strongly depolarized modes at 705, 2990, and 3035 cm^{-1} exhibit Δ values of comparable magnitude. It is striking that the CH stretching modes generally possess the higher Δ values. This could be due to the large amplitude of hydrogen stretching motions that may produce fairly large perturbations of the optical activity tensors. The band at 2740 cm^{-1} with the large Δ value is probably due to a CH stretch–ring pucker combination mode.[6] Other modes which possess large Δ values also seem to occur in regions likely to contain CH deformation and ring breathing modes. The modes which are largely C=O and C=C stretching (1648, 1675 cm^{-1}), although giving the largest $I_R - I_L$ values, do not exhibit comparably large Δ values. Correlation of these results with the vibrational fine structure in electronic circular dichroism[7] should yield structural information not presently available.

Differential circular intensity was also observed in the Rayleigh line of the two enantiomers; the magnitudes were roughly equal and the signs opposite. Quantitative determination of the circular intensity differential in the Rayleigh line was, however, prevented by instrumental difficulties.

The apparatus used to observe the phenomenon consisted of a Jarrell Ash Model 25-100 double monochromator fitted with an ITT FW-130 photomultiplier detector operated at −25°. The exciting source was a Spectra Physics Model 125A He–Ne laser. A Victoreen Model VTE-1 electrometer amplifier was used to measure the dc signals. CDR spectra were obtained using 400 Hz, $\lambda/4$ sinusoidal modulation (CML McCarr Model 120 NS with a step-up transformer) of an electrooptical modulator (Lasermetrics Model EOM 703). Since alignment of the modulator is exceedingly critical, a micrometer-adjustable housing was constructed and utilized. First and second harmonic detection was accomplished with a PAR Model 126 lock-in amplifier operated in the external modes. Zero base line was established using several achiral liquids and racemic modifications.

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Intramolecular Fluorine Exchange in Diphenyltrifluorophosphorane

Sir:

Recently, Cowley[1] and coworkers presented evidence from a ^{1}H nmr line shape study for a second-order intermolecular fluorine exchange process in the phosphorus(V) fluorides $(CH_3)_3PF_2$ and $(CH_3)_2PF_3$. Earlier reports[2] on these compounds and other phosphorus(V) fluorides indicated that the fluorine exchange proceed *via* an intramolecular "pseudorotation" mechanism first proposed by Berry.[3] The purpose of this communication is to report strong evidence for intramolecular fluorine exchange in diphenyltrifluorophosphorane, Ph_2PF_3.

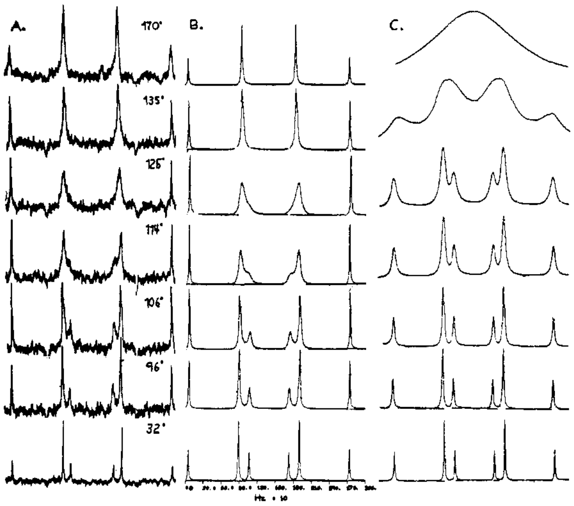

Figure 1. (A) Experimental ^{31}P nmr spectra of neat Ph_2PF_3 in Teflon cells, (B) calculated ^{31}P nmr spectra using matrix I, and (C) calculated ^{31}P nmr spectra using matrix II. The calculated τ values (sec) as a function of temperature are: 0.20, 32°; 0.015, 96°; 0.0075, 106°; 0.0030, 114°; 0.0018, 125°; 0.00040, 135°; 0.00010, 170°.

The compound was prepared by the fluorination of Ph_2PCl with AsF_3. The product was purified by repeated fractional vacuum distillation over NaF and its properties correspond well with reported values.[4] The nmr samples were prepared in a glove bag dried with P_2O_5 under nitrogen atmosphere. It was necessary to use Teflon cells (NMR Specialties) because samples prepared in Pyrex tubes did not give reproducible ^{31}P nmr line shapes. The Teflon cells were sealed in the glove bag and placed in standard nmr Pyrex tubes which were sealed with pressure caps. All ^{31}P nmr studies were carried out at 40.5 MHz with ^{1}H decoupling at 100 MHz. The spectra were calibrated using the side-band technique.

In this work the rate constants ($1/\tau$) for fluorine exchange were obtained by comparing experimental ^{31}P nmr line shapes with those calculated using the Kubo-Sack[5] method. Figure 1 shows (A) the experimental ^{31}P nmr line shapes as a function of temperature, (B) the calculated line shapes at different τ values using matrix I, and (C) the calculated line shapes using matrix II.

