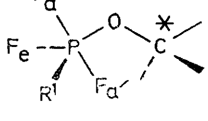
Non-equivalence of the Apical Fluorine Atoms on Pentaco-ordinate Phosphorus Studied by ^{19}F Nuclear Magnetic Resonance Spectroscopy

By Dominique U. Robert, D. Jean Costa, and Jean G. Riess*

(*Laboratoire de Chimie Minérale, Institut de Mathématiques et Sciences Physiques, Parc Valrose,* 06034 *Nice Cedex, France*)

Summary The non-equivalence of the apical fluorine atoms was observed in the low temperature ^{19}F n.m.r. spectra of the alkoxyfluorophosphoranes (I) and (II), and is attributed to the adjacent asymmetric carbon atom and not to a hindered rotation of the alkoxy-group.

Several cases of non-equivalence of the apical fluorine atoms have been reported for thioalkyl[1] or aminoalkyl[2] substituted trigonal bipyramidal fluorophosphoranes and were attributed to hindered rotation of the substituents about the P–S or P–N bonds. We now report the first examples of non-equivalence of the apical fluorine atoms due to the presence of an adjacent fast-rotating asymmetric alkoxy-group.



(I) R^1 = Me or Ph

At low temperature the ^{19}F n.m.r. spectra of the alkoxyfluorophosphoranes of general formula $R^1PF_3OR^2$ (I) were in all the cases examined consistent with trigonal bipyramidal geometry in which the alkoxy-group occupies one of the equatorial positions.[3] In these compounds the apical fluorine atoms are diastereotopic when R^2 is an asymmetric group. This is now confirmed by the observation of two distinct signals of equal intensity for the apical fluorine atoms in the low temperature ^{19}F n.m.r. for (I) when R^2 = MeCHEt, MeCHPr, $MeCHCH_2Cl$, $MeCHCH_2OMe$, MeCHCN, 2-chlorocyclohexyl, bornyl, and menthyl. Typical n.m.r. data, for R^2 = MeCHEt, at −60°, are: $\delta\,(F_a)$ 41·50, $\delta\,(F_a)$ 42·30, $\delta(F_e)$ 65·47 ($CFCl_3$ standard); $J(P–F_a)$ 830, $J(P–F_{a'})$ 834, $J(P–F_e)$ 960, $J(F_a–F_e) = J(F_{a'}–F_e)$ 64, $J(F_a–F_{a'})$ 10·5 Hz.

The spectra were not significantly influenced by temperature between −100 and −30°. At higher temperatures the three fluorine atoms become magnetically equivalent due to a pseudorotation process which, in the alkoxy-derivatives studied, is considerably faster than in the corresponding sulphur[1] or nitrogen[4] analogues.

That the observed effect is due to the asymmetry of the substituent and not to its hindered rotation about the P–O is supported by the following observations: (i) the magnetic non-equivalence disappears when the asymmetric substituent is replaced by a non-asymmetric but otherwise comparable group, for example MeCHEt by MeCHMe or by EtCHEt; (ii) it also disappears when the diastereotopic character of the fluorine atoms is removed by substitution of the equatorial fluorine in (I) by a second identical R^1 group [compound $R^1{}_2PF_2(OR^2)$ with R^1 = Ph, R^2 = MeCHEt]; (iii) the non-equivalence is again observed in the phenylethyldifluoroalkoxyphosphoranes $PhEtPF_2(OR^2)$ (II) when the alkoxy-group is asymmetric as for example with R^2 = CNCHMe.

No evidence for the freezing of the rotation around the P–O bond was ever observed even with bulky groups, such as menthyl (to $-110°$).

*The alkoxy*fluorophosphoranes were prepared in methylene chloride solutions by cleavage of the Si–O bonds in trimethylsilyl ethers by phenyl- or methyl-tetrafluorophosphoranes, or by diphenyl-, dimethyl-, or phenylethylfluorophosphoranes.[3,5]

(*Received*, 16*th July* 1973; *Com.* 1004.)

[1] S. C. Peake and R. Schmutzler, *Chem. Comm.*, 1968, 1662; S. C. Peake and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 1049.

[2] V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *Zhur. strukt. Khim.*, 1969, **10**, 142; J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, 1971, **10**, 1538; M. J. C. Hewson and R. Schmutzler, *Z. Naturforsch.*, 1972, **27b**, 879.

[3] D. U. Robert, G. N. Flatau, C. Demay, and J. G. Riess, *J.C.S. Chem. Comm.*, 1972, 1127.

[4] R. Schmutzler, *J. Chem. Soc.*, 1965, 5630; M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zhur. strukt. Khim.*, 1967, **8**, 1097.

[5] R. Schmutzler, in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, London and New York, 1967, vol. 2.