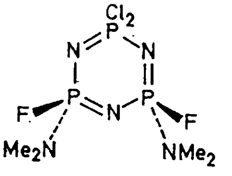
Relationships of Nuclear Magnetic Resonance Parameters to Structure for Cyclotriphosphazatrienes

By **Philip Clare** and **D. Bryan Sowerby**, Department of Chemistry, The University, Nottingham NG7 2RD
Robin K. Harris * and **Mohamed I. M. Wazeer**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

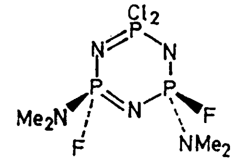
The ^{19}F n.m.r. spectra of a number of fluorinated cyclotriphosphazatrienes were measured and analysed, using iterative fitting by computer, to give the relevant coupling constants and chemical shifts. Some of the ^{31}P spectra were also recorded and used in the computer iteration. The relationships of the n.m.r. parameters with molecular structure are discussed.

ALTHOUGH a substantial number of cyclotriphosphazatrienes has been studied [1-6] by n.m.r., relatively few of them have contained fluorine substituents, and only a small number of such compounds have been subjected to detailed n.m.r. spectral analysis.[6-8] The relationship of the n.m.r. parameters, particularly the (F,F) coupling constants, to chemical structure has not been adequately documented hitherto. Consequently, we decided to study in detail the n.m.r. spectra of a number of fluorinated cyclotriphosphazatrienes containing Cl, Br, and NMe_2 substituents. These compounds, together with the appropriate spin systems,[9] are listed below:

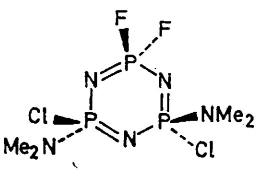
(I)	*cis*- 1,3,5-$P_3N_3F_3Cl_3$	$[AX]_3$
(II)	*cis*- 1,3,5-$P_3N_3F_3Br_3$	$[AX]_3$
(III)	*trans*-1,3,5-$P_3N_3F_3Cl_3$	$AX[BY]_2$
(IV)	*trans*-1,3,5-$P_3N_3F_3Br_3$	$AX[BY]_2$
(V)	*cis* -1,3-$P_3N_3F_2Cl_4$	$A[BX]_2$
(VI)	*trans*-1,3-$P_3N_3F_2Cl_4$	$A[BX]_2$
(VII)	*trans*-1,3-$P_3N_3F_2Br_4$	$A[BX]_2$
(VIII)	*cis* -1,3-$P_3N_3F_2Br_4$	$A[BX]_2$



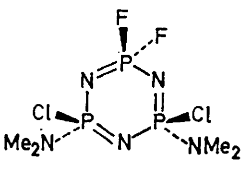
(IX) *cis* $A[BX]_2$



(X) *trans* $A[BX]_2$



(XI) *trans* $A[BX]_2$



(XII) *cis* AB_2XY

In the spin-system notation A and B stand for ^{31}P, whereas X and Y refer to ^{19}F. In the case of compounds (IX) to (XII) it is assumed that the protons are decoupled. It is also assumed throughout that the nitrogen, chlorine, and bromine atoms do not cause any splittings in the ^{19}F or ^{31}P n.m.r. spectra, but they certainly contribute substantially to linewidths because quadrupolar relaxation is insufficiently rapid to give very sharp lines. Indeed, complete and accurate analysis of the n.m.r. spectra of cyclotriphosphazatrienes is not always feasible because of the large linewidths (up to $\Delta\nu_{\frac{1}{2}} \sim 3$ Hz in some of our cases) and because of the extensive overlapping that sometimes occurs. Bandshapes have been shown [10] in certain cases to exhibit features which cannot be explained on a simple basis, but this type of problem has been ignored in the present treatment since it does not seem to affect the derived n.m.r. parameters greatly. Earlier analyses of fluorinated compounds [7,8] have not used *iterative* computational methods, but, even in cases where explicit expressions are available for certain transitions, the accuracy of the results may be improved by iteration using as many observed lines as is feasible.

Spectral Analysis.—The general approach of this work was to use primarily the ^{19}F spectra [in the case of compounds (IX)—(XII) $^{19}F-\{^1H\}$ spectra were used] to obtain as much information as possible by inspection (making use of explicit features of the appropriate spin systems), and then to carry out an iterative fitting using the computer program LACX [11,12] [in the case of (XII) the program UEANMR [12,13] was used to take advantage of magnetic equivalence]. Some ^{31}P spectra were also obtained [but not for (I)—(III), (VII), and (VIII) since these compounds were no longer available in sufficient quantity by the time access to ^{31}P facilities was possible]. For compounds (V), (VI), and (IX)—(XII) the ^{31}P data were used in the computer iteration, but for (IV) they

---

[1] E. G. Finer and R. K. Harris, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61.

[2] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.

[3] P. Clare, D. B. Sowerby, and B. Green, *J.C.S. Dalton*, 1972, 2374.

[4] C. W. Allen, *J. Magnetic Resonance*, 1971, **5**, 435.

[5] E. Niecke, H. Thamm, and G. Flaskerud, *Chem. Ber.*, 1971, **104**, 3729.

[6] A. A. Volodin, V. V. Kireev, A. A. Fomin, M. G. Edelev, and V. V. Korshak, *Doklady Chem.*, 1973, **209**, 168.

[7] M. L. Heffernan and R. F. White, *J. Chem. Soc.*, 1961, 1382.

[8] F. Heatley and S. M. Todd, *J. Chem. Soc.* (*A*), 1966, 1152.

[9] C. W. Haigh, *J. Chem. Soc.* (*A*), 1970, 1682.

[10] R. K. Harris, E. G. Finer, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 72.

[11] C. W. Haigh, *Ann. Rep. N.M.R. Spectroscopy*, 1971, **3**, 311.

[12] R. K. Harris and M. Kinns, 'A Library of Computer Programs for N.M.R. Spectroscopy,' Atlas Computer Laboratory, Chilton, Berks, 1974.

[13] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magnetic Resonance*, 1970, **3**, 84.

were simply compared with spectra predicted by computer using parameters obtained from the ^{19}F spectra.

