177. *The Nuclear Magnetic Resonance Spectra of Some Perfluoroalkyl Phosphorus Derivatives.*

By K. J. Packer.

The phosphorus and fluorine chemical shifts and the phosphorus–fluorine spin–spin coupling constants of a series of perfluoroalkylphosphorus derivatives have been measured and related to the nature of substituents. The results for the phosphorus chemical shifts are consistent with the dominance of a paramagnetic contribution to chemical shifts of nuclei having *p*- and/or *d*-electrons associated with them.

Because of the failure of Ramsey's theoretical equation [1] for any but the simplest molecules, the magnetic shielding of nuclei in molecules has been considered as consisting of four "atomic" contributions: [2] (i) the diamagnetic term for the atom containing the nucleus in question; (ii) the corresponding paramagnetic term, which may be regarded as a magnetic field-induced mixing of ground and excited electronic states; (iii) the contributions from other atoms in the molecule; and (iv) interatomic currents. The last effect is only of significance in aromatic systems. The coupling of nuclear spins has been discussed theoretically [3] but, except for proton–proton couplings, little progress has been made in interpretation of observed values.

[1] Ramsey, *Phys. Rev.*, 1950, **78**, 699.

[2] (*a*) Saika and Slichter, *J. Chem. Phys.*, 1954, **22**, 26; (*b*) McConnell, *ibid.*, 1957, **27**, 226; (*c*) Pople, *Proc. Roy. Soc.*, 1957, *A*, **239**, 541.

[3] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, Chapter 8.

The nuclear magnetic resonance spectra reported here were studied to see if a correlation existed between some property of the substituent X in $(CF_3)_2PX$, and the two chemical shifts and the phosphorus-fluorine spin-spin coupling constant. The results are summarised in Table 1, together with some other measurements on related compounds.

TABLE 1.

The ^{19}F and ^{31}P chemical shifts (ϕ_F and δ_P) and the phosphorus–fluorine spin–spin constants [$J(P–CF_3)$] for compounds containing trifluoromethyl phosphorus groups.

Compound	δ_P *†	ϕ_F †‡	$J(P–CF_3)$ §
$(CF_3)_2PF$	$-123·9 \pm 0·6$	$66·5 \pm 0·05$	$89·6 \pm 0·20$
$(CF_3)_2PCl$	$-50·0 \pm 0·4$	$61·4 \pm 0·10$	$85·1 \pm 0·10$
$(CF_3)_2PBr$	$-33·7 \pm 0·1$	$59·5 \pm 0·02$	$80·6 \pm 0·05$
$(CF_3)_2PI$	$-0·8 \pm 0·04$	$55·4 \pm 0·05$	$73·2 \pm 0·03$
$(CF_3)_2P·CN$	$40·7 \pm 0·2$	$51·3 \pm 0·20$	$85·6 \pm 0·10$
$(CF_3)_2P·NCO$	$-34·5 \pm 0·2$	$63·2 \pm 0·20$	$88·0 \pm 0·10$
$(CF_3)_2P·NCS$ ¶	—	$61·9 \pm 0·05$	$87·3 \pm 0·10$
$(CF_3)_2P·OEt$	$-92·3 \pm 0·3$	$65·3 \pm 0·20$	$86·6 \pm 0·04$
$(CF_3)_2P·NMe_2$	$-46·3 \pm 0·2$	$60·0 \pm 0·10$	$85·6 \pm 0·10$
$(CF_3)_2P·S·CF_3$	$-12·8 \pm 0·1$	$55·6 \pm 0·20$	$83·8 \pm 0·40$
$(CF_3)_2P·Se·CF_3$	$-14·1 \pm 0·1$	$53·7 \pm 0·10$	$77·2 \pm 0·10$
$(CF_3)_2PH$ ¶	—	$47·5 \pm 0·04$	$68·6 \pm 0·10$
$(CF_3)_3P$	$2·6 \pm 0·0$	$50·8 \pm 0·05$	$85·5 \pm 0·10$
$(CF_3)_2PCl_3$ ¶	—	$78·8 \pm 0·10$	$193·3 \pm 0·20$
$(CF_3)_3P\rightarrow O$	$-2·3 \pm 0·15$	$66·2 \pm 0·05$	$113·4 \pm 0·10$
$[(CF_3)_3P]_2Ni(CO)_2$	$-52·6 \pm 0·5$	$56·6 \pm 0·12$	$91·4 \pm 0·10$

* In p.p.m. from H_3PO_4 (85%). † High-field shift positive. ‡ In p.p.m. from CCl_3F (ref. 4). § In cycles/sec. ¶ The ^{31}P nuclear magnetic resonance spectra of these compounds were not obtained, not enough material being available. In all cases, average error is taken from 5 to 18 measurements, depending on the linearity of the sweep-rate.

