that a symmetry-forbidden transformation proceeds in the presence of a transition metal catalyst should not imply the intervention of the forbidden-to-allowed process. Stepwise catalytic processes reasonably explain the nickel-catalyzed cycloaddition of butadiene[25] and the rhodium-catalyzed valence isomerization of cubane,[19] for example. The overall chemistry associated with the catalysis of symmetry-forbidden reactions will unquestionably involve a number of distinguishable stepwise processes in addition to the special case addressed here. In describing postulated stepwise reaction paths, particular attention has been directed toward the "nonconcertedness" of the catalytic process.[19,23] All molecular transformations to distinct intermediates, of course, are concerted processes, and orbital symmetry restraints necessarily intervene. In the catalysis of [2 + 2] cycloaddition, symmetry restraints similar in kind to those discussed here can appear.[26] The ligand-field restraints encountered by the stepwise cycloaddition process are essentially those that would be associated with the forbidden-to-allowed process proceeding *via* monodentate coordination.[21] The two paths thus exhibit quite similar orbital symmetry patterns in their modes of catalysis.

We feel that the forbidden-to-allowed process will play an important role in the catalysis of symmetry-forbidden reactions. Catalytic systems are presently known which are best interpreted through forbidden-to-allowed concepts;[2d,f] the striking ease of these catalytic transformations suggests that significant levels of activity are achievable with appropriate metal systems. Indeed, most unusual catalytic systems have been reported in which trace elements (apparently entrained during purification of reagents over stainless steel spinning bands) catalyze the valence isomerization of quadricyclene derivatives to norbornadiene products, and do so with remarkable facility.[27] The nature of these elements is unknown. However, the apparent high levels of activity pose some interesting questions regarding their mode of catalysis. The real breadth of the chemistry associated with the forbidden-to-allowed process is essentially unknown, remaining the subject of experimental research. The dynamics of this process would seem to depend on the thermodynamic driving force of the [2 + 2] ligand transformations, the changes in metal-to-ligand coordinate bonding, and the attendant energy barriers associated with the ligand fields of the nonreacting ligands.

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[26] Consider the oxidative-cycloaddition mechanism proposed for both olefin cyclobutanation and cyclobutane ring-opening processes.[19] For the ring-opening path, the oxidative-addition step, to be symmetry allowed, should be considered a $[{}_{d}2_{a} + {}_{\sigma}2_{s}]$ process (1) (the subscripts d and a on the first term refer to a metal d orbital which is antisymmetric to the symmetry plane bisecting the two reaction participants). The metal thus supplies an electron pair through one of its antisymmetric atomic orbitals. The second step, however, corresponds to a $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ process and the metal thus must withdraw from the transforming ligand system an electron pair through one of its symmetric (with respect to the plane of symmetry passing through metallo–ring) atomic orbitals. Orbital symmetry restraints due to the ligand-field effects discussed above could enter here, introducing energy barriers to the second step. The transition metal, however, has a larger number of symmetric atomic orbitals than antisymmetric and thus can be in a variety of ligand fields which split the d orbitals in a way allowing the unhindered introduction of valence electrons into a symmetric atomic orbital. This would particularly be the case for metal systems with fewer d electrons, where a broader number of symmetric atomic orbitals would be available to accommodate the returning electron pair. The reverse, however, is true for reactions proceeding in the opposite direction. The oxidative-addition step now is described $[{}_{d}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s}]$ and the second step (extrusion) $[{}_{\sigma}2_{a} + {}_{\sigma}2_{s}]$. The second step, extrusion of a cyclobutane ring, can experience significant orbital symmetry restrictions due to ligand-field effects, particularly in the d-electron-rich metal systems, since the metal must withdraw an electron pair through an antisymmetric orbital.

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Preparation and Spectroscopic Properties of Methylamino Derivatives of Some Difluoro- and Bis(trifluoromethyl)phosphorus Compounds

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received April 6, 1970*

Abstract: The preparation and characterization of four new compounds of the type $(CF_3)_2P(E)N(H)CH_3$ and $F_2P(E)N(H)CH_3$ (E = O, S) by aminolysis of the appropriate chlorophosphorus compound is described. Infrared and nmr spectra of the compounds indicate that no conformational preference is adopted on the latter time scale although the presence of conformational isomers may be indicated by infrared. Some hydrogen bonding is indicated by infrared studies especially for the compound $F_2P(O)N(H)CH_3$, which appears to be strongly hydrogen bonded in all states. The nmr spectral behavior indicates the presence of coupling of the N–H proton to the methyl proton. Second-order intensity variations are observed when the N–H chemical shift is close to that of the CH_3 group. The nmr spectra of the phosphines $X_2PN(H)CH_3$ (X = F, CF_3) show the same features.

