$ could not be isolated from the reaction of PF_5 with CH_3NH_2,[6] it could be obtained in good yields by the low-temperature reaction of PF_5 with $CH_3N[Si(CH_3)_3]_2$, *viz.*

$$2PF_5 + 2CH_3N[Si(CH_3)_3]_2 \longrightarrow (CH_3NPF_3)_2 + 4(CH_3)_3SiF \quad (2)$$

This reaction has subsequently been reported independently by Schmutzler.[7]

The synthesis of $(CH_3)_2NSF_3$ was first attempted by the reaction of SF_4 with $(CH_3)_2NH$, but only unidentified nonvolatile solid and oily materials were obtained; however, the low-temperature reaction of SF_4 with $(CH_3)_2NSi(CH_3)_3$ gave good yields of $(CH_3)_2NSF_3$, *viz.*

$$SF_4 + (CH_3)_2NSi(CH_3)_3 \longrightarrow (CH_3)_2NSF_3 + (CH_3)_3SiF \quad (3)$$

The ^1H and ^{19}F nmr spectra of $(CH_3)_2NPF_4$ and $(CH_3)_2NSF_3$ are consistent with those of other monosubstituted derivatives of PF_5 and SF_4 and suggest trigonal bipyrimidal structures in which the dimethylamino group occupies an equatorial site.[8-12] The room-temperature proton spectrum of $(CH_3NPF_3)_2$ consisted of a well-defined triplet which is consistent with the previously postulated symmetrical cyclic structure.[3] Harris and Woodman[13] have subsequently shown that the complex ^{19}F nmr spectrum of this compound is also consistent with this structure.

Experimental Section

All work was performed in a Pyrex (borosilicate) vacuum system. The syntheses were carried out in a 100-ml round-bottom flask fitted with a blow-off manometer. Vapor pressures were recorded in a glass tensimeter (mercury manometer) which had been pretreated with a sample of the material for a period of 12–16 hr. Melting points were determined by the magnetic plunger technique. Mass spectra were obtained with a Consolidated Electrodynamics Model 21-30 spectrometer. Infrared absorption spectra were recorded with a Perkin-Elmer 137B Infracord spectrophotometer on the gas phase at room temperature with the sample confined in a 10-cm cell fitted with KBr windows cemented to the cell with Glyptal resin.

Reagents.—$(CH_3)_2NSi(CH_3)_3$ (mol wt found 116.5, calcd 117.0; vapor pressure at 0.20° found 26.8 mm, lit.[14] 26.9 mm; confirmed by infrared spectrum[14]) was prepared from $(CH_3)_2NH$ and $(CH_3)_3SiCl$.[15] $CH_3N[Si(CH_3)_3]_2$ (confirmed by infrared spectrum[14]) was synthesized from CH_3NH_2 and $(CH_3)_3SiCl$. Commercial SF_4 (confirmed by infrared spectrum[16]) was purified according to the method of Bartlett and Robinson.[17] Commercial PF_5 (mol wt found 125.1, calcd 126.0; vapor pressure at −132.5° found 17.4 mm, lit.[18] 17.6 mm; confirmed by infrared spectrum[19]) was used without further purification.

Synthesis of $(CH_3)_2NSF_3$.—$(CH_3)_2NSi(CH_3)_3$ (5.661 mmoles) and SF_4 (6.002 mmoles) were condensed in the reaction flask. Reaction occurred while warming to room temperature. The contents of the flask were refrozen and were allowed to warm to room temperature. This operation was repeated several times to ensure complete mixing of reactants. Distillation through a series of traps held at −126, −83.5, and −23° yielded $(CH_3)_3SiF$ (5.507 mmoles; 97.4% yield; mol wt found 91.5, calcd 92.0; confirmed by infrared spectrum[20]) in the −126° trap and $(CH_3)_2NSF_3$ (4.267 mmoles; 75.4% yield; mol wt found 132.6, calcd 133.0) in the −83.5° trap.

Anal.[21] Calcd for $C_2H_6NSF_3$: C, 18.04; H, 4.51; N, 10.52; S, 24.06; F, 42.85. Found: C, 18.25; H, 4.63; N, 10.65; S, 23.96; F, 42.79.

The pure compound melted at −78.7 ± 0.1°.

