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Phosphoranes. 11. Barriers to Permutational and/or Rotational (P–N) Processes in (Trifluoromethyl)aminophosphoranes and Related Compounds

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Barriers to pseudorotational processes in the aminophosphoranes (as $\Delta G^{\ddagger}_{298}$ in kcal) $F_4PN(H)CH_3$ (13.5 ± 0.4), $F_4PN(CH_3)CH_2C_6H_5$ (8.3 ± 0.4), $F_3(CF_3)PN(CH_3)_2$ (15.6 ± 0.6), $CH_3(CF_3)_2P(F)N(CH_3)_2$ (14.2 ± 0.5), $CH_3(CF_3)_2P(F)N(H)CH_3$ (17.6 ± 1.0), $(CF_3)_2P[N(CH_3)_2]_2$ (15.3 ± 0.4), $F(CF_3)_3PN(CH_3)_2$ (12.2 ± 0.3), $F(CF_3)_3PN(H)CH_3$ (14.5 ± 0.5), $F(CF_3)_3PN(CH_3)_3CH_2C_6H_5$ (13.3 ± 0.3 (average of ^{31}P and ^{13}C results)), $CH_3(CF_3)_3PN(H)CH_3$ (16.4 ± 0.3), and $Cl(CF_3)_3PN(CH_3)_2$ (9.8 ± 0.3) have been obtained by line-shape analysis of ^{31}P or in some cases $^{13}C(CF_3)$ dynamic NMR spectra. Evidence for hydrogen bonding of primary-amino hydrogen atoms to axial fluorine atoms was obtained. Very low-temperature dynamic ^{13}C (CH_3) NMR spectroscopy of $F(CF_3)_3PN(CH_3)_2$ provided evidence for cessation of P–N rotation in this one case with a barrier of about 7.5 kcal. In no other case could the P–N barrier be clearly separated from the barrier to the permutational process. Synthetic considerations and the low-temperature limiting and normal-temperature NMR spectral parameters for those compounds that have been newly synthetized are described herein.

Introduction

Although there has been considerable recent interest in the dynamic behavior of five-coordinate phosphorus compounds, much of our knowledge of barrier energetics has been derived from compounds containing bidentate substituents.[2,3] We have been interested in phosphoranes containing monofunctional substituents, and in these cases the energetic barriers will be independent of ring constraints. We have recently reported the barriers to exchange processes in $CF_3(CH_3)PF_3$,[4] the series $CH_3(CF_3)_3PY$[5] (Y = F, Cl, OCH_3, SCH_3, $N(CH_3)_2$, and CF_3), and a series of (methylthio)phosphoranes (F_4PSCH_3, $F_3(CF_3)PSCH_3$, $CF_3(CH_3)F_2PSCH_3$, $F_2(CF_3)_2PSCH_3$, and $F(CF_3)_3PSCH_3$).[6] In the latter series rotation about the P–S bond was separable from the CF_3 permutation process in $F_3(CF_3)PSCH_3$ with barriers of 10.2 and 12.6 kcal, respectively.

As part of a study of the chemistry and stereochemistry of simple phosphoranes, we have now determined barriers to fluxional processes for a series of fluoro- and (trifluoromethyl)aminophosphoranes with symmetrical and asymmetrical amino substituents.

Experimental Part

Volatile compounds were manipulated in a standard vacuum system with greased (Apiezon N) stopcocks. Nonvolatile materials were transferred in a nitrogen-filled drybox.

Reagent grade commercially available materials were dried and fractionated under vacuum before use to remove dissolved gases. Solvents for dynamic NMR studies were carefully dried. (Trifluoromethyl)phosphines were prepared from CF_3I and P in an autoclave.[7] (Trifluoromethyl)halophosphoranes were prepared by literature procedures[7-9] as were $F_4PN(CH_3)_2$,[10] $(CF_3)_3P[N(CH_3)_2]_2$,[11] $CH_3(CF_3)_2P(F)N(CH_3)_2$,[12] $(CF_3)_3P(Cl)N(CH_3)_2$,[13] and $(CF_3)_3P(F)N(CH_3)_2$.[13] $(CH_3)_3SiN(H)CH_3$ was prepared from the reaction of $(CH_3)_3SiCl$ and methylamine in the gas phase and condensed, followed by vacuum fractionation, whereupon the compound was obtained in a −78 °C trap. Also isolated was $((CH_3)_3Si)_2NCH_3$. This preparation differs from the standard preparation[14] only in that we have carried it out in the gas phase under dilute conditions in the absence of solvent.

Hydrolysis reactions were carried out in degassed water and in degassed, saturated NaOH solution for 48 h at room temperature. The quantities of compound, the yields of fluoroform, which was characterized by infrared spectroscopy, and the anions remaining in the hydrolysate, which were characterized by ^{19}F NMR spectroscopy,[15] are given in Tables I and II.

Mass spectra were obtained on an AEI MS9 mass spectrometer, operating at an ionizing voltage of 70 eV. Compounds were introduced as gases with use of a heated inlet system. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer in a 9-cm gas cell with potassium bromide windows or on potassium bromide plates for liquid samples.

Proton NMR spectra were recorded at 60.0 MHz and fluorine NMR spectra at 56.4 MHz with a Varian A56/60 instrument. Higher resolution spectra were obtained with a Varian HA 100 (continuous-wave) instrument, equipped with a V6040 temperature controller. Recording ^{31}P (36.4-MHz) spectra at low temperatures required the heteronuclear lock system of the Bruker HFX-90 system operating in the pulsed Fourier transform mode. Carbon-13 NMR spectra (22.6 MHz) were recorded on the Bruker HFX-90 in the pulsed FT mode also. All Fourier transform mode spectra were done with 2000-, 2500-, or 5000-Hz sweep widths, which were collected in 2K data points on the Nicolet 1085 computer associated with the system. Samples of volatile products for NMR measurements were prepared under vacuum in 5-mm-o.d. medium-wall sample tubes consisting of about 30% by volume of the compound in suitable mixtures of solvents depending on the temperature requirements. Involatile products were investigated as solutions in CD_3CN, CD_2Cl_2, or H_2O. Fluorine chemical shifts were measured relative to internal $CFCl_3$ solvent or to external (capillary) $CFCl_3$ if other solvents were used. Proton and phosphorus chemical shifts were measured relative to internal tetramethylsilane or an external capillary of P_4O_6 (neat),[16] respectively.

Dynamic NMR studies [$^{31}P\{^1H\}$ or $^{13}C\{^{19}F\}$ as appropriate] were carried out in the pulsed FT mode with the Bruker HFX-90 system described above by using solutions or neat liquid samples as appropriate. The Bruker temperature controller was calibrated periodically, and temperatures are accurate to ±1 °C. Calibration also established that no significant temperature gradients >0.1 °C existed along the length of the sample tube.

Preparation of New Compounds. Fluorotris(trifluoromethyl)(methylamino)phosphorane. Gaseous methylamine (0.168 g, 5.15 mmol) was slowly admitted to a sample of gaseous $(CF_3)_3PF_2$[8] (1.018 g, 3.69

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(2) Holmes, R. R. *Acc. Chem. Res.* **1972**, *5*, 296.

(3) (a) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*. (b) *Ibid.* **1980**, *No. 176*.

(4) Yap, N. T.; Cavell, R. G. *Inorg. Chem.* **1979**, *18*, 1301.

(5) Cavell, R. G.; Gibson, J. A.; The, Kwat I. *Inorg. Chem.* **1978**, *17*, 2880.

(6) Cavell, R. G.; The, Kwat I.; Gibson, J. A.; Yap, N. T. *Inorg. Chem.* **1979**, *18*, 3400.

(7) Bennett, F. W.; Emeleus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1565.

(8) Mahler, W. *Inorg. Chem.* **1963**, *2*, 230.

(9) Emeleus, H. J.; Haszeldine, R. N.; Paul, R. C. *J. Chem. Soc.* **1955**, 563.

(10) Demitras, G. C.; Kent, R. A.; McDiarmid, A. G. *Chem. Ind.* (*London*) **1964**, 1712. Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 753. Brown, D. H.; Fraser, G. W.; Sharp, D. W. A. *J. Chem. Soc. A* **1966**, 171.

(11) Poulin, D. D.; Cavell, R. G. *Inorg. Chem.* **1974**, *13*, 2324; **1975**, *14*, 2022 (erratum).

(12) The, Kwat I.; Cavell, R. G. *Inorg. Chem.* **1977**, *16*, 1463.

(13) The, Kwat I.; Cavell, R. G. *Inorg. Chem.* **1976**, *15*, 2518.

(14) Sauer, R. O.; Hasek, R. H. *J. Am. Chem. Soc.* **1946**, *68*, 241.

(15) Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1971**, *10*, 2720.

(16) Chapman, A. C.; Horner, J.; Mowthorpe, D. J.; Jones, K. T. *J. Chem. Soc., Chem. Commun.* **1965**, 121. The chemical shift of 85% H_3PO_4 is +112 ppm (high field) of P_4O_6.

Table I. Hydrolysis of (Trifluoromethyl)phosphoranes

	conditions	quantity of compd, wt, g (mmol)	yield of CF_3H, wt, g (mmol)	ions remaining in hydrolysate[a]
$(CF_3)_3P(F)NH(CH_3)$	neutral	0.082 (0.29)	0.021 (0.30)	$(CF_3)_2PO_2^-$
	alkaline	0.174 (0.61)	0.82 (1.16)	$CF_3PO_3^{2-}$
$(CF_3)_3P(F)NCH_3(CH_2C_6H_5)$	neutral	0.076 (0.20)	0.015 (0.21)	$(CF_3)_2PO_2^-$
	alkaline	0.166 (0.44)	0.061 (0.87)	$CF_3PO_3^{2-}$
$CH_3(CF_3)_2P(F)NH(CH_3)$	neutral	0.066 (0.28)	0.017 (0.24)	$[CH_3(CF_3)PO_2^-]$
	alkaline	0.074 (0.32)	0.045 (0.64)	$[CH_3PO_2N(H)CH_3^-] + CH_3PO_3^{2-}$

[a] Species in brackets have been tentatively identified by NMR spectroscopy. Others have been established previously.

Table II. NMR Data of Phosphorus-Containing Hydrolysis Products of $CH_3(CF_3)_2P(F)NH(CH_3)$

	τ[a]	ϕ_F[b]	ϕ_{CF_3}[b]	$^2J_{PF}$[h]	$^2J_{PH}$	$^3J_{PH}$	$^3J_{FH}$	$^4J_{FH}$	$^5J_{FH}$
$CH_3PO_3^{2-}$	8.87[e]	120.6			15.8				
$CH_3PO_2NH(CH_3)^-$	7.51[c,e]					12.7			
	8.7[b,e]				15.6				
$CH_3(CF_3)PO_2^-$	7.4[c,f]		77.1[g]	91.0				0.7	6.0
	8.54[d,g]				15.25		0.8		

[a] τ relative to internal tetramethylsilane, $\tau = 10.0$. [b] ϕ relative to internal (solvent) $CFCl_3$ standard with positive values indicating resonance to high field of standard. [c] CH_3 group attached to nitrogen. [d] CH_3 group attached to phosphorus. [e] Doublet. [f] Quartet. [g] Doublet of quartets. [h] All J values in hertz.

