125. Fluorine Nuclear Magnetic Resonance Spectra of Some Perfluoroalkylhalogenophosphines.

By John F. Nixon.

Fluorine chemical shifts and phosphorus–fluorine spin–spin coupling constants are reported for trifluoromethyldihalogenophosphines $CF_3{\cdot}PX_2$ (where X is F, Cl, Br, and I), heptafluoropropyldihalogenophosphines $C_3F_7{\cdot}PY_2$ and bisheptafluoropropylhalogenophosphines $(C_3F_7)_2PY$ (Y is F, Cl, and I). The chemical shift of the fluorines on the carbon atom α to phosphorus varies with the halogen attached to phosphorus, and increases to higher field in the order I < Br < Cl < F. The two fluorine atoms of the α-C atom in $(C_3F_7)_2PI$ are magnetically non-equivalent and give rise to the typical *AB* spectrum, whereas the corresponding chloro- and fluoro-derivatives exhibit equivalence at room temperature as a result of fast positional exchange of the halogen atom between the two lone-pair positions of the phosphorus atom.

During study [1-5] of phosphorus–fluorine compounds, the fluorine-19 nuclear magnetic resonance spectra of some fluorophosphines and related compounds were recorded. These exhibit interesting chemical shift and spin-coupling correlations, and give evidence about the positional exchange of the halogen atom in the bisheptafluoropropylhalogenophosphines.

Experimental

Trifluoromethyldihalogenophosphines were made by known methods [6,7] and carefully purified by fractional condensation in the vacuum line. Their purity was confirmed by infrared spectroscopy and molecular weight determinations. Bisheptafluoropropyliodophosphine, bisheptafluoropropylchlorophosphine, heptafluoropropyldi-iodophosphine and heptafluoropropyldichlorophosphine were synthesised by the method of Emeleus and Smith,[8] and used to make the corresponding new fluorophosphines as follows.

Heptafluoropropyldifluorophosphine. The phosphine was prepared by heating heptafluoropropyldi-iodophosphine (4·8 g.) with antimony trifluoride in a sealed glass tube (*ca.* 50 ml. volume) at 80° for 7 hr. Vacuum fractionation of the volatile material yielded *heptafluoropropyldifluorophosphine*, 1·9 g. (75 % yield) which was collected at $-116°$ (Found C_3F_7 (attached to

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[1] Nixon, *Chem. and Ind.*, 1963, 1555.
[2] Nixon, *J.*, 1964, 2469.
[3] Nixon and Cavell, *J.*, in the press.
[4] Cavell and Nixon, *Proc. Chem. Soc.*, 1964, 229.
[5] Nixon and Schmutzler, *Spectrochim. Acta*, 1964, **20**, 1835.
[6] Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.
[7] Kulakova, Zinovev, and Soborovskii, *Zhur. obshchei. Khim.*, 1959, **29**, 3957.
[8] Emeléus and Smith, *J.*, 1959, 375.

phosphorus, measured at C_3F_7H), 70·1; P, 13·2%; *M*, 238. C_3F_9P requires C_3F_7, 71·0; P, 13·0%; *M*, 238). Further confirmation of the structure resulted from the ^{31}P n.m.r. spectrum which showed the expected 1–2–1 triplet due to spin–coupling with the two fluorine atoms directly attached to phosphorus, each resonance being further split into a triplet by the fluorines of the α-CF_2 group. The details of this spectrum are published elsewhere.[5] The difluorophosphine is a colourless, mobile liquid whose vapour pressure in the range -45 to 0° is given by the equation $\log_{10} p$ (mm.) $= 7{\cdot}873 - 1443/T$ leading to an extrapolated b. p. of 15·8° and Trouton constant 22·8 cal./deg. mole. The infrared spectrum, recorded on a Perkin-Elmer Infracord spectrophotometer, showed bands at 1350s, 1280sh, 1240vs, 1225vs, 1190sh, 1160ms, 1125s, 1065ms, 1030ms, 935ms, 870vs (P–F), 746s, 671ms cm.$^{-1}$.