Seven of the compounds have spectra of the $A[BX]_2$ type, and only three other spectral types are represented. In all cases some simplifications result from the fact that $|^1J_{PF}|$ is much larger than any of the other coupling constants. Thus the PF groups of compounds (I)—(X) give a large doublet splitting in ^{19}F resonance, often with much fine structure. In particular, compounds (I) and (II) are examples of the $[AX]_3$ spin system with $|^1J_{AX}| \gg |J_{AA}| \gg |^3J_{AX}| > |J_{XX}|$, and the ^{19}F spectra show (Figure 1) the expected [14,15] approximate ' doublet of quintets ' pattern, which allows much information to be obtained directly. For instance, it can be immediately concluded that $^1J_{PF}$ and $^3J_{PF}$ are of opposite sign. Some preliminary results for these compounds have already been reported.[3] The high and low frequency moieties of these spectra are mirror images. The spectrum of (II) had appreciably greater linewidths than that of (I), and the derived parameters are correspondingly less accurate. It is doubtful, for instance, whether the value of $^4J_{FF}$ for (II) (—0·5 Hz) is meaningful. Even for (I) the coupling $^4J_{FF}$ does not lead to clearly resolved splittings, as it would in an ideal case. LACX Is not, of course, an ideal program for handling $[AX]_3$ spectra since it factorizes the Hamiltonian for a twofold element of symmetry only; it can, nevertheless, be used.

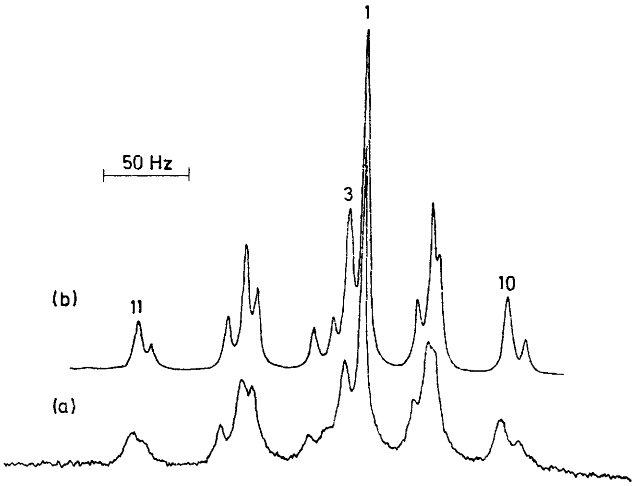


FIGURE 1 (a) Observed and (b) computed 94·075 MHz ^{19}F n.m.r. spectrum (high frequency half) of *cis*-$P_3N_3F_3Cl_3$ (I). Peaks marked 1 and 3 are at $\nu_F + \frac{1}{2}|^1J_{PF} + 2\,^3J_{PF}|$ and $\nu_F + \frac{1}{2}|^1J_{PF}|$ respectively. The separation of peaks marked 10 and 11 is $2|^2J_{PP}|$ (see ref. 15)

The $A[BX]_2$ spin system has also already been discussed in detail,[16,17] but some special features of the present cases require explanation. In the $A[MX]_2$ limit, the M and X regions consist of two $[mx]_2$ subspectra,[18] characterized by the two possible values for the *z* component of the A spin. In the present cases, since $|^1J_{PF}|$ is large, the subspectra are further simplified, and each consists of two five-line moieties. For the M region when J_{XX} is small the overall appearance is that of a pair of quintets (see Figure 2), since $J_{MM} \approx J_{AM}$. The X region will contain, *inter alia*, a pair of intense lines (corresponding to $A[M]_2$ spin states ααα and βββ) separated by $|J_{AX} + J_{MX} + J_{MX}'|$, and a further pair (from $A[M]_2$ states αββ and βαα) separated by $|J_{MX} + J_{MX}' - J_{AX}|$. However, the latter pair are perturbed and split when second-order effects occur if $|\nu_A - \nu_M|$ is comparable to the coupling constants involved. In many instances it is still possible to identify both sets of lines and to assign them correctly by inspection so as to give the approximate magnitudes of J_{AX} and $J_{AX} + J_{BX}'$, plus their relative signs. However, we have shown, by a series of computations (Figure 3) with variation of $|\nu_A - \nu_B|$, that this information is no longer available directly when $|\nu_A - \nu_B \pm \frac{1}{2}(J_{BX} + J_{BX}')|$ is comparable to $|J_{AB}|$. For compounds (IX) and (X) $|\nu_A - \nu_B| \sim 250$ Hz and it proved feasible to obtain the relative sign information. The second-order effects lead to changes in transition frequencies in the X region, but in the present cases the only lines additional to those for the $A[MX]_2$ case are those produced by the splittings mentioned above. However, further relative sign information for the coupling constants becomes available.

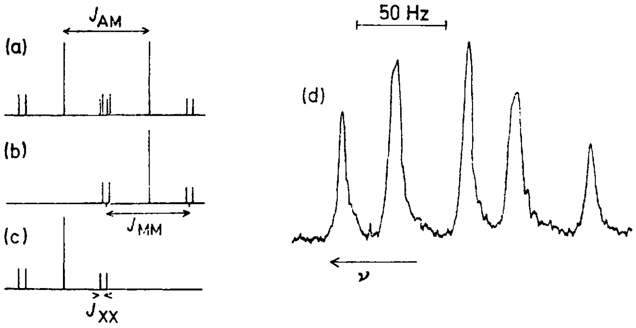


FIGURE 2 (a) Low frequency moiety for the M region of an A $[MX]_2$ spin system with $|L_{MX}| \gg |J_{AA}| \approx |J_{AM}| \gg |J_{XX}|$; (b) and (c) are component subspectra; (d) is the low frequency part of the observed $^{31}P-\{^1H\}$ noise-decoupled n.m.r. spectrum for *cis*-$P_3N_3F_2Cl_2(NMe_2)_2$ (IX). The quintet in (d) is not evenly spaced, both because J_{MX}' is non-zero and because J_{MM} is not negligible with respect to J_{MX}

The $A[BX]_2$ spin system of compound (XI) has very different parameters from those of compounds (V)—(X), especially in that $|J_{BX} - J_{BX}'|$ is now small instead of very large. In fact the spectrum is nearly deceptively simple [16,18] and may be discussed most readily from the viewpoint of an AB_2X_2 system, which has been described

---

[14] E. G. Finer and R. K. Harris, *J. Chem. Soc.* (*A*), 1969, 1972.