Synthesis of $(CH_3)_2NPF_4$.—PF_5 (3.411 mmoles) and $(CH_3)_2NSi(CH_3)_3$ (1.293 mmoles) were condensed at −196° in the reaction vessel and the mixture was allowed to warm to room temperature. The reaction flask was immediately surrounded by a −134° bath. After 10 min the reaction flask was opened to a trap surrounded by liquid nitrogen. Volatile material ceased to condense in the liquid nitrogen trap after a period of 90 min. The liquid nitrogen trap contained PF_5 (2.110 mmoles; mol wt found 126.1, calcd 126.0; confirmed by infrared spectrum[19]). These data indicated that the white solid residue in the −136° trap was composed of PF_5 and $(CH_3)_2NSi(CH_3)_3$ in the molar ratio of 1.08:1.00. The adduct appeared to be stable at −78°.

In another experiment, $(CH_3)_2NSi(CH_3)_3$ (8.073 mmoles) and PF_5 (10.930 mmoles) were condensed into the reaction vessel and were allowed to react while warming to room temperature. The materials were refrozen and were allowed to warm to room temperature several times to ensure complete mixing. The white solid adduct which formed decomposed completely during approximately 1 hr at room temperature. Distillation of the products through a series of traps held at −134, −83.5, and −45° yielded $(CH_3)_3SiF$ (8.072 mmoles, 100.0% yield; mol wt found 91.7, calcd 92.0; confirmed by infrared spectrum[20]) in the −134° trap and $(CH_3)_2NPF_4$ (6.439 mmoles; 79.5% yield; mol wt found 150.2, calcd 151.0) in the −83.5° trap.

Anal.[21] Calcd for $C_2H_6NPF_4$: C, 15.90; H, 4.00; N, 9.27; P, 20.50; F, 50.31. Found: C, 16.09; H, 4.17; N, 9.57; P, 20.22; F, 50.24.

The pure compound melted at −80.0 ± 0.1°.

Synthesis of $(CH_3NPF_3)_2$.—PF_5 (5.540 mmoles) and $CH_3N[Si(CH_3)_3]_2$ (3.250 mmoles) were condensed at −196° into the reaction flask which contained a Kel-F coated magnetic stirring bar. After stirring at room temperature for approximately 5 min, the materials were refrozen at −196° and were again stirred at room temperature until there was no pressure change in the reaction system. Distillation of the products through a series of traps held at −134, −83.5, and −37° yielded $(CH_3)_3SiF$ (6.350 mmoles; 97.7% yield; mol wt found 92.7, calcd 92.0; confirmed by infrared spectrum[20]) in the −134° trap and $(CH_3NPF_3)_2$ (1.075 mmoles; 66.2% yield; mol wt found 232.8, calcd 234.1) in the −83.5° trap.

Anal.[21] Calcd for $C_2H_6N_2P_2F_6$: C, 10.25: H, 2.58; N, 11.93; P, 26.59; F, 48.70. Found: C, 10.50; H, 2.77; N, 11.70; P, 26.37; F, 48.25.

The pure compound melted at −10.3 ± 0.1°.

Vapor Pressure Data. (A) $(CH_3)_2NSF_3$.—It was observed that $(CH_3)_2NSF_3$ decomposed during the study of its vapor pressure over a 6-hr period between 23 and 50° as evidenced by

---

[5] D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *Chem. Ind.* (London), 367 (1964).

[6] D. W. A. Sharp, private communication, 1964.

[7] R. Schmutzler, *Chem. Commun.*, 19 (1965).

[8] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

[9] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 615, (1963).

[10] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[11] R. Schmutzler, "International Review of Halogen Chemistry," V. Gutmann, Ed., Academic Press Inc., New York, N. Y., in press.

[12] W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962); R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

[13] R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).

[14] H. A. Kriegsmann, *Z. Elektrochem.*, **61**, 1088 (1957).

[15] E. A. V. Ebsworth and H. J. Emeléus, *J. Chem. Soc.*, 2150 (1958).

[16] R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **52**, 1052 (1956).

[17] N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 3417 (1961).

[18] R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," 2nd ed, Elsevier Publishing Co., New York, N. Y., 1957, p 211.

[19] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

[20] H. A. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **294**, 113 (1958).

[21] Schwarzkopf Micro-Analytical Laboratories, Woodside, 77, N. Y. Samples were transported at liquid nitrogen temperature.

the fact that as the temperature of the material was lowered, the apparent vapor pressure remained essentially constant. It was therefore necessary to gather the observed vapor pressure data using four separate, pure samples at four different temperatures. In this way, vapor pressure data could be obtained before any appreciable thermal decomposition occurred. Vapor pressures in the range 23.4–53.5° are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{2115.3}{t + 273.16} + 8.2936$$

The extrapolated boiling point is 117.5°, the molar heat of vaporization is 9.68 kcal, and Trouton's constant is 24.7 cal $\deg^{-1}$ mole^{-1}.