Recently much interest has developed in the structural properties of P–N compounds especially in connection with the question of π bonding and restricted rotation about the phosphorus–nitrogen bond in amino derivatives of trivalent phosphorus compounds.[1-6] As part of a continuing study on the prop-

Table I. Synthesis of Methylaminophosphorus Compounds

	Reaction quantities				Analyses,							
					Calcd				Found			
	EPX_2Cl taken, mmol	EPX_2Cl recovered, mmol	Amine taken, mmol	EPX_2-$NHCH_3$ yield, mmol (%)	N	P	S	CF_3[c]	N	P	S	CF_3[c]
$OPF_2N(H)CH_3$	5.4	0.4	10.3	4.67 (94)	12.17	26.96			12.00	26.28		
$OPF_2N(D)CH_3$	2.95	0	6.0									
$SPF_2N(H)CH_3$	6.11	0.33	11.8	4.85 (84)	10.69	23.7	24.4		10.46	22.8	23.1	
$SPF_2N(D)CH_3$	3.09		6.07									
$PF_2N(H)CH_3$	6.05	0.8	10.9	5.05 (96)[a]								
$PF_2N(D)CH_3$	4.10[b]		4.14									
$(CF_3)_2P(O)N(H)CH_3$	1.01	0	2.03	0.4 (40)								
$(CF_3)_2P(O)N(D)CH_3$	0.99	0.50	1.04	0.49 (94)								
$(CF_3)_2P(S)N(H)CH_3$	1.06	0	2.25	0.99 (93)				29.9				29.7
$(CF_3)_2P(S)N(D)CH_3$	0.95	0	2.0									

[a] A trace of PF_3 was also obtained. [b] PF_3 was used in place of PF_2Cl for this synthesis only. Unreacted PF_3 was recovered. [c] Determined as CF_3H.

erties of volatile fluorophosphorus compounds, we now wish to report the results of synthetic and spectroscopic studies of some four-coordinated pentavalent monomethyl aminophosphorus fluorides and their trifluoromethyl analogs and further studies on related phosphines.

Experimental Section

Standard vacuum techniques using Pyrex glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon "N" grease. Infrared spectra were obtained with a Perkin-Elmer 421 dual-interchange (4000–300 cm^{-1}) instrument. Low-temperature spectra were obtained with a cell similar to that described by Wagner and Hornig.[7] Mass spectra were obtained with an AEI-MS-9 double-focusing mass spectrometer, and nmr spectra with Varian A-56/60 or HA-100 instruments. Proton spectra were measured at 60 and 100 MHz relative to TMS. Fluorine spectra were measured at 94.1 or 56.4 MHz relative to $CFCl_3$ and phosphorus spectra were measured at 40.5 MHz relative to P_4O_6. (PBr_3 was used as a reference to obtain low temperature ^{31}P spectra.) Vapor pressures were measured with a glass spiral microtensimeter[8] using the null-point technique with both ascending and descending temperature.

Materials. Chlorophosphoryl and chlorothiophosphoryl difluorides were prepared by partial fluorination of phosphoryl or thiophosphoryl trichloride with antimony trifluoride, followed by vacuum fractionation. Methylamine-d_2 was prepared by several successive exchanges of monomethylamine with concentrated NaOD in D_2O solution and checked by ir, molecular weight (mol wt calcd for CH_3ND_2, 33.0; found, 33.0), and mass spectroscopy including mass measurement of the parent ion (m/e calcd for CH_3D_2N, 33.0548; found, 33.0546). Trifluoromethylphosphorus iodides were obtained from the reaction of CF_3I with phosphorus.[9] Chlorobis(trifluoromethyl)phosphine,[10] chlorobis(trifluoromethyl)phosphine sulfide,[11] and chlorobis(trifluoromethyl)phosphine oxide[12] were prepared by literature methods as was $(CF_3)_2PN(H)CH_3$.[13] The N-deuterated analog of the latter was prepared by the identical procedure using CH_3ND_2 in place of monomethylamine.

Preparation of Monomethylamino Derivatives. Method A. Methylamine (2 mol equiv) was condensed into a stopcocked side arm of a 1-l. reaction vessel and 1 mol equiv of the appropriate chlorophosphorus difluoride was condensed into the reaction vessel and allowed to expand into the 1-l. volume. The amine was warmed and slowly admitted to the gaseous chlorophosphorus compound at room temperature through the stopcock provided on the side arm. Reaction occurred immediately on contact of the gaseous reagents with the visible formation of a white solid. After allowing 15 min for complete mixing of the reactants, the volatile materials were admitted to the vacuum system and the constituents separated by fractional condensation. The desired products were trapped at −45°, except in the case of $F_2PN(H)CH_3$, which passed −63° and was trapped at −96°. Excess chlorophosphorus compound was usually used because of easier separation of this constituent from the products. Reactant and product quantities are given in Table I.

Method B. Methylamine (2 mol equiv) and 1 mol equiv of chlorophosphine were condensed into a sealed tube which was then allowed to warm to room temperature, whereupon visible reaction was immediately observed. The volatile materials were taken into the vacuum system and separated as above.

Vapor pressures of the thiophosphoryl compounds were determined. The data are given in Table II and the volatility constants in Table III. Mass spectral results of all new compounds are given in Tables IV and V.

Table II. Vapor Pressure Data

$SPF_2N(H)CH_3$						
Temp, °C	0.0	6.7[a]	9.9	15.5[a]	20.8	25.3[a]
P(obsd), mm	2.3	3.5	4.0	6.0	8.2	10.6
P(calcd),[b] mm	2.3	3.5	4.2	5.9	8.0	10.3
Temp, °C	30.9	35.6[a]	39.8	45.7[a]	52.0	
P(obsd), mm	14.2	17.0	21.5	28.7	39.8	
P(calcd),[b] mm	13.9	17.7	21.8	29.1	39.0	

$(CF_3)_2P(S)N(H)CH_3$									
Temp, °C	19.8	25.7	32.0	36.0	39.2	45.5	51.2	59.5	69.0
P(obsd), mm	4.4	6.2	8.7	10.8	12.6	16.1	23.1	31.6	48.2
P(calcd),[b] mm	4.5	6.2	8.6	10.6	12.5	16.9	22.1	32.1	48.2

[a] Observed with temperature descending from maximum value obtained. All others measured with ascending temperature. [b] Pressures calculated from the equation log P (mm) $= A - B/T$, using the volatility constants given in Table III.

