Barrier to Rotation about the Phosphorus–Nitrogen Bond in Aminofluorophosphoranes. Relevance to Rearrangements in Five-Coordinate Compounds

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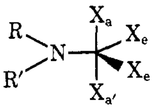
Abstract: An analysis of the temperature-dependent ^{19}F nmr line shapes for $PF_3(NH_2)_2$ established that the internal rotation about the two equivalent P–N bonds is essentially uncorrelated and that the free energy of activation ($\Delta G^{\ddagger}$) for this process is 12.3 kcal/mol at 250°K. The activation energy (E_a) is 11.15 kcal/mol, and this value represents a minimum estimate for the P–N π-bonding interaction in this fluorophosphorane. The contribution of this π interaction in raising barriers to intramolecular rearrangements (permutation of fluorine atom positions) in fluorophosphoranes is discussed.

There is ample experimental[2–6] and theoretical evidence[7] for π bonding in amino and alkylthio derivatives of pentacoordinate phosphorus(V). The data and the symmetry considerations[7] agree in placing the orientation of these donor ligands in the $P(X_a)_2$ axial plane as in **1** and **2** to allow for maximal π bonding in the equatorial plane. To date there has been no estimate of the π interaction energy in this aminophosphorane. We present data for the barrier to P–N bond rotation which is a minimal estimate for the π interaction and a discussion of the relevance of this interaction to Berry[8] rearrangements in molecules of the type XPF_4.



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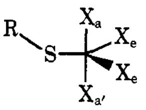

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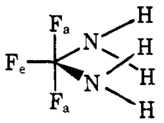
For $PF_3(NH_2)_2$, the ^{19}F, ^{31}P, and ^{1}H nmr data[9] establish a stereochemically rigid molecule (nmr time scale at 25°) with respect to fluorine atom permutations and a stereochemistry depicted in **3**. The axial fluorine nuclei are equally spin coupled to all four hydrogen nuclei at 25°. This indicates that P–N bond rotation is relatively rapid at this temperature. We anticipated and found the slow exchange (P–N rotation) spectrum below −40° to show "strong" coupling of the axial fluorine nuclei to only two hydrogen atoms, consistent with the stereochemistry for **3**.



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The left-hand column of Figure 1 shows the upfield half (large PF splitting) of the temperature-dependent 84.66-MHz ^{19}F nmr spectra associated with the axial fluorine atoms. The low-temperature limit ^{19}F spectrum assigned to the axial fluorine atoms consists of a near doublet ($|J_{F_aP}|$ = 665 Hz) of doublets ($|J_{F_aF_e}|$ = 39 Hz) of triplets ($|J_{F_aH}|$ = 41.5 Hz) of triplets ($|J_{F_aH'}|$ = 1 Hz). As the temperature is raised from the low-temperature limit, some of the lines begin to broaden while other lines remain sharp. As the temperature is raised still further, the broad lines broaden further until at a sufficiently high temperature the spectrum coalesces into a doublet of doublets of quintets. Since the small doublet splitting (39 Hz) is approximately twice the quintet splitting (the averaged F_aH coupling constant is 21.25 Hz), the high-temperature limit spectrum is a doublet of nonbinomial septets (Figure 1).

The process which averages the F_aH coupling constants is assumed to be internal rotation about the P–N bonds.[10] The internal rotation about the two P–N bonds may be at one extreme completely correlated (an internal rotation about one bond occurs whenever an internal rotation about the other bond occurs, *i.e.*, a "cog wheel" effect) or at the other extreme completely uncorrelated (independent internal rotation about the P–N bonds). These two mechanisms are distinguishable by the temperature dependence of the nmr line shapes associated with them. Figure 2 shows the nmr line shapes simulated for these two models using the density matrix method (see Experimental Section). Column 1 of Figure 2 shows the results for the uncorrelated mechanism and column II shows the spectra

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(3) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, **8**, 1097 (1967); V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, **10**, 142 (1969); M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, **10**, 1113 (1969).

