Rearrangements in Fluxional Trifluorophosphoranes: ^{1}H Nuclear Magnetic Resonance Study

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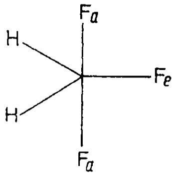
Summary Dynamical ^{1}H n.m.r. studies of the fluxional trifluorophosphoranes, H_2PF_3 (**1**) and $CF_3(H)PF_3$ (**2**) are reported and the observations are discussed in terms of rearrangement modes.

Many fluxional five-co-ordinate phosphorus compounds have been investigated by n.m.r. spectroscopy.[1] However, only for Me_2NPF_4 has detailed information been secured for the ligand permutational process(es) in an acyclic species.[2] Since no such information is available for systems of the type X_2PF_3 or $XYPF_3$ we have undertaken dynamical n.m.r. (d.n.m.r.) studies of the fluxional trifluorophosphoranes H_2PF_3 (**1**)[3] and $CF_3(H)PF_3$ (**2**).[4]



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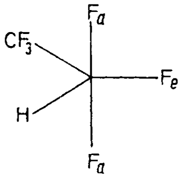

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† On sabbatical leave from the Chemistry Department, University of Hawaii, Honolulu, Hawaii, during the 1972—1973 academic year.

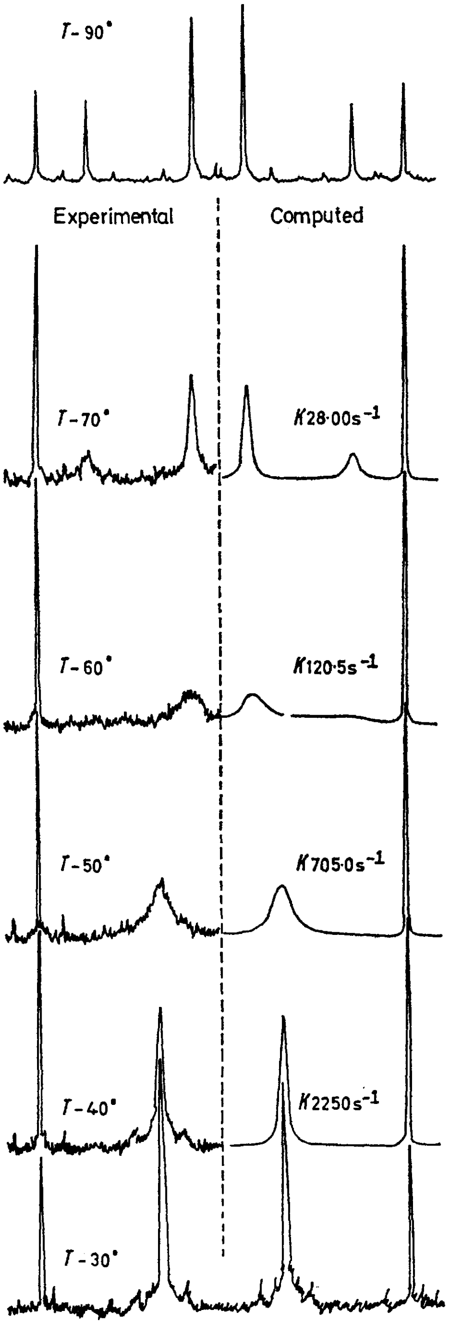
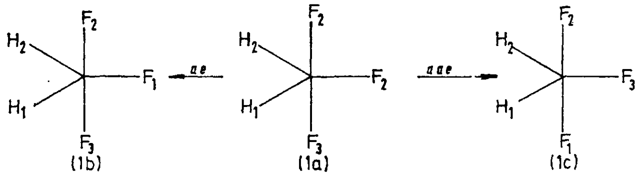


FIGURE Experimental and computed ^{1}H n.m.r. spectra of H_2PF_3 (**1**). Only the pertinent portions of the low field P–H multiplet are reproduced. The spectra of $CF_3(H)PF_3$ (**2**) were very similar to those of (**1**) since F–C–P–H coupling in (**2**) is unresolved.