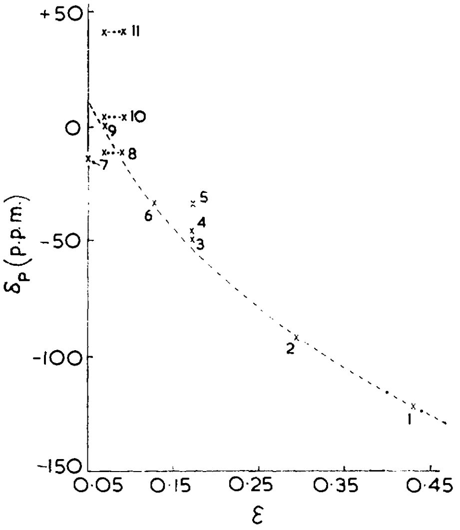
Some general points in the results may be noted. (i) The range of phosphorus chemical shifts (δ_P) is of an order of magnitude larger than the fluorine chemical shifts (ϕ_F).[4] This is not really surprising as the substituent X is bound directly to the phosphorus atom but is relatively remote from the fluorine nuclei. As a result of the small range of observed ϕ_F values in this series ($\sim$20 p.p.m.) and the usually large range of these values (>600 p.p.m.) it will be very difficult to interpret the changes occurring, because they will be caused by relatively subtle effects. (ii) In general, apart from one or two minor reversals in ϕ_F values, increasing δ_P corresponds to decreasing ϕ_F.

Phosphorus Chemical Shifts.—Muller *et al.*[5] and Parks [6] have obtained a semi-empirical equation for δ_P values in PX_3 molecules, in terms of the orbital hybridisation of the phosphorus atom and the ionic character of the P–X bonds. Their work was based on that of Saika and Slichter,[2a] who showed that fluorine chemical shifts, and chemical shifts of any nucleus with other than *s*-electrons associated with it, are determined, to a first order, by the paramagnetic contribution. The use of this equation depends on accurate knowledge of bond angles, small errors in which can cause large errors in the calculated δ_P values.[7] In the series of compounds, $(CF_3)_2PX$, considered here, only one substituent on the phosphorus atom is altered and it is reasonable to assume that very little change in hybridisation or bond angle will occur. Some evidence in favour of this assumption is that in the series H_3SiX, where X = F, Cl, Br, or I, the total variation in the bond angles is less than 15′.[8] If this assumption is valid and other effects are negligible, then the change in phosphorus chemical shift should be linearly related to the change in ionic character of the P–X bond. (This follows from the work of Saika and Slichter.[2a]) The

---

[4] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.
[5] Muller, Lauterbur, and Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557.
[6] Parks, *J. Amer. Chem. Soc.*, 1957, **79**, 757.
[7] Finegold, *Ann. N.Y. Acad. Sci.*, 1958, **70**, 875.
[8] Kewley, Murty, and Sugden, personal communication.