[15] R. K. Harris, J. R. Woplin, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 134.

[16] R. J. Abraham, 'Analysis of High Resolution N.M.R. Spectra,' Elsevier, Amsterdam, 1971.

[17] P. Diehl, R. G. Jones, and H. J. Bernstein, *Canad. J. Chem.*, 1965, **43**, 81.

[18] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.

in the n.m.r. spectral analysis of various compounds.[7,19,20] It may be discussed using ' composite particle ' factorization.[16,18] The A and B regions simply consist of three

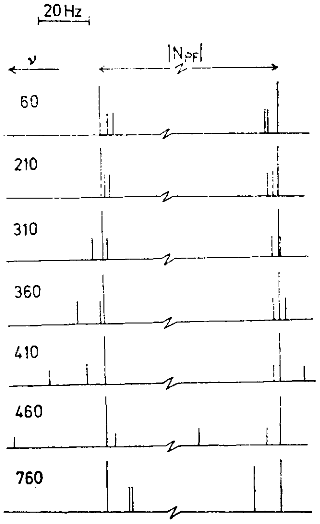


FIGURE 3 Computer stick-plots for the X region of the n.m.r. spectrum for an $A[BX]_2$ spin system with $J_{BB} = 69{\cdot}0$ Hz, $J_{XX} = 0{\cdot}0$ Hz, $J_{AB} = 66{\cdot}7$ Hz, $J_{AX} = 9{\cdot}2$ Hz, $J_{BX} = 920{\cdot}0$ Hz, and $J_{BX}' = -4{\cdot}7$ Hz. The values taken by $\nu_A - \nu_B$ are indicated beside the spectra, in Hz. Only transitions related to lines at $|J_{AX} + J_{BX} + J_{BX}'|$ and $|J_{BX} + J_{BX}' - J_{AX}|$ in the semi-first-order $A[MX]_2$ limit are indicated

ab_2 subspectra with weightings 1 : 2 : 1, and give ν_A, ν_B, $|J_{AB}|$, $|J_{AX}|$, and $|J_{BX}|$, together with the relative signs of J_{AX} and J_{BX}. The X region consists of DTT and DST subspectra. The former gives, *inter alia*, two strong lines separated by $|J_{AX} + 2J_{BX}|$ and the latter gives (only) two lines separated by $|J_{AX}|$. When $|J_{AB}| \sim |\nu_A - \nu_B|$, and only then, the X region as a whole is asymmetric, leading to information about the relative signs of J_{AB} and J_{AX}.

The $AX[BY]_2$ spectra may be treated as logical extensions of the $A[BX]_2$ cases (V) to (X). Such an extension is simplified by the fact that $|\nu_X - \nu_Y|$ is normally greater than the value of $|J_{XY}|$, so ' X approximation ' principles [16,18] may be applied. The A, B, and Y regions then consist of two $a[by]_2$ subspectra.

Composite particle factorization may be employed for the AB_2XY spin system [compound (XII)]. When $|\nu_X - \nu_Y| \gg |J_{XY}|$ the A and B regions consist of four ab_2 subspectra. The X and Y regions contain an axy subspectrum (when the B_2 spins are in the S state). In the AM_2XY limit the effect of the M_2 spins is to split each line into a 1 : 2 : 1 triplet (of spacing $|J_{MX}|$ or $|J_{MY}|$, as appropriate, when $|\nu_X - \nu_Y| \gg |J_{XY}|$). For compound (XII) such a simple pattern only occurred in the low frequency X and Y regions; the high frequency parts are more complex because $|\nu_A - \nu_B| \approx \frac{1}{2}|J_{AX} + J_{AY}|$. The spectrum is thus partially first order (Figure 4).

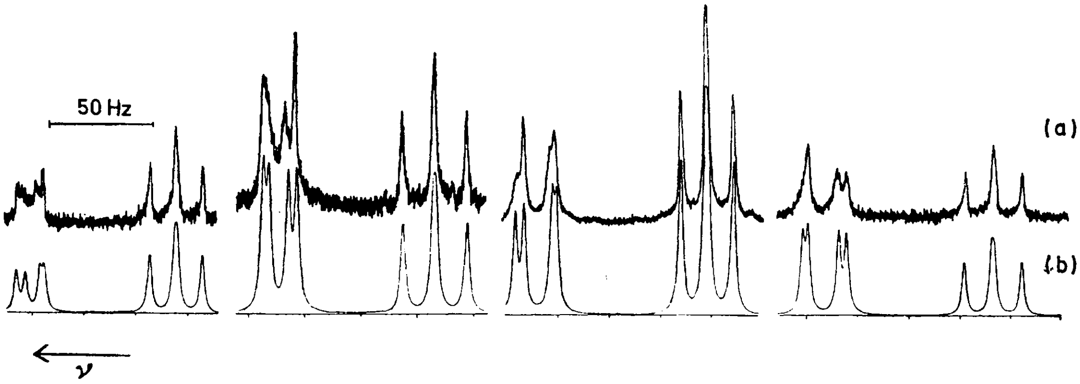


FIGURE 4 (a) Observed and (b) computed 94·075 MHz $^{19}F-\{^1H\}$ n.m.r. spectrum of *cis*-$P_3N_3F_2Cl_2(NMe_2)_2$ (XII), showing the partially first-order character (triplets). The intensities are not relatively correct between the four regions

Comments on special features in the spectral analyses of certain of the compounds follow at this point.

