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Pseudorotation in $(\text{CH}_3)_2\text{NPF}_4$

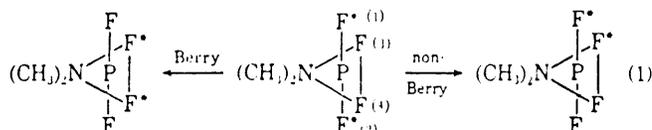


George M. Whitesides and H. Lee Mitchell

Pseudorotation in $(\text{CH}_3)_2\text{NPF}_4^1$

Sir:

The rapid intramolecular interchange of axial and equatorial fluorine atoms observed² for compounds of the formula XPF_4 is commonly believed to occur by a mechanism proposed by Berry,³ in which isomerization of one ground-state trigonal bipyramid to another (pseudorotation) takes place by a transition state or intermediate of square-pyramidal geometry. The simplicity and high symmetry of this mechanism make it attractive. However, a number of distinct mechanistic alternatives for the process which results in fluorine interchange can be envisioned,^{4,5} and clear experimental distinctions between these alternatives have not been reported. We wish to describe ^{31}P nmr studies of $(\text{CH}_3)_2\text{NPF}_4^6$ (1) which confirm a fundamental prediction of the Berry mechanism, *viz.* that pseudorotation of this compound results in *simultaneous* interchange of both axial fluorine atoms with equatorial fluorines, rather than in interchange of only one pair of axial and equatorial fluorine atoms. In what follows, we will arbitrarily refer to *any* exchange reaction resulting in interchange of both pairs of fluorines as a "Berry" pseudorotation, and to any reaction interchanging only one pair as a "non-Berry" pseudorotation (eq 1), without implying further details of the interchange.



The ^{31}P nmr spectrum of 1 at -100° is the triplet of triplets ($J_{\text{P,F}} = 768$ Hz, $J_{\text{P,F}'} = 904$ Hz) expected for a static trigonal-bipyramidal structure having the $(\text{CH}_3)_2\text{N}$ - group in an equatorial position (Figure 1).² At -50° pseudorotation is rapid on the nmr time scale, and the spectrum shows a 1:4:6:4:1 quintet resulting from coupling of ^{31}P to four magnetically equivalent fluorines. The slow-exchange spectrum can be considered as the summation of resonances of ^{31}P nuclei in the characteristic magnetic environments of the fluorine nuclear spin configurations represented by the 16 possible ^{19}F spin eigenfunctions of 1; as a result of degeneracies, these 16 fluorine spin configurations give rise to only nine distinct ^{31}P resonances (Figure 2). For the purposes of this discussion, these spin eigenfunctions can be approximated by the symmetrized spin functions for four nuclei in C_{2v} symmetry.⁷ The problem of describing the ^{31}P spectral behavior of 1 in the region of intermediate pseudorotation rates can then be treated as a problem of describing the transfer of magnetization between these nine lines and 16 sites by the pseudorotation process.

(1) Supported by the National Institutes of Health, Grant GM 16020.

(2) E. L. Muettterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); E. L. Muettterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); R. Schmutzler in "Halogen Chemistry," Vol. 2, V. Gutman, Ed., Academic Press, New York, N. Y., 1967, pp 33 ff.

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

(4) E. L. Muettterties, *J. Amer. Chem. Soc.*, **91**, 1636, 4115 (1969), and references therein.

(5) For infrared studies pertinent to this problem, see L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967); R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, **7**, 2229 (1968).

(6) D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc., A*, 171 (1966).

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, Chapter 8. The chemical shift difference between axial and equatorial fluorine atoms ($\delta\nu = 1660$ Hz at 23 kG) and the fluorine-fluorine coupling constant ($J = 62$ Hz) of 1 are such that mixing of these functions is small. Use of the correct eigenfunctions for 1 in the following discussion does not quantitatively change our conclusions, but does obscure their physical foundation.

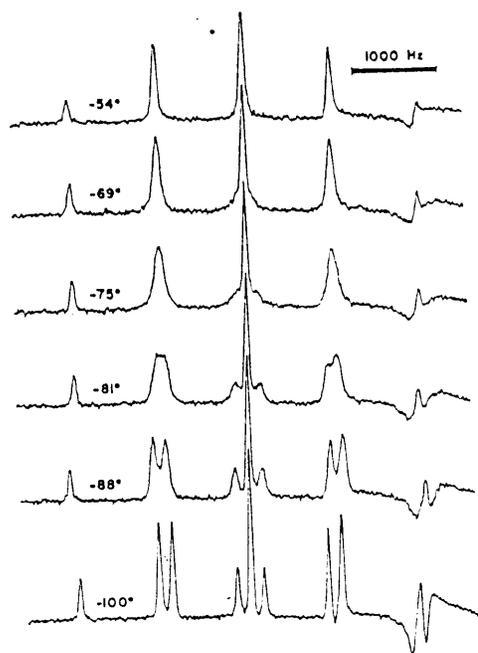


Figure 1. ^{31}P nmr spectra of $(\text{CH}_3)_2\text{NPF}_4$ as a function of temperature (nonspinning sample containing $\sim 10\%$ TMS). These spectra were taken using 2.5-kHz audiomodulation; the shapes of the three highest field lines (lines 7, 8, and 9) are distorted by superposition on center-band resonances. Lines 1-6 are undistorted.