Figure shows a plot of ε, the ionic character of the P–X bond, against the chemical shifts, δ_P. ε is taken from Coulson's " Valence " and is strictly applicable only to diatomic molecules. However, as Muller *et al.*[5] pointed out, this approximation is one of the least in this type of consideration. In the case where X is a group of atoms, the electronegativity of the first atom has been used to calculate ε. The plot is not linear. The change in chemical shift is qualitatively in the right direction for the dominance of a paramagnetic shielding term, *i.e.*, the greater the ionic character of the P–X bond, the greater the paramagnetic shielding term on the phosphorus atom and the greater the chemical shift to low field. (This is in the opposite direction from that for fluorine, where the more covalent the bond the larger the paramagnetic term, because fluorine and phosphorus, in general, form opposite ends of the dipole in a bond with a given atom of intermediate electronegativity.) Reasons for the deviations from linearity cannot be given with certainty, but a few points are worth considering. It is possible that, as the ligand X becomes smaller and more electronegative, the energy of the 3*d*-orbitals drops, owing to their contraction about the atom. This is similar to the behaviour of the 3*d*-orbitals in sulphur, as proposed by Craig and Magnusson.[9] When this occurs, ligands having lone pairs of electrons can probably participate in *dπ–pπ* bonding with the phosphorus. This interaction and change in 3*d*-orbital energy will be more significant at higher values of ε. However, it is impossible to estimate the magnitude or sign of this effect on the paramagnetic shielding term in the absence of more detailed knowledge of the electronic systems involved. Again, the anisotropic magnetic susceptibility in the P–X bond or X atom has been invoked many times to explain observed chemical shifts,[10,11] and in some cases calculations of the magnitudes of these effects have been carried out.[12,2c] If the ligand X has one or more lone pairs of electrons and the P–X bond is axially



Relation of effective ionic character (ε) of the P–X bond to δ_P from H_3PO_4.
1, F. 2, OEt. 3, Cl. 4, NMe_2. 5, –NCO. 6, Br. 7, Se·CF_3. 8, S·CF_3. 9, I. 10, CF_3. 11, –CN.

---

[9] Craig and Magnusson, *J.*, 1956, 4895.

[10] Narisimhan and Rogers, *J. Phys. Chem.*, 1959, **63**, 1388; Pople, Schneider and Bernstein, *J. Chem. Phys.*, 1958, **28**, 601; Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80**, 1728; Whipple, Stewart, Reddy, and Goldstein, *J. Chem. Phys.*, 1961, **34**, 2136; Whipple, Goldstein, and Stewart, *J. Amer. Chem. Soc.*, 1959, **81**, 4761; Whipple, Goldstein, and Mandell, *J. Chem. Phys.*, 1959, **30**, 1109; *J. Amer. Chem. Soc.*, 1960, **82**, 3010; Whipple, Goldstein, and McClure, *ibid.*, p. 3812; Jackman and Wiley, *J.*, 1960, 2881.

[11] Spiesecke and Schneider, *J. Chem. Phys.*, 1961, **35**, 722.

[12] Narisimhan and Rogers, *J. Chem. Phys.*, 1959, **31**, 1302; Musher, *ibid.*, 1961, **35**, 1159; Reddy, Mandell, and Goldstein, *J. Amer. Chem. Soc.*, 1951, **83**, 4729, 1300; Pople, *Proc. Roy. Soc.*, 1957, *A*, **239**, 550.

symmetric, which it is considered to be at least for the halogens, then, when the external magnetic field is parallel to the axis, free diamagnetic circulation of the bonding and lone-pair electrons can occur, giving rise to a large diamagnetic susceptibility in this direction. When the external magnetic field is perpendicular to the bond, however, this circulation is highly hindered, leading to an overall anisotropic diamagnetic susceptibility which gives rise to increased shielding of a nucleus on the bond axis when the magnetic field is averaged over all orientations of the molecule. In a similar manner the P–X bond or X atom can have an anisotropic paramagnetic susceptibility. (How far these two susceptibilities can be considered as separable or independent is a matter for debate, but they have been considered as such before.[11]) This susceptibility is usually greatest, especially for bonds containing halogens, when the external magnetic field is perpendicular to the P–X axis.[11] It is zero in the direction of the bond axis if the bond is axially symmetric.[11] This type of anisotropy also gives rise to an increased shielding of the phosphorus nucleus when the magnetic field is averaged over all orientations. (This can be seen by considering the induced magnetic field as a point magnetic dipole, situated somewhere in the bond, and by drawing out the requisite lines of force.) Both these anisotropies will increase in magnitude from fluorine to iodine, the diamagnetic because of increasing orbital radius of the X atom's electrons, and the paramagnetic, because of the closer approach of energy levels with increasing atomic number. Thus, if anisotropy effects are significant we might expect deviations to high field at lower values of ε for ligands with lone pairs of electrons, as is to be seen in the Figure.