trans-$P_3N_3F_3Cl_3$ (III). It is clear from the ^{19}F spectrum that $|^1J_{PF}| \gg |\nu_X - \nu_Y| \gg |^4J_{FF}|$. Thus the two types of fluorine nuclei are weakly coupled and the spectrum consists of two moieties because of the large value of $|^1J_{PF}|$. In each moiety an intense doublet and a corresponding 1 : 2 : 1 triplet can be seen. These first-order patterns arise from phosphorus spin states $\alpha\alpha\alpha$ and $\beta\beta\beta$. They give, by inspection, good approximations to ν_X, ν_Y, $|J_{XY}|$, $|^1J_{BY} + {}^3J_{BY} + {}^3J_{AY}|$, and $|^1J_{AX} + 2\,{}^3J_{BX}|$. Using these measured values and the information gained from the other compounds, trial spectra could be computed, but the difficulty lay in estimating $\nu_A - \nu_B$, since the ^{31}P spectrum was not available. In fact the ^{19}F region was very sensitive to $\nu_A - \nu_B$, which was found eventually to be rather small in magnitude (2·4 Hz).

trans-$P_3N_3F_3Br_3$ (IV). The analysis for this compound was easier than for (III) since the $^{31}P-\{^{14}N\}$ double-resonance spectrum was at hand, and both $|\nu_X - \nu_Y|$ and $|\nu_A - \nu_B|$ are larger than for (III). The calculated ^{31}P spectrum (Figure 5) is in good agreement

---

[19] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Canad. J. Chem.*, 1957, **35**, 1487.

[20] R. C. Hirst, D. M. Grant, and E. G. Paul, *J. Chem. Phys.*, 1966, **44**, 4305.

with the observed one, even though this region was not used in the iterative calculations.

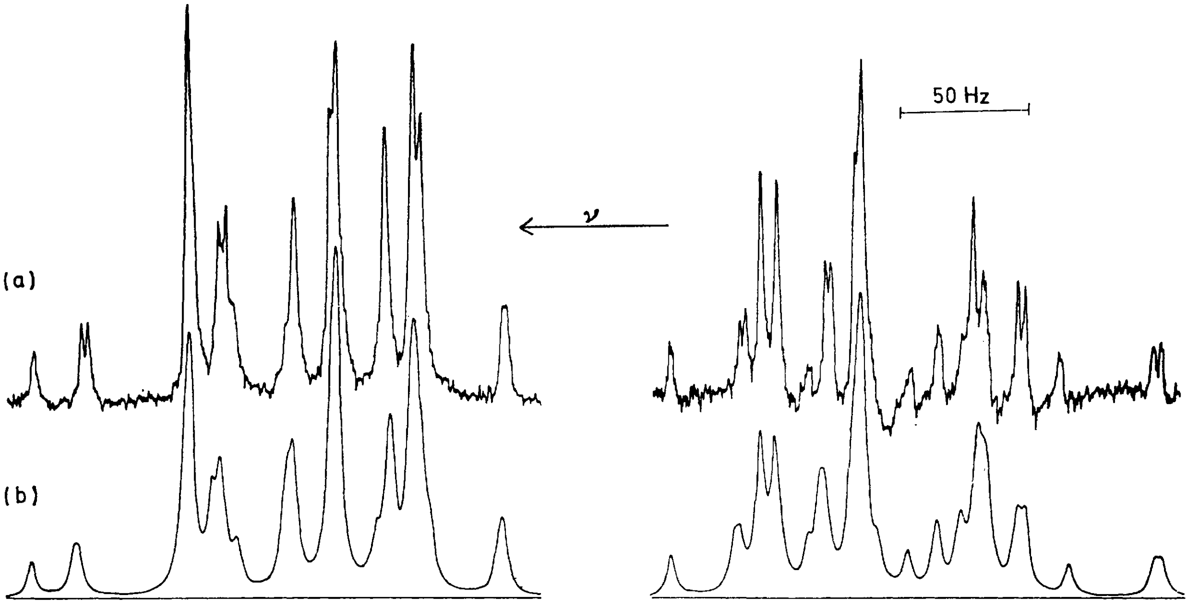


FIGURE 5 (a) Observed $^{31}P-\{^{14}N\}$ and (b) computer-simulated n.m.r. spectrum of *trans*-$P_3N_3F_3Br_3$ (IV)

cis (V)- *and* trans (VI)-$P_3N_3F_2Cl_4$. These two isomers could not be separated by gas chromatography, and the spectral analysis was conducted on the mixture. The ^{19}F signals (Figure 6a) from (V) and (VI) overlap, but the presence of four strong lines in two pairs, each separated by *ca.* 1000 Hz, indicated that the two isomers were present in comparable amounts. A distinction can be made by noting from the results for other compounds that $^4J_{FF}$ (*cis*) ~ -1 Hz whereas $^4J_{FF}$ (*trans*) $\sim +12$ Hz. The spectral analyses for the two isomers (Figure 6) were carried out in parallel, since changes of assignment in one spectrum necessarily affected the other. As for (IV), the $^{31}P-\{^{14}N\}$ spectra were also obtained, but for (V) and (VI) the ^{31}P information was used, with the ^{19}F data, in the iterative computation process. Most of the parameters could be obtained accurately from the ^{19}F spectra alone, but evaluation of $\nu_A - \nu_B$ and J_{AB} required use of the ^{31}P transitions.

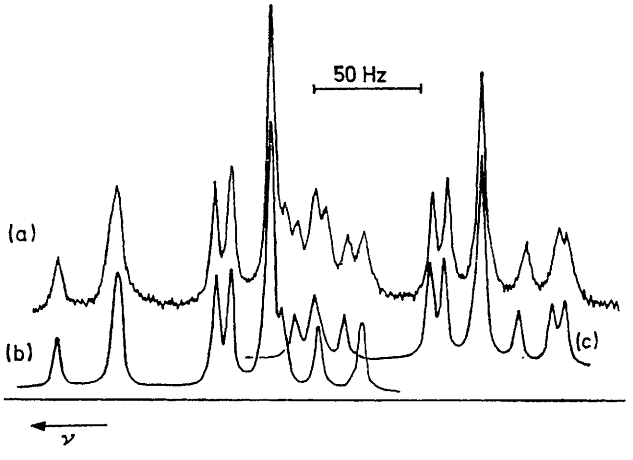


FIGURE 6 (a) Observed 94·075 MHz ^{19}F n.m.r. spectrum (high frequency region) of a mixture of *cis*-$P_3N_3F_2Cl_4$ (V) and *trans*-$P_3N_3F_2Cl_4$ (VI); (b) and (c) are the corresponding computer-simulated spectra for (VI) and (V) respectively

trans (VII)- *and* cis (VIII)-$P_3N_3F_2Br_4$. As for (V) and (VI), the spectral analysis was carried out on a mixture of the isomers. The ^{19}F spectra showed that $|\nu_A - \nu_B| \gg |J_{AB}|$ so that the ' X approximation ' could be applied. A full analysis of the ^{19}F spectrum of (VII) was therefore carried out by inspection, and computation was then used merely to average errors. However, $|\nu_A - \nu_B|$ and $|J_{AB}|$ could not be varied during iteration; they were maintained at estimated values. For (VIII) the ^{19}F spectrum is poorly resolved (partly because $^4J_{FF}$ is very small), and the reliability of the derived data is uncertain; it was not feasible to use computation in this case.