Table III. Infrared Spectral Data for New Phosphoranes[a]

$F_4PN(CH_3)$-$CH_2C_6H_5$	$CH_3(CF_3)_3$-$PN(H)CH_3$	$(CF_3)_3P$-$(F)NH(CH_3)$	$(CF_3)_3P(F)NCH_3$-$(CH_2C_6H_5)$[b]	$CH_3(CF_3)_2P$-$(F)N(CH_3)_2$	$CH_3(CF_3)_2P$-$(F)NHCH_3$	
	3463 s	3454 w			3500 s	ν(N–H)
			3270 w	2965 m		
3080 sh	2977 s	2952 sh	3080 w sh	2940 sh	3000 sh	ν(C–H)
3040 s	2859 s	2832 w	3040 w	2900 m	3980 m	
2940 m			2970 w sh	2820 w	2920 sh	
					2850 w	
1610 w						
1500 m		1572 w	1500 w			$\sigma_{asym}(CH_3)$
1450 s	1494 s	1463 vw	1460 m	1473 m	1470 m	
		1442 vw			1438 sh	
1420 m		1362 vw	1370 m		1380 w	$\sigma_{sym}(CH_3)$
			1340 vw		1320 w	
		1282 vw	1300 m	1295 m		
	1202 w		1210 vw	1210 s	1220 s	ν(C–F) and CH_3 rock
	1168 w	1192 s	1190 vs	1172 s	1190 vs	
	1151 m	1162 vs	1150 vs	1150 s	1170 vs	
1175 s[c]	1120 s	1140 s	1120 s	1120 m	1160 vs	
	1105 s	1105 vs		1089 s	1120 s	
		1074 vs				
1028 m	1090 m	1044 m	1000 m	1012 s	1090 s	$\nu(PNC_2)$
	962 s		960 w	970 m	970 m	
962 vs	878 s	872 vw		890 ms	895 s	ν(P–F)
874 vs	808 s	840 w			850 s	
		782 s	780 m	795 sh	765 m	$\sigma_{sym}(CF_3)$(?)
		742 s	750 s	780 s	760 m	
762 s			720 m	740 w	730 m	ν(PN)(?)
700 s	675 m	690 vs	690 m	672 s	680 s	ν(PF)
		631 w	630 m	648 s		
		604 s	590 s	570 w	600 sh	$\sigma_{asym}(CF_3)$(?)
580 m	571 m	583 m			550 m	
540 w	502 m	542 sh			530 sh	
510 w	465 m	522 vw				
480 w	440 m	510 vw			490 w	
470 w		460 w	480 w sh	440 w	455 m	
					430 sh	

[a] Gas-phase spectra all values in cm^{-1}. s = strong, m = medium, w = weak, v = very, sh = shoulder, ν = stretching, σ = deformation, sym = symmetric, asym = asymmetric, ? = a very tentative assignment. [b] Liquid-film spectrum. [c] CH_3 rock only.

mmol) contained in a 1-L gas-phase reactor (described elsewhere[17]) at room temperature. A white solid formed immediately upon contact of the two vapors. After $^1/_2$ h at room temperature, separation of the volatile products under vacuum gave fluorotris(trifluoromethyl)(methylamino)phosphorane $F(CF_3)_3PN(H)CH_3$ (0.353 g, 1.23 mmol, 65%), which was trapped at −45 °C, and a mixture of unreacted $(CF_3)_3PF_2$ and methylamine (0.0380 g), trapped at −196 °C. The compound $(CF_3)_3P(F)N(H)CH_3$ was characterized by its spectroscopic properties (IR, Table III; NMR, Table IV), mass spectral data (Table V), and hydrolysis (Table I).

The ^{19}F NMR spectrum of a deuterated methylene chloride solution of the remaining white solid showed three multiplets, centered at ϕ 68.8, 88.1, and 103.3 (J_{PF} = 854 Hz), which were consistent with those reported[18] for $(CF_3)_3PF_3^-$. The ^1H NMR spectrum of this solution showed two singlets of equal relative intensity at τ 7.52 and

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(17) Cavell, R. G. *J. Chem. Soc.* **1964**, 1992.

(18) Bishop, E. O.; Carey, P. R.; Nixon, J. F.; Swain, J. R. *J. Chem. Soc. A* **1970**, 1074. Chan, S. S.; Willis, C. J. *Can. J. Chem.* **1968**, *46*, 1237.

Table IV. Phosphorus and Fluorine NMR Data for Aminophosphoranes

	temp, °C	τ^a	$\phi_F{}^b$	$\phi_{CF_3}{}^b$	$\sigma_{^{31}P}{}^c$	$^1J_{PF}{}^{ss}$	$^2J_{PF}$	other
$PF_4N(CH_3)CH_2C_6H_5{}^d$	+31	7.43^{d-f}	65.9^h		182.4^{k--m}	855^n		$^3J_{PH} = 11.6$
		$5.94^{g,h}$						$^3J_{PH} = 14.5$
		$2.88^{i,j}$						$^4J_{FH} = 2.25$
	−90				$182.4^{l,o}$	920^q		
						784^r		
	−100		$73.2^{p,q}$			920^q		$^2J_{FF} = 74.0$
			$59.1^{o,p,s}$			779^s		$^2J_{FF} = 74.0$
			$56.7^{o,p,t}$			786^t		$^2J_{FF} = 74.0$
$CH_3(CF_3)_2P(F)N(H)CH_3$	+31	$7.32^{u,w}$	30.1^y	$67.2^{z,aa}$	$177.1^{l,cc}$	$754^{m,s}$	$125.3^{z,aa}$	$^3J_{PH} = 6.5$
								$^3J_{FF} = 15.0$
								$^4J_{FF} = 12.5$
		$8.27^{v,x}$				756^l	$124.6^{l,aa}$	
				$71.3^{z,bb}$			$35.0^{z,bb}$	$^3J_{FF} = 15.75$
								$^4J_{FF} = 12.5$
							35.4^l	
$(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$	+30	$7.15^{e,h}$	30.4^{ee}	60.6^y	$180.8^{l,ff}$	866^s	108^n	$^3J_{PH} = 11.4$
		$5.56^{g,h}$					$106^{l,hh}$	$^4J_{FH} = 2.0$
								$^5J_{FH} = 0.5^{dd}$
		$2.76^{i,j}$						$^3J_{PH} = 11.4$ (CH_2)
	−40		31.8^{ii}	$59.0\ (1)^{bb,jj,kk}$	$180.1^{l,gg}$	858^s	$53.7^{l,bb}$	$^4J_{PH} = 2.0^{ll}$
				$61.5\ (2)^{aa,jj,mm}$			$130.6^{l,aa}$	$^3J_{FF} = 17.6$, $^4J_{FF} = 15.0$
$(CF_3)_3P(F)N(H)CH_3$	+30	7.16	29.2^{ff}	64.1^y	$186^{l,ff,hh}$	843^s	$102^{l,ff}$	$^3J_{PH} = 11.5$
						$844^{l,hh}$		
	−40		49.6^{nn}	$65.2\ (1)^{bb,jj,oo}$	$185.7^{l,gg}$	834^s	$49.6^{l,bb}$	*ll*
				$63.7\ (2)^{aa,jj,mm}$			$133.1^{l,aa}$	$^3J_{FF} = 16.1$
								$^4J_{FF} = 12.3$
$CH_3(CF_3)_3PN(H)CH_3$	+30	8.37^v		$64.8\ (1)^{aa,jj}$	189.6^l		109.4^{aa}	$^2J_{PH} = 12.0$, $^3J_{FF} = 15.0$
		7.7^u		$61.3\ (2)^{bb,jj}$			40.3^{bb}	$^3J_{PH} = 14.0$, $^4J_{PH} = 1.0$
		7.43						br ^1H signal
$(CF_3)_3P[N(CH_3)_2]_2{}^{pp}$	+10				$169.6^{l,pp}$		53.0^{aa}	see ref 11
							106.0^{bb}	
$CH_3(CF_3)_2(F)PN(CH_3)_2$	−40				166.4^l	750.6^s	35.5^{aa}	see ref 12
							121.4^{bb}	
$CF_3PF_3N(CH_3)_2$	+30	7.39^{rr}		68.5^{aa}				$^3J_{PH} = 11.0$, $^4J_{FH} = 4.0$
	−50				$179.3^{l,qq}$	993.2^q	163.8^{aa}	$^3J_{FF} = 14.0$
						885.3^s		
$F_4PN(H)CH_3$	−90				180.2^l	744.1^s		
						766.4^t		
						915.9^q		

[a] τ relative to internal tetramethylsilane, $\tau = 10.0$. [b] ϕ relative to internal (solvent) $CFCl_3$ standard with positive values indicating resonance to *high field* of standard. [c] ppm vs. P_4O_6 as external standard (capillary), positive values indicating resonance to *high field* of standard. [d] In agreement with data of ref 19. [e] CH_3 region. [f] Doublet of quintets. [g] CH_2 region. [h] Doublet. [i] C_6H_5 region. [j] Sharp singlet. [k] Quintet. [l] Obtained from $^{31}P\{^1H\}$ spectra. [m] At −40 °C. [n] Average value of axial and equatorial environments. [o] Triplet of triplets. [p] Doublet of triplets. [q] F equatorial. [r] Average of two axial environments. [s] F axial. [t] F′ axial. [u] CH_3 group attached to nitrogen. [v] CH_3 group directly bound to phosphorus. [w] Doublet of doublets. [x] Doublet of doublets of multiplets. [y] Broad doublet. [z] Doublet of doublet of overlapped quartets. [aa] CF_3 equatorial. [bb] CF_3 axial. [cc] Doublet of quartets of quartets. [dd] Doublet of decets obtained from expansion of CH_3 region. [ee] Doublet of quartets of decets. [ff] Doublet of decets. [gg] Doublet of septets of quartets. [hh] Obtained at 55 °C. [ii] Doublet of multiplets. [jj] Relative intensity in arbitrary units in parentheses. [kk] Two overlapped septets. [ll] Axial signal is broad and unresolved; therefore, the coupling constant cannot be obtained from the ^{19}F spectra. [mm] Doublet of two overlapped quartets. [nn] Doublet of broad multiplets. [oo] Broad multiplets. [pp] Phosphoranes 1,[11] ^{31}P shift value therein is in error. [qq] Doublet of triplets of quartets. [rr] Doublet of quartets. [ss] All *J* values in hertz.

Table V. Mass Measurement Data for Some New Phosphoranes

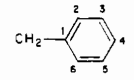
compd	ion[a]	calcd *m/e*	found *m/e*
$(CF_3)_3P(F)N(H)CH_3$	$(CF_3)_3P(F)NCH_3{}^+$	285.9844	285.9855
	$(CF_3)_3PNHCH_3{}^+$	267.9938	267.9928
	$(CF_3)_3PF^+$	256.9578	256.9588
$(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$	$(CF_3)_2P(F)N(CH_3)(CH_2C_6H_5)^+$	308.0439	308.0444
	$(CF_3)_3PF^+$	256.9578	256.9585
	$CF_3{}^+$	68.9706	68.9707
$CH_3(CF_3)_2P(F)N(H)CH_3$	$CH_3(CF_3)_2PNH(CH_3)^+$	214.0221	214.0223
	$CH_3(CF_3)_2PF^+$	202.9861	202.9862
	$CH_3(CF_3)P(F)NH(CH_3)^+$	164.0253	164.0252
$PF_4N(CH_3)CH_2C_6H_5$	$PF_4NH(CH_3)^+$	137.0018	137.0016
	$PF_4{}^+$	106.9674	106.9673
	$PF_3{}^+$	87.9690	87.9690

[a] A reasonable structural formula rather than the molecular formula is given for each fragment ion for convenience only.

4.42, assigned to CH_3 and NH_3 protons of $CH_3NH_3{}^+$. The other signals from the same sample (^{19}F, 64.0 and 49.0 ppm) were assigned to a small amount of $(CF_3)_3P(F)N(H)CH_3$ that had been trapped in the solid.

