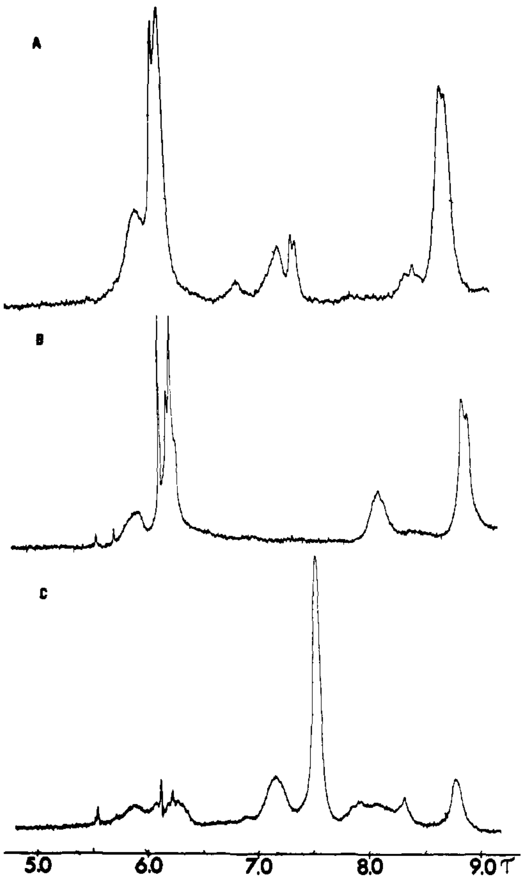

Figure 1. 100-MHz spectra of (A) 2,4-dimethyl-2-pentyl cation at −114°, (B) 2,5-dimethyl-2-hexyl cation at −95°, (C) 2,6-dimethylheptyl cation at −95°.

information was obtained by strong irradiation at −60° of the α-methyl resonance which caused a marked decrease in the intensity of the δ-methyl peak and *vice versa.*

Ion III was more difficult to obtain than ion I or II. Most of the attempts at preparation led to oxidation to the ditertiary cation. This dication is characterized by an intense peak at τ 5.9 and has previously been reported by Olah.[5] When ion I was successfully prepared its spectrum was less well resolved than those for the lower homologs. The interesting feature in the spectrum at −95° (Figure 1C) is the broad peak centered at τ 7.5 which is at the average of the shifts expected for the α and ϵ methyls. We take this as evidence for a rapidly occurring degenerate 1,5-hydride transfer in the ion with an activation energy of no more than 6 or 7 kcal/mol. Upon heating above −85°, this peak rapidly disappears with the appearance of the peak for the dication at τ 5.9.

Several mechanisms for the 1,3-hydride shift can be imagined (Figure 2). Consecutive 1,2 shifts (Figure 2B) are inconsistent with the observed spectral changes as previously noted. The 1,3 shift could conceivably go *via* a protonated cyclopropane (Figure 2C). However, the occurrence of the 1,4- and 1,5-hydride transfers (the latter requiring *less* energy than the 1,3 shift) in ions where no such intermediate can be considered argues against this pathway. Furthermore, cases in which the intermediacy of such protonated cyclopropanes has been firmly established[6-8] indicate that the transition state for corner-to-corner migration in this kind of intermediate lies at least 15 kcal higher in energy than a tertiary ion. The process which converts the 2,4-dimethyl-2-pentyl cation into the 2,3,3-dimethyl-2-butyl cation requires 17 kcal of activation energy[9] and most likely involves a protonated cyclopropane.

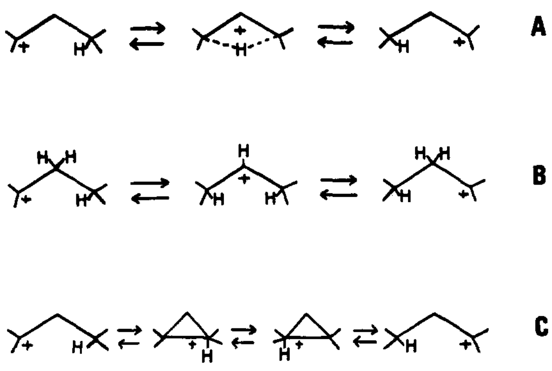

Figure 2. Mechanisms considered for the 1,3 hydride shift: (A) simple 1,3 shift, (B) consecutive 1,2 shifts, (C) hydride shift *via* protonated cyclopropane.