In the region of slow exchange the ^{1}H spectra of (**1**) and (**2**) consist of a doublet of triplets of doublets centred at τ 2·9 and 2·7, respectively, with J(PH) 865, J(HPF$_a$) 105, J(HPF$_e$) 34 Hz for (**1**) (−90°); and J(PH) 955, J(HPF$_a$) 117, and J(HPF$_e$) 35 Hz for (**2**) (−150°). Assuming trigonal bipyramidal stereochemistry these data establish the ground state geometries.‡

As the temperature increases the twelve-line spectra of (**1**) and (**2**) collapse and are replaced by eight-line spectra (doublet of quartets) when exchange becomes rapid on the n.m.r. time scale (Figure). The preservation of an appropriately weighed H–P–F coupling [80 Hz for (**1**), 88 Hz for (**2**)] indicates that the exchange process is intramolecular, a view which is substantiated by the insensitivity of the spectra to changes in solute concentration.

The spectra in the intermediate exchange region were simulated[6] (Figure) by assembling a probability matrix such that the equatorial fluorine ligand of (**1**) or (**2**) had an equal probability of exchanging with either of the axial fluorine ligands. Satisfactory agreement between the computed and experimental spectra was not attainable with any other probability matrix. The following activation parameters were calculated in the usual manner assuming a transmission coefficient of unity; (**1**) $\Delta H^{\ddagger}$ 14·2 kcal mol^{-1}; $\Delta G^{\ddagger}_{218}$ 10·2 kcal mol^{-1}; (**2**), $\Delta H^{\ddagger}$ 8·8 kcal mol^{-1}; $\Delta G^{\ddagger}_{133}$, 6·3 kcal mol^{-1}.



Several authors[7] have discussed the important differentiation between modes and mechanisms of rearrangement. The rearrangement modes are merely permutational in character and do not contain any information regarding the pathway (mechanism) *via* which a species proceeds from the initial to the final state. In the case of trigonal bipyramidal systems the complete set of rearrangements has been described in terms of six such modes, M_i.[7b] Thus d.n.m.r. data, which are interpreted within the framework of the 'jump model,' are best discussed with reference to the pertinent rearrangement modes. In contrast to Me_2NPF_4 [which rearrranges *via* (M_1, M_5)§] (**1**) and (**2**) rearrange by the previously unreported modes (M_2, M_4) with the built-in ambiguity of corresponding to either the *ae* or *aae* one-step processes (or a mixture of these) due to the spectroscopic indistinguishability of (**1b**) and (**1c**).

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‡ These structures are easily assignable because previous work[5] has established that J(HPF$_a$) lies in the range 100—140 Hz whilst J(HPF$_e$) falls between 20 and 40 Hz. Earlier ^{19}F data[3a] had been used to deduce the ground state geometry of (**1**). However, the spectral resolution was such that no H–P–F coupling was observed.

§ The symbol (M_i, M_j) is taken to mean that no differentiation between modes M_i and M_j (or combinations thereof) is possible with the available data.

We have indicated how the rearrangements might take place, but a sequence of multi-step processes involving higher energy species with an axial hydride ligand could also be accommodated by modes (M_2, M_4).

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[6] The spectra were calculated using the many-site program, NMRLS which is based on the equations of Anderson and Kubo (P. W. Anderson, *J. Phys. Soc. Japan*, 1954, **9**, 316; R. Kubo, *ibid.*, p. 935; R. Kubo, *Nuovo Cim., Suppl.*, 1957, **6**, 1063). The program was devised by M. Saunders, *Tetrahedron Letters*, 1963, 1699; M. Saunders in 'Magnetic Resonance in Biological Systems', eds. A. Ehrenberg, A. G. Mahlstrom, and T. Vanngard, Pergamon Press, Oxford, 1967, p. 85.

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