Tris(trifluoromethyl)fluoro(methylbenzylamino)phosphorane. Methylbenzylamine, $CH_3(CH_2C_6H_5)NH$ (0.541 g, 4.48 mmol), weighed under nitrogen by difference into a reaction tube in the drybox, was added to a tube containing diethyl ether (0.33 g) which was chilled

Table VI. ^{13}C NMR Data

	temp, °C	region	$\delta_{^{13}C}$[a]	J_{PC}, Hz	$^1J_{CH}$, Hz
$F(CF_3)_3PN(CH_3)CH_2C_6H_5$	+31	CH_3	38.4[b,i]		56.0[d,f]
		CH_2	58.4[b,e]	12.2	68.0[d,g]
		C_1	136.3[b,e]	2.0	
		$C_{2,6}$	129.4[b,i]	6.0	162.0[e,h]
		$C_{3,5}$	128.1[b,i]		158.0[e]
		C_4	128.7[b,i]		uncertain
	+45	CF_3	124.9[c,e]	200 [av][j]	
	+60	CF_3	125.1[e]	198 [av][j,k]	
	−80	CF_3(eq)	123.4[e]	263 [2][l,m]	
		CF_3(ax)	126.5[e]	59 [1][l,n]	
$F_4PN(CH_3)CH_2C_6H_5$	+36	CH_3	38.5		
		CH_2	58.4		
		C_1	n.o.		
		$C_{2,6}$	128.5		
		$C_{3,5}$	126.8		
		C_4	127.4		
$F(CF_3)_3PN(CH_3)_2$	−50	CH_3	42.7	<15 (fwhm)	
	−123	CH_3	44.1	17	
			40.0	~0	
$F_3(CF_3)PN(CH_3)_2$[c]	+32	CF_3	123.0	418.7 sharp doublet	
	−10	CF_3	122.6	418.1 sharp doublet	
	−50	CF_3	122.2	417.6 sharp doublet	
	−90	CF_3	121.8	417.5 sharp doublet	
		CH_3	39.9	$^1J_{CH} = 137.0$, $^2J_{PC} = 6.2$, $^3J_{CH} = 3.6$ (quartet of sextets)	

[a] Measured values (vs. CD_2Cl_2; $\sigma = 53.8$ ppm) have been converted to the $(^{13}CH_3)_4Si$ reference scale. Positive values indicate resonance downfield of standard. [b] Obtained from $^{13}C\{^1H\}$ spectra. [c] Obtained from $^{13}C\{^{19}F\}$ spectra. [d] Obtained from off-resonance decoupling technique. [e] Doublet. [f] Quartet overlapped with the signals from $CD_3C_6D_{11}$. [g] Triplet of doublets. [h] Doublet of doublets. [i] Singlet. [j] The weighted average of the axial and equatorial $^1J_{PC}$ values. [k] With methylcyclohexane-d_{14} as the solvent for high-temperature measurement. [l] Relative intensity in arbitrary units. [m] CF_3 equatorial. [n] CF_3 axial.

and evacuated. $(CF_3)_3PF_2$[8] (1.128 g, 4.09 mmol) was condensed into the reaction tube, and the tube was sealed. Upon slow warming from −196 °C to room temperature, a white solid was first formed, which subsequently dissolved to form a yellow, oily liquid. Separation of the volatile products gave $(CF_3)_3P(F)NCH_3(CH_2C_6H_5)$, tris(trifluoromethyl)fluoro(methylbenzylamino)phosphorane (0.593 g, 1.57 mmol) trapped at −45 °C, unreacted $(CF_3)_3PF_2$ (0.013 g, 0.05 mmol) trapped at −116 °C, and diethyl ether (0.323 g) trapped at −196 °C. $(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$ was characterized by its spectroscopic properties (IR, Table III; NMR, Tables IV and VI), mass spectral data (Table V), and hydrolysis (Table I).

The ^{19}F NMR spectrum of the yellow, oily liquid in deuterated methylene chloride showed three multiplets, centered at 67.2, 88.0, and 103.2 ppm (J_{PF} = 859 Hz), which are consistent with those reported[18] for $(CF_3)_3PF_3^-$. The other signals (a doublet and a broad singlet, centered at 60.5 ppm, belong to the CF_3 region of $(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$ and there is also a doublet of multiplets, centered at 30.4 ppm, that is due to the unique fluorine of the same compound) arise from a portion of the volatile product that had been trapped in the solid residues.

(Methylbenzylamino)tetrafluorophosphorane from Thermal Decomposition of the Methylbenzylamine–Phosphorus Pentafluoride Adduct. Phosphorus pentafluoride (0.466 g, 3.70 mmol) was condensed onto a solution of methylbenzylamine (0.380 g, 3.13 mmol) in toluene (1.0459 g) at −196 °C. The pale yellow solid methylbenzylamine–phosphorus pentafluoride adduct was formed upon warming the mixture to room temperature. After 2 h at room temperature the volatile products were removed under vacuum to leave a solid adduct, which was then heated to 75 °C in the same vessel. (Methylbenzylamino)tetrafluorophosphorane $[PF_4N(CH_3)CH_2C_6H_5]$ was evolved and trapped in a U-tube at −78 °C. Excess phosphorus pentafluoride and a trace of toluene were more volatile. Spectral characterization of the (benzylamino)phosphorane, given in Tables III and IV, is in good agreement with data given for this same compound prepared elsewhere by reaction of $Me_3SiN(CH_3)CH_2C_6H_5$ with PF_5.[19]

Methylbis(trifluoromethyl)fluoro(methylamino)phosphorane. $CH_3(CF_3)_2PF_2$ (0.244 g, 1.23 mmol) and CH_3NH_2 (0.042 g, 1.35 mmol) reacted immediately on contact at room temperature in the gas phase in a 1-L gas-phase reactor.[17] After 1 h at room temperature, separation of volatile products from the less volatile white solid under vacuum gave methylbis(trifluoromethyl)fluoro(methylamino)phosphorane, $CH_3(CF_3)_2P(F)N(H)CH_3$ (0.140 g, 0.603 mmol, ~50%), trapped at both −45 and −78 °C and unreacted $CH_3(CF_3)_2PF_2$ and CH_3NH_2 (0.011 g) at −196 °C. The compound $CH_3(CF_3)_2P(F)N(H)CH_3$ was characterized by its spectroscopic properties (IR, Table III; NMR, Table IV), mass spectral data (Table V), and hydrolysis (Tables I and II).

The ^{19}F NMR spectrum of a solution of the remaining white solid in deuterated acetonitrile showed two multiplets centered at 67.2 and 69.1 ppm, two doublets at 78.3 and 80.5 ppm with $^2J_{PF}$ = 86.5 and 79.5 Hz, respectively, which were assigned to ^{19}F signals of $CH_3(CF_3)_2PF_3^-$.

The ^{1}H NMR spectrum of the same sample showed two singlets of equal intensity ratio at τ 7.85 and 3.56, which were assigned to protons of $CH_3NH_3^+$. The other signals in the same sample were due to the CH_3 group directly bound to the phosphorus atom in $CH_3(CF_3)_2PF_3^-$, centered at τ 9.17.

$CH_3(CF_3)_3PN(H)CH_3$. (Methylamino)trimethylsilane (0.327 g, 3.17 mmol) and $CH_3(CF_3)_3PF$[20] (0.793 g, 2.91 mmol) were combined in a sealed tube at room temperature for 1 h with shaking. Separation of the volatile contents under vacuum gave $CH_3(CF_3)_3PN(H)CH_3$ (0.771 g, 2.72 mmol, 93%) trapped at −45 °C and $(CH_3)_3SiF$ (0.205 g, 2.23 mmol) trapped at −196 °C. A small amount of unreacted $(CH_3)_3SiN(H)CH_3$ (0.11 g) was collected in a −96 °C trap. A small amount (0.011 g) of a compound identified by IR spectroscopy as $F(CF_3)_2CH_3PN(H)CH_3$ was collected at −63 °C. NMR data are given in Table IV.

$F_4PN(H)CH_3$. Methylamine was slowly introduced into a 1-L gas-phase reactor[17] containing PF_5 at room temperature. Reacting ratios ranging from 0.5/1.0 to 1.0/1.0 for amine/PF_5 gave $F_4PN(H)CH_3$ in yields >50% and an unidentified white solid. The (methylamino)phosphorane was purified by passage through a −78 °C trap and collected at −96 °C as a white solid. The properties of the product are in agreement with those reported elsewhere.[21] Sealed-tube reactions gave mainly $F_3P(N(H)CH_3)_2$ and PF_5·2MeNH$_2$ as reported elsewhere.[22] Larger amine/PF_5 ratios gave substantial yields of

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(19) Peake, S. C.; Hewson, M. J. C.; Schlak, O.; Schmutzler, R.; Harris, R. K.; Wazeer, M. I. M. *Phosphorus Sulfur* **1978**, *4*, 67.

(20) The, Kwat I.; Cavell, R. G. *Inorg. Chem.* **1977**, *16*, 2887.

(21) Harman, J. S.; Sharp, D. W. A. *Inorg. Chem.* **1971**, *10*, 1538.

(22) Harman, J. S.; Sharp, D. W. A. *J. Chem. Soc. A* **1970**, 1138.

$F_3P(N(H)CH_3)_2$ and $(F_3PNMe)_2$.

$F_3(CF_3)PN(CH_3)_2$.[23] This compound was prepared by reaction of CF_3PF_4 with $(CH_3)_3SiN(CH_3)_2$ at room temperature, followed by fractionation under vacuum, whereupon the desired product was collected at −78 °C. The purest product was obtained when a small excess of CF_3PF_4 was employed. The only other product of the reaction was $(CH_3)_3SiF$. The NMR spectral properties of this aminophosphorane, which agreed with those obtained by earlier workers,[23] are given in Table IV.

Results and Discussions

Synthetic Considerations. The syntheses are relatively straightforward in that either the silyl reagent

$$X_4PF + (CH_3)_3SiL \rightarrow X_4PL + (CH_3)_3SiF \quad (1)$$

or the direct aminolysis reaction

$$2X_4PF + 2RR'NH \rightarrow X_4PNRR' + RR'NH_2{}^+X_4PF_2{}^- \quad (2)$$

is effective. The first reaction is more efficient with respect to consumption of phosphorus(V) species because no salt formation is involved, but the direct aminolysis avoids the need for preliminary preparations of the silyl reagent. While the disubstituted silylamines, $(CH_3)_3SiNR_2$, are easily stored, the primary-amino species, $-N(H)R$, are subject to further condensations and direct aminolysis may be preferable. We have had very good success with direct aminolysis in the gas phase with controlled admission of one reagent into another, thus minimizing the partial pressure of one reactant. The method is essentially a "high-dilution" reaction system. The success of this method is illustrated by the successful synthesis of $F_4PN(H)CH_3$ by this route, albeit in only moderate yield, whereas previous workers[22] combining the reagents in a sealed tube were not able to isolate the desired aminophosphorane. This aminophosphorane has been prepared in good yield from PF_5 and $(CH_3)_3SiN(H)CH_3$.[21]

We found the silane route to be the method of choice for the preparation of $CH_3(CF_3)_3PN(H)CH_3$, as was the case in related systems.[13] Direct aminolysis gave principally the phosphazene ring $[CH_3(CF_3)_2PN(CH_3)]_2$ described elsewhere.[24]

The benzylamine derivatives are best synthesized by direct aminolysis in a sealed tube because of the low volatility of this amine although $F_4PN(CH_3)CH_2C_6H_5$ has also been prepared[19] by the silylamine route. As in similar studies, the amine first formed a solid adduct, which upon pyrolysis at moderate temperatures (e.g., 75 °C) yielded the fluorophosphorane.

$$X_4PF + RR'NH \rightarrow [X_4PF{\cdot}RR'NH] \xrightarrow{75\ °C} {}^1/_2X_4PNRR' + {}^1/_2RR'NH_2{}^+X_4PF_2{}^- \quad (3)$$

Both $F(CF_3)_3PN(CH_3)CH_2C_6H_5$ and $F_4PN(CH_3)CH_2C_6H_5$ were obtained in good yields by this route.