Method A was used to prepare $F_2PN(H)CH_3$ (also prepared elsewhere by a different method[14]), $F_2P(O)N(H)CH_3$, $F_2P(S)N(H)CH_3$, and their deuterated analogs because method B consistently gave poor yields of the desired monosubstituted product and

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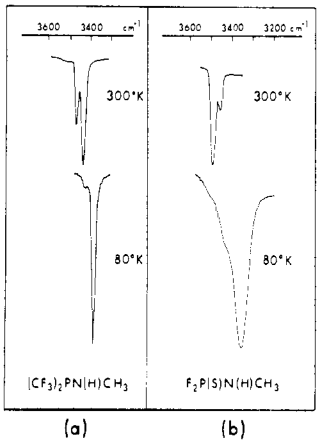


Figure 1. Gas-phase (300°K) and solid-phase (80°K) infrared spectra of the N-H stretching region of $(CF_3)_2PN(H)CH_3$ and $F_2P(S)N(H)CH_3$.

significant proportions of disubstituted products. With reaction temperatures as low as −95°, method B gave improved yields of the desired products but the reactions were not as clean as those done in the gas phase. Reagent quantities, yields, and characterizations are given in Table I.

Table III. Volatilities of Thiophosphorylamines

	$SPF_2N(H)CH_3$	$(CF_3)_2P(S)N(H)CH_3$
Volatility constants		
A	8.065	7.836
B	2105	2105
ΔH_{vap}, cal/mol	9633	9634
Extrapolated bp, °C	132.9	151.7
Trouton constant, eu	23.7	22.7

Table IV. Mass Measurement of Parent Ions

	m/e	
	Calcd	Found
$F_2P(O)N(H)CH_3$	114.9999	114.9991
$F_2P(O)N(D)CH_3$	116.0062	116.0062
$F_2P(S)N(H)CH_3$	130.9761[a]	130.9759[a]
$F_2P(S)N(D)CH_3$	131.9834[a]	131.9830[a]
$F_2PN(H)CH_3$	99.0050	99.0050
$F_2PN(D)CH_3$	100.0113	100.0108
$(CF_3)_2P(O)N(H)CH_3$	214.9935	214.9936
$(CF_3)_2P(O)N(D)CH_3$	215.9998	215.9990
$(CF_3)_2P(S)N(H)CH_3$	230.9707[a]	230.9706[a]
$(CF_3)_2P(S)N(D)CH_3$	231.9769	231.9754

[a] Accurate masses calculated and measured for ^{32}S isotope.

An alternative preparation of methylaminophosphoryl difluoride involved reaction of difluorophosphoric acid anhydride, $(OPF_2)_2O$ (0.99 g, 5.31 mmol), with methylamine (0.34 g, 10.97 mmol) in the gas phase according to method A. Immediate reaction was observed upon mixing of the reagents. The only volatile product obtained was $F_2P(O)N(H)CH_3$ (0.44 g, 3.79 mmol, 72% yield). A white solid and a small amount of an involatile colorless liquid remained in the reaction vessel.

The compounds $(CF_3)_2P(O)N(H)CH_3$, $(CF_3)_2P(S)N(H)CH_3$, and their deuterated analogs were prepared by method B. Reactant and product quantities are given in Table I.

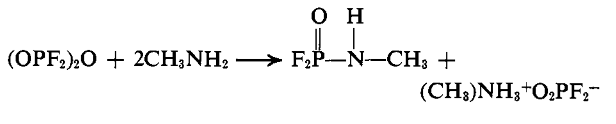
Results and Discussion

A. Preparations. The general synthetic reaction

$$X_2P(E)Cl + 2CH_3NH_2 \longrightarrow X_2P(E)N(H)CH_3 + CH_3NH_3Cl \quad (1)$$

where X = CF_3, F; E = O, S, involving preferential aminolysis of the P–Cl group can be straightforwardly applied to the CF_3 system by simple combination of the required reagents. In order to obtain good yields of the fluoro compounds, it was necessary to conduct the reaction in the gas phase with the chlorophosphorus compound in excess; otherwise concomitant aminolysis of the P–F groups occurs, which yields undesired products. Although P–Cl reacts preferentially with methylamine it is well known that P–F groups also react readily with amines;[15–17] hence it is necessary to dilute the reagents in order to obtain good yields of the desired products. In one case, synthesis of $PF_2N(D)CH_3$, readily available PF_3 was used in place of PF_2Cl.

An alternate route to the synthesis of *N*-methyl(difluorophosphoryl)amine was provided by the gas-phase reaction of monomethylamine with difluorophosphoric anhydride



$$(OPF_2)_2O + 2CH_3NH_2 \longrightarrow F_2\overset{\overset{\displaystyle O}{\|}}{P}-\overset{\overset{\displaystyle H}{|}}{N}-CH_3 + (CH_3)NH_3{}^+O_2PF_2{}^- \quad (2)$$

a reaction which is analogous to the synthesis of $F_2P(O)NH_2$ from $(OPF_2)_2O$ and ammonia[18] except that the latter was done in solution rather than the gas phase.