(4) J. J. Harris and B. Rudner, *J. Org. Chem.*, **33**, 1392 (1968).

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

(6) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); F. N. Tebbe and E. L. Muetterties, *ibid.*, **7**, 172 (1968).

(7) (a) P. C. Van Der Voorn and R. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966); (b) P. C. Van Der Voorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, **43**, 3457 (1965); (c) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

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

(9) M. Lustig and H. W. Roesky, *Inorg. Chem.*, **9**, 1289 (1970).

(10) We are assuming either that the NH_2 groups are planar or that they are pyramidal but inverting rapidly on the nmr time scale at all temperatures observed in these studies.

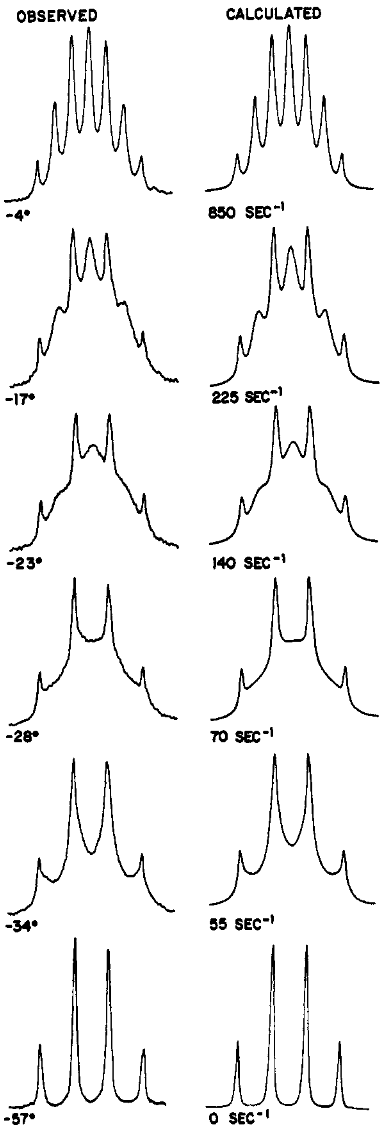


Figure 1. Observed and calculated 84.66-MHz ^{19}F nmr spectra of $PF_3(NH_2)_2$ at several temperatures (exchange rates). Only the upfield half of resonances assigned to the axial fluorine atoms is shown here. The spectra are calculated for uncorrelated internal rotation about the P–N bonds.

simulated on the basis of completely correlated internal rotation about the two P–N bonds. The spectra simulated on the basis of the uncorrelated internal rotation are in very good agreement with the observed spectra and are compared with the observed spectra at a few selected temperatures (exchange rates) in Figure 1. The spectra simulated assuming correlated internal rotation are in poor agreement with the observed spectra throughout the exchange region and are in good agreement with the observed spectra only near the fast and slow exchange limits. The real motion may of course be partially correlated internal rotation about the P–N bonds, and in this case the nmr line shapes could be simulated using a linear combination of the exchange operators (in Liouville space) for correlated and uncorrelated internal rotation. However, the excellent agreement obtained for the completely uncorrelated mechanism indicates that for $PF_3(NH_2)_2$ the internal rotations must be essentially uncorrelated.

The rate data for internal rotation about the P–N bond are presented as an Arrhenius plot in Figure 3.