The gas-phase aminolyses of PF_5, $(CF_3)_3PF_2$, and $CH_3(CF_3)_2PF_2$ with methylamine formed the (methylamino)phosphorane directly rather than the initial adducts, which might have been expected from the above behavior of benzylamine and previous studies.[22] Although adduct formation was not prominent in these three cases, the moderate yields obtained by this route may be due to the formation of the adduct, which is only partially decomposed under the reaction conditions. More aminophosphorane might have been obtained upon pyrolysis, but this aspect was not investigated particularly in view of the report that the phosphorus pentafluoride–methylamine adducts formed in the condensed-phase reaction of these two reactants could not be successfully pyrolyzed to the aminophosphorane $F_4PN(H)CH_3$.[22]

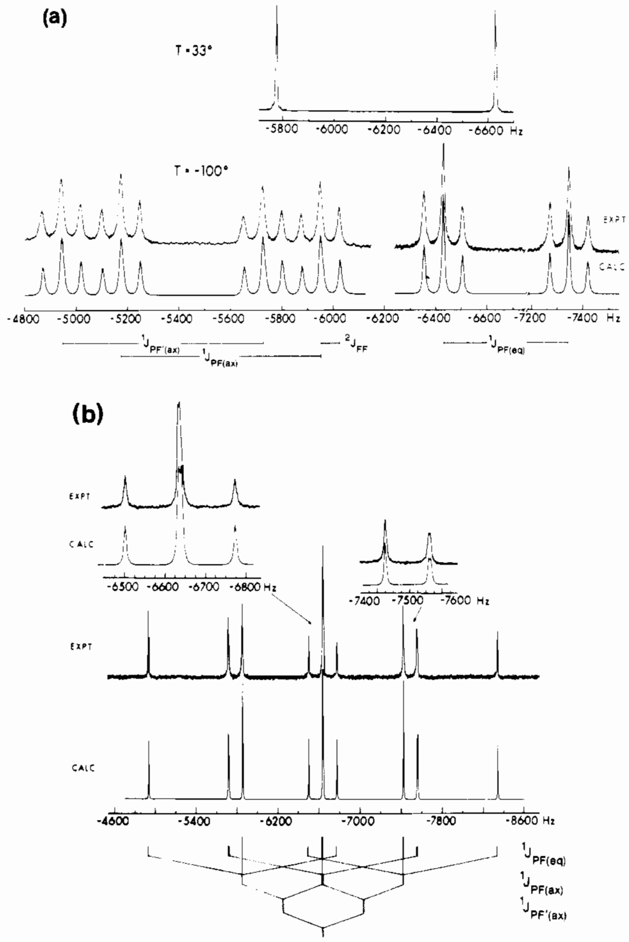

Figure 1. ^{19}F (CW) and ^{31}P NMR (FT) spectra of $F_4PN(CH_3)CH_2C_6H_5$ at +33 (^{19}F) and at −100 °C (^{31}P). Spectra were obtained on a solution of the compound in $CFCl_3$. Shifts are given in Hz, negative values indicating resonance to high field of the standards: ^{19}F ($CFCl_3$), ^{31}P (P_4O_6).

NMR Spectroscopic Properties: Limiting Stereochemistry. At the lowest temperatures (−90 to −100 °C), the limiting ^{19}F and ^{31}P NMR spectra of the two tetrafluorides with asymmetric amine substituents, $F_4PN(H)CH_3$[21] and $F_4PN(CH_3)CH_2C_6H_5$[19] (Figure 1), show distinct axial and equatorial fluorine environments, with the former further separated into distinct environments consistent with the cessation of rotation about the P–N bond as well as the cessation of fluorine atom permutations. It was our interest in the relationship between these two motions that prompted the investigation of the barriers existent in these two molecules. While the distinction between the two axial environments is very prominent in the low-temperature ^{19}F NMR spectrum of $F_4PN(H)CH_3$[21] and in the low-temperature ^{31}P NMR spectrum, it is not so prominent in the case of $F_4PN(CH_3)CH_2C_6H_5$. In this latter case the two axial fluorine atoms have very similar phosphorus–fluorine coupling constants (but the values are not exactly equal as reported[19] initially). The chemical shift distinction between axial fluorines is clear in both cases and shows that both of the permutational exchange processes have ceased at the lowest temperatures.

Our limiting ^{19}F spectrum of $F_4PN(H)CH_3$ is in good agreement with that of Harman and Sharp.[21] Iterative simulation of the ^{19}F spectrum by means of NUMARIT yields the coupling constants given in Table V. All coupling constant assignments of previous workers stand and in addition we can identify $^3J_{HF}$(eq) as 1.9 Hz. It is interesting to note that only one of the axial fluorine atoms shows a coupling with the amino hydrogen; presumably the fluorine that is involved in hydrogen-bonding interactions with the hydrogen on nitrogen is also

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[23] Sawin, S. S. Ph.D. Thesis, University of Wisconsin, 1971. We thank Dr. P. M. Treichel for a copy of this thesis.

[24] Vande Griend, L.; Cavell, R. G. *Inorg. Chem.* **1980**, *19*, 2070.

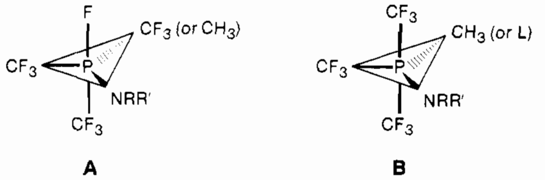

Figure 2. Isomers of (trifluoromethyl)phosphoranes.

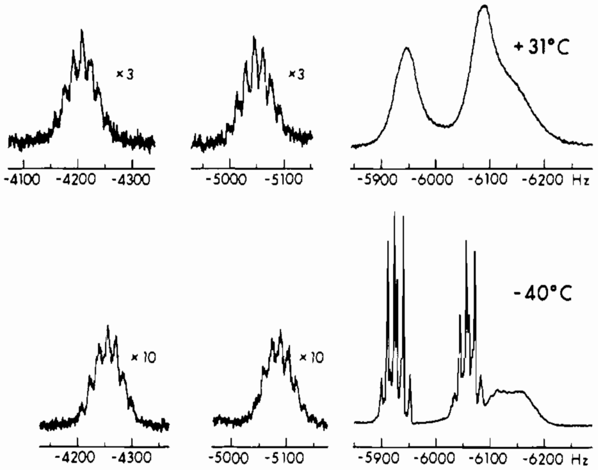

Figure 3. Fluorine-19 NMR spectra of $F(CF_3)_3PN(H)CH_3$ at +31 °C showing exchange of CF_3 environments and at −40 °C showing two CF_3 environments. The shift scale in Hz (negative values indicate resonance to high field of standard) is relative to the solvent, $CFCl_3$.

coupled to it. The other axial fluorine shows no (or very small) couplings to the NH proton nor to the CH_3 group.

The only trifluoride studied, $F_3(CF_3)PN(CH_3)_2$, shows permutational behavior for the fluorine atoms resolving at −50 °C to axial and equatorial fluorine atom environments with 2/1 relative intensity ratio, respectively. The CF_3 group parameters, principally $^2J_{PF}$ (163.8 Hz) and $^1J_{PC}$ (418 Hz), are compatible with an equatorial CF_3 environment as expected,[25] and the axial and equatorial directly bound couplings between phosphorus and fluorine are appropriate; the largest value is clearly associated with the equatorial environment.[3] The CF_3 signal at intermediate temperatures (0 °C) is essentially a quartet of doublets although the central members of the quartet are significantly broader than the outermost lines as a result of the permutational averaging of the fluorine atoms directly bound to P. The ^{19}F signals were not examined in detail at low temperatures.

The tris(trifluoromethyl)- and methylbis(trifluoromethyl)-phosphoranes exhibit varying degrees of lability so that limiting spectra are observable at temperatures ranging from normal probe temperatures (ca. +30 °C) to −40 °C. The spectra (and structures) fall into two categories; those with a fluorine atom directly bound to phosphorus have ground-state structure A (Figure 2), in which the F is axial and the CH_3 (if present) and NRR′ groups are equatorial, leaving one CF_3 axial and one (or two) CF_3 equatorial substituents. This structure has been previously identified for $F(CF_3)_3PN(CH_3)_2$[13] and $CH_3(CF_3)_2P(F)N(CH_3)_2$[12] (with slightly revised NMR parameters given in Table IV) and here is newly identified for $F(CF_3)_3PN(CH_3)CH_2C_6H_5$, $F(CF_3)_3PN(H)CH_3$ (Figures 3 and 4), and $F(CH_3)(CF_3)_2PN(H)CH_3$. In all cases the CF_3 groups are characterized[25] by a large $^2J_{PF}$ (and $^1J_{PC}$) when in the equatorial position (relative intensity 1 or 2 in these cases as appropriate) and a relatively small value of these coupling constants when occupying the axial position (relative intensity 1). We have previously suggested that the chloro compound $Cl(CF_3)_3PN(CH_3)_2$ possesses the ground-state structure A with Cl occupying the axial position on the basis of similar arguments.[13,25]

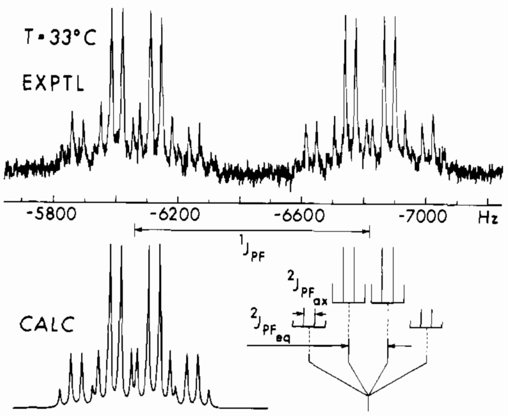

Figure 4. FT proton-decoupled ^{31}P NMR spectrum of $CH_3(CF_3)_2(F)PN(H)CH_3$ at +33 °C. The frequency scale gives chemical shift in Hz, negative values indicating resonance to high field of the standard, P_4O_6.

The nonhalogenated tris(trifluoromethyl) derivatives have ground-state structure B (Figure 2), in which two CF_3 groups occupy axial positions (with concomitantly small values of $^2J_{PF}$ and $^1J_{PC}$ associated with the more intense (relative intensity 2) CF_3 signals). The arguments for $(CF_3)_3P[N(CH_3)_2]_2$[11,25] and $CH_3(CF_3)_3PN(CH_3)_2$[20,25] have been given earlier. New data for $CH_3(CF_3)_3PN(H)CH_3$ (Table IV) and its ^{31}P NMR spectrum at +20 °C (Figure 5) show features consistent with structure B.

The major effect visible in the NMR spectra of all of the above trifluoromethyl systems is permutational exchange of CF_3 groups. In one case, $F(CF_3)_3PN(CH_3)_2$, a clear indication of the cessation of the rotation about the P–N bond was also derived from very low-temperature ^{13}C NMR spectra. In this case the dissimilar axial substituents (the ground-state structure is A according to arguments described above) on phosphorus destroy the magnetic equivalence at −123 °C in the ^{13}C (CH_3) NMR spectrum of the CH_3 groups on nitrogen. Two resonances of equal intensity were observed: $\delta(^{13}C)$ 44.1, $^2J_{PC} = 17$ Hz, and $\delta(^{13}C)$ 40.0, $^2J_{PC} = 0$ (<1.5) Hz, only one of which is observably coupled to phosphorus. This spectrum is most reasonably ascribed to cessation of P–N rotation at this temperature, the CF_3/F permutational process having ceased at a higher temperature (vide infra). The fast-exchange ^{13}C NMR spectrum of the $N(CH_3)_2$ group at −30 °C shows only a broad resonance with fwhm ~ 15 Hz. It is interesting that only one of the amino methyl substituents is strongly coupled to phosphorus. We have observed similar features in the low-temperature ^{13}C NMR spectra of aminophosphines, wherein a large and a small $^2J_{PC}$ (of opposite sign) arise from the separate CH_3 environments.[26] Of further interest are the very complex ^{31}P and ^{19}F (CF_3) spectra of $F(CF_3)_3PN(CH_3)_2$ at these same temperatures, which indicates that the magnetic equivalence in the *axial* CF_3 group has been destroyed, creating an AB_2 or ABC system but, as in many other cases,[11,12,27] the ^{19}F and ^{31}P spectra generated by this magnetic inequivalence within the CF_3 group were too complicated to analyze. Similarly, the very low-temperature (below −100 °C) ^{19}F and ^{31}P NMR spectra of $CH_3(CF_3)_2P(F)N(CH_3)_2$ clearly show a degree of complexity that is consistent with the onset of magnetic nonequivalence within the CF_3 group in the axial position (axial and equatorial CF_3 groups are distinctly resolved at −50 °C). Both these cases are presumably due to the cessation of rotation about the P–N bond as the result of a

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(25) Cavell, R. G.; Gibson, J. A.; The, Kwat I. *J. Am. Chem. Soc.* **1977**, *99*, 7841.

(26) Cavell, R. G.; Choot, E. H.; Yap, N. T., unpublished.