For these reasons, it seems likely that the process under observation in all of these ions is simply a hydride transfer between the two tertiary centers with no direct bonding between the carbons at these centers (Figure 2A).

The magnitude of the energy barriers for the hydride shifts (1,4 > 1,3 > 1,5) is likely a reflection of the steric and conformational factors operative in these systems. It is interesting that the order of rates found in these acyclic systems is the same as the order of rates for reaction involving hydride shifts in medium-sized rings which have been studied by other techniques.[10,11]

Acknowledgment. The stimulation for this work was the prepublication disclosure by Professor D. Arigoni of several reactions induced by polyphosphoric acid which were convincingly demonstrated to occur *via* 1,5 hydride shifts (see Q. Branca and D. Arigoni, *Chimia*, **23**, 189 (1969), and Q. Branca, Dissertation, Federal Institute of Technology, Zurich, 1970). This work was supported by a grant from the National Science Foundation.

---

(5) J. M. Bollinger, C. A. Capas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

(6) M. Saunders, E. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882(1968).

(7) M. Saunders and J. Rosenfeld, *ibid.*, **91**, 7756 (1969).

(8) E. Hagen, Ph.D. Thesis, Yale University, 1969.

(9) D. M. Brouwer and J. M. Oelderich, *Recl. Trav. Chim. Pays-Bas*, **87**, 721 (1969).

(10) V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Wiley-Interscience, New York, N. Y., 1963, p 593.

(11) A. E. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966).

Martin Saunders,* John J. Stofko, Jr.
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520

Received June 9, 1972

Circular Differential Raman Spectra of Carvone

Sir:

Recently, Bosnich, *et al.*,[1] reported the observation of Raman "circular dichroism" or circular differential

---

(1) B. Bosnich, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **94**, 4750 (1972).