Matrix I[6] is for an intramolecular exchange between

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[5] (a) R. Kubo, *Nuovo Cimento, Suppl.*, 6, 1063 (1957); (b) R. A. Sack, *Mol. Phys.*, 1, 163 (1958).

[6] A more detailed discussion of the derivation of matrices I and II is given in C. S. Johnson, Jr., and C. G. Moreland, *J. Chem. Educ.*, in press.

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & 1/2 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 1/2 & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

I

$$\begin{bmatrix} -1/2 & 1/3 & 1/6 & 0 & 0 & 0 \\ 1/6 & -1/2 & 0 & 1/6 & 1/6 & 0 \\ 1/6 & 0 & -1/2 & 0 & 1/3 & 0 \\ 0 & 1/3 & 0 & -1/2 & 0 & 1/6 \\ 0 & 1/6 & 1/6 & 0 & -1/2 & 1/6 \\ 0 & 0 & 0 & 1/6 & 1/3 & -1/2 \end{bmatrix}$$

II

either axial fluorine and the equatorial fluorine where τ is the mean time between fluorine exchanges. In the fluorine configurations, $\alpha\alpha\alpha$ and $\beta\beta\beta$, the intramolecular exchange of the equatorial fluorine with either of the axial fluorines leads to the same configurations; thus fluorine intramolecular exchanges have no effect on the first and last lines in the ^{31}P nmr spectrum. This can be seen as one of the main features in the experimental spectra in Figure 1A. Also, at high temperature where the fluorine lifetimes are very short, the three fluorines should become equivalent on the ^{31}P nmr time scale and therefore the ^{31}P nmr spectrum should show a 1:3:3:1 quartet as observed at 170° in Figure 1A and B.

Matrix II[6] is for an intermolecular exchange of fluorines where it is assumed that the three fluorines have the same mean lifetimes between exchanges. The principal feature of these spectra is the decoupling of the fluorines from the phosphorus which is not observed in the experimental spectra over the temperature range covered.

Since the spectra calculated using matrix I (B) are almost identical with the experimental spectra (A) and those calculated using matrix II are extremely different, the conclusion reached is that the fluorine exchange in Ph_2PF_3 is intramolecular. Also, a concentration study using nitrobenzene as a solvent showed that the spectra at all concentrations and temperatures were identical with those of the neat Ph_2PF_3 and indicates that the exchange process is first order in Ph_2PF_3.

On the other hand, ^{31}P nmr spectra obtained on Ph_2PF_3 in Pyrex tubes showed extreme line broadening and partial collapse of the quartet multiplet at $\sim$140°. In fact, the temperature-dependent spectra closely resembled the calculated spectra given in Figure 1C and indicated an intermolecular fluorine exchange process. Concentration studies in nitrobenzene, however, showed no effect on the ^{31}P nmr line shapes and thus indicate a first-order process. We have tentatively concluded that Ph_2PF_3 in Pyrex tubes attacks the glass to produce phosphoryl compounds and F^- (or HF) which exchanges with the Ph_2PF_3. Cowley, *et al.*,[1] also observed collapse of the $^{31}P-^{19}F$ coupling at $\sim$140° in the ^{19}F nmr spectrum of $(CH_3)_2PF_3$ and $(CH_3)_3PF_2$, in Pyrex tubes. Since they did not report on the concentration dependence of the multiplet collapse, it is possible they were not observing the same exchange process at high temperatures as they observed at low temperatures.

The caption for Figure 1 gives the τ values which were used to obtain the spectra shown in Figures 1B and C. Each τ value is reported with the temperature of the experimental spectrum in A that most nearly matches the calculated spectrum in B. An Arrhenius plot of these data excluding the limiting cases gives a $E_a \sim$ 20 kcal. A more precise value of E_a is being obtained by following the disappearance of $^{19}F-^{19}F$ coupling by ^{19}F nmr.

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A Model Conformational Study of Nucleic Acid Phosphate Ester Bonds. The Torsional Potential of Dimethyl Phosphate Monoanion

Sir:

Knowledge of the conformational behavior of biopolymers has increased considerably in recent years, due to (1) the vast accumulation of experimental structure data from X-ray crystallography, nmr, and other physical methods,[1,2] and (2) the feasibility of carrying out large-scale potential-energy and statistical-mechanical calculations, using a variety of empirical and semiempirical techniques.[2a,3,4] Although the bulk of previous theoretical work has been directed toward polypeptide conformations,[3] several studies on polynucleotides have also been reported.[4] Associated with the three structural subunits of polynucleotides—the ribose sugar, the pyrimidine or purine base, and the phosphate group—are three major conformational problems: (1) the internal conformations of the ribose group; (2) the conformation between the ribose and the base (the glycosidic linkage); and (3) the conformations involving the phosphodiester linkage. The first two problems have been thoroughly examined in the

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