All of these compounds were clear colorless liquids of relatively low volatility. The thiophosphoryl compounds were the most volatile, as is usually observed. The low volatility of the fluorophosphoryl amines made their handling in the vacuum system slow and inconvenient.

B. Nmr Spectral Properties. The nmr spectral properties of these compounds are of interest because of the importance of this technique in conformational studies.[1–6] The methyl-region spectra ($\tau \cong 7.0$) of $F_2P(O)N(H)CH_3$ and $(CF_3)_2P(O)N(H)CH_3$ are perfectly symmetric and are satisfactorily interpreted by first-order analysis. The methyl-region spectrum of $F_2P(S)N(H)CH_3$ is not symmetric, but shows an intensity bias, as illustrated in Figure 1; otherwise, the spectral pattern is similar to the symmetric pattern displayed by the above molecules. The fluoro compounds typically show triplet structure in all of the above cases due to $^4J_{FH}$, whereas the $^5J_{FH}$ coupling was not resolved in any of the CF_3 compounds studied here or elsewhere.[1] A notable feature of all of the spectra is the presence of a coupling of the amino hydrogen (H′) with the methyl hydrogens ($^3J_{HH'}$) of the order of 5 cps, even though the N–H′ signal is broad and poorly defined. The effect of $^3J_{HH'}$ and $^3J_{PH}$ couplings is to split the methyl-group resonance into a doublet of doublets. This interpretation is further confirmed by the observations that (1) the spacings within the methyl doublet of doublets are identical at 60 and 100 MHz, indicating that the spectral pattern arises from coupling interactions and not chemically shifted isomers, and also (2) this pattern is not observed in the N-deuterated aminomethyl compounds; rather the $X_2P(E)N(D)CH_3$ analogs show only a doublet for the methyl resonance with the $^3J_{PH}$ coupling nearly identical with that found in the $N(H)CH_3$

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Table V. Mass Spectra

m/e	Intensity[a]	Assignment[b]	m/e	Intensity[a]	Assignment[b]
	$(CF_3)_2P(O)N(H)CH_3$			$(CF_3)_2P(S)N(H)CH_3$	
215	2.1	$C_2F_6PONCH_4$	233	0.6	M + 2
214	1.1	$C_2F_6PONCH_3$	232	0.8	M + 1
164	1.6	$CF_3PFONCH_3$	231	7.5	$C_2F_6PSNCH_4$(M)
147	0.8	CF_4PNCH_2	164	1.1	162 + 2
146	23.3	CF_3PONCH_4, CF_4PNCH	163	1.3	162 + 1
114	1.8	F_2PONCH_3, CF_3PN	162	16.7	CF_3PSNCH_4
107	2.0	CF_2PNC	133	0.7	CF_4PN
96	12.3	$FPONCH_4$, F_2PNCH	130	1.4	F_2PSNCH_3
81	0.7	F_2PC	119	1.3	CF_3PF
80	15.2	$FPNCH_4$	114	0.9	CF_3PN, 112 + 2
78	3.8	$FPNCH_2$	113	1.2	CF_2PS, 112 + 1
76	2.3	$PONCH_3$, FPCN	112	16.1	$FPSNCH_4$
69	7.5	PF_2, CF_3	100	0.6	C_2F_4, CF_3P
67	1.3	FPOH	93	1.0	$PSNCH_4$
60	2.4	$PNCH_3$	92	1.6	$PSNCH_3$
59	1.3	$PNCH_2$	83	1.7	F_2PN
51	1.0	CF_2H, PFH	81	1.1	F_2PC
50	1.0	PF, CF_2	80	13.9	$FPNCH_4$
49	1.5	H_2PO	78	1.6	$FPNCH_2$, HNPS
48	0.7	HPO	69	5.6	CF_3, PF_2
47	11.2	PO	65	0.8	FPNH
46	2.9	PNH	64	1.0	FPN
33	0.7	PH_2	63	9.7	PS
31	1.5	P	61	1.0	$PNCH_4$
			60	2.8	$PNCH_3$
			59	1.2	$PNCH_2$
	$SPF_2N(H)CH_3$		51	0.9	CF_2H, PFH
133	1.4	M + 2	50	0.9	CF_2, PF
132	1.1	M + 1	46	2.8	PNH
131	28.8	SPF_2NCH_4	32	1.3	S
130	2.6	SPF_2NCH_3	31	0.8	P
112	2.0	$SPFNCH_4$		$OPF_2N(H)CH_3$	
110	2.0	$SPFNCH_2$	115	22.2	OPF_2NCH_4
103	1.7	SPF_2H_2	114	23.7	OPF_2NCH_3
102	1.7	SPF_2H	112	2.6	OPF_2NCH
101	8.9	SPF_2	104	2.1	OPF_3
98	25.6	F_2PNCH_4	98	1.3	F_2PNCH_3
80	1.1	$FPNCH_4$	96	2.8	$OPFNCH_4$
78	1.7	$FPNCH_2$	94	5.4	$OPFNCH_2$
69	12.9	PF_2	87	10.8	OPF_2H_2
63	1.1	PS	86	2.1	OPF_2H
60	0.9	$PNCH_3$	85	8.2	OPF_2
50	1.7	PF	69	7.7	PF_2
47	0.9	PNH_2	67	4.4	POFH
46	1.4	PNH	66	1.3	OPF
45	0.9	PN	50	1.0	PF
32	1.1	S	47	1.8	PO

[a] Ions such as NCH_4, NCH_3, and NCH_2 arising from the fragmentation of the methylamino group are not included in the listing. Intensities are expressed relative to the total ionization defined as Σ_n(intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Positive ion spectra. Masses of sulfur-containing fragments are calculated for the ^{32}S isotope. The symbol M refers to the molecular ion.

compounds. Because D–H coupling constants are about one-seventh the size of H–H coupling constants, the former were not usually resolved, although one case, illustrated in the spectrum of $F_2P(S)N(D)CH_3$ (Figure 1), did show this splitting owing to a fortuitous coincidence of $^4J_{FH}$ and $^3J_{DH}$ which gave an easily resolved overlapping pattern. The spectral parameters are given in Table VI.