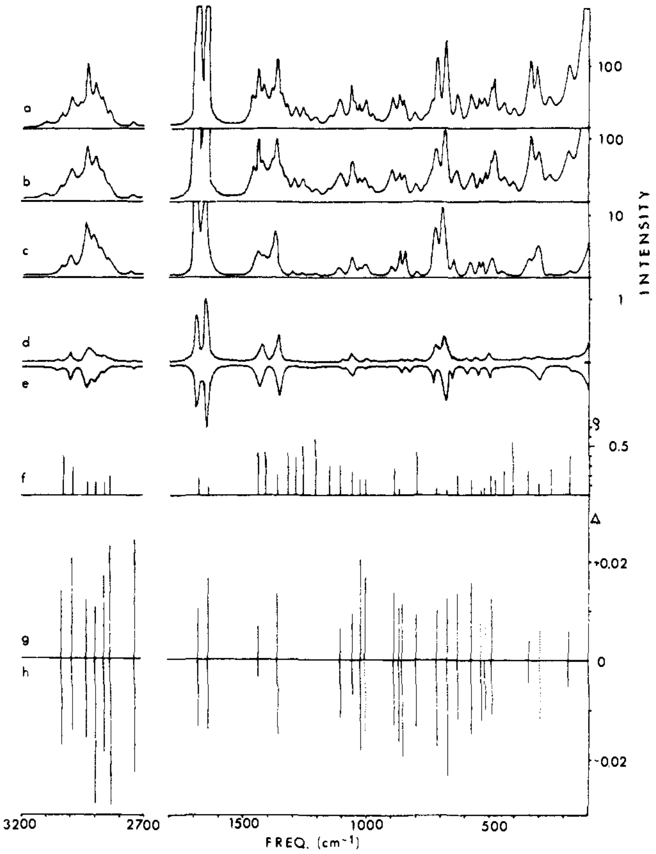

Figure 1. Raman and CDR spectra for (+)- and (−)-carvone: (a) ordinary Raman spectrum without polarizer, (b) dc component of the CDR spectrum, (c) second harmonic component of the CDR spectrum, (d) first harmonic component of the CDR spectrum of (+)-carvone ($[\alpha]^{25}\mathrm{D}$ + 59.8°), (e) first harmonic component of the CDR spectrum of (−)-carvone ($[\alpha]^{25}\mathrm{D}$ − 60.5°), (f) depolarization ratios of the ordinary Raman bands, (g) Δ values for (+)-carvone, (h) Δ values for (−)-carvone. Numbers on the intensity scale for a–e indicate relative intensities. Intensities were estimated from peak heights for f–h. Dotted lines indicate values which were partially obscured by noise.

Raman scattering in α-phenylethylamine; the effect had been predicted earlier by Barron and Buckingham[2] and by Barron.[3] We wish to report observation of the circular differential Raman (CDR) spectra of both enantiomers of carvone by excitation with a 632.8-nm He–Ne laser line producing *ca.* 70 mW at the sample. Our observations generally substantiate the report of Bosnich, *et al.*, but indicate that use of ordinary Raman intensities to normalize CDR intensities may result in misleading conclusions. In fact, observation of both the first and second harmonic components of the signal along with the dc component is required for proper normalization. Furthermore, we find that in the carvones, there is no distinctly apparent correlation between the polarization of an ordinary Raman mode and its normalized CDR intensity. In addition, preliminary data on α-phenylethylamine tend to substantiate our observations with the carvones.

The appropriate measure of intensity in CDR spectra[2] is

$$\Delta = (I_{\mathrm{R}} - I_{\mathrm{L}})/(I_{\mathrm{R}} + I_{\mathrm{L}}) \qquad (1)$$

where I_{R} and I_{L} are the intensities of scattered right-hand and left-hand circularly polarized light, respectively. When linearly polarized light is passed through an electrooptical modulator driven with λ/4 sinusoidal voltage, the emerging elliptically polarized light can be represented as a superposition of circularly and linearly polarized light with time varying intensities. The time variation of light intensity scattered from a sample can be represented by

$$\begin{aligned} I(\omega t) &= L\cos(\pi/2\sin\omega t) + \\ &\qquad I_{\mathrm{R}}[1 - \cos(\pi/2\sin\omega t)]\ (-\pi \le \omega t \le 0) \\ &= L\cos(\pi/2\sin\omega t) + \\ &\qquad I_{\mathrm{L}}[1 - \cos(\pi/2\sin\omega t)]\ (0 \le \omega t \le \pi) \qquad (2) \end{aligned}$$

where ω is the modulation frequency and L is the intensity of scattered linearly polarized light. Using the approximation[4]

$$\cos(\pi/2\sin\omega t) = \cos^2\omega t + A\sin^2 2\omega t \qquad (3)$$

followed by Fourier expansion of $I(\omega t)$ in the interval −π to π, it can be shown that

$$\Delta = 1.73V_{\omega}/(V_{\mathrm{DC}} - 1.35V_{2\omega}) \qquad (4)$$

where V_{DC} is the dc signal under modulation conditions while V_{ω} and $V_{2\omega}$ are the measured first and second harmonic signals as obtained by synchronous detection with a lock-in amplifier. Appropriate root mean square (rms) correction factors for the ac measurements are included in eq 4.[5]

The ordinary Raman and the various components of the CDR spectra are illustrated in Figure 1. Comparison of the bands at 330, 895, and 1430 cm^{-1} in Figure 1a–c indicates that the relative intensities of these bands are not the same in the three spectra. Thus, normalization of $I_{\mathrm{R}} - I_{\mathrm{L}}$ by use of the ordinary Raman spectrum rather than by eq 4 is likely to generate anomalous results.