trans-$P_3N_3F_2Cl_2(NMe_2)_2$ *with geminal chlorines* (X). This compound was used as a test-case to determine the relative signs of the coupling constants, since both $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ spectra were available and well-resolved. It was assumed (*a*) that $^1J_{PF}$ is invariably negative,[21,22] (*b*) that the two different values of $^3J_{PF}$ have the same sign, and (*c*) that the two different values of $^2J_{PP}$ have the same sign. Furthermore, inspection of the ^{19}F spectrum showed that $^1J_{PF}$ and $^3J_{PF}$ are of opposite sign. Spectra were then computed (using reasonable values of the parameters) for the four

---

[21] C. Schumann, H. Dreeskamp, and O. Stelzer, *Chem. Comm.*, 1970, 619.

[22] D. L. Vanderhart, H. S. Gutowsky, and T. C. Farrar, *J. Chem. Phys.*, 1969, **50**, 1058.

remaining possibilities of relative signs. Visual comparison of the simulated and observed spectra ruled out the cases with J_{PP} and $^4J_{FF}$ (*trans*) of opposite sign (the relative signs of J_{PP} and J_{FF} affect the ^{19}F region, but not the ^{31}P). Iteration was performed for the remaining two cases. The r.m.s. error for J_{PP} positive was 0·9; that for J_{PP} negative was 2·1. It was concluded that the former is correct, and that the signs of Table 1 are established, subject to some uncertainty in the case of $^4J_{FF}$ (*cis*).

trans-$P_3N_3F_2Cl_2(NMe_2)_2$ *with geminal fluorines* (XI). The fluorine spectrum for this compound was asymmetric, and therefore, as mentioned earlier, this gives the relative signs of J_{PP} and J_{PF}. Computation also gave the relative signs of $^1J_{PF}$ and $^3J_{PF}$. Because the spectrum approximates to that of an AB_2X_2 system, the values of J_{BB} and J_{XX} were set at reasonable values and not iterated. The result for $J_{BX} + J_{BX}'$ is accurate but that for $J_{BX} - J_{BX}'$ is very inaccurate.

cis-$P_3N_3F_2Cl_2(NMe_2)_2$ *with geminal fluorines* (XII). This compound is the only one for which $^2J_{FF}$ can be determined. Computation showed that the sign of this parameter affected the ^{19}F spectrum (but not the ^{31}P spectrum), and it was concluded that it is negative.

The results obtained for all the compounds are summarised in Table 1.

DISCUSSION

Phosphorus Chemical Shifts.—The known[23] relative shielding constants (ref. 23, page 391) of the phosphorus nucleus in various situations are $PBr_2 > PF_2 > PFCl > PCl_2 > PClNMe_2$, and this enabled the correct order to be used in the computations of the chlorofluoro-compounds. There were no data available for the corresponding PFBr group in cyclotriphosphazatrienes, but it might be expected that $\sigma_{PFBr} < \sigma_{PBr_2}$. This suggestion is confirmed by comparison of the ^{31}P results for (IV) with literature values[23] of δ_P for the PBr_2 group. It is also consistent with evidence from computation of the *trans*-$P_3N_3F_2Br_4$ case with $\sigma_{PFBr} > \sigma_{PBr_2}$; the final solution is very close in all other respects to the alternative case, but the r.m.s. error of frequencies is 1·11 Hz compared to 0·25 Hz. There appears to be sufficient interaction between the two types of phosphorus nucleus for the effect to be transmitted to the fluorine region even though the X-approximation ($|J/\Delta\nu| \approx 0{\cdot}04$) is good.

The second-order nature of the phosphorus region for *cis*- and *trans*-$P_3N_3F_2Cl_4$ arises both from chemical equivalence and from the smaller chemical-shift difference between the PFCl and PCl_2 groups. There are relatively large standard deviations (*ca.* 10 Hz) on these shift differences when only ^{19}F transitions are used in the iterative computations. For the *trans*-trisubstituted derivatives, (III) and (IV), on the other hand, the very small differences between the chemically equivalent pair of phosphorus nuclei and the unique nucleus allows *all* the phosphorus parameters to be determined from the ^{19}F spectra, and in these cases the standard deviations are no larger than for fluorine parameters, suggesting the phosphorus chemical-shift difference is numerically reliable.

TABLE 1

N.m.r. parameters for cyclotriphosphazatrienes determined by iterative computation [a,b]