The intensity bias in the methyl nmr spectrum of $F_2P(S)N(H)CH_3$ can be ascribed to the proximity of NH and CH_3 resonances, whereupon the ratio J/σ indicates that second-order spectral interpretation is required. Second-order spectra calculated[19] from the parameters listed in Table VI give both line positions and intensities in excellent agreement with observed spectra. The greater chemical shift differences between N–H and CH_3 in the compounds $(CF_3)_2P(O)N(H)CH_3$ and $F_2P(O)N(H)CH_3$ (where τ_{NH} ~4.0–5.0) allows a first-order interpretation. We have obtained similar results to the above for $(CF_3)_2PN(H)CH_3$, in agreement with a recent reinterpretation of the methyl-region nmr spectrum of this compound. Thus the doublet of doublets observed[1] can be ascribed to amino hydrogen and phosphorus coupling with the methyl protons. The constancy of the four-line CH_3 pattern at both 60 and 100 MHz and the collapse of the four-line pattern to a simple doublet in the N-deuterated derivative supports this interpretation[6] and does not support the proposed presence of rotational isomers.[1]

The methyl proton spectrum of $F_2PN(H)CH_3$ is, in agreement with a previous report,[14] a broad complex multiplet at both 60 and 100 MHz for reasons which are

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(19) Spectra were calculated by the program NSPECT III kindly supplied by Dr. J. S. Martin of this department.

Table VI. Nuclear Magnetic Resonance Parameters of Methylamino Compounds

	Chemical shifts[a]			Coupling constants[b,c]					
	τ(NH)	$\tau(CH_3)$	ϕ(F)	J_{PF}	J_{PH}	$J_{PH'}$	J_{FH}	$J_{FH'}$	$J_{HH'}$
$(CF_3)_2PN(H)CH_3$[d]	7.7	7.16	64.5	82.4	11.6	NR	NR	NR	5.2
$(CF_3)_2PN(D)CH_3$		7.11	60.8	82.0	11.4		0.6		
$(CF_3)_2P(O)N(H)CH_3$	4.5	7.08	72.2	111	11.5	NR	0.6	NR	5.6
$(CF_3)_2P(O)N(D)CH_3$		7.09	72.2	112	11.5		0.5		
$(CF_3)_2P(S)N(H)CH_3$	~7	7.08	72.3	106	13.2	NR	NR	NR	4.6
$(CF_3)_2P(S)N(D)CH_3$		6.99	72.4	106	13.3		0.6		
$F_2PN(H)CH_3$ (in CCl_3F)[e]	?	7.4	70.2	1197	Complex		2.0	10.35	NR
$F_2PN(H)CH_3$ (in py–CCl_3F)		7.9	69.5	1177	7.05		2.4	11.0	5.8
$F_2PN(D)CH_3$		7.2	70.5	1190	NR		NR		
$F_2P(O)N(H)CH_3$	?	7.23	80.5	991	13.7	20	1.2	1.5	5.6
$F_2P(O)N(D)CH_3$		7.22	81.5	986	13.8		NR		
$F_2P(S)N(H)CH_3$[f]	?	7.07	52.4	1083	14.3	20.7	1.0	5.2	5.8
$F_2P(S)N(D)CH_3$		7.06	52.2	1083	14.2		~1.0		

[a] Hydrogen chemical shifts are measured relative to tetramethylsilane τ 10.0. Fluorine chemical shifts are given relative to CCl_3F. [b] Values in cps. H′ refers to the NH proton. [c] NR = not resolved. [d] In agreement with ref 1 and 6. [e] In agreement with ref 16. [f] ^{31}P chemical shift = 42.6 ppm *vs.* P_4O_6.

identical with those outlined above. In this case further evidence is provided by the pronounced simplication of the 60-MHz proton spectrum of $F_2PN(H)CH_3$ to a doublet of doublets of triplets upon addition of pyridine to the sample solution. The ^{19}F spectrum of this solution shows a doublet of doublets of quartets as expected for the above structure in which all possible spin-$^1/_2$ couplings are resolved into a first-order spectrum. It seems reasonable to suggest that interaction of pyridine serves to shift the amino proton to lower field, removing the accidental coincidence of chemical shifts which gave rise to the complex multiplet pattern. The coupling of the amino proton to the methyl group is observed as in all other compounds in this system.