Bisheptafluoropropylfluorophosphine. This compound was prepared in a similar way from bisheptafluoropropyliodophosphine (1·7 g.) and collected at -78° (Found: C_3F_7 (attached to phosphorus, measured as C_3F_7H), 84·0; P, 7·87%; *M*, 388. $C_6F_{15}P$ requires C_3F_7, 87·1; P, 7·99%; *M*, 388). The *bisheptafluoropropylfluorophosphine* (1 g.; 75% yield) is a colourless mobile liquid, m. p. $-48{\cdot}8$ to $-49{\cdot}2$°, whose vapour pressure in the range 0—65° is given by $\log_{10} p$ (mm.) $= 8{\cdot}228 - 1954/T$, giving an extrapolated b. p. of 92·2° and a Trouton constant of 24·4 cal./deg. mole. The identity was confirmed by ^{31}P n.m.r. which showed the expected broad doublet.[5] The infrared spectrum recorded as above showed bands at 1340s, 1280sh, 1240vs, 1222vs, 1190s, 1155s, 1133s, 1115s, 1060ms, 917ms, 844s (P–F), 744s, 666ms cm.$^{-1}$.

Nuclear Magnetic Resonance Spectra.—The ^{19}F nuclear magnetic resonance spectra were obtained at 40 Mc./sec. on a Varian Associates V.4300 B n.m.r. spectrometer and 12-inch electromagnet with flux stabilisation and a Varian V.4356 field homogeneity control unit. The samples were sealed in Pyrex tubes of 5 mm. outside diameter with CCl_3F as solvent and standard. The concentrations were usually 30—50% v/v; however in order to get good resolution of the α-CF_2 group in $(C_3F_7)_2PI$ the pure liquid was employed. The samples were spun in the magnetic field at room temperature and the spectra calibrated by means of sidebands of the resonance of the compound or the standard. Values quoted are in general the average of at least five determinations. No correction was made for solute–solvent interaction. Chemical shifts are considered accurate to ±0·4 p.p.m., and spin-coupling constants to ±0·5 c.p.s. except where indicated.

RESULTS

The fluorine-19 n.m.r. spectra of the compounds listed in the Table appear as multiplets arising from spin–spin coupling between the various nuclei. The trifluoromethyl-di-iodo-, -dichloro-, and -dibromo-phosphines all give rise to simple doublets as expected because of

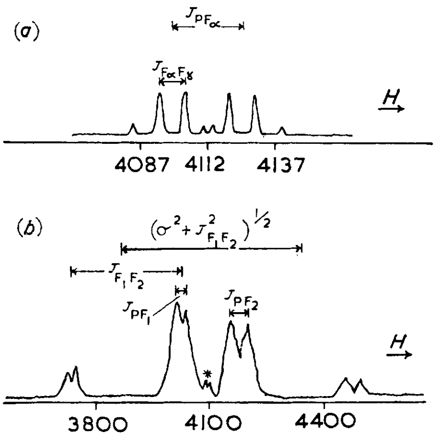
^{19}F Chemical shifts ϕ and phosphorus–fluorine spin–spin constants J(P–CF) for perfluoroalkylhalogenophosphines.

Compound	$\phi(CF_3)$[a]	$\phi(\beta\text{-}CF_2)$	$\phi(\alpha\text{-}CF_2)$	$J(PF_\alpha)$ (c./sec.)	$J(PF_\beta)$ (c./sec.)	$J(PF_\gamma)$ (c./sec.)
$CF_3{\cdot}PI_2$	61·0	—	—	52·1	—	—
$CF_3{\cdot}PBr_2$	67·8	—	—	69·6	—	—
$CF_3{\cdot}PCl_2$	72·1	—	—	79·9	—	—
$CF_3{\cdot}PF_2$ *	80·7	—	—	87·2	—	—
$(CF_3)_2PI$[b]	55·4	—	—	73·2	—	—
$(CF_3)_2PBr$[b]	59·5	—	—	80·6	—	—
$(CF_3)_2PCl$[b]	61·4	—	—	85·1	—	—
$(CF_3)_2PF$[b]†	66·5	—	—	89·6	—	—
$C_3F_7{\cdot}PI_2$[c]	81·1	119·7	102·8	25·3	37·2	9·7
$C_3F_7{\cdot}PCl_2$[d]	81·1	122·6	120·0	58·2	36·2	9·6
$C_3F_7{\cdot}PF_2$ ‡	81·3	125·9	131·9	90·5	19·3	9·3
$(C_3F_7)_2PI$[e]	80·4	120·5	98·3 106·9	20 47	37·4	7·8
$(C_3F_7)_2PCl$[f]	80·8	122·4	113·3	54·8	36·0	8·2
$(C_3F_7)_2PF$ §	80·5	124·2	121·3	62·1	33·5	8·3