Depolarization ratios (ρ) and Δ values for the vibrational modes of the carvones are given in Figure 1f–h. The differences in magnitudes of the Δ values for the two enantiomers are attributed to the low *S/N* when using relatively low power, red exciting light. I_{R} and I_{L} have also been measured directly, with less precision, using unmodulated circularly polarized light; except for differences in magnitude attributed to long term instrumental drift, the resulting Δ values are substantially the same as those obtained by ac measurement.

Several features of the carvone CDR spectra deserve comment. As observed by Bosnich, *et al.*,[1] the sign of Δ values for all modes of a given enantiomer is the same; but, this may be due to a fortuitous choice of sample rather than to some fundamental molecular property. For the carvones, large Δ values are not directly correlated with strongly polarized modes in the ordinary Raman spectrum. Whereas the strongly polarized modes at 518, 533, 681, and 2740 cm^{-1} exhibit medium to large Δ values, the

---

(2) L. D. Barron and A. D. Buckingham, *Mol. Phys.*, 20, 1111 (1971).

(3) L. D. Barron, *J. Chem. Soc. A*, 2899 (1971).

(4) A was fit so that the approximation is valid to within 99%.

(5) M. Moskovits, in a personal communication, has described his derivation of similar expressions for the Δ_x and Δ_z components of Δ by use of the complete scattering matrix. Our use of eq 4, however, is adequate to describe Δ as measured in the absence of an analyzer between the sample and monochromator. Low *S/N* precluded our measurement of the two components separately.

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.

Acknowledgments. We thank The University of Toledo and the Research Corporation for partial support of this work. We are grateful to Mr. D. Clay and to Mr. G. Buenning for aid in the design and construction of electronic and mechanical components and to Professor H. B. Thompson for valuable discussions.

(6) J. R. Durig and L. A. Carriera, *J. Chem. Phys.*, **56**, 4956 (1972).
(7) D. J. Caldwell and H. Eyring, "The Theory of Optical Activity," Wiley-Interscience, New York, N. Y., 1971, pp 194–204.

M. Diem, James L. Fry, D. F. Burow*
Department of Chemistry, The University of Toledo
Toledo, Ohio 43606

Received August 31, 1972

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.

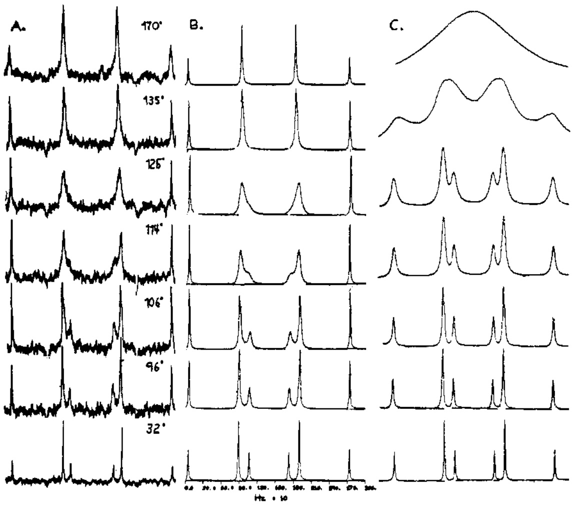

Figure 1. (A) Experimental ^{31}P nmr spectra of neat Ph_2PF_3 in Teflon cells, (B) calculated ^{31}P nmr spectra using matrix I, and (C) calculated ^{31}P nmr spectra using matrix II. The calculated τ values (sec) as a function of temperature are: 0.20, 32°; 0.015, 96°; 0.0075, 106°; 0.0030, 114°; 0.0018,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

---

(1) T. A. Furtsch, D. S. Dierdorf, and A. H. Cowley, *J. Amer. Chem. Soc.*, **92**, 5759 (1970).

(2) (a) R. Schmutzler in "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967; (b) G. M. Whitesides and L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5389 (1969); (c) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); (d) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

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

(4) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).

(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.