

Pseudo-rotation in $(\text{PCF}_3)_5$

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PSEUDO-ROTATION in five-membered-ring compounds has been discussed theoretically by several authors,¹⁻⁵ with particular attention to cyclopentane, but to our knowledge there have been no experimental studies of the kinetic parameters for such an intramolecular process. We offer n.m.r. evidence here for the existence of pseudo-rotation in the 5-membered phosphorous ring compound $(\text{PCF}_3)_5$ and give an experimental lower value for ΔG^\ddagger .

A mixture of $(\text{PCF}_3)_5$ and $(\text{PCF}_3)_4$ was prepared

by the method of Mahler and Burg.⁶ By ^{19}F n.m.r. integration our final sample was a solution of the pentamer (46 mole %) in the tetramer (54 mole %).

The temperature dependence of the 56.4 Mc./sec. (14 kgauss) ^{19}F spectrum of $(\text{PCF}_3)_5$ is shown in Figure 1. At 42° the pentamer yields two bands, of intensity ratio 2:3 within experimental error, exhibiting a complex structure which is presumably due to ^{31}P - ^{19}F coupling, but may reflect hindered rotation of the CF_3 groups about the P-C bonds. This structure blurs on heating to 147° and has

vanished at 165°. On further heating to 202° (the upper limit of our Varian A56/60 spectrometer), the two main bands broaden and start to merge, but are still below coalescence. The spectrum of the tetramer component remains sharp up to 202°. On cooling a solution of mixed pentamer and tetramer in CCl_3F to -60° (not shown), the pentamer spectrum sharpens somewhat in its detailed structure, but the major features remain unchanged. We could detect no significant temperature dependence of the ^{19}F chemical shifts.

The 40.5 Mc./sec. (25 kgauss) ^{31}P spectrum of mixed tetramer and pentamer at 33° is given in

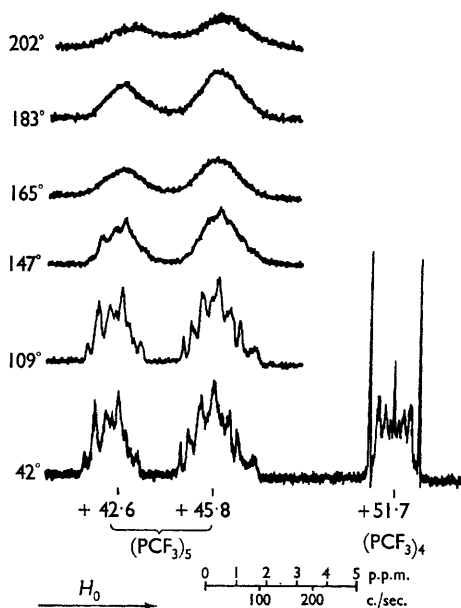


FIGURE 1. Temperature dependence of the 56.4 Mc./sec. ^{19}F spectrum of $(\text{PCF}_3)_5$ in solution with $(\text{PCF}_3)_4$. The figures below are the ^{19}F shifts, in p.p.m., from external CFCl_3 .

Figure 2. The spectrum is similar to the ^{19}F spectrum in that again the pentamer absorption is to the low field of the tetramer and again the pentamer signal is a 2:3 doublet. However, the ^{31}P chemical shifts are larger, and the pentamer doublet is inverted by comparison with the fluorine resonance. Some broadening of the ^{31}P pentamer signal at 200° was observed but the signal-to-noise ratio of the spectra at elevated temperatures is poor. Due to the larger ^{31}P shifts, we expect the spectrum here to be further from coalescence at 200° than the ^{19}F spectrum.

The crystal structure of $(\text{PCF}_3)_5$ at -100° has been studied by Spencer and Lipscomb⁷ and by

Donohue.⁸ The P_5 ring is found to be sterically distorted and nonplanar, with the CF_3 groups

^{31}P spectrum 40.5 Mc./sec.

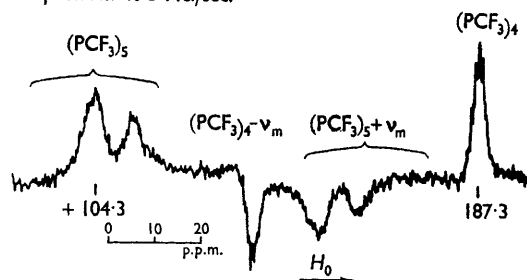


FIGURE 2. 40.5 Mc./sec. ^{31}P spectrum of a solution of $(\text{PCF}_3)_5$ in $(\text{PCF}_3)_4$ at 32° . The figures represent the ^{31}P shifts, in p.p.m., from external P_4O_6 ; μ_m is 1976 c./sec.

staggered as far as possible (see Figure 3). Assuming the structure in solution to be similar to that found in the solid, we suppose the unique CF_3 groups and the unique P atoms to be at ring positions 2 and 4 with low ring angles, or at positions 3 and 4 where adjacent substituents are on the same side of the ring.

We ascribe the motion which scrambles the CF_3 groups at high temperatures to pseudo-rotation, a cyclic interchange of the role of the P atoms, and hence of the CF_3 groups, around the ring through a torsional vibration. This results in an apparent rotation of the ring-puckering. However, at least four other mechanisms should be considered, (i) intermolecular CF_3 exchange, (ii) ring opening, (iii) hindered rotation of the CF_3 groups, and (iv) inversion at a single P atom.

The fact that the exchanging fluorine doublet of the pentamer is below coalescence at 200° leads to a lower limit of ΔG^\ddagger for the exchange process of

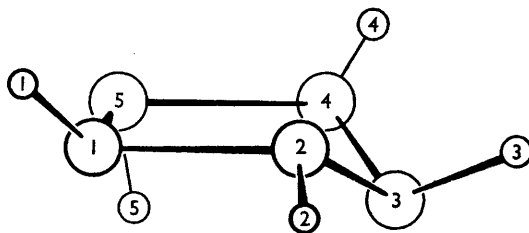


FIGURE 3. The structure of $(\text{PCF}_3)_5$ in the solid, after Spencer and Lipscomb (reference 7); F atoms are not shown.

about 22.5 kcal., and to an estimated value of 23.5 kcal. It is desirable to follow the exchange

through coalescence by achieving a higher temperature, or by working at a lower H_0 field, Heteronuclear decoupling of the ^{31}P nuclei from the ^{19}F nuclei is necessary to obtain values for ΔH^\ddagger and ΔS^\ddagger , and to elucidate the details of the complex spectra. Such studies will be reported elsewhere.

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¹ J. Waser and V. Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 2014.

² J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483.

³ K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 1959, **81**, 2313.

⁴ R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

⁵ J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537; 1963, **86**, 4059.

⁶ W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.

⁷ C. J. Spencer and W. N. Lipscomb, *Acta Cryst.*, 1961, **14**, 250; 1962, **15**, 509.

⁸ J. Donohue, *Acta Cryst.*, 1962, **15**, 708.