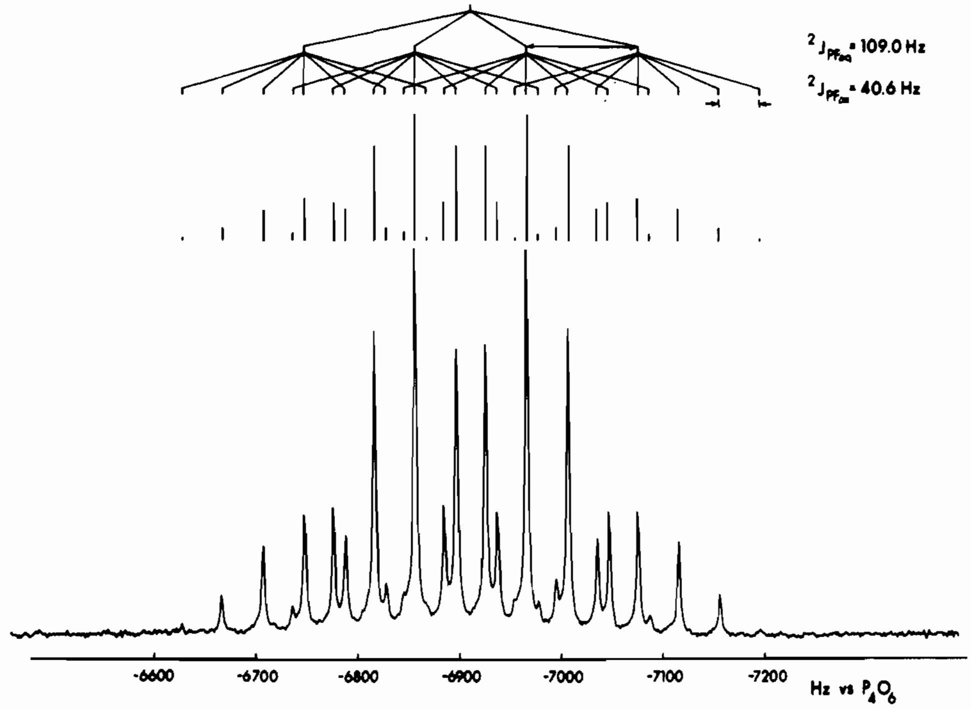

Figure 5. Proton-decoupled ^{31}P FT NMR spectrum of $CH_3(CF_3)_3PN(H)CH_3$ at +20 °C showing the two coupling constants associated with axial and equatorial environments. The frequency scale gives chemical shift (negative values to high field of standard) relative to P_4O_6.

Table VII. Permutational Barriers for Aminophosphoranes[a]

	$\Delta G^{\ddagger}_{298}$, kcal	$\Delta G^{\ddagger}_{T}$, kcal	T,[b] K	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	E_a, kcal	$10^{-12}A$, s^{-1}	E_a,[c] kcal	$\Delta H^{\ddagger}$,[c] kcal	note
$F_4PN(CH_3)_2$[d]	9.4 ± 0.2	8.9 ± 0.2	193	8.0 ± 0.1	−4.9 ± 0.6	8.3 ± 0.1	0.80 ± 0.28	9.4 ± 0.2	8.9 ± 0.2	*h*
	9.9 ± 0.2	8.2 ± 0.1	177	5.8 ± 0.1	−13.7 ± 0.6	6.1 ± 0.1	0.010 ± 0.003	8.7 ± 0.5	8.2 ± 0.5	*i*
$F_4PN(H)CH_3$	13.5 ± 0.3	13.4 ± 0.3	274	12.6 ± 0.2	−3.3 ± 0.8	13.1 ± 0.2	2.9 ± 1.2	14.0 ± 0.2	13.4 ± 0.2	*j*
	13.4 ± 0.3	13.4 ± 0.3	278	14.3 ± 0.2	3.1 ± 0.7	14.8 ± 0.2	72 ± 27	14.0 ± 0.2	13.4 ± 0.1	*k*
$F_4PN(CH_3)CH_2C_6H_5$	8.1 ± 0.4	9.2 ± 0.3	207	11.4 ± 0.2	11.1 ± 1.0	11.8 ± 0.2	3176 ± 1677	9.70 ± 0.3	9.2 ± 0.3	*l*
$F(CF_3)_3PN(CH_3)_2$[e]	12.2 ± 0.3	12.2 ± 0.4	263	12.1 ± 0.2	−0.1 ± 1.0	12.7 ± 0.3	12.0 ± 0.7	12.7 ± 0.1	12.2 ± 0.1	*m*
$F(CF_3)_3PN(H)CH_3$	14.5 ± 0.5	14.5 ± 0.5	296	16.5 ± 0.3	6.6 ± 1.2	17.1 ± 0.3	478 ± 277	15.1 ± 0.2	14.5 ± 0.2	*l*
$F(CF_3)_3PN(CH_3)CH_2C_6H_5$	13.0 ± 0.3	12.8 ± 0.3	266	11.5 ± 0.2	−4.9 ± 0.8	12.0 ± 0.2	1.2 ± 0.5	13.4 ± 0.16	12.8 ± 0.16	*n*
	13.6 ± 0.2[f]	13.6 ± 0.2	298	12.4 ± 0.1	−4.1 ± 0.5	12.9 ± 0.1	2.1 ± 0.5	14.1 ± 0.2	13.6 ± 0.2	*o, p*
$Cl(CF_3)_3PN(CH_3)_2$	9.8 ± 0.2	9.0 ± 0.2	194	7.7 ± 0.1	−7.0 ± 0.7	8.05 ± 0.1	0.31 ± 0.10	9.57 ± 0.3	9.05 ± 0.3	*o, q*
$CH_3(CF_3)_3PN(H)CH_3$	16.4 ± 0.3	16.9 ± 0.3	347	13.4 ± 0.2	−10.2 ± 0.6	14.1 ± 0.2	0.11 ± 0.04	17.5 ± 0.4	16.9 ± 0.5	*r*
$(CF_3)_3P[N(CH_3)_2]_2$	15.1 ± 0.4	15.3 ± 0.4	314	12.5 ± 0.3	−8.7 ± 0.9	13.2 ± 0.3	0.22 ± 0.10	15.8 ± 0.3	15.3 ± 0.3	*s*
$F(CH_3)(CF_3)_2PN(CH_3)_2$	14.7 ± 0.2[g]	14.7 ± 0.2	303	13.2 ± 0.2	−5.5 ± 0.6	13.8 ± 0.2	3.5 ± 1.0	14.3 ± 0.4	14.7 ± 0.4	*r*
	14.2 ± 0.2	14.3 ± 0.5	303	9.9 ± 0.3	−14.5 ± 1.1	10.5 ± 0.3	0.012 ± 0.007	14.8 ± 0.5	14.3 ± 0.5	*o, t*
$F(CH_3)(CF_3)_2PN(H)CH_3$	17.5 ± 1.4	17.6 ± 1.5	330	16.8 ± 1.0	−2.4 ± 3.1	17.5 ± 1.0	5.5 ± 8.7	18.1 ± 0.1	17.6 ± 0.1	*l*
$F_3(CF_3)PN(CH_3)_2$	15.6 ± 0.5	15.5 ± 0.6	321	16.3 ± 0.3	2.3 ± 1.3	16.9 ± 0.4	58 ± 37	16.1 ± 0.1	15.5 ± 0.1	*r*

[a] Errors are statistical line-fit values; systematic errors have not been evaluated. Determined from ^{31}P NMR line-shape analysis unless otherwise noted. [b] T is the average temperature of the range investigated, not a coalescence temperature. [c] Results of a constrained fit to the Arrhenius equation with $A = 10^{13.2}$ and to the Eyring equation with $\Delta S^{\ddagger} = 0$. [d] Reference 30 reported $\Delta G^{\ddagger}_{189} = 8.8$ kcal. [e] See Table VII. [f] Average data obtained from two separate analyses, one in CD_2Cl_2 solution and one in methylcyclohexane-d_{14}. [g] Averaging of fitting of each (slightly second-order) ^{31}P half-spectrum separately. [h] 60% solution in CF_2Cl_2. [i] 25% solution in C_2H_5Cl. [j] 50% solution in $CFCl_3$. [k] 50% solution in $Cl_2C{=}C(Cl)CF_3$. [l] $CFCl_3$ solution. [m] $CFCl_3/CD_2Cl_2$ solution. [n] Mixed solvent $CF_2Cl_2/CFCl_3$. [o] Determined from ^{13}C (CF_3) NMR spectrum. [p] CD_2Cl_2 solution or $CD_3C_6D_{11}$ solution. [q] 50% in 60/40 CF_2Cl_2/CD_2Cl_2 solution. [r] Neat liquid. [s] 33% in $CD_3C_6D_{11}$ solution. [t] 90% in CD_3CN solution.

"cogwheel" interaction between a methyl group on nitrogen and one of the CF_3 groups, presumably that in the axial position, with spectral results similar to those successfully analyzed for $CH_3(CF_3)_2P(OCH_3)_2$[12] and $(CF_3)_2(CH_3)_2PSCH_3$[27] in terms of AB_2 patterns within the axial CF_3. These data suggest that cessation of P–N bond rotation may be generally observable as a separate process from permutational interchange and that the barrier to P–N bond rotation, estimated from the very much lower temperatures required to observe this inequivalence, is significantly lower than that associated with permutations on phosphorus in the less mobile phosphoranes.

Carbon-13 data for the carbon nuclei in several molecules containing CF_3 substituents are given in Table VI. The results are consistent with ground-state stereochemistries discussed above. The assignments of the benzyl group spectra in $F(CF_3)_3PN(CH_3)CH_2C_6H_5$ (Figure 6) and $F_4PN(CH_3)CH_2C_6H_5$ are also given in Table VI.

Dynamic NMR Studies. (a) Pseudorotation Barriers. Rates were obtained by fitting spectra calculated by either the program EXCHSYS[28] or DNMR3[29] to the observed spectra at

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(27) Cavell, R. G.; The, Kwat I. *Inorg. Chem.* **1978**, *17*, 355.

(28) A locally adapted version of the programs EXCHSYS (described by: Krieger, J. K.; Deutsch, J. M.; Whitesides, G. J. *Inorg. Chem.* **1973**, *12*, 1535) was used for these calculations. Details of the program and the description of the construction of the kinetic magnetization-transfer matrix are given by: Kreiger, J. K. Ph.D. Thesis, MIT, Cambridge MA, 1971.

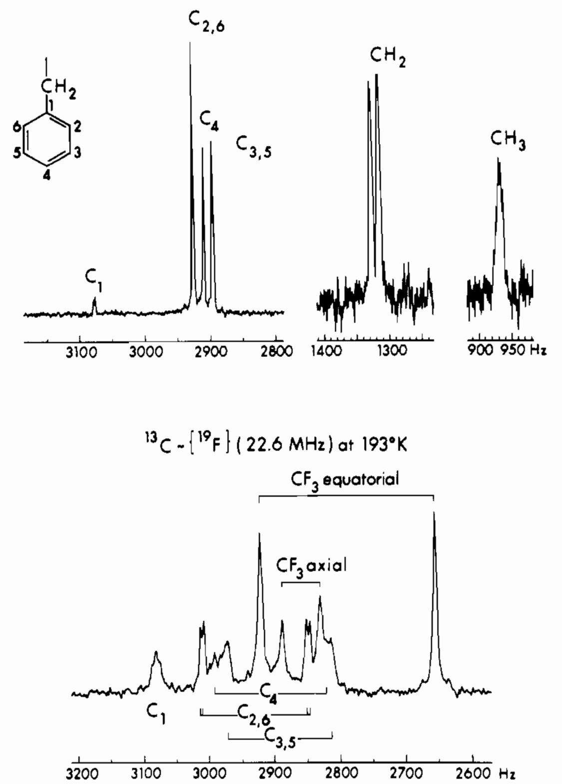

Figure 6. Top: $^{13}C\{^1H\}$ NMR spectrum of $(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$ at +31 °C (304 K) obtained in a solution of CD_2Cl_2. Bottom: $^{13}C\{^{19}F\}$ spectrum of the same compound at −80 °C (193 K) also in CD_2Cl_2. The frequency scales give chemical shift values from $(^{13}CH_3)_4Si$ (in Hz) for both cases, positive values indicating resonance to low field of standard.