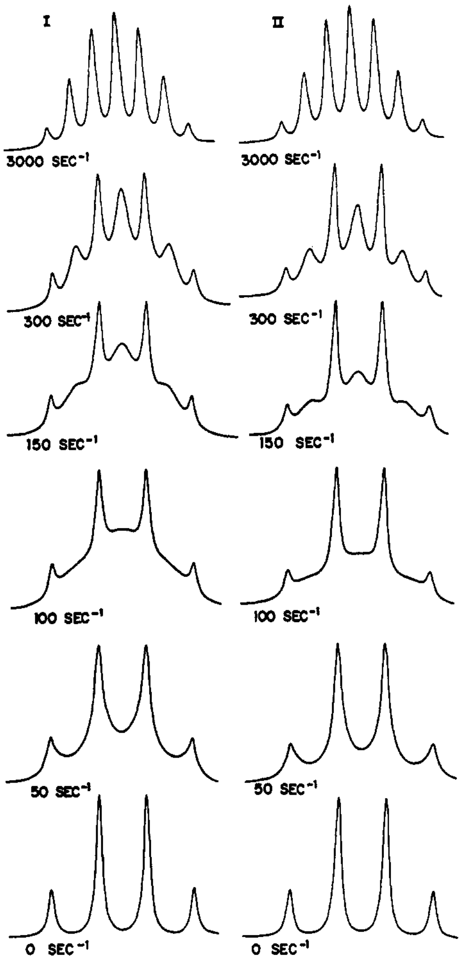


Figure 2. Calculated first-order line shapes for uncorrelated (I) and correlated (II) internal rotation about the P–N bonds. The rates are for internal rotation about a particular P–N bond.

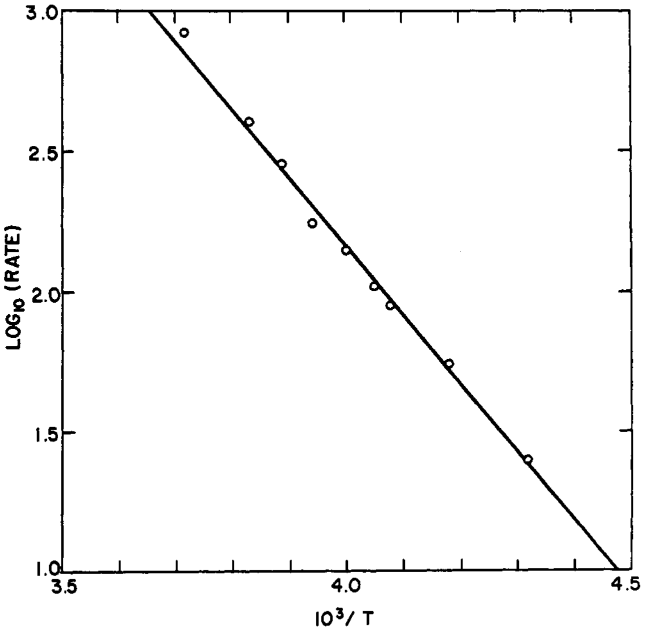


Figure 3. Arrhenius plot for the rates of internal rotation about the P–N bonds in $PF_3(NH_2)_2$.

The straight line in Figure 3 represents the rate expression

$$R(T) = 10^{11.75}e^{-11,150/RT}$$

Alternatively, the temperature dependence of the internal rotation rate can be expressed in terms of the Eyring equation

$$R(T) = K(kT/h)e^{-\Delta G^{\ddagger}/RT}$$

with the activation parameters

$$\Delta G^{\ddagger} = 12.25 \text{ kcal mol}^{-1}$$

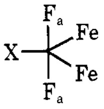
$$\Delta H^{\ddagger} = 10.65 \text{ kcal mol}^{-1}$$

$$\Delta S^{\ddagger} = -6.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

at 250°K.

The Arrhenius activation energy of 11.15 kcal mol^{-1} provides an approximate[11] value for the barrier to internal rotation about the P–N bond. In this case the reduced moment of inertia for the internal rotation is small and quantum tunneling may provide effective, lower energy paths for the internal rotation. Also, the correction for the zero-point torsional energy will be larger than usual, and these two effects combined will give an Arrhenius activation energy somewhat smaller than the barrier height. The barrier to internal rotation about the P–N bond can be taken as a reasonable lower limit to the P–N π-interaction energy in this molecule and serves as a general qualitative measure of the π-interaction energy in aminofluorophosphoranes.[12]

Essentially all XPF$_4$ molecules in which there is no extensive π bonding between X and P or those in which that π bonding is cylindrical undergo a very rapid intramolecular rearrangement to average fluorine atom environments at all temperatures attainable in solution. The slow exchange limit is not detected.[13] This is explicable[6,13] in terms of the Berry[8] rearrangement. In sharp contrast, the amino- and alkylthiotetrafluorophosphoranes show the slow exchange limit ^{19}F nmr spectra expected for **4** at temperatures of −30 to −85°.