The spectra of all of the $X_2P(E)N(H)CH_3$ compounds with the exception of $(CF_3)_2P(S)N(H)CH_3$ are essentially unchanged with temperature down to about −90°, which was the lowest temperature available to us. The methyl-region spectrum of $(CF_3)_2P(S)N(H)CH_3$ did, however, show some temperature variations. At normal probe temperatures (35°) a doublet ($J \cong 13.4$ cps) of relatively broad and nonsymmetric lines is observed. Cooling the sample to about −20° results in the resolution of two components from each broad line: one apparently about twice as intense as the other member. Further cooling improves the separation of the two components until at −40° the spectrum is similar in appearance to that of $(CF_3)_2PN(H)CH_3$ except that the weaker components of the second-order A_3 part of the A_3BX spectrum appear on the high-field rather than low-field side. Further cooling has little effect on the spectrum except that at −80° a broad signal which can be assigned to the N–H resonance emerges from the low-field side of the methyl multiplet and so accounts for the direction of the intensity bias. The spectrum is best interpreted in a way consistent with that of all of the other $X_2P(E)N(H)CH_3$ compounds with the only differences being due to the position of the N–H chemical shift. The temperature behavior of the CH_3 spectrum of $(CF_3)_2P(S)N(H)CH_3$ is best interpreted as the result of changes of the NH′ chemical shift with temperature. The N–H′ proton, however, couples with the methyl protons as in the other compounds, creating the characteristic A_3BX pattern observed in all cases here. The N-deuterated derivative shows only a sharp doublet which is unchanged in shape and position down to −90°, confirming the above interpretation. The 100-MHz spectrum at normal probe temperatures (+40°) is similar in appearance to the 60-MHz spectrum obtained at −20° and shows the characteristic intensity-biased doublet of doublets. The resolution of these features at the ordinary probe temperature (40°) of the 100-MHz instrument probably occurs because of the increased separation of CH_3 and NH′ resonances at the higher field. The sense of the intensity bias is the same as that shown by the −20 to −60° spectra obtained at 60 MHz.

All of these compounds therefore exhibit A_3BX spectra characterized by coupling of phosphorus and the amino proton to the methyl group. They differ only in the position of the NH chemical shift relative to that of the CH_3 chemical shift and its relationship to the coupling constants. Although the N–H resonance is usually well separated from that of CH_3, occasional accidental proximity must be expected, particularly when the nitrogen contains such strongly modifying substituents as $(CF_3)_2P$ or F_2P groups. It is possible that the geometry at the nitrogen is planar or nearly so in these compounds as it is in crystalline $F_2PN(CH_3)_2$[20] and this feature may be responsible for the observed chemical shifts. The nmr spectra, however, provide no evidence of distinct rotational isomers in any of these compounds down to −90°. Recent indications[6] that rotational isomers can be distinguished in the nmr spectra of $(CF_3)_2PN(H)CH_3$, $Cl_2PN(CH_3)_2$, and $(CF_3)_2PN(CH_3)$ at temperatures of the order of −120° indicate that the spectra observed here from +40° to −90° are averages of all rotational conformations. The barriers to rotation about the P–N bond in the presently investigated series of compounds are probably similar to the values of 8–9 kcal estimated for the above phosphines.[6] We are attempting to extend the temperature range of our measurements in order to obtain a clearer picture of rotational barriers in the pentavalent P(O) and P(S) compounds.

C. Infrared Spectral Studies. In general, the gas-phase infrared spectra of compounds of the type $X_2P(E)NHR$ show two rather than one band in the N–H stretching region. The bands are best described in terms of a poor-to-well-resolved shoulder on a peak of

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(20) E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

Table VII. Infrared Frequencies of Methylamino Compounds[a]

$(CF_3)_2PN(H)CH_3$		$(CF_3)_2P(O)N(H)CH_3$		$(CF_3)_2P(S)N(H)CH_3$		$F_2PN(H)CH_3$		$F_2P(O)N(H)CH_3$		$F_2P(S)N(H)CH_3$		
Gas[b]	Solid	Gas	Solid	Gas	Solid	Gas[c]	Solid	Gas	Solid	Gas	Solid	Assignment
3465 m	3375 s	3490 m	3180 s	3435 m	3290 s	3458 m	3415 s	3256 m	3265 s	3482 m	3330 s	N—H stretch
3430 ms		3455 m				3395 w, sh				3446 w	3230 wsh	
	3000 m						3015 sh		3000 vw			
2980	2975 w					3013 sh	2980 w					
2945	2945 m	w, br	2940 m	2980 vw	2900–2975		2955 w	2955 brw	2958 m	2960 m	2992 vw	
2920	2920 w	NR	2890 m	2950 vw	w, br	2963 s	2925 m		2922 vw	2920 w	2960 vw	
	2885 w			2910 vw		2915 sh	2905 sh				2938 w	CH_3 stretch
2840	2840 w		2830 m	2830 w	2830 vw	2830 m	2830 w		2850 vw	2850 w	2843 vw	
	2790 w										2792 vw	
2260												
												CF overtone
2240												
	1488 m		1485 m		1485 w	1460 w	1480 m		1488 m		1478 w	
1476	1447 w		1460 m		1470 w		1420 sh		1445 m		1451 w	
1436	1441 w		1425 m						1429 m		1433 vw	
1388	1400 m			1392 m	1400 w	1384 s	1390 s	1416 m PQR	1390 wsh	1390 ms	1396 s	
				1386 m								
		1324 m	1293 s					1327 s	1309 vs			P=O stretch
1279												
	1215 sh	1215 s	1221 s	1218 s	1218 s							
1200	1204 s	1185 s	1211 s	1189 vs								
1165	1152 vs	1158 s	1170 vs	1170 vs	1173 vs							CF_3 stretch
1155	1134 vs	1130 m	1126 s	1159 s	1129 s							
1108	1109 m			1127 m								
							1260 s					
							1155 sh	1125 mbr				
1095	1091 s	1080 m	1089 s	1091 ms	1090 ms				1153 m	1110 s	1135 wsh	
	1085 s					1100 vs	1102 vs	987 s	1119 s		1108 vs	PNC stretch
	1073 m										1017 w	
			1000 w				950 w	937 m	991 m	982 m	969 vw	
						892 s[d]	890 vw				951 w	
						828 vs	800 s	916 s	937 vs	920 vs	910 vs	P—F stretch
						823 vvs	775 s	890 m PQR	893 vs	876 vs	864 vs	
809	833 s	877 m	865 m	872 ms	867 s	787 vs	725 vvs	864 ms	872 wsh			
						779 s, sh			803 w			
782				777 w								
				764 m	761 m							CF_3 antisym def
739				720 w	708 m							
											692 wsh	
				696 ms	682 s					697 m	685 vs	P=S stretch
563	570 m		586 ms		551 m							CF_3 sym def
540	563 ms	575 m	566 ms	544 m	547 m							
	524 m									458 m		
	490 s						550 s			410 m		
	478 s	490 m	515 m	485 ms	495 ms		495 s	460 m				
			503 m		460 m							
464	446 m									383 m		