Three ligands are anomalous, CF_3, –CN, and –NCO. The CF_3 ligand would be expected to have an electron-withdrawing power similar to that of chlorine,[13] and hence would seem to be anomalous. However, we are, strictly, considering only PY_2X molecules, whereas $P(CF_3)_3$ is a PY_3 molecule and its energy levels may be significantly different, leading to a difference in the paramagnetic contribution to the shielding. At first it was thought that the high-field deviations for the –CN and –NCO compounds were due to anisotropy. Calculation of the order of magnitude of such effects for the cyanide derivative, with values for the paramagnetic and diamagnetic susceptibilities similar to those used for acetylene by Pople [2c] and for cyanide by Reddy *et al.*,[12] gave only +6 p.p.m., the centres of the anisotropies being taken to be the mid-point of the C≡N bond. It seems that a more likely explanation of the magnitude of these deviations to high field is interaction of the π-electron systems with the phosphorus 3*d*-orbitals. This would not only shift the anisotropy centres nearer to the phosphorus, giving a rapidly increasing contribution from these effects due to an R^{-3} dependence, but would also involve the use of the 3*d*-orbitals of the phosphorus. This effect apparently also gives rise to high-field deviations (see Figure at high ε values.)

It is interesting that, on co-ordination of $(CF_3)_3P$ to an oxygen atom, very little change in the δ_P value occurs ($\Delta\delta_P = -4{\cdot}6$ p.p.m.). However, on co-ordination of the same molecule to a nickel atom the change is much greater ($\Delta\delta_P = -55{\cdot}2$ p.p.m.). It is perhaps instructive to consider the changes in δ_P on co-ordination of PX_3 molecules to oxygen or nickel(0). Table 2 shows some available values. On co-ordination to oxygen, those compounds having the lowest-field δ_P values, and thus presumably the largest paramagnetic contribution, exhibit the largest high-field shift on co-ordination. This could be taken to indicate that a large proportion of the paramagnetic term arises from the lone pair of electrons. On co-ordination to nickel(0) no such pattern is observable.

Phosphorus–Fluorine Spin–Spin Coupling Constants.—The range over which these vary is about a quarter of their absolute value. The order of decreasing *J*(P–F) is: $F > NCO > NCS > OEt > CN \sim NMe_2 > CF_3 > Cl > SCF_3 > Br > SeCF_3 > I > H$. A qualitative correlation is that the more electron-withdrawing X the larger is *J*(P–F). The compounds $(CF_3)_3P\rightarrow O$, $[(CF_3)_3P]_2Ni(CO)_2$, and $(CF_3)_2PCl_3$ have values of *J*(P–F)

---

[13] Lagowski, *Quart. Rev.*, 1959, **13**, 233.

of 113·4, 91·4, and 193·3 c./sec., respectively. This indicates, possibly, that increasing use of the 3*d*-orbitals corresponds to an increase in *J*(P–F). Certainly, in the last compound mentioned, where the formal orbital hybridisation is sp^3d, a very substantial increase in *J*(P–F) occurs. It has also been suggested by Petrakis and Sederholm[14] that contributions to fluorine–fluorine spin–spin coupling constants can arise by interactions direct through space, leading to strong stereochemical dependence of such couplings, and this mechanism may be important in P–F couplings.

TABLE 2.

Some changes in δ_P in PX_3 molecules on co-ordination to oxygen or nickel(0).

X	δ_P *	$\Delta\delta_P$(O) †	$\Delta\delta_P$(Ni) ‡	X	δ_P *	$\Delta\delta_P$(O) †	$\Delta\delta_P$(Ni) ‡
F	−97	No value	−30	Br	−222	+324·9	No value
NMe_2	−122	+100	No value	SEt	−115·6	+54	No value
OPh	−127	+144	−21	CF_3	+2·3	−4·6	−54
OEt	−138	+138·9	−20	Et	+20·4	−69	−39·8
Cl	−215	+210	+34				

* In p.p.m. from H_3PO_4. † Values taken from ref. 3, Chapter 12, section 8; $\Delta\delta_P(O) = \delta_P(POX)_3 - \delta_P(PX_3)$. ‡ Values taken from ref. 19· $\Delta\delta_P(Ni) = \delta_P(X_3P\rightarrow Ni) - \delta_P(PX_3)$.