The influence of pseudorotation on the ^{31}P resonances is determined by the extent to which the magnetic environment "seen" by the phosphorus is changed by the fluorine interchange. If pseudorotation results in isomerization of a starting configuration of fluorines to a final configuration which is magnetically indistinguishable from the vantage of the ^{31}P nucleus, no broadening will be observed for the phosphorus transition characteristic of this configuration. If, on the other hand, pseudorotation converts the starting configuration of fluorine nuclei to a final configuration characterized by a different ^{31}P resonance frequency, the two (or more) slow-exchange phosphorus lines coupled by the exchange will broaden and coalesce as the pseudorotation rate increases. The final configurations of fluorine nuclei obtained from a particular starting configuration following pseudorotation by Berry and non-Berry mechanisms are easily determined by inspection, and representative examples are given in Table I.

Table I. Representative Starting and Final Fluorine Spin Configurations for Pseudorotation of **1**

Berry		Non-Berry	
Final	Start- ing	Final	Start- ing
ϕ_1	$\leftarrow \phi_1 \rightarrow$	ϕ_1	$\leftarrow \phi_1 \rightarrow$
ϕ_4	$\leftarrow \phi_2 \rightarrow$	$1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$	$\leftarrow \phi_2 \rightarrow$
ϕ_5	$\leftarrow \phi_3 \rightarrow$	$1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$	$\leftarrow \phi_3 \rightarrow$
ϕ_{11}	$\leftarrow \phi_6 \rightarrow$	$1/4\phi_7 + 1/4\phi_8 + 1/4\phi_9 + 1/4\phi_{10}$	$\leftarrow \phi_6 \rightarrow$
ϕ_7	$\leftarrow \phi_7 \rightarrow$	$1/4\phi_6 + 1/4\phi_7 + 1/4\phi_8 + 1/4\phi_9 + 1/4\phi_{10} + 1/4\phi_{11}$	$\leftarrow \phi_7 \rightarrow$
ϕ_9	$\leftarrow \phi_8 \rightarrow$	$1/4\phi_6 + 1/4\phi_7 + 1/4\phi_8 + 1/4\phi_9 + 1/4\phi_{10} + 1/4\phi_{11}$	$\leftarrow \phi_8 \rightarrow$

In these examples, the axial and equatorial fluorine sites are labeled using the numbering scheme of eq 1, and, e.g., $\phi_2 \rightarrow 1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$ indicates that a molecule of **1** whose fluorines are originally described

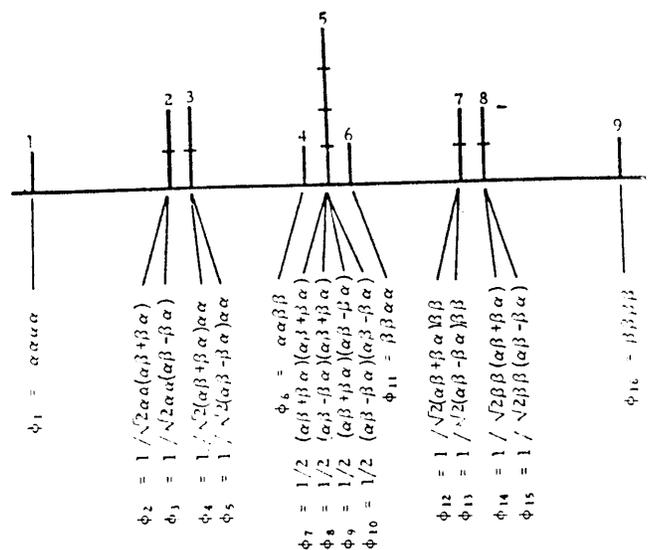


Figure 2. Spectral assignments for the ^{31}P spectrum of $(\text{CH}_3)_2\text{NPF}_4$.

by the spin function $1/\sqrt{2}\alpha(1)\alpha(2)[\alpha(3)\beta(4) + \beta(3)\alpha(4)]$ will be converted on pseudorotation to the configurations $1/\sqrt{2}\alpha\alpha(\alpha\beta + \beta\alpha)$, $1/\sqrt{2}\alpha\alpha(\alpha\beta - \beta\alpha)$, $1/\sqrt{2}(\alpha\beta + \beta\alpha)\alpha\alpha$, and $1/\sqrt{2}(\alpha\beta - \beta\alpha)\alpha\alpha$ with equal probabilities.⁸