Compound	δ_F [c]	δ_P [d]	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	$^4J_{FF}(cis)$	$^4J_{FF}(trans)$	R.m.s. error	No. transitions [e] obs.	comp. [f]
cis-$P_3N_3F_3Cl_3$ (I)	−31·68	*g*	−1001·6 (0·2)	8·9 (0·1)	105·3 (0·2)	−1·0 (0·2)		0·85	27	44 (46)
cis-$P_3N_3F_3Br_3$ (II)	−22·24	*g*	−1051·6 (0·3)	3·7 (0·2)	83·1 (0·3)	−0·5 (0·3)		1·30	26	42 (44)
trans-$P_3N_3F_3Cl_3$ (III)	−30·81	0·06 [h]	−997·7 (0·3)	12·6 (0·2)	107·8 (0·3)	−1·5 (0·3)	12·5 (0·1)	0·75	62	99 (130)
			$\underline{-966\cdot1}$ (0·4)	$\underline{12\cdot1}$ (0·3)	$\underline{103\cdot7}$ (0·2)					
	$\underline{\underline{-29\cdot73}}$			$\underline{\underline{16\cdot0}}$ (0·2)						
trans-$P_3N_3F_3Br_3$ (IV)	−20·49	2·64	−1048·2 (0·3)	8·7 (0·2)	87·2 (0·3)	−2·3 (0·3)	11·9 (0·2)	0·83	63	103 (130)
		$\underline{3\cdot31}$	$-\underline{1042\cdot3}$ (0·4)	$\underline{10\cdot5}$ (0·3)	$\underline{77\cdot0}$ (0·2)					
	$\underline{\underline{-18\cdot26}}$			$\underline{\underline{13\cdot5}}$ (0·2)						
cis-$P_3N_3F_2Cl_4$ (V)	−31·01	18·50	−1002·5 (0·3)	11·2 (0·3)	100·2 (0·3)	−1·2 (0·3)		0·76	42	55 (66)
		$\underline{26\cdot65}$		$\underline{8\cdot8}$ (0·3)	$\underline{81\cdot6}$ (0·3)					
trans-$P_3N_3F_2Cl_4$ (VI)	−29·95	18·39	−998·8 (0·3)	14·0 (0·3)	97·6 (0·3)		12·5 (0·3)	0·75 [i]	47	51 (66)
		$\underline{26\cdot40}$		$\underline{12\cdot1}$ (0·3)	83·0 (0·3)					
trans-$P_3N_3F_2Br_4$ (VII)	−18·86	~−50 [h]	−1048·1 (0·1)	11·8 (0·1)	70·4 (0·1)		11·9 (0·1)	0·25	20	22 (22)
				$\underline{7\cdot5}$ (0·1)	*g*					
cis-$P_3N_3F_2Br_4$ (VIII) [j]	−21·19	*g*	−1051·2	5·7	77	*k*				
				$\underline{2\cdot8}$	*g*					
cis-$P_3N_3F_2Cl_2(NMe_2)_2$ (IX)	−64·89	18·90	−925·7 (0·3)	5·8 (0·3)	70·5 (0·4)	−1·1 (0·4)		0·97	46	63 (66)
		$\underline{26\cdot09}$		$\underline{8\cdot6}$ (0·3)	$\underline{67\cdot1}$ (0·3)					
trans-$P_3N_3F_2Cl_2(NMe_2)_2$ (X)	−66·34	18·95	−901·1 (0·5)	12·4 (0·5)	75·8 (0·6)		14·0 (0·6)	0·9	46	52 (63)
		$\underline{25\cdot55}$		$\underline{11\cdot5}$ (0·5)	$\underline{69\cdot1}$ (0·4)					
trans-$P_3N_3F_2Cl_2(NMe_2)_2$ (XI)	−71·32	$\left\{\begin{matrix}31\cdot27\\3\cdot61\end{matrix}\right\}$	−905·3 (0·2)	$\left\{\begin{matrix}14\cdot7\ [l]\\13\cdot2\ [l]\end{matrix}\right.$	$\left.\begin{matrix}g\\ \underline{82\cdot0}\ (0\cdot2)\end{matrix}\right\}$			0·54	30	46 (50)
cis-$P_3N_3F_2Cl_2(NMe_2)_2$ (XII) [m]	−73·61 [n]	31·90	−909·5 [n] (0·4)	15·1 [n] (0·3)	$\underline{82\cdot3}$ (0·3)			0·9	52	64 (64)
	−69·53	$\underline{4\cdot63}$	−904·6 (0·4)	13·3 (0·3)						

[a] The chemical shifts are in p.p.m. (see the Experimental section). The coupling constants are in Hz. The single underlining indicates a parameter involving a unique ^{31}P; the double underlining refers to a unique ^{19}F. [b] The numbers in brackets are the standard errors from the computer-fitting. [c] Estimated (from the spectra) to be accurate to ±0·01. [d] The relative values of δ_P are accurate to ±0·03 p.p.m., but the absolute values are only estimated to ±0·1 p.p.m. [e] For compounds (I)—(IV) and (VII) data for the ^{19}F region only are given. [f] Transitions of intensity >0·1. The number in brackets includes unassigned lines. [g] Not obtained. [h] These values are δ_P(unique) − δ_P(equiv.). [i] The ^{19}F transitions were weighted by 2 since they are considered to be more accurate than the ^{31}P transitions. [j] Data determined directly from the spectrum, not from computation. [k] Judged to be <1·5 Hz in magnitude. [l] The average of these coupling constants is accurate; the difference is uncertain (see the text). [m] $^2J_{FF} = -76{\cdot}0\ (\pm0{\cdot}4)$ Hz. [n] These results refer to the same ^{19}F nucleus.

---

[23] V. Mark, C. H. Dungan, M. V. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

Since the full information on ^{31}P chemical shifts of all the compounds studied here is not available, further discussion is not warranted.

Fluorine Chemical Shift.—In fluorinated cyclotriphosphazatriene spectra, there are usually two sharp lines in the fluorine region which are stronger than all the others and which are centred about the fluorine chemical shift. Consequently the values of δ_F reported in the literature are usually reliable if they are obtained from field-frequency locked spectra. Ranges of chemical shifts for PFX groups in cyclotriphosphazatrienes are fairly well defined for different X-substituents and are quoted in Table 2. Correlation between the electronegativity of X in a PFX group and the fluorine chemical shift is observed.[27] For the simple mixed halides the correlation is reasonable, but comparison with dimethylamino-substituted fluorides shows that π-bonding of X to phosphorus reduces the paramagnetic contribution to shielding at the fluorine nucleus, causing a shift to low frequency of that expected using electronegativity correlations alone. Similar effects occur for groups such as NCS and Ph which can also undergo π-interaction with phosphorus.

TABLE 2

^{19}F Chemical-shift ranges for the PFX group of cyclotriphosphazatrienes

X	Range of values for δ_F (p.p.m.)	Ref.
F	−67·7 to −73·6	3, 24, 25, this work
NMe_2	−59·2 to −66·4	2, 3, 26, this work
NCS	−49·6	25
Ph	−49·1 to 51·5	24
Cl	−29·7 to −31·7	3, 25, this work
Br	−18·2 to −22·3	3,[a] 25, this work

[a] Ref. 3 also gives one value at −15·9.