EXPERIMENTAL

Preparations.—Compounds were handled and purified by conventional high-vacuum techniques. Compounds $(CF_3)_2PX$ where X = I, Cl, –CN, NMe_2, CF_3, $S{\cdot}CF_3$, $Se{\cdot}CF_3$, H, or OEt were prepared by recorded methods.[15-19] The compounds $(CF_3)_2PCl_3$, $(CF_3)_3P\rightarrow O$ and $[(CF_3)_3P]_2Ni(CO)_2$ were available in the laboratory and were purified by vacuum-fractionation, their purity being checked by infrared spectroscopy and molecular-weight determinations.

Fluorobistrifluoromethylphosphine. Formation of this compound from the corresponding iodophosphine and antimony trifluoride has been reported to occur at room temperature.[16] Attempts to repeat this failed and the reactants had to be heated to 60° for 40 hr. to give quantitative yields. An attempt to prepare this compound from silver fluoride and the iodophosphine caused an explosion.

Bromobistrifluoromethylphosphine. The corresponding arsine has been reported.[17] The phosphine was prepared by the reaction of the iodophosphine with silver bromide. The reaction was very slow and entailed shaking with several batches of silver bromide, for 4—5 days, until no yellow colour remained in the liquid. Vacuum-fractionation of the volatile material yielded *bromobistrifluoromethylphosphine*, which was collected at −95° [Found: CF_3 (attached to phosphorus, measured as CF_3H), 54·1; Br, 32·3; P, 12·1%; *M*, 250. C_2BrF_6P requires CF_3, 55·4; Br, 32·1; P, 12·5%; *M*, 249]. This is a colourless mobile liquid, whose vapour pressure from −40° to 20° is given by: $\log_{10} p$ (mm.) = $-1510/T + 7{\cdot}68$, giving an extrapolated b. p. of 41·8°. The infrared spectrum, recorded on a Perkin-Elmer Infracord spectrophotometer, showed bands at 2330w, 2295w, 2250w, 1213vs, 1170vs, 1140vs, 1092s, 815w, 764w, and 750ms cm.$^{-1}$.

Isocyanatobistrifluoromethylphosphine. This compound was prepared in a similar way to the bromo-derivative, silver cyanate being used instead of silver bromide. Two treatments with an excess of silver cyanate were necessary. The *phosphine* was collected at −95° [Found: CF_3 (attached to phosphorus, measured as CF_3H), 67·0; C, 16·9; N, 7·5%; *M*, 210. C_3F_6NOP requires CF_3, 65·5; C, 17·0; N, 6·6%; *M*, 211]. It is a colourless, mobile liquid, whose vapour pressure (−33° to 31°) is given by $\log_{10} p$ (mm.) = $-1775/T + 8{\cdot}3$, giving an extrapolated b. p. of 53·8°; the spectrum, recorded as above, showed bands at 2370sh, 2310vs, 1436m, 1218s, 1180vs, 1130s, and 700m cm.$^{-1}$.

Thiocyanatobistrifluoromethylphosphine was prepared analogously [Found: CF_3 (attached

---

[14] Petrakis and Sederholm, *J. Chem. Phys.*, 1961, **35**, 1243.

[15] (*a*) Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565; Harris, *J.*, 1958, 512; Emeléus and Smith, *J.*, 1959, 375; Emeléus, Packer, and Welcman, *J.*, 1962, 2529; (*b*) Burg and Mahler, *J. Amer. Chem. Soc.*, 1957, **79**, 4242.

[16] Burg and Brendel, *J. Amer. Chem. Soc.*, 1958, **86**, 3198.

[17] Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552.

[18] Miller and Carlson, *Spectrochim. Acta*, 1961, **17**, 977.