By identifying the sets of transitions which are kinetically coupled by fluorine interchange, the entries in Table I, together with parallel descriptions for the starting configurations not explicitly listed in this table, make it possible to calculate the influence of pseudorotation by either mechanism on the shapes of the lines in the ^{31}P spectrum of **1**. Thus, qualitatively, the configuration ϕ_1 is transformed into itself by Berry or non-Berry pseudorotations; consequently, line 1 of the spectrum is not affected by pseudorotation, regardless of mechanism. Both mechanisms transfer magnetization between lines 2 and 3; however, the rate constant for this transfer by a Berry mechanism is twice that by a non-Berry mechanism, since half of the non-Berry pseudorotation events do not change the phosphorus precession frequency.

A Berry mechanism transfers magnetization between lines 4 and 6, but does not couple any of the transitions making up line 5 with transitions of different frequency; in contrast, a non-Berry mechanism transfers magnetization between lines 4 and 5, and between 5 and 6, but not directly between 4 and 6. Thus, in a Berry mechanism lines 4 and 6 should broaden and coalesce in the intermediate exchange region, while line 5 remains sharp. In a non-Berry mechanism lines 4, 5, and 6 should all broaden in the intermediate exchange region.

These arguments can be used as the basis for quantitative calculations of line shapes using unexceptional procedures.⁹ The kinetic exchange matrices **K** describing transfer of magnetization between the lines of the observed spectra are given by eq 2 and 3. The rows and columns of these matrices are numbered to

(8) These relative probabilities are based on the assumption that the transition from starting to final configurations is instantaneous. The spectral consequences of an intermediate of C_{2v} nuclear symmetry and finite lifetime along the pseudorotation coordinate will be discussed in a full paper.

(9) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965); G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 2245 (1969), and references in each.

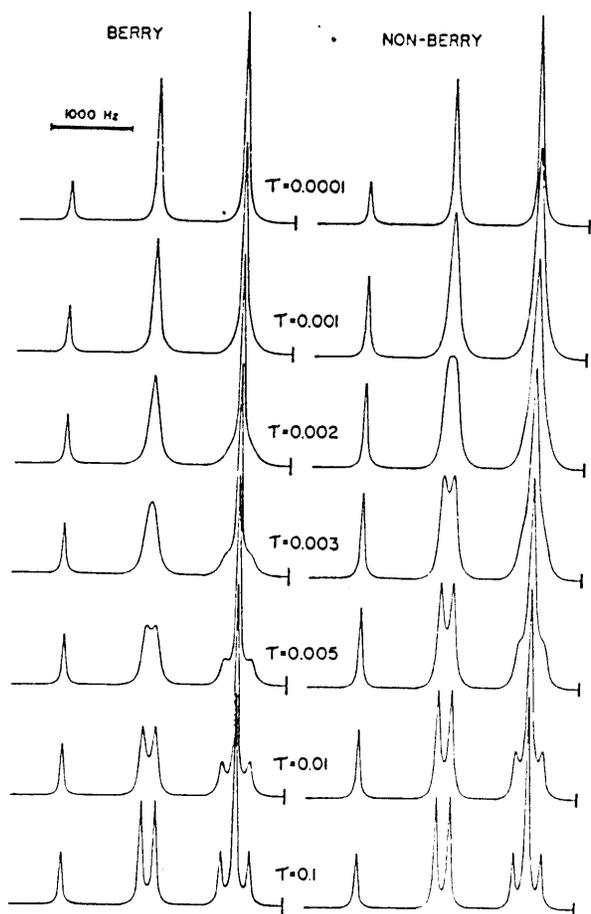


Figure 3. Spectra calculated for pseudorotation by Berry and non-Berry mechanisms. To save space, only the kinetic behavior of lines 1-6 is shown.

correspond with the lines of the observed static spec-

trum. Spectra calculated for a range of preexchange lifetimes τ are given in Figure 3.

$$K_{\text{Berry}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & -9 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (2)$$

$$K_{\text{non-Berry}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & -1/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/4 & -1/2 & 1/4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (3)$$

Comparisons of two features of these calculated and observed spectra clearly demonstrate that a Berry mechanism is responsible for pseudorotation in 1. First, in agreement with spectra calculated assuming this mechanism, line 5 of the observed spectra remains sharp throughout the temperature range responsible for the broadening and complete collapse of lines 4 and 6; by contrast, line 5 is appreciably broadened for intermediate non-Berry exchange rates. Second, the relative rates of broadening and collapse of lines 2, 3, 4, and 6 are compatible with those calculated on the basis of a Berry mechanism, but are incompatible with relative rates based on a non-Berry process.

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