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[a] Solid spectra were obtained at approximately 80°K, gas-phase spectra at room temperature. Abbreviations represent: br = broad, m = medium, s = strong, sh = shoulder, w = weak, v = very, NR = not resolved. [b] See ref 1. [c] See ref 14. [d] In contrast to ref 14, we only observe a very weak band at 892 cm^{-1} in the infrared spectrum of this compound, and it is likely that this peak arises from an impurity.

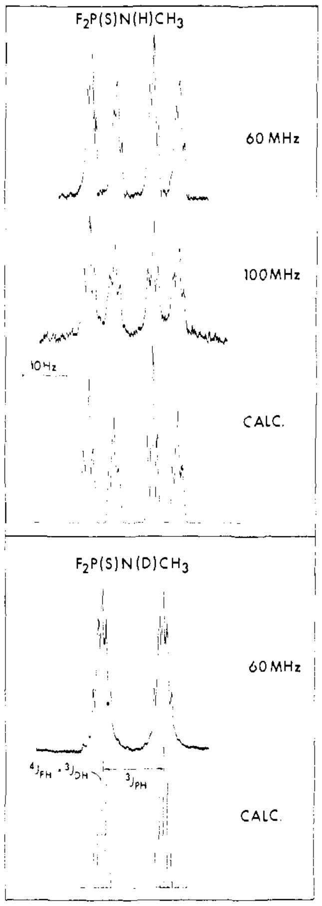
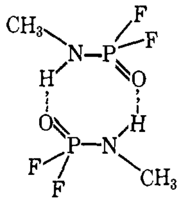


Figure 2. A comparison of observed methyl region (τ ~7.0) of $F_2P(S)N(H)CH_3$ at 60 and 100 MHz with the calculated spectrum and with the spectrum of the N-deuterated analog. All spectra were obtained on an approximate 15% solution of the compounds in CCl_3F and all spectra are shown on the same sweep-width scale (100 cps) with field increasing to the right.

reasonable intensity. A typical example is illustrated in Figure 2.

Gas-phase spectra of $(CF_3)_2P(O)N(H)CH_3$ and $F_2P(S)N(H)CH_3$ have a relatively sharp absorption in the N–H region at values generally assigned to an unassociated[21] N–H group (3400–3500 cm^{-1}) with a shoulder at lower energy. The gas-phase spectra of $(CF_3)_2P(S)N(H)CH_3$ and $F_2P(O)N(H)CH_3$ are different, however; the former shows only one fairly sharp band at 3435 cm^{-1} and the latter has a relatively broad band centered at 3256 cm^{-1}. Condensing the above compounds to the solid state at approximately 80°K resulted in three cases in a pronounced broadening of the N–H band and a significant shift to lower wave-number values as shown in Table VII. The relatively broad band at 3256 cm^{-1} in the gas-phase spectrum of $F_2P(O)N(H)CH_3$ did not, however, significantly change its shape or position upon condensing the compound to the solid phase at 80°K. A 10% solution of $F_2P(O)N(H)CH_3$ in CCl_4 showed the same broad band at 3260 cm^{-1}. The shape and position of this band were unchanged upon dilution of the solution to 0.05%. It seems reasonable to postulate that the observed spectral changes are due to two effects, hydrogen-bonding interactions of the N–H group and differences of interaction in conformational isomers.

The lack of change of the spectrum of $F_2P(O)N(H)CH_3$ with change of state suggests that this compound exists primarily in the hydrogen-bonded form in gas, solution, and solid states. In view of the persistence of the association and the low volatility of the compound, it seems reasonable to propose that the hydrogen-bond association is intermolecular; perhaps through the formation of a dimer (**1**) or perhaps extended-chain polymers. Intramolecular hydrogen bonding would appear to be less likely because of unfavorable steric requirements.