[19] Meriweather and Leto, *J. Amer. Chem. Soc.*, 1961, **83**, 3192.

to phosphorus, measured as CF_3H), 62·5; C, 15·7; N, 7·0%; *M*, 225. C_3F_6NPS requires CF_3, 61·0; C, 15·9; N, 6·2%; *M*, 227]. It is a colourless liquid which becomes brown at room temperature. Its vapour pressure (20° to 40°) is given by $\log_{10} p$ (mm.) $= -1715/T + 7{\cdot}68$, giving an extrapolated b. p. 84·0°. The infrared spectrum, recorded as above, has bands at 2610w, 2100w, 2060m, 2020vs, 1218s, 1180vs, 1135s, 1040w, 750w cm.$^{-1}$.

Nuclear Magnetic Resonance Spectra.—(*A*) *Measurement.* (*a*) Phosphorus-31 spectra. These were obtained, at 16·2 Mc./sec., by using a Varian Associates V4300A nuclear magnetic resonance spectrometer and 12″ electromagnet with flux stabilisation and a Varian V4356 field-homogeneity control unit. The samples were sealed under a vacuum in Pyrex tubes of 10 mm. outside diameter. The standard, 85% phosphoric acid, was sealed in capillaries, of at least 2 mm. internal diameter, which were placed inside the 10 mm. sample tubes before these were filled with the compound to be studied. Owing to the large spread of most of the spectra (the largest covers ~1600 c./sec.) sidebands of the compounds themselves could not be used for calibration and in these cases the phosphorus–fluorine spin–spin coupling constant, as measured from the fluorine-19 spectra, was used for calibration. When the compound's resonance signals were far enough removed from that of the standard, some sidebands of the standard resonance were used as a check of the scale calibration. The chemical shifts given are, in general, the average of at least six runs.

(*b*) Fluorine-19 spectra. These were recorded on the same instrument, at 40 Mc./sec. The samples were sealed in Pyrex tubes of 5 mm. outside diameter with trichlorofluoromethane as solvent and standard. The concentrations were usually 50% v/v. The samples were spun in the magnetic field; the phosphorus-31 samples were not. The calibration of these spectra was carried out by means of sidebands of the compound's or the standard's resonance. These sidebands were generated by a Muirhead–Wigan D695A decade oscillator. Values given are, in general, the average of at least six determinations.

(*c*) Proton spectra. The proton spectra of the compounds $(CF_3)_2P{\cdot}OEt$, $(CF_3)_2PH$, and $(CF_3)_2P{\cdot}NMe_2$ were recorded on a Perkin-Elmer nuclear magnetic resonance spectrometer. This spectrometer operates at a frequency of 40 Mc./sec. for protons. It employs a permanent magnet and the spectrum is scanned by small changes in the magnetic field whilst the frequency is maintained constant.

(*B*) *Description.*—(*a*) Phosphorus-31 spectra. The spectra of compounds $(CF_3)_2PX$ where X = Cl, Br, I, –CN, –NCO, or NMe_2 consisted of a septet. The spectra of the Cl, Br, I, and –CN derivatives were sharp and intense, whereas those of the –NCO and NMe_2 derivatives were broad and weak. For the NMe_2 derivative, part of this broadening is due to phosphorus–proton spin–spin coupling which is 9·03 c./sec. (from proton spectrum). However, a similar splitting was easily resolvable in the phosphorus-31 spectrum of $(CF_3)_2P{\cdot}OEt$, whereas it was not so in this case, indicating that significant broadening was due to direct bonding of the quadrupolar ^{14}N nuclei to phosphorus. This leads to the conclusion that the –NCO group is bonded to phosphorus through nitrogen: hence the isocyanate nomenclature assigned to this compound. The infrared spectrum of this derivative shows a band at 1436 cm.$^{-1}$ which has been claimed to show the presence of a covalent isocyanate groups.[18] The phosphorus spectra of $(CF_3)_3P$, $(CF_3)_3P{\rightarrow}O$, and $[(CF_3)_3P]_2Ni(CO)_2$ should theoretically contain ten lines of appropriate intensities. Only eight lines were obtained, presumably because of the very low relative intensity of the two outer lines which become merged with the background noise. The spectra of $(CF_3)_2P{\cdot}S{\cdot}CF_3$ and $(CF_3)_2P{\cdot}Se{\cdot}CF_3$ consisted of a septet of quartets, arising from the two phosphorus–fluorine spin–spin coupling constants in the molecules. Only the central two lines of the two outer quartets were visible, owing to their small relative intensity. The spectrum of $(CF_3)_2P{\cdot}OEt$ consisted of a septet of well-resolved triplets, the triplet structure arising from the coupling of the phosphorus nucleus with the methylene protons of the ethoxy-group. The spectrum of $(CF_3)_2PF$ consisted of two septets, the large splitting between the two groups being due to the directly bound P–F coupling.