[a] In p.p.m. to high field of CCl_3F. [b] Data from Ref. 11. [c] $J(F_\alpha F_\gamma) = 9{\cdot}7$ c./sec. [d] $J(F_\alpha F_\gamma) = 9{\cdot}6$ c./sec. [e] $J(F_\alpha F_\gamma) = 9{\cdot}7$ c./sec. Chemical shift values for two non-equivalent fluorine atoms on α-C atom (see text). [f] $J(F_\alpha F_\gamma) = 9{\cdot}9$ c./sec. * ϕ(F) for fluorine directly bound to P = 104·1 p.p.m.; J(PF) = 1245 c./sec.; J(FF) = 5·8 c./sec. † ϕ(F) for fluorine directly bound to P = 219·0 p.p.m.; J(PF) = 1013 c./sec.; J(FF) = 3·5 c./sec. ‡ ϕ(F) for fluorine directly bound to P = 102·5 p.p.m.; J(PF) = 1257 ± 3 c./sec.; $J(F,F_\beta) = 7{\cdot}9$ c./sec.; $J(F_\alpha F_\gamma) = 9{\cdot}3$ c./sec.; $J(FF_\gamma) = 1{\cdot}5$ c./sec. § ϕ(F) for fluorine directly bound to P = 215·5 p.p.m.; J(PF) = 1025 c./sec.

coupling between the fluorine and ^{31}P nuclei ($I = \frac{1}{2}$). In trifluoromethyldifluorophosphine, each line of the doublet resonance of the CF_3 group is split into a triplet by the two fluorine atoms directly bound to phosphorus. The resonance of the latter appears to higher field as a widely spaced doublet of quartets, from spin coupling with both the phosphorus and the three fluorine atoms of the CF_3 group.

The spectra of heptafluoropropyldichloro- and heptafluoropropyldi-iodo-phosphines, $C_3F_7PCl_2$ and $C_3F_7PI_2$, consist of three well resolved groups of bands, whose relative peak intensities were useful in assigning each absorption to a particular group. In the di-iodo compound the quartet at lowest field is due to the CF_3 group and arises from the perfect overlap of two triplets formed by spin-coupling with both the phosphorus nucleus and the fluorine atoms of the α-CF_2 group. The α-CF_2 resonance shown in the Figure (*a*) appears at higher field as two partly overlapping quartets arising from coupling with the phosphorus nucleus and with the CF_3 group, while the β-CF_2 absorption occurs at highest field as a doublet containing some unresolved fine structure presumably arising from coupling with the α-CF_2 group. The spectrum of heptafluoropropyldichlorophosphine was very similar in appearance to that of the iodo-compound, except that the α-CF_2 group absorption consisted of two separate quartets.



α-CF_2 resonances of (*a*) $C_3F_7PI_2$ and (*b*) $(C_3F_7)_2PI$.

Scale is in c.p.s. to high field of CCl_3F.
* Trace of $C_3F_7PI_2$ impurity.

These spectra are identical with those previously reported by Pitcher, Buckingham, and Stone for bisheptafluoropropyliodophosphine $(C_3F_7)_2PI$ and bisheptafluoropropylchlorophosphine $(C_3F_7)_2PCl$ [9] where it appears that the compounds were incorrectly identified,[10] but in no way affects their conclusions concerning the comparison of fluorine chemical shifts of perfluoroalkyl derivatives of transition metals and main-group elements.

The spectrum of heptafluoropropyldifluorophosphine showed a low field quartet for the CF_3 group with further small triplet splitting evident (~1·5 c.p.s.). The α-CF_2 resonance this time occurs at highest field as a doublet of quartets, while the β-CF_2 resonance lay between those of the CF_3 and the α-CF_2 groups as a doublet of overlapping triplets formed by spin coupling with phosphorus and the two fluorines directly bound to it. The absorption due to these fluorine atoms attached to phosphorus occurs between the resonances of the CF_3 and the β-CF_2 groups as a widely spaced doublet each line of which shows triplet structure from coupling with the β-CF_2 group. The phosphorus–fluorine spin–spin coupling constants were in excellent agreement with the values obtained from the ^{31}P n.m.r. spectra.[5]

A characteristic feature of the spectra of all the bisheptafluoropropylhalogenophosphines $(C_3F_7)_2PX$ was the presence of much more detailed fine structure which led to broadening of the absorption bands. The CF_3 resonance of all three compounds studied appeared at lowest field as a slightly distorted quartet arising from imperfect overlap of two triplets, with considerable extra fine structure apparent. The β-CF_2 resonance occurred at highest field as an unsymmetrical broad doublet again exhibiting much extra structure.