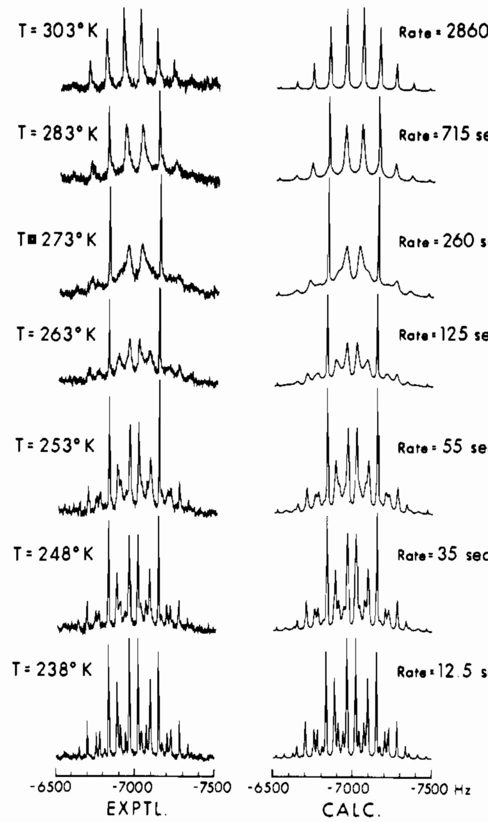

Figure 7. Experimental and calculated $^{31}P\{^1H\}$ (36.4 MHz) FT NMR spectra at various temperatures and appropriate rates of exchange of magnetization for $(CF_3)_3P(F)N(CH_3)CH_2C_6H_5$. The experimental spectra were obtained in a solution of $CFCl_3/CF_2Cl_2$. The calculated spectra were obtained by using a K-matrix constructed for a pairwise exchange mechanism. The frequency scale gives chemical shift values relative to P_4O_6 (negative values indicating resonance to high field of the standard) but was measured by heteronuclear techniques relative to ^2D of CD_2Cl_2. The spectrum shown is half of the $^1J_{PF}$ doubled spectrum.

Table VIII. 16 × 16 Matrix for $(CF_3)_2P$ Systems (1 Axial, 1 Equatorial)

			eq	aaa	βaa	ββa	βββ	aaa	βaa	ββa	βββ	aaa	βaa	ββa	βββ	aaa	βaa	ββa	βββ	
	ax	eq	ax	aaa	aaa	aaa	aaa	βaa	βaa	βaa	βaa	ββa	ββa	ββa	ββa	βββ	βββ	βββ	βββ	
1	aaa	aaa		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	*
2	aaa	βaa		0	-1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	
3	aaa	ββa		0	0	-1	0	0	0	0	0	1	0	0	0	0	0	0	0	
4	aaa	βββ		0	0	0	-1	0	0	0	0	0	0	0	0	1	0	0	0	
5	βaa	aaa		0	1	0	0	-1	0	0	0	0	0	0	0	0	0	0	0	
6	βaa	βaa		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	*
7	βaa	ββa		0	0	0	0	0	0	-1	0	0	1	0	0	0	0	0	0	
8	βaa	βββ		0	0	0	0	0	0	0	-1	0	0	0	0	0	1	0	0	
9	ββa	aaa		0	0	1	0	0	0	0	0	-1	0	0	0	0	0	0	0	
10	ββa	βaa		0	0	0	0	0	0	1	0	0	-1	0	0	0	0	0	0	
11	ββa	ββa		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	*
12	ββa	βββ		0	0	0	0	0	0	0	0	0	0	0	-1	0	0	1	0	
13	βββ	aaa		0	0	0	1	0	0	0	0	0	0	0	0	-1	0	0	0	
14	βββ	βaa		0	0	0	0	0	0	0	1	0	0	0	0	0	-1	0	0	
15	βββ	ββa		0	0	0	0	0	0	0	0	0	0	0	1	0	0	-1	0	
16	βββ	βββ		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	*

* unchanged by exchange

various temperatures. In general ^{31}P spectra were evaluated by means of the former and ^{13}C spectra by the latter. The results are summarized in Table VII. The compounds $F_4PN(CH_3)_2$ and $F_4PN(CH_3)CH_2C_6H_5$ were evaluated by means of EXCHSYS using the matrix given initially by Eisenhut et al.,[30] which is appropriate for the latter case because the axial fluorine distinguishability appears only at the very lowest temperatures, near the limiting spectrum. In the case of $F_4PN(H)CH_3$, where the differentiation is visible in the intermediate-exchange region, the matrix given (Table II of ref 6) for the permutationally equivalent system F_4PSCH_3 was used. The molecules $F(CF_3)_3PN(CH_3)_2$, $F(CF_3)_3PN(H)CH_3$, and $F(CF_3)_3PN(CH_3)CH_2C_6H_5$ (Figure 7), for which only half of the $^1J_{PF}$ doubled ^{31}P spectrum was fitted (the halves were identical in all cases), were analyzed by means of the kinetic magnetization-transfer matrix for a $(CF_3)_3P$ system with two equatorial and one axial CF_3 groups. This matrix has been given previously as supplementary material.[6] The compound $F(CF_3)_3PN(CH_3)CH_2C_6H_5$ was also analyzed by means of ^{13}C (CF_3) NMR spectroscopy using DNMR3 as was $Cl(CF_3)_3PN(CH_3)_2$. The trifluoride $F_3(CF_3)PN(CH_3)_2$ was analyzed by ^{31}P NMR spectroscopy and calculated with the program EXCHSYS using the matrix given previously (Table VIA of ref 6). Analysis of $CH_3(CF_3)_3PN(CH_3)_2$ and $(CF_3)_3P[N(CH_3)_2]_2$ by means of EXCHSYS employed the matrix for $(CF_3)_3P$ systems with two axial and one equatorial CF_3 groups, which is given as supplementary material to this paper.[31] Finally, the compounds $CH_3(CF_3)_2(F)PN(H)CH_3$ and $CH_3(CF_3)_2(F)PN(CH_3)_2$ were analyzed by ^{31}P NMR spectroscopy, and spectra were calculated by the program EXCHSYS using the matrix for two CF_3 groups on P, one axial and one equatorial, given in Table VIII. In the former case, the two

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(29) Binsch, G.; Kleier, D. L. "DNMR3, a Computer Program for the Calculation of Exchange Broadened NMR Spectra", Program 165; Quantum Chemistry Program Exchange: Indiana University, Bloomington, IN.

(30) Eisenhut, M.; Mitchell, H. L.; Traficante, D. D.; Kaufman, R. J.; Deutsch, J. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 5385.

(31) Supplementary material.

half-spectra were superimposable and only one of the $^1J_{PF}$ doubled portions of the spectra was fitted. In the latter compound the halves of the ^{31}P spectra were in general not identical because of a small second-order effect. In this case both halves were fitted independently and the rates averaged. The barrier in this case was further checked by a ^{13}C (CF_3) temperature-dependent study fitted by DNMR3, and good agreement with the barrier derived from ^{31}P dynamic NMR analysis was obtained.

The energetics of the rearrangement processes given in Table VII were obtained by fitting the rate data obtained from line-shape analyses to Arrhenius and Eyring equations.[32] In most cases $\Delta S^{\ddagger}$ and A terms are reasonable. The trends as indicated by $\Delta G^{\ddagger}_{298}$ values, generally the most reliable indicator,[33] indicate that the highest barriers are provided by methylamino derivatives in which an axial F atom is present on phosphorus, providing an opportunity for intramolecular hydrogen bonding. The magnitude of the contribution from hydrogen bonding can be discerned by comparing $F_4PN(CH_3)_2$ (9.4 kcal)[30,36] with $F_4PN(H)CH_3$ (13.4 kcal), a difference of 5 kcal, $F(CF_3)_3PN(CH_3)_2$ (12.2 kcal) with $F(CF_3)_3PN(H)CH_3$ (14.5 kcal), a difference of 2.3 kcal, and $CH_3(CF_3)_2P(F)N(CH_3)_2$ (14.2 kcal) with $CH_3(CF_3)_2P(F)N(H)CH_3$ (17.5 kcal), a difference of 3.3 kcal. In the absence of an axial F atom the barriers of $N(H)CH_3$ and $N(CH_3)_2$ compounds are virtually identical (cf. $CH_3(CF_3)_3PN(H)CH_3$ (16.4 kcal) and $CH_3(CF_3)_3PN(CH_3)_2$ (16.5 kcal));[5] thus we conclude that $N(H)CH_3$ and $N(CH_3)_2$ are electronically (except for hydrogen-bonding effects) and sterically equivalent. The hydrogen-bonding contribution can be tentatively assessed at 2.5 kcal for each axial F present and presumably arises because the trigonal-bipyramidal ground state with N(H)Me in an equatorial position with additional bonding to an axial fluorine atom is stabilized relative to the square-pyramidal or other intermediates involved in the rearrangement process.

The bulk of the amine seems to have only a small effect on the barriers, and the effect is irregular. Thus, comparison of $F(CF_3)_3PN(CH_3)_2$ (12.2 kcal) with $F(CF_3)_3PN(CH_3)CH_2C_6H_5$ (13.0 kcal) indicates that the bulkier amine may be associated with a higher barrier, but in contrast, the barrier to exchange in $F_4PN(CH_3)CH_2C_6H_5$ is lower (8.3 kcal) than that in $F_4PN(CH_3)_2$ (9.4 kcal).[36] These systems also illustrate that, in contrast to the suggestion of Holmes,[34] the element effect of a CF_3 group is not equal to that of F. This is further demonstrated by the following comparisons: the barriers of $(CF_3)_3P[N(CH_3)_2]_2$ (15.1 kcal) vs. that of the permutationally equivalent molecule $F_3P[N(CH_3)_2]_2$ (19.6 kcal);[35] the barrier of $F(CF_3)_3PN(CH_3)_2$ (12.2 kcal) vs. that of $CF_3PF_3N(CH_3)_2$ (15.6 kcal). Similarly the barriers in $F(CF_3)_3PSCH_3$ (11.5 kcal) and $F_3(CF_3)PSCH_3$ (12.8 kcal) are not identical although in this case the difference is within the limits of reliability. Equating the element effects of F and CF_3 results in the prediction of equal barriers for the above systems whereas the observed differences are substantial. The situation is discussed in more detail below.

The system $F_4PN(H)CH_3$ is permutationally equivalent to F_4PSCH_3, which we investigated earlier.[6] The limiting spectrum clearly demonstrates that both the permutational equilibrium of the PF_4 set and P–N bond rotation have ceased at the lowest temperatures. It is not possible to separate these processes because, as in the case of F_4PSCH_3,[6] either process transfers magnetization between the same sets of lines. Furthermore, the ^{31}P spectral line pattern generated by the particular values of the coupling constants is not so amenable to the discernment of such subtle differences in the line shape that may arise from uncorrelated BPR[38] and rotation or a fully correlated process wherein P–N bond rotation is intimately coupled with PF_4 permutations. In view of the observation however that, in some cases, P–N rotation is separable (e.g., by dynamic ^{13}C NMR of the $N(CH_3)_2$ group) from CF_3 permutations of $(CF_3)_3P(F)N(CH_3)_2$ and that the P–N barrier in this case is substantially lower than the BPR, we suspect that BPR and P–N rotations are separate processes in $F_4PN(H)CH_3$ but that the rates are comparable. An observable that distinguishes the two processes should reveal the processes independently if the barriers are significantly different, but in neither $F_4PN(H)CH_3$ nor $F_4PN(CH_3)CH_2C_6H_5$ are the two axial coupling constants sufficiently different to warrant additional scrutiny of the spectral line shapes in the intermediate-exchange region. A detailed analysis of the ^{19}F temperature dependence, although fraught with more difficulties than the present ^{31}P NMR spectral analyses, may be rewarding because the chemical shift differences between the two axial fluorines are reasonably large.