TABLE I

VAPOR PRESSURES OF $(CH_3)_2NSF_3$

Temp, °C	P, mm, obsd	P, mm, calcd
23.5	14.6	14.6
29.0	20.0	19.6
36.8	28.8	29.5
53.5	66.7	65.9

(B) **$(CH_3)_2NPF_4$**.—Vapor pressures of $(CH_3)_2NPF_4$ in the range −23.2 to 30.5° are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{1764.75}{t + 273.160} + 8.12015$$

Additional measurements to those given in Table II were used in deriving this relationship. The reversibility of the curve on decreasing the temperature indicates that no observable decomposition took place during the 12-hr experiment. The infrared spectrum of the compound recovered was identical with that of the pure material. The extrapolated boiling point is 63.7°, the molar heat of vaporization is 8.08 kcal, and Trouton's constant is 23.9 cal $\deg^{-1}$ mole^{-1}.

TABLE II

VAPOR PRESSURES OF $(CH_3)_2NPF_4$

Temp, °C	P, mm, obsd	P, mm, calcd	Temp, °C	P, mm, obsd	P, mm, calcd
2.1	47.3	51.1	26.4[a]	170.0	169.5
10.5	79.1	79.2	20.8[a]	129.2	130.7
15.2	99.9	100.0	13.4[a]	91.4	91.6
23.4	147.1	147.7	9.1[a]	73.3	73.1
30.5	204.1	203.5	2.0[a]	50.9	50.9
29.2[a]	191.8	191.1	−23.2[a]	11.7	11.5

[a] Pressures observed while decreasing the temperature.

(C) **$(CH_3NPF_3)_2$**.—Vapor pressures of $(CH_3NPF_3)_2$ in the range 0.1–46.5° are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{2021.24}{t + 273.160} + 8.46782$$

Additional measurements to those given in Table III were used in deriving this relationship. The reversability of the curve on decreasing the temperature indicates that no observable decomposition took place during the 12-hr experiment. The infrared spectrum of the compound recovered was identical with that of the pure material. The extrapolated boiling point is 87.9°, the molar heat of vaporization is 9.24 kcal, and Trouton's constant is 25.5 cal $\deg^{-1}$ mole^{-1}.

Mass Spectra.—The mass spectra were recorded at an ionizing voltage of 76.0 v and at an ionizing current of 20 μa.

(A) **$(CH_3)_2NSF_3$**.—A molecular ion peak of mass number 133 had a relative intensity of 1% of the major peak. Possible assignments for the major fragments in decreasing order of abundance are $C_2H_4N^+$, $C_2H_5N^+$, $C_2H_6N^+$, $C_2H_2NSF_2^+$, and $C_2H_3NSF_3^+$.

TABLE III

VAPOR PRESSURES OF $(CH_3NPF_3)_2$

Temp, °C	P, mm, obsd	P, mm, calcd	Temp, °C	P, mm, obsd	P, mm, calcd
0.1	11.4	11.8	46.5	138.7	139.5
3.9	14.9	14.9	41.1[a]	109.9	108.2
6.5	16.8	17.3	35.5[a]	83.9	83.1
19.5	36.7	36.5	29.7[a]	62.2	62.1
23.8	46.2	45.9	26.6[a]	45.3	45.4
29.3	61.0	61.0	12.9[a]	24.5	25.2
34.7	81.1	81.1	5.3[a]	16.7	16.2

[a] Pressures observed while decreasing the temperature.

(B) **$(CH_3)_2NPF_4$**.—A molecular ion peak at mass number 151 had a relative intensity of 19% of the major peak. Possible assignments for the major fragments in decreasing order of abundance are PF_4^+, $C_2H_4N^+$, $C_2H_5N^+$, CH_3^+, and $C_2H_6NPF_3^+$.

(C) **$(CH_3NPF_3)_2$**.—A molecular ion peak at mass number 234 had a relative intensity of 15% of the major peak. Possible assignments for the major fragments in decreasing order of abundance are $CH_3NPF_3^+$, $CHNPF_3^+$, CH_3N^+, $CH_2NPF_3^+$, PF_2^+, and $C_2H_6N_2P_2F_5^+$.