The α-CF_2 resonance of bisheptafluoropropyliodophosphine $(C_3F_7)_2PI$ is shown in the Fig.

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[9] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.
[10] Stone, personal communication.

(*b*); it shows the typical basic four-line *AB* spectrum expected for two non-magnetically equivalent fluorine atoms attached to the same carbon atom. Each line is split further by spin coupling with the phosphorus nucleus into a doublet, but it is clear that the two J(P–F) coupling constants are unequal. Further fine structure arises from spin coupling with the other fluorine nuclei in the molecule.

A simplified assignment of the bands was made by direct inspection of the spectrum shown in the Fig. (*b*), (cf. Drysdale and Phillips [11]). The separation between the doublet centres of the two *gem.*-fluorine atoms is $(\delta^2 + J(FF))^{\frac{1}{2}}$, where δ is the chemical shift between the two *gem.*-fluorine atoms and J(FF) is the spin coupling constant between them. Analysis of the spectrum yields the values $\delta = 344$ c./sec., $J(FF) = 296$ c./sec., $J(PF_1) = 23$ c./sec., and $J(PF_2) = 43$ c./sec. A rigorous analysis of the spectrum using accurate expressions for the transition energies for the *ABX* system calculated by Bernstein, Pople, and Schneider [12] leads to the values $\delta = 348$ c./sec., $J(FF) = 296$ c./sec., $J(PF_1) = 20$ c./sec., and $J(PF_2) = 47$ c./sec. The accuracy of these measurements was limited because of some broadening of the bands due to spin–spin coupling with other fluorine nuclei, and the values quoted are accurate only to ±2 or 3 c./sec.

In contrast to the iodo-compound, the corresponding bisheptafluoropropylchlorophosphine and bisheptafluoropropylfluorophosphine both showed only a simple broad doublet band for the α-CF_2 resonance, thus indicating apparent equivalence of fluorine atoms. A widely spaced doublet at very high field in the spectrum of bisheptafluoropropylfluorophosphine, arises from the fluorine atom directly attached to phosphorus, and showed further unresolved fine-structure.

Discussion

The data summarised in the Table include values previously reported for bistrifluoromethylhalogenophosphines for completeness,[13] and indicate the following trends: (i) The chemical shift of the fluorine atoms on the α-C atom in all the perfluoroalkylhalogenophosphines is influenced by the nature of the halogen, and moves progressively to lower field in the series $F < Cl < Br < I$. (ii) In the heptafluoropropylhalogenophosphines, the chemical shift of the CF_3-group is constant, while the β-CF_2 group shows a much smaller but similar trend to the α-CF_2 group. (iii) The fluorines on the α-C atom in the R_FPX_2 systems are more highly shielded than those of the corresponding $(R_F)_2PX$ compounds. (iv) The ^{31}P–^{19}F coupling constants for the fluorines on the α-C atom increase in magnitude as their chemical shift increases to higher field. (v) The fluorine atoms attached directly to phosphorus are more highly shielded in the $(R_F)_2PF$ systems than in the R_FPF_2 series.

The theory first outlined by Saika and Slichter [14] showed that ^{19}F chemical shifts are largely determined by the paramagnetic contribution to the local nuclear screening constant. This paramagnetic contribution which represents a shift to low field (decreased screening) arises from the mixing of ground and excited states by the magnetic field, and is zero for the spherically symmetrical fluoride ion, but increases as the ionic character of the bond to fluorine decreases.

A correlation of ^{19}F chemical shifts with the electronegativity of the atom attached to fluorine has been obtained for binary fluorides.[15] Additional factors which have been forwarded to explain ^{19}F chemical shifts include π-bonding [16-18] and " repulsive unshielding of large neighbouring groups." [19] The latter explanation was suggested to account for the observed order of unshielding of ^{19}F resonances in –CF_2–X compounds, $I > Br > Cl > F$, which is *opposite* to that expected from the simple electronegativity approach.