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We[6,13] had earlier suggested that the difference in rearrangement rates for these two classes of XPF$_4$ molecules was due to P–N multiple bonding; the P–N bond rotation and a Berry rearrangement are inextricably coupled. This view appears supported by all data now available. Previous estimates for the rearrangement barrier (permutation of fluorine atoms positions) in dialkylaminotetrafluorophosphoranes were in the range 6–12 kcal/mol. We have recalculated $\Delta G^{\ddagger}$ for (CH$_3$)$_2$NPF$_4$ with the data of Whitesides and Mitchell[14] and obtain a value of 9.5 kcal/mol for this molecule. The magnitude of the rearrangement barriers relative to the P–N rotational barrier in PF$_3$(NH$_2$)$_2$ would seem to suggest that the resistance to P–N bond rotation makes a major contribution to the Berry rearrangement barrier in R$_2$NPF$_4$ molecules. It is not possible, however, to truly quantify this statement. Note simply that if one assumes the Berry[8] rearrangement in R$_2$NPF$_4$,[15] the transition state is approximately a square pyramid with the amino group at an apex. The barrier to P–N rotation in this idealized state,[16] or one approximating it, must be substantially lower than in the ground state because of the fourfold character of the barrier. The coupling of P–N rotation and the fluorine atom permutational process in R$_2$NPF$_4$ molecules simply does not allow a mechanistic factoring of the overall process; factoring would involve at best a circular argument of which process comes first.

Experimental Section

PF$_3$(NH$_2$)$_2$ was prepared by the procedure of Lustig and Roesky.[9] The fluorine nmr spectra were run over the temperature range of −60 to 25° using a Bruker HFX-90 spectrometer. The solution medium was 50/50 acetonitrile–dichloromethane. Temperatures were measured with a copper–constantan thermocouple located just below the sample tube and were calibrated using a similar thermocouple held coaxially in the spinning sample tube partially filled with solvent.

The nmr line shapes were calculated using the density matrix method of Kaplan[17] and Alexander.[18] Since the ^{19}F spectra at 84.66 MHz are very nearly first order, the spectra were treated as if they were exactly first order. This considerably simplifies the line-shape calculations. Details concerning the nmr line-shape calculations are given elsewhere.[19] The rates for the internal rotation were determined by varying the exchange rate used in the calculation until a best visual fit was obtained between calculated and observed spectra. The coupling constants were not varied as they seem to be almost temperature independent, and excellent agreement was obtained between calculated and observed spectra at all temperatures using the coupling constants obtained from the low-temperature limit spectra. The line width in the absence of exchange can be determined from those lines that are invariant to the exchange process.

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(11) M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).

(12) For a related case, see the discussion of π interaction and bond rotation in metal-olefin complexes: R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

(13) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(14) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

(15) Whitesides and Mitchell[14] showed the rearrangement in (CH$_3$)$_2$NPF$_4$ to be consistent with the Berry[8] rearrangement (other non-Berry mechanisms are also consistent with the observed line shape changes; *i.e.*, they are of the same permutational character as the Berry[8] mechanism).

(16) For a detailed discussion of idealized rearrangement mechanisms in five coordination, see P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(17) J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).

(18) S. Alexander, *ibid.*, **37**, 967, 974 (1962); **38**, 1787 (1963); **40**, 2741 (1964).

(19) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).