Infrared Absorption Spectra.—The infrared spectrum of $(CH_3)_2NSF_3$ was recorded at 5 mm pressure, that of $(CH_3)_2NPF_4$ was recorded at 66 and 1.5 mm pressure; and that of $(CH_3NPF_3)_2$ was recorded at 19.5 and 2.0 mm pressure. Absorption maxima are listed in Tables IV and V and the spectra are given in Figures 1–3.

TABLE IV

INFRARED ABSORPTION MAXIMA OF $(CH_3)_2NSF_3$ (CM^{-1})

	Assignment	Ref
2950 s	C–H str	*a, b*
1480 s	Asym CH_3 def	*a, b*
1373 m	Sym CH_3 def	*b, c*
1350 m	Unassigned	
1225 vs	C–N str	*b, d*
1060 m	Unassigned	
993 vs	S–F str	*e*
946 s	Impurity[f]	
769 vs	SF_3 def	*e*
704 712 ds	S–N str	*e, g, h*
677 w	Unassigned	

[a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958. [b] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962. [c] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1964. [d] J. Goubeau and J. Jimenéz-Barberá, *Z. Anorg. Allgem. Chem.*, **303,** 217 (1960). [e] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963. [f] The intensity of this band varied somewhat from one sample to another. [g] R. Schmutzler, private communication. [h] It seems likely that this may be an S–N stretch, in view of the similarity of the masses of ^{31}P and ^{32}S and the fact that the P–N stretch in the compounds $(CH_3)_2NPF_2$, $(C_2H_5)_2NPF_4$, and $(C_6H_5)_2NPF_2$ has been assigned bands at 705, 680, and 691 cm^{-1}, respectively. See ref 9 and 10 and footnotes *f* and *g* of Table V.

Nuclear Magnetic Resonance Spectra.—The proton spectra of both $(CH_3)_2NPF_4$ (τ 7.49; $J_{\mathrm{HF}} = 2.1$ cps; $J_{\mathrm{HP}} = 11.7$ cps) and $(CH_3NPF_3)_2$ (τ 7.58; $J_{\mathrm{HP}} = 14.5$ cps) [pure liquids, $(CH_3)_4Si$ external standard] were recorded on a Varian A60 spectrometer, and that of $(CH_3)_2NSF_3$ (τ 6.85; no HF coupling; pure liquid, C_6H_{12} external standard) was studied by means of a Varian HR60 instrument.

Fluorine spectra were recorded on a Varian HR60 instrument at 56.4 Mc. The ^{19}F spectrum of $(CH_3)_2NPF_4$ [25% (volume)

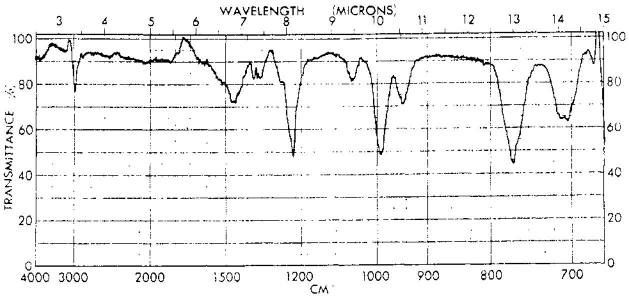

Figure 1.—Infrared absorption spectrum of $(CH_3)_2NSF_3$.

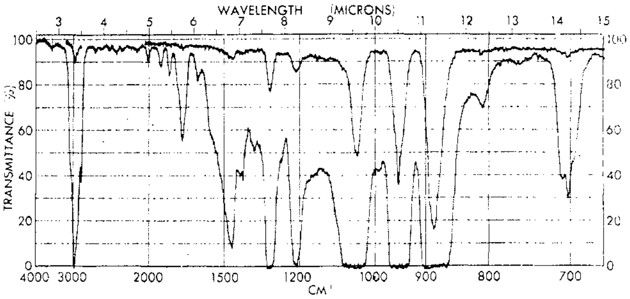

Figure 2.—Infrared absorption spectra of $(CH_3)_2NPF_4$.