Table IX. Magnetization-Transfer Matrix for ^{13}C (CH_3) Exchange in $(CF_3)_3P(F)N(\mathit{CH}_3)_2$

line		P spin state	rel int	freq, Hz	1	2	3	4
1	C_1	α	$^1/_4$	250.0	−1.0	0	0	1.0
2	C_1	β	$^1/_4$	250.0	0	−1.0	1.0	0
3	C_2	β	$^1/_4$	334.0	0	1.0	−1.0	0
4	C_2	α	$^1/_4$	351.0	1.0	0	0	−1.0

(b) P–N Rotational Barriers. Our best evidence that Berry permutational interchange is *not* correlated with P–N bond rotation is provided by the observation that inequivalent ^{13}C (CH_3) environments are developed in $F(CF_3)_3PN(CH_3)_2$ at very low temperatures after permutational rearrangement has ceased. Line-shape analysis of this system (^{13}C (CH_3) dynamic NMR spectra were fitted by means of the program EXCHSYS[28] using the exchange matrix given in Table IX), although not without difficulty due to solubility and hence S/N difficulties at the low temperatures involved, gave a barrier to P–N rotation estimated from $\Delta G^{\ddagger}_{162}$ (and a constrained E_a) as 7.3 kcal[39] with a caution that the errors are relatively high in this case. This value is to be compared with P–N barriers for the non-hydrogen-bonded systems $F_3(CH_3)PN(CH_3)$-i-C_3H_7 (E_a = 10.6 kcal),[40] $F_2(C_6H_5)_2PN(CH_3)CH_2C_6H_5$ ($\Delta G^{\ddagger}_{210}$ = 9.8 kcal),[19] and $F_2(C_6H_5)_2P\overline{N(CH_2)_4C}H(CH_3)$ ($\Delta G^{\ddagger}_{210}$ = 10.4 kcal).[19] The remaining systems that have been studied are all potentially hydrogen bonded, having an N(H) function that may, as we have seen above, interact with the axial F on phosphorus. These systems provide P–N rotational barrier values (E_a) from 5.0 to 8.1 kcal for X_2F_2PNHR systems (Table X). The reliability of these numbers may be questionable because of unusually low values of A. The compound $F_3P(NH_2)_2$ exhibits a barrier of ($\Delta G^{\ddagger}_{250}$) 12.2 kcal[37] to P–N rotation (PF_3 permutation has ceased at room temperatures),

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(32) Laidler, K. "Chemical Kinetics"; McGraw-Hill: New York, 1950.

(33) Binsch, G. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1979.

(34) Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433.

(35) Moreland, C. G.; Doak, G. O.; Littlefield, L. B.; Walker, N. S.; Gilge, J. W.; Braun, R. W.; Cowley, A. H. *J. Am. Chem. Soc.* **1976**, *98*, 2161.

(36) We have repeated measurements on $F_4PN(CH_3)_2$ and obtained $\Delta G^{\ddagger}_{298}$ = 9.4 kcal and $\Delta G^{\ddagger}_{193}$ = 8.9 kcal, in good agreement with the original result of $\Delta G^{\ddagger}_{189}$ = 8.8 kcal obtained by earlier workers.[30] Reanalysis of the original data[30] for $F_4PN(CH_3)_2$ gave $\Delta G^{\ddagger}_{298}$ = 9.5 kcal.

(37) Muetterties, E. L.; Meakin, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *94*, 5674.

(38) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(39) The poor S/N conditions that prevailed gave very unreasonable values of $\Delta S^{\ddagger}$, and we are reluctant to accept the lower $\Delta G^{\ddagger}_{298}$ value derived therefrom because of the very long extrapolation from the measurement temperature (in contrast to all other cases herein). We favor the constrained E_a value of 7.3 kcal and suggest that this is probably the upper limiting value for this process in this molecule.

(40) Sokal'skii, M. A.; Drozd, G. I.; Landau, M. A.; Dubov, S. S. *Zh. Strukt. Khim.* **1969**, *10*, 1113.

Table X. Barriers to P–N Bond Rotation in Five-Coordinate Aminophosphoranes

	E_a, kcal	A, s^{-1}	T,[a] K	$\Delta G^{\ddagger}_T$, kcal	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{298}$, kcal	ref
$F(CF_3)_3PN(CH_3)_2$	10.5 ± 0.3	5.9×10^{16}	162	7.3 ± 0.4	10.2 ± 0.3	17.4 ± 1.9	5.0 ± 0.7	this work[b]
$F_2(C_6H_5)_2PN(CH_3)CH_2C_6H_5$			210	9.8 ± 0.5	9.4 ± 0.5	−1.9 ± 2.9		19
$F_2(C_6H_5)_2PN(CH_2)_4C(H)CH_3$			210	10.4 ± 0.5	8.8 ± 0.5	−6.9 ± 2.9		19
$F_3P(NH_2)_2$	11.15	5.6×10^{11}	250	12.25	10.65	−6.4		37[c]
$F_2(CH_3)_2PN(H)CH_3$	5.0 ± 1.5	10^5						41
$F_2(CH_3)_2PN(H)C_2H_5$	6.7 ± 2.5	10^8						41
$F_2(CH_3)(H)PN(H)(i\text{-}C_3H_7)$	8.1 ± 1.2	10^8						41
$F_3(C_2H_5)PN(H)C_2H_5$	11.0 ± 0.5	3×10^9						41
$F_3(CH_3)PN(H)(i\text{-}C_4H_9)$	11.5 ± 1.5	3×10^9						41
$F_3(C_6H_5)PN(H)CH_3$	12.0 ± 1.0	5×10^9						41
$F_3(CH_3)PN(CH_3)(i\text{-}C_3H_7)$	10.6 ± 0.2							40

[a] T is an average temperature, not a coalescence temperature. [b] A constrained fit to the Arrhenius equation with $A = 10^{13.2}$ gave $E_a = 7.3$ kcal, in good agreement with $\Delta G^{\ddagger}_{162}$. [c] No errors given.

similar to those given for the system $X_3RPN(H)R'$ (E_a = 11.0–12.0 kcal),[41] wherein F_3P permutational processes may be competitive.

The P–N rotational barrier seems to be smaller than that of P–S ($\Delta G^{\ddagger}_{298}$ = 10.2–11.0 kcal) obtained earlier;[6] however, the poorer reliability of the single value extracted herein renders comparisons speculative at this stage. It does, however, seem to be clear that the two types of motions are not correlated, as discussed elsewhere,[6] and nonseparability can be attributed to accidental similarity of barrier magnitudes or the inadequate differences of NMR spectral parameters, each of which renders distinction impossible.

If we consider this rotational barrier to be representative of the strength of π-bonding interactions in this molecule, the magnitude of such effects is seen to be substantial and to be of the same order as the barriers to permutational interchange. It is notable that the nitrogen need not carry exceptionally bulky substituents in order to provide a substantial barrier to P–N bond rotation. Relatively large substituents seem to be without a prominent effect on P–N rotation since fluxional barriers in benzylamine compounds are not substantially different from those of dimethylamino derivatives, although such bulky substituents appear to have a role in creating more readily discernible NMR environmental effects, which more readily reveal the cessation of the rotational averaging processes. The magnitude of the effects suggests that π-bonding contributions may provide a significant contribution to the overall fluxional barrier in five-coordinate molecules. Electronic and steric contributions arising from the substituents on nitrogen, except for the apparently substantial hydrogen-bonding contribution in N(H)R systems, are of less importance.

Parameterized Estimations of Permutational Barriers. While it is clear that the effect of a CF_3 group cannot be equated with the "element effect" for C derived from hydrocarbon substituents, the appropriate value for CF_3 is not obvious. As a first step toward evaluating the appropriate value of the element effect for CF_3, we have herein attempted to estimate the CF_3 parameters from the apparent electronegativity of 3.3[42] of the group, linearly interpolating the "element" contribution for CF_3 in equatorial and axial locations in a trigonal bipyramid and apical and basal locations in a square pyramid relative to the values given by Holmes[3] for Cl, O, and F substituents. Judging from the shape of the curves given in Figure 6 of ref 34, such linear interpolations appear to be quite reasonable, especially at the high electronegativity end of the scale. The resultant "element-effect" terms for CF_3 are given in Table XI along with apicophilicity values deduced therefrom, which appear also to be quite reasonable. In the application of these new CF_3 parameters to the (trifluoromethyl)phosphoranes, we have used the values given originally for H for the SCH_3 group plus a "π-loss" value of 2 kcal/mol for this group as suggested by Holmes[3] on the basis of the similarities of electronegativity values for H and the SCH_3 group. The "π-loss" for OCH_3 was 4 kcal/mol.[3] Our results are given in Table XII. We have also used the element-effect value for OCH_3 given by Holmes in Table 2.1 of ref 3b rather than equate OCH_3 to O as was done for previous calculations on some of these molecules.[3]

Table XI. Electronegativity-Interpolated Element-Effect Parameters for CF_3[a]

X	3.35
TP: eq	2.6
ax	1.9
A(ax–eq)	−0.7
−A(ref (C=O))	7.7
SP: ap	4.6
bas	0.7
−A(bas–ap)	−3.9
A(ref (C=O))	7.9

[a] These parameters are used in combination with those given in Table 2.1 of ref 3b.

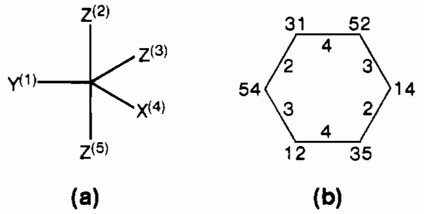

Figure 8. (a) Site labels and group designation scheme for $PXYZ_3$ phosphoranes. (b) Portion of the topological diagram for rearrangement of $PXYZ_3$ phosphoranes (adapted from Figure 1 of ref 34). The vertices represent trigonal-bipyramidal structures with the numbered groups indicated in the axial position. Along connecting lines are given the numerical label of the square-pyramidal apical substituent.

For all of the compounds discussed herein the permutational process can be represented (Figure 8) by a portion of the topological diagram given by Holmes (Figure 1 of ref 34), in which the tbp isomers are represented by specification of their axial groups at the vertex of the diagram and the Berry pivot is designated by number on the line connecting the isomers. The numbering of sites (Figure 8) and classification of groups are consistent with those given by Holmes.[3] In the molecules **1–6**, **11**, **12**, **14**, and **16**, the ground state is the (52) isomer

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[41] Sheluchenko, V. V.; Sokal'skii, M. A.; Landau, M. A.; Drozd, G. I.; Dubov, S. S. *Zh. Strukt. Khim.* **1969**, *10*, 142.

[42] Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111.

[43] Cavell, R. G.; Vande Griend, L. *Inorg. Chem.*, in press.

[44] Gilge, J. W.; Braun, R. W.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1974**, 15.

Table XII. Barriers for Exchange in (Trifluoromethyl)phosphoranes: $PXYZ_3$

compd	no.	substituent (original site)			exchange pathway[a]	calcd $\Delta G^‡$, kcal		exptl $\Delta G^‡$, kcal	ref to exptl $\Delta G^‡$	notes
		X (4)	Y (1)	Z (2, 3, 5)		case I[b] $CF_3 = F$	case II CF_3 unique			
$CH_3(CF_3)_3PH$	1	CH_3	H	CF_3	A(B)	14.9 (16.4)	11.5 (11.8)	14.2	43	
$CF_3(H)PF_3$	2	H	CF_3	F	A	7.9	9.0	6.4	44	
$CH_3(CF_3)_3POCH_3$	3	CH_3	OCH_3	CF_3	A(B)	16.6[c] (17.0)	13.2	12.9	5	
$CH_3(CF_3)_3PSCH_3$	4	CH_3	SCH_3	CF_3	A(B)	16.9[d] (18.4)	13.5 (13.8)	15.5	5	
$CH_3(CF_3)_3PN(CH_3)_2$	5	CH_3	$N(CH_3)_2$	CF_3	A(B)	19.0[d] (19.6)	15.6	17.2	5	
$(CF_3)_3P(CH_3)_2$	6	CH_3	CH_3	CF_3	A(B)	18.0[d] (20.0)	14.6 (15.4)	>17.2	5	
$CH_3(CF_3)_3PCl$	7	CH_3	Cl	CF_3	A(B)	13.0 (13.6)	9.6	11.1	5	ground-state anomaly; see text
					C	9.4[d]	8.3			
$CH_3(CF_3)_3PF$	8	CH_3	F	CF_3	C(D)	11.0[d,e]	9.9 (10.0)	9.6	5	
$(CF_3)_3P(Cl)N(CH_3)_2$	9	$N(CH_3)_2$	Cl	CF_3	A	14.0	10.6	9.8	this work	ground-state anomaly; see text
					C	10.4[d]	9.3			
$(CF_3)_3P(F)N(CH_3)_2$	10	$N(CH_3)_2$	F	CF_3	C	12.0[d,e]	10.9	12.2	this work	
$CF_3PF_3N(CH_3)_2$	11	CF_3	$N(CH_3)_2$	F	A	12.0[f]	13.1	15.6	this work	
$CF_3PF_3SCH_3$	12	CF_3	SCH_3	F	A	9.9[d]	11.0	12.8	6	
$(CF_3)_3P(F)SCH_3$	13	SCH_3	F	CF_3	C	9.9[d]	8.8	11.5	6	
$CF_3(CH_3)PF_3$	14	CH_3	CF_3	F	A(B)	11.0[d,e]	12.1 (12.3)	8.8	4	
$CF_3(CH_3)PCl_3$	15	CH_3	CF_3	Cl	C	6.4	8.8	n.o.	4	ground-state anomaly; see text
					A	10.0	7.5			
$(CF_3)_2PF_3$	16	CF_3	CF_3	F	A	4.0	5.5	n.o.	25	
CF_3PF_4	17	CF_3	F	F		4.0	3.0	n.o.	25	path $52 \overset{4}{\rightleftharpoons} 13$ provides provides the lowest barrier given here
$(CF_3)_3P[N(CH_3)_2]_2$	18	$N(CH_3)_2$	$N(CH_3)_2$	CF_3	A[f]	20.0	16.6	15.1	this work	