Smaller changes in chemical shift within these ranges are intimately associated with finer structural details, and these differences have been used to assign structures. For dimethylamino- and phenyl-cyclotriphosphazatrienes it has been shown conclusively [2,24,26] that fluorine groups in a *cis*-configuration with respect to the plane of the ring resonate to high frequency of those groups with a *trans*-configuration, whereas the opposite order is observed for the mixed halides. This is yet another manifestation of the '*cis*-effect' postulated earlier [28] and later modified to account for π-bonding interactions affecting reaction mechanisms.[24] Thus it would seem that a particular P–F bond is made more ionic by a dimethylamino group *cis* than by one *trans* or by a fluorine atom *cis* in dimethylamino-substituted compounds. In the case of the mixed halogeno-compounds, where chlorine and bromine are considered not to give strong π-back bonding, it is the fluorine that causes the low frequency shift. The theoretical reasons for this effect are not understood.

It is interesting to note that the ^{19}F chemical shift for (XI) is near to the average for (XII). This probably indicates that the variations are structural in origin.

Signs of Coupling Constants.—We regard the signs of the coupling constants, with the possible exception of $^4J_{FF}$ (*cis*), as well-established following the work reported here. All the signs of Table 1 are presented on the assumption that $^1J_{PF}$ is negative.[21,22] In the cases where we have carried out computation for a variety of signs, we found both $^3J_{PF}$ and $^2J_{PP}$ to be positive, which is in agreement with the work of Heffernan and White [7] and of Heatley and Todd.[8] The relative signs of $^1J_{PF}$ and $^3J_{PF}$ are, in fact, quite explicit in a number of our spectra (*e.g.* *cis*-$P_3N_3Cl_3F_3$). The positive sign for $^4J_{FF}$ (*trans*) was obtained from the study of (X), as described above. It may be noted that positive signs have been reported for ^4J(FPNPF) in $MeN(PF_2)_2$ [29] and $[MeNPF_2Bu^t]_2$.[30] The negative sign for $^4J_{FF}$(*cis*) is both less certain and less important, because of its small magnitude. The consistency with which the iterative computations result in a negative $^4J_{FF}$(*cis*) is regarded as reasonably good evidence for the sign, though some of the spectra appear to be virtually independent of sign. The sign of $^2J_{FF}$, obtained for (XII) is as expected [30,31] from results for other PF_2 groups.

One-bond (P,F) *Coupling.*—The values of $|^1J_{PF}|$ fall into four categories, for the groups PFBr, PFCl, $PFNMe_2$, and PF_2. Those for the first two cases are in well-defined regions, 1042—1052 Hz for PFBr, and 996—1002 Hz for PFCl (though Heatley and Todd [8] report 1012 Hz for $P_3N_3Cl_5F$). Within these categories the variations are consistent with the supposition that substituents *cis* to the F nucleus in question have little effect, but *trans*-substituents cause changes, the values of $|^1J_{PF}|$ being higher when there are *trans* Cl or Br atoms rather than F. However, this pattern is not followed in the case of Heatley and Todd's result,[8] which is appreciably higher than the values for (I) and (V) although the *trans*-substituents are the same in all three cases. The values for the $PFNMe_2$ and PF_2 groups are substantially smaller, being in the range 904—910 Hz for the latter (the value reported by Heffernan and White [7] for *gem*-$P_3N_3Cl_4F_2$ is appreciably higher, 934 Hz), and having values 901 and 925 Hz for the former. It is generally recognised [32] that $^1J_{PF}$ depends on several factors, including substituent electronegativity and the position of substituents in the periodic table (see, for example, ref. 33). The variations in the present

---

[24] C. W. Allen and T. Moeller, *Inorg. Chem.*, 1968, **7**, 2177, 2183.

[25] T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc.* (*A*), 1970, 2324.

[26] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.

[27] J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 1.

[28] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1677.

[29] R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

[30] R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.

[31] H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Comm.*, 1970, 671.

[32] G. Mavel, *Ann. Rep. N.M.R. Spectroscopy*, 1973, **5B**, 1.

[33] R. K. Harris, J. R. Woplin, M. Murray, and R. Schmutzler, *J.C.S. Dalton*, 1972, 1590.

examples cannot therefore be simply explained in terms of *s*-character. The order for $|^1J_{PF}|$ with PFBr > PFCl > PF_2 is in accord with previous results[33] for the $-SP(\dot{:}S)FX$ system, but the values for $PFNMe_2$ are substantially higher than anticipated. Variations in phosphorus hybridisation would be expected to cause geometry changes, and certainly the *X*-ray crystallography results[34,35] show (see also ref. 36) that the X–P–X angle increases in the series $P_3N_3F_6$ (99·3°), *cis*-$P_3N_3F_3Cl_3$ (99·8°), and *cis*-$P_3N_3F_3Br_3$ (100·3°); steric effects may also be of importance here, as well as electronegativity effects. More results are, however, needed before a link between $^1J_{PF}$ and geometry can be established.

Three-bond (P,F) *Coupling*.—Table 1 lists 24 values of $^3J_{PF}$, and although the accuracy is variable, there are sufficient data for detailed appraisal. For non-rigid structures such as diazadiphosphetidines and related compounds $^3J_{PF}$ has been found[37] to be strongly dependent on both stereochemistry and on the nature of the substituents. In the fluorinated cyclotriphosphazatrienes considered here the structure is rather more rigid, and discussion must centre on (*a*) the nature of X for the group PFX, (*b*) the nature of substituents at the other P atom involved in the coupling, plus their orientation (*cis* or *trans*) to the coupled F nucleus, and (*c*) similar effects for substituents at the uninvolved P atom. Since we have not studied any mixed chlorobromo-species, attention needs to be focussed separately on the brominated and chlorinated series (compounds containing NMe_2 groups being more complicated). The ranges of $^3J_{PF}$ for PFBr (2·8 to 13·5 Hz) and PFCl (8·5 to 16·0 Hz) groups overlap. Within these categories there are consistent trends with the nature and orientation (relative to the coupled F) of groups attached to the other P atoms. These may be summarised as additive contributions (in Hz) for replacements Br ⟶ F or Cl ⟶ F as follows:

	trans Br → F	*cis* Br → F	*trans* Cl → F	*cis* Cl → F
P involved in $^3J_{PF}$	+7	+1	+4	+0·5
P not involved in $^3J_{PF}$	+2·5	−1·5	+1·5	−2·5