(*b*) Fluorine-19 spectra. The spectra of the compounds $(CF_3)_2PX$ consisted of a doublet to high field of the standard resonance (CCl_3F). The spectrum of $(CF_3)_2PH$ has been reported qualitatively in the literature.[15b] The spectrum consisted, as reported, of a pair of doublets, the major doublet splitting being the phosphorus–fluorine coupling constant and the minor one the fluorine–proton coupling constant [J(F–H) $= 9{\cdot}73 \pm 0{\cdot}05$ c./sec.]. The spectra of the $-S{\cdot}CF_3$ and $-Se{\cdot}CF_3$ derivatives consisted of a doublet of quartets to high field of a doublet of septets, all being to high field of the CCl_3F signal. The quartets arise from coupling of fluorine of $(CF_3)_2P$ with fluorine of $S(Se)\cdot CF_3$, and the septets by the reversal of this process [J(F–F) = 1·11 c./sec. for the $-S\cdot CF_3$ derivative and 1·09 c./sec. for the $-Se\cdot CF_3$ derivative). The spectrum of $(CF_3)_2P\cdot NMe_2$ consisted of a doublet of septets, the septet splitting arising from fluorine–proton coupling [J(F–H) = 0·52 c./sec.]. The spectrum of $(CF_3)_2PF$ consisted of a doublet of doublets to low field of a doublet of septets [the chemical shift of the single fluorine was $\phi_F = +219{\cdot}0 \pm 0{\cdot}2$ p.p.m.; and J(P–F) = 1013 ± 2 c./sec.; J(F–F) = 3·46 ± 0·04 c./sec.]. The spectra of $(CF_3)_3P\rightarrow O$ and $[(CF_3)_3P]_2Ni(CO)_2$ were simple doublets.

(*c*) Proton spectra. The spectrum of $(CF_3)_2P\cdot NMe_2$ was a doublet of septets. The doublet splitting corresponds to the phosphorus–proton spin–spin coupling constant [J(P–H) = 9·03 c./sec.]. The chemical shift of the protons is $\tau = 7{\cdot}11$. The spectrum of $(CF_3)_2PH$ was found, as reported,[15b] to consist of a doublet of septets [J(P–H) = 218·0 c./sec.; $\tau = 5{\cdot}45$]. The spectrum of $(CF_3)_2P\cdot OEt$ consisted of a doublet of quartets (overlapping) to low field of a triplet. The former represent the methylene protons' resonance split by coupling with the methyl protons and the phosphorus nucleus. The triplet represents the methyl protons' resonance [$\tau(CH_2) = 5{\cdot}87$; $\tau(CH_3) = 8{\cdot}66$; $J(CH_2–CH_3) = 6{\cdot}87 \pm 0{\cdot}2$ c./sec.; $J(P–CH_2) = 9{\cdot}91 \pm 0{\cdot}1$ c./sec.]. The lower-field quartet of the methylene resonance, corresponding to one spin state of the phosphorus nucleus was consistently more intense than the higher-field quartet. This part of the spectrum was investigated at different sweep-rates to see if this effect was due to a difference in relaxation times for the two states. No change was observed. It was concluded that this difference in intensity probably arose because the system approaches an A_2B_3X system rather than A_2R_3X. The triplet methyl resonance was also slightly unsymmetrical, but not as noticeably so as the methylene resonance.

The author thanks Professor H. J. Emeléus for his interest, Dr. E. A. V. Ebsworth and Dr. A McLachlan for useful discussions, Messrs. E. Liddell and A. Gray for obtaining the proton spectra, and the Department of Scientific and Industrial Research for a Research Studentship.

INORGANIC CHEMISTRY DEPARTMENT, THE UNIVERSITY, CAMBRIDGE.
[Present address: EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.,
WILMINGTON 98, DEL., U.S.A.]

[*Received, July* 10*th*, 1962.]