[a] Except where noted otherwise, the barrier for pathway A is identical with that of pathway B and that for pathway C is identical with that of pathway D. [b] Calculated according to the method and program given in ref **3**; parameters are given in Table 2.1 of ref 3b. [c] The value of 12.6 kcal was given in Table 1.13 of ref 3b; however this was obtained by equating the element effect of OCH_3 to that of O. We have used the element-effect value for OCH_3 given in Table 2.1 of ref **3b** for the OCH_3 substituents. A π-loss value was not given for OCH_3 in ref 3, but it seems reasonable to assign a value of 4.0 kcal in keeping with the value of 6.0 kcal assigned to $N(CH_3)_2$[3,34] and 2.0 kcal assigned to SCH_3.[3] [d] Given in Table 1.13 of ref 3b. [e] All paths have equal barriers (A = B = C = D) and the energy of the (52) ground state is identical with that of the (31) ground state—thus the ground state and the path are indeterminate. [f] No steric interactions between the $N(CH_3)_2$ groups were assigned to this system.

with either F or CF_3 in apical locations. Rearrangement can occur by either pathway A or pathway B. Only in the case

$$52 \overset{(4)}{\rightleftharpoons} 31 \overset{(2)}{\rightleftharpoons} 54 \overset{(3)}{\rightleftharpoons} 12 \overset{(4)}{\rightleftharpoons} 35 \tag{A}$$

$$52 \overset{(3)}{\rightleftharpoons} 14 \overset{(2)}{\rightleftharpoons} 35 \tag{B}$$

of compounds **1**, **4**, and **6** is there a difference in barrier energy of the two paths, and even in those cases the difference is very small. Therefore, in general, no path distinction is provided by the calculated barriers.

The molecules **8**, **10**, and **13** have a different ground state, (31); that is, when Y = F, it will be preferentially located in the axial position of a trigonal bipyramid. The rearrangement pathways in these cases are

$$31 \overset{(4)}{\rightleftharpoons} 52 \overset{(3)}{\rightleftharpoons} 14 \overset{(2)}{\rightleftharpoons} 35 \overset{(4)}{\rightleftharpoons} 12 \tag{C}$$

$$31 \overset{(2)}{\rightleftharpoons} 54 \overset{(3)}{\rightleftharpoons} 12 \tag{D}$$

and in all cases considered, there is again no distinction of pathway provided by the barrier calculations.

The three molecules containing Cl substituents provide an interesting anomaly. If, as we have argued elsewhere,[4-6,25] Cl is preferentially located in the axial position, then the proper ground state for compounds **7** and **9** is (31), similar to the case of their fluorine analogues, and the rearrangement pathway is either (C) or (D) with, again, identical predicted barrier values. If, however, the electronegativity rule prevails, these parameters, which are extracted from an electronegativity-based scale, indicate that the proper ground state is (52), being the isomer with the lowest energy. In that case the rearrangement pathway is either (A) or (B) and the barrier is higher by about 1.3 kcal, as indicated in Table XI. Holmes adopted our indicated ground states[3] (with Cl preferentially axial) and selected pathway C (≡D). Compound **15** presents a similar dilemma; the parameters indicate that (31) is the ground state and the resultant barrier to rearrangement via pathway A (≡B) is 7.5 kcal. However, if Cl is the preferential axial substituent, then the ground state is (52) and the resultant barrier is 8.8 kcal via pathway C (≡D). In contrast to the case of **7** and **9**, there are no NMR data that establish the ground state for these latter systems and, although a rearrangement process appears to be involved, no barrier has been determined.

The interpolated CF_3 parameter derived herein thus does not resolve the question of the ground states of chlorophosphoranes. Adoption[3] of CF_3 parameters equal to those of F does not resolve the difficulty either; in general, the ground states were predicted to be those with CF_3 rather than Cl axial by an even greater margin because no distinction between F and CF_3 was made. If the ground states are indeed those with Cl preferentially axial, then both Holmes' values and the present electronegativity-interpolated CF_3 values fail one reasonable test of parameter validity: that of the correct prediction of the ground state.

The barriers calculated for all compounds with the present value for CF_3 are similar to those given by Holmes.[3b] In some cases ours are in better agreement with experiment, and in some cases the barriers estimated by assuming the equality of F and CF_3 element effects[3] are in closer agreement with experiment. Our present set of estimated barriers are generally lower than those given elsewhere[3b] when the molecules contain three CF_3 groups, and our estimated barriers are higher than those given for molecules that contain three F substituents, as would be expected given the relationship of our electronegativity-interpolated values for CF_3 relative to the equality of F and CF_3 parameters. Equating the CF_3 element effect to that of F however makes it impossible to differentiate between the cases $(CF_3)_3P(F)L$ and CF_3PF_3L whereas the present interpolated parameters do so in a satisfactory way. For example, the experimental barriers of **10** and **11** differ by

3.4 kcal, with **11** having the larger barrier. The earlier calculation predicted zero difference;[3b] our calculations predict **11** to have the larger barrier by 2.2 kcal. Similarly, the barriers of **12** and **13** differ experimentally by 1.3 kcal, with **12** having the larger barrier. The modified CF_3 parameters predict **12** to have the larger barrier, also with a difference of 2.2 kcal. Compounds **8** and **14** provide a similar pair, but our prediction of a difference of 2.2 kcal, with the larger barrier associated with **14**, disagrees with the experimental result that the barrier of **8** is the larger of the two by 0.8 kcal. While the predictions seem in many cases to be rather good, there are sufficient disagreements with experiment to indicate that the approach must be used cautiously.[3] The barrier results are actually not strongly dependent on the values chosen for the parameters whereas the ground-state predictions are. A set of calculations in which CF_3 was assigned an element effect equal to that of Cl gave reasonable barrier values also, although in this case there was a tendency to substantially underestimate the barriers in cases where the molecules contained several CF_3 groups. In this case also, the ground-state predictions for the fluorides are of course in agreement with experiment but, because of the equality of CF_3 and Cl effects, the ground states for chlorides were indeterminate. In view of the uncertainty surrounding the ground states of chlorophosphoranes, this state of affairs may be appropriate. It would seem that some effort to revise the parameters in order to lift the gross dependency on electronegativity might be useful particularly in the development of more reliable prediction of the correct ground states, but we suspect that the "correct" CF_3 parameters would not on the whole give a better set of barrier values than either the simple equation of CF_3 to F or the electronegativity-interpolated values given herein.

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Registry No. $F_4PN(CH_3)_2$, 51922-00-0; $F_4PN(H)CH_3$, 33099-40-0; $F_4PN(CH_3)CH_2C_6H_5$, 84926-50-1; $F(CF_3)_3PN(CH_3)_2$, 51874-41-0; $F(CF_3)_3PN(H)CH_3$, 84895-93-2; $F(CF_3)_3PN(CH_3)CH_2C_6H_5$, 84895-94-3; $Cl(CF_3)_3PN(CH_3)_2$, 51874-40-9; $CH_3(CF_3)_3PN(H)CH_3$, 84926-51-2; $(CF_3)_3P[N(CH_3)_2]_2$, 51874-38-5; $F(CH_3)(CF_3)_2PN(CH_3)_2$, 51888-43-8; $F(CH_3)(CF_3)_2PN(H)CH_3$, 84926-52-3; $F_3(CF_3)PN(CH_3)_2$, 84926-53-4; $(DF_3)_3PF_2$, 79549-41-0; $CH_3(CH_2C_6H_5)NH$, 103-67-3; PF_5, 7647-19-0; $CH_3(CF_3)_2PF_2$, 51874-46-5; $(CH_3)_3SiN(H)CH_3$, 16513-17-0; $CH_3(CF_3)_3PF$, 56396-13-5; CF_3PF_4, 79549-39-6; $(CH_3)_3SiN(CH_3)_2$, 7083-91-2; CH_3NH_2, 74-89-5; $PF_5 \cdot NH(CH_3)CH_2C_6H_5$, 84895-95-4.

Supplementary Material Available: A matrix for $(CF_3)_3P$ systems with two axial and one equatorial CF_3 groups (1 page). Ordering information is given on any current masthead page.

Notes

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Symmetry of the Intermediate in the Hydroxylamine–Nitrous Acid Reaction[1]

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The reaction between hydroxylamine and nitrous acid leads to the products nitrous oxide and water (eq 1). A tracer

$$H_2NOH + ONOH \rightarrow N_2O + H_2O \qquad (1)$$

investigation reported by Bothner-By and Friedman,[2] in which ^{15}N-labeled nitrite was caused to react with hydroxylamine of natural isotopic abundance, established that the N_2O product emerges from an N–N bound precursor and that HNO is therefore not an intermediate. It was further reported that the isomers $^{14}N^{15}NO$ and $^{15}N^{14}NO$ are produced in equal amounts at low acidity but that $^{14}N^{15}NO$ predominates over $^{15}N^{14}NO$ in 2:1 ratio when the reaction is carried out in 0.1 M HCl. (The pH at "low acidity" is not specified in ref 2, but from reactant concentrations given it was clearly below 7 and may have been as low as 3.) It was concluded that reaction occurs via a symmetric intermediate (hyponitrous acid) at low acidity but that a competing pathway involving an unsymmetric intermediate (perhaps *N*-nitrosohydroxylamine) becomes important in acid solution. The experiments were carried out in $H_2{}^{18}O$, and the incorporation of solvent oxygen in N_2O product (mainly in the form $^{14}N^{15}N^{18}O$) appeared to be substantially greater in the acid solution case, an observation considered to strengthen the asymmetric intermediate hypothesis.

The production of equal amounts of $^{14}N^{15}NO$ and $^{15}N^{14}NO$ at low acidity was confirmed by Clusius and Effenberger.[3] Kinetic and mechanistic studies of the HNO_2–NH_2OH reaction have been reported by Doering and Gehlen[4] and in a series of papers by Stedman et al.[5–7] The latter have demonstrated the existence of three pathways, one acid catalyzed, one anion catalyzed, and one (at low acidity) second order in HNO_2. Oxygen-18 solvent studies reported in ref 5 appeared to corroborate the appearance of an asymmetric intermediate in acid solution: with the assumption of isotopic equilibrium between HNO_2 and solvent, the ratio of ^{18}O atom excess in product N_2O to that in solvent H_2O should be very nearly 0.5 if equimolar quantities of the two isomers are present. This ratio was observed to rise from 0.50 (low acidity) to 0.60 (pH 4 to 5 M $HClO_4$),[5] in rough agreement with the value 0.66 reported for acid solution in ref 2. In a more extensive series reported in ref 7, however, the appearance of intermediate asymmetry was observed only at very high acidity (4.2–4.9 M H_2SO_4 and $HClO_4$). More recently, in the course of a study of the oxidation of hydroxylamine by nitric acid, Pembridge and Stedman[8] observed that the nitrogen from $^{15}NH_2OH$ becomes equally distributed between the two nitrogens of N_2O produced by its reaction with the HNO_2 product of the main reaction, at HNO_3 concentrations up to ca. 5 M.

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[2] Bothner-By, A.; Friedman, L. *J. Chem. Phys.* **1952**, *20*, 459.

[3] Clusius, K.; Effenberger, E. *Helv. Chim. Acta* **1955**, *38*, 1834.

[4] Doering, C.; Gehlen, H. *Z. Anorg. Allg. Chem.* **1961**, *312*, 32.

[5] Hughes, M. N.; Stedman, G. *J. Chem. Soc.* **1963**, 2824.

[6] Morgan, T. D. B.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 344.

[7] Hussain, M. A.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 597.

[8] Pembridge, J. R.; Stedman, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1657.