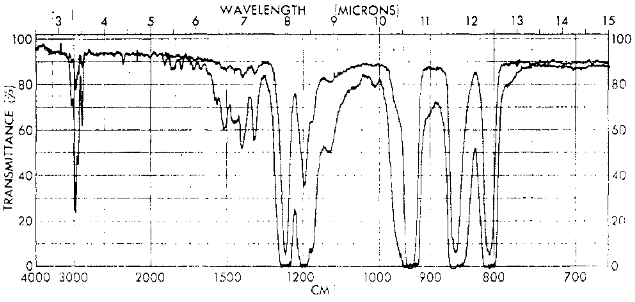

Figure 3.—Infrared absorption spectra of $(CH_3NPF_3)_2$.

solution in pentane; δ 0.18 ppm upfield from (external) $FCl_2C\text{-}CCl_2F$; $J_{HF} = 2.0$ cps; $J_{PF} = 836$ cps] was similar in form to that of $(C_2H_5)_2NPF_4$, both at room temperature and at low temperature.[10,11] The room-temperature ^{19}F spectrum of $(CH_3)_2NSF_3$ [25% (volume) solution in pentane; δ 118 ppm downfield from (external) CF_3COOH] consisted of a moderately broad signal, but at −100° it appeared as two signals (δ −136 ppm; relative intensity 2, and δ −107, relative intensity 1). The fact that the average value of these signals (121.5 ppm) is close to that of the room-temperature ^{19}F signal suggests that no great structural change occurs between room temperature and −100°.[10]

The ^{31}P spectrum of $(CH_3NPF_3)_2$, which was recorded on a Varian HR60 spectrometer at 19.5 Mc, consisted of a complex multiplet 69.5 ppm upfield from H_3PO_4.

TABLE V

INFRARED ABSORPTION MAXIMA OF $(CH_3)_2NPF_4$ AND $(CH_3NPF_3)_2$ (CM⁻¹)

$(CH_3)_2$-NPF_4	$(CH_3NPF_3)_2$	Assignment	Ref
2970 w	2960 w	C–H str	*a*, *b*
2010 vvw	1525 vw	Unassigned	
1900 vvw		Unassigned	
1840 vvw		Unassigned	
1745 vw		Unassigned	
1461 w	1430 vw	Asym CH_3 def	*a*, *b*
	1375 vw	Sym CH_3 def	*b*, *c*
1300 m		CH_3 def in CH_3–N–P group	*a*
1210 w	1260 s 1195 m	C–N str	*a*, *b*
	1170 sh	Unassigned	
1041 s		C–N str	*a*, *b*, *d*
952 s	938 vs	Equatorial P–F str	9
885 vs	858 s	Axial P–F str	9
809 vvw		Unassigned	
703 vw	807 s	P–N str	*a*, *e*–*g*

[a] See Table IV, footnote *a*. [b] See Table IV, footnote *b*. [c] See Table IV, footnote *c*. [d] See Table IV, footnote *d*. [e] B. Holmstedt and B. Larson, *Acta Chem. Scand.*, **5**, 1179 (1951). [f] M. A. Fleming, Ph.D. Thesis, University of Michigan, 1963. [g] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

Acknowledgment.—The authors are greatly indebted to Dr. E. L. Muetterties and Dr. R. Schmutzler, E. I. du Pont de Nemours and Co., Wilmington, Del., and Mr. G. D. Vickers, Olin Mathieson Chemical Corp., New Haven, Conn., for their assistance with the nuclear magnetic resonance studies.

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

The Crystal and Molecular Structure of Sulfur Nitride–Boron Trifluoride[1]

BY MICHAEL G. B. DREW, DAVID H. TEMPLETON, AND ALLAN ZALKIN

Received February 6, 1967

The structure of $S_4N_4 \cdot BF_3$ has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.114 \pm 0.005$, $b = 10.418 \pm 0.007$, $c = 10.754 \pm 0.008$ A, and $\beta = 95.40 \pm 0.06°$. The BF_3 group is bonded *via* the boron atom to a nitrogen atom of the S_4N_4 eight-membered ring. The four sulfur atoms in this ring are near the corners of a square, while the nitrogen atoms are alternately above and below the plane of the square. This conformation is very similar to that of $S_4N_4 \cdot SbCl_5$, but unlike that of S_4N_4 itself.

Introduction

In a recent study of the reaction of sulfur nitride, S_4N_4, with the boron trihalides Wynne and Jolly[2] isolated compounds of the composition $S_4N_4 \cdot BF_3$ and $S_4N_4 \cdot BCl_3$. Several other adducts of S_4N_4 with Lewis acids have been prepared in the past,[3] and Neubauer

---

[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, **6**, 107 (1967).

[3] See citations listed in ref 2.