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The remaining compounds, including $(CF_3)_2P(O)N(H)CH_3$, do not provide evidence in favor of strong hydrogen bonding in the gas phase; rather the molecules appear to exist as equilibrium mixtures of two conformations in the gas phase as indicated by the presence of two N–H frequencies which can be assigned to two conformations of the $N(H)CH_3$ group with respect to the X_2P group. Condensation to the solid state, however, gives rise to substantial shifts in the N–H stretching frequency which are compatible with the formation of hydrogen-bonded N–H groups in the solid. The most marked shift of the N–H frequency upon condensation to the solid state is about 300 cm^{-1} in the case of $(CF_3)_2P(O)N(H)CH_3$. The solid-state N–H absorption is then similar in both phosphoryl compounds. Both of the thiophosphoryl compounds exhibited smaller shifts of 135–180 cm^{-1} upon condensation to the solid state, which suggests that hydrogen bonding to the P═O or P═S group is involved in all systems rather than hydrogen bonding to fluorine atoms. Finally, the lowest shifts are those shown by the phosphines, 55 cm^{-1} from the strongest gas band to the solid-state band in the case of $(CF_3)_2PN(H)CH_3$ and 42 cm^{-1} in the case of $F_2PN(H)CH_3$. The sharpness of the bands in the solid-state spectra of the phosphines suggests that the molecules have been stabilized in one conformation at this temperature, but it is not possible to decide from the available evidence which conformation is preferred. The broadness of the bands in the other compounds, particularly the P═O compounds, may arise from the existence of more than one conformation or from various forms of intermolecular association in the solid state. It is unfortunate that all of our attempts to produce narrow bands in the solid-state spectra of P═O and P═S compounds by means of various annealing and condensation procedures have been unsuccessful.

The two bands which are observed in the gas-phase spectra of all $X_2P(E)N(H)CH_3$ compounds except $(CF_3)_2P(S)N(H)CH_3$ (which shows only one band) are most probably due to the presence of different rotational isomers in the compounds in which the N–H stretching frequency is affected by its relationship to the substituents on phosphorus. Both frequencies occur

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[21] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958.

in the nonassociated region and may be reasonably assigned to the cis and trans orientations of the N–H group relative to the X_2P group.[21] The detailed assignments are further complicated by the possibility that the nitrogen may be planar in these molecules;[20] thus the bands may arise through the existence of three conformations (Figure 3, I–III), of which two (I and II) will probably have similar N–H environments and thus similar N–H stretching frequencies, whereas the third pyramidal nitrogen conformation (III) will have a different stretching frequency from the other two. If on the other hand the nitrogen is planar, the two most likely conformations (Figure 3, IV and V) provide cis and trans orientations of the CH_3 groups relative to the $(CF_3)_2P$ group. In the absence of the appropriate dipole moment data a definite interpretation of the intensity patterns cannot be made at this time. If, however, following others,[6] we assume a nearly planar nitrogen environment and that steric arguments suggest that the *trans*-CH_3 (V) structure is the most abundant and assign the lower frequency to the cis conformation and the higher to the trans,[21] we are led to the conclusion that the cis form is the least abundant form observed in the spectra of $F_2PN(H)CH_3$ and the pentavalent $X_2P(E)N(H)CH_3$ compounds except $F_2P(O)N(H)CH_3$, which appears to be wholly hydrogen bonded, and $(CF_3)_2P(S)N(H)CH_3$, which shows only one band in the N–H region. In this latter case the observation of only one band suggests that either only one conformation exists (which is unlikely in view of the nmr results which suggest that the $N(H)CH_3$ group is freely rotating on the nmr time scale at 25°) or that there is little difference in the N–H stretching frequencies of the cis and trans conformations.

In the case of $(CF_3)_2PN(H)CH_3$ the weaker component of the N–H absorptions is found to high energy rather than low energy, in contrast to the behavior of $F_2PN(H)CH_3$. As a consequence, either the cis (IV) form must be the more abundant of the two conformations (perhaps through strong intramolecular interactions or substantially different dipole moments in each conformation) or the reverse assignment of the frequencies should be made in this case. The infrared spectrum of the compound $(CF_3)_2PN(H)CH_3$ is also anomalous in the series of molecules studied here in that it shows the largest splitting between the two gas-phase N–H frequencies. It has been clearly established, however, by overtone and isotopic substitution spectra[1] that both the 3465- and 3430-cm^{-1} bands arise from N–H stretch vibrations. The very pronounced shift of the N–H stretching region to one sharp band in the solid state further suggests that the two bands in the gas phase arise from different conformers, only one of which is favored in the solid. Unfortunately, the available evidence does not permit a decision as to whether the solid structure contains the cis or the trans conformers. It is interesting to note also that the relative intensities of the two bands in the NH region of the spectrum of $(CF_3)_2PN(H)CH_3$ did not change over the temperature range 20–90°, which suggests that the relative populations are not greatly affected by temperature in this region, in contrast to the pronounced effect observed upon solidifying the compound. Further understanding of the behavior of $(CF_3)_2PN(H)CH_3$ will only be achieved with additional gas- and solid-state structural data, particularly on the conformation and geometry of the $N(H)CH_3$ group in both states.

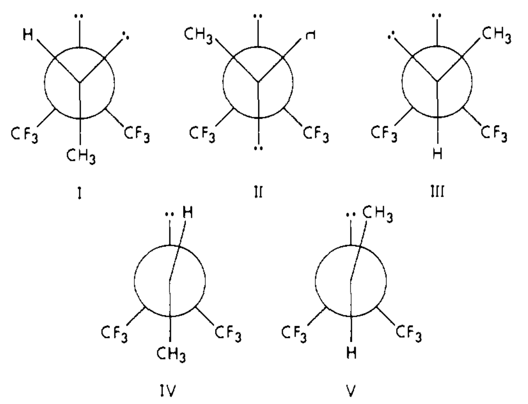

Figure 3. A representation of the conformations of $(CF_3)_2PN(H)CH_3$.

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