[11] Drysdale and Phillips, *J. Amer. Chem. Soc.*, 1957, **79**, 319.
[12] Bernstein, Pople, and Schneider, *Canad. J. Chem.*, 1957, **35**, 65.
[13] Packer, *J.*, 1963, 960.
[14] Saika and Slichter, *J. Chem. Phys.*, 1954, **22**, 26.
[15] Gutowsky and Hoffmann, *J. Chem. Phys.*, 1951, **19**, 1259.
[16] Meyer and Gutowsky, *J. Phys. Chem.*, 1953, **57**, 481.
[17] T. S. Smith and E. A. Smith, *J. Phys. Chem.*, 1959, **63**, 1701.
[18] Coyle and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6223.
[19] Tiers, *J. Amer. Chem. Soc.*, 1956, **78**, 2914.

However a more satisfactory explanation for this behaviour has been proposed by Pitcher, Buckingham, and Stone,[9] who attributed the very low field shifts of the α-CF_2 resonances in perfluoroalkyl–transition metal compounds to a large paramagnetic contribution arising from the presence of low lying excited states in the bonds between the transition-metals and the carbon atoms of the α-CF_2 groups. They suggested that in the RCF_2–X systems, the paramagnetic contribution would be expected to decrease in the order $I > Br > Cl > F$, because of the presence of higher principal quantum numbers, which increase the availability of low-lying excited states.

This same effect, though less pronounced, would account for the observed order of unshielding of the α-CF_2 group in the perfluoroalkyl halogenophosphines reported in this work, though the halogen atom is now one further bond removed from the CF_2 group than in the RCF_2X system. It is noteworthy that a similar but smaller trend has been reported for the shielding of the α-CF_2 group in $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CH_2X$ compounds.[19]

The spectra of the $(C_3F_7)_2PX$ compounds show interesting differences. In these compounds, the three groups and the lone pair attached to phosphorus will be nearly tetrahedral in disposition, so that the two fluorine atoms on the α-C atom will not be magnetically equivalent even if fast rotation about the C–P bond takes place. These *gem.*-fluorines would therefore be expected to form the *AB* part of an *ABX* spectrum for the $-CF_2-P<$ group. This *gem.*-inequivalence however does not extend to the β-CF_2 group. Non-equivalence of the methylene protons in diethyl sulphide–borane adduct,[20] diethyl sulphoxide,[20] and diethyl sulphite [21] has been reported in the literature.

The ^{19}F spectrum of the α-CF_2 group of $(C_3F_7)_2PI$ shown in the Fig. (*b*) shows clearly the typical *AB* spectrum expected. Secondary splitting of each line into a doublet arises from coupling with the phosphorus atom, and the two distinctly different coupling constants may reflect differences in the two F–C–P bond angles. The spectrum is similar to that reported recently for octafluoro-1,4-di-iodo-1,4-diphosphane,[22] where the two fluorines on the carbon atom are non-equivalent as a result of the lack of a plane of symmetry through the ring.

The spectra at room temperature of $(C_3F_7)_2PCl$ and $(C_3F_7)_2PF$ however show only a broad doublet for the α-CF_2 resonance, indicating apparent equivalence of the two fluorine atoms. This could arise by a rapid exchange process in which the halogen atom occupies the two lone pair positions of the phosphorus atom. Since the geminal inequivalence is produced by inequivalence of rotamer residence times and environmental variations in the rotamers, changes in X will result in different inversion rates for effective averaging.* A variable-temperature study of these systems would therefore be of particular interest.

The observation of ^{31}P–^{19}F spin-coupling between the phosphorus and the fluorine attached to it in $(C_3F_7)_2PF$ would suggest that such an exchange process is intramolecular. This type of exchange has previously been reported for the boron trifluoride adducts of ethers and sulphides.[20,23]

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* The author is indebted to the Referee for pointing this out.

[20] Coyle and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 4138.
[21] Finegold, *Proc. Chem. Soc.*, 1960, 283.
[22] Krespan, *J. Org. Chem.*, 1962, 3586.
[23] Craig and Richards, *Trans. Faraday Soc.*, 1963, **59**, 1962.