Such quantitative data need to be accepted with caution in view of the variations and errors involved, but the consistency of the overall pattern is good and extends to the literature results[7,8] for $P_3N_3Cl_5F$ and *gem*-$P_3N_3Cl_4F_2$. Our values for $^3J_{PF}$ involving the fluorine of the $PFNMe_2$ group range from 5·8 to 12·4 Hz, while those involving a PF_2 group are markedly higher (13·3 to 15·1 Hz), but there is insufficient variety in the other substituents for detailed comment.

Fluorine–Fluorine Coupling.—The values of $^4J_{FF}$ fall into two distinct groups, *ca.* +12 and *ca.* −1 Hz, which can be assigned to *trans*- and *cis*-fluorine pairs respectively. There are no previously-reported values for this coupling in cyclotriphosphazatrienes, but the result (13·5 Hz) given[38] for 1,1,5-trimethyl-3,3,5,7,7-pentafluorocyclotetraphosphazatetraene was attributed to the *cis*-arrangement by analogy with perfluoromethylcyclohexane and other saturated organic molecules.[39] However our work shows this assignment is incorrect. In fact it is clear that $^4J_{FF}$ is extremely useful for structure determination in cyclophosphazenes. It may, of course, be suggested that the low magnitude for $^4J_{FF}(cis)$ is the result of competing mechanisms or pathways giving contributions of opposite sign. In this context it might be noted that a ' through-space ' effect would be negligible for *trans*-fluorines (separation[34] *ca.* 5·0 Å) but may become relevant for *cis*-fluorines (separation *ca.* 3·3 Å).

The magnitude and sign for $^2J_{FF}$, obtained only for compound (XII), are as expected, but our result is the first reported value for a cyclotriphosphazatriene.

Phosphorus–Phosphorus Coupling.—It was suggested[8] some years ago that $^2J_{PP}$ in cyclotriphosphazatrienes depends on the electronegativities of the four substituents at the phosphorus nuclei concerned. This relationship was placed on an empirical quantitative basis by Finer,[40] who assigned a parameter λ_L to each ligand L such that effects of the two ligands attached to a given phosphorus atom were additive. This idea correlated the observed coupling constants reasonably well, but Allen showed later[4] that there were serious errors for compounds containing only phenyl and fluorine substituents (see also ref. 1). These errors were attributed both to (*a*) non-additivity of the substituent effects, and to (*b*) the influence of substituents at the phosphorus atom not involved in the coupling. In view of the involvement of phosphorus orbitals in ring bonding, and possibly even direct overlap of phosphorus orbitals in the plane of the ring,[41] an effect on J_{PP} from the uninvolved phosphorus is not unreasonable. The data presented here (Table 1) throw further light on the factors which influence $^2J_{PP}$ in cyclophosphazatrienes. At least three facts should be noted.

(i) There is a significant, though small, influence of stereochemistry on J_{PP}. Thus the two values for (III) differ by *ca.* 4 Hz, and neither of them equal that for (I). Moreover *both* results for (VI) differ from the corresponding values for (V). The discrepancies appear to be larger for the brominated series—the two values for (IV) differ by *ca.* 10 Hz. Variations are also apparent for compounds (IX) and (X). Although experimental errors may be significant with respect to the discrepancies in some of the examples this cannot be true in all the cases.

(ii) The value of $^2J_{PP}$ for (V) (100·2 Hz) is, within

---

[34] P. Clare, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1974, 2071.

[35] M. W. Dougill, *J. Chem. Soc.*, 1963, 3211.

[36] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[37] R. K. Harris, J. R. Woplin, R. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft. Phys. Chem.*, 1972, **46**, 44.

[38] T. N. Ranganathan, S. M. Todd, and N. L. Paddock, *Inorg. Chem.*, 1973, **12**, 316.

[39] R. J. Abraham, *J. Chem. Soc.* (*B*), 1969, 1022.

[40] E. G. Finer, *J. Mol. Spectroscopy*, 1967, **23**, 104.

[41] D. R. Armstrong, G. H. Langmuir, and P. G. Perkins, *J.C.S. Chem. Comm.*, 1972, 464.

experimental error, equal to that reported by Heffernan and White [7] for *gem*-$P_3N_3Cl_4F_2$ (100 Hz), which has the same grouping (PCl_2) at the uninvolved phosphorus. Thus the coupling J(PFCl, PFCl) cannot be distinguished from $J(PF_2, PCl_2)$, and it appears that for the chlorofluoro-compounds each similar substituent change affects J_{PP} by the same factor, even for multiple substitution.

(iii) The effects of substituents at the uninvolved phosphorus atom are clearly important. As these change from FCl to Cl_2 $^2J_{PP}$ decreases from 105·3 Hz (I) to 100·2 Hz (V) for J(PFCl, PFCl) and from 81·6 Hz (V) to 78·3 Hz [8] ($P_3N_3Cl_5F$) for $J(PFCl, PCl_2)$. The introduction of a second Cl atom at the uninvolved phosphorus reduces $^2J_{PP}$ by a factor 0·95 and 0·96, respectively, in the two examples.

The change in $^2J_{PP}$ from *gem*-$P_3N_3Cl_4F_2$ (100 Hz) [7] to $P_3N_3Cl_5F$ (78·3 Hz) [8] represents a reduction by a factor of 0·78 when Cl replaces F as a substituent. If this reduction factor and that for replacement at the uninvolved phosphorus, given under (iii) above, are considered to be constants, the value of $^2J_{PP}$ in $P_3N_3F_6$ may be estimated to be *ca.* 179 Hz (the observed spectrum is suggestive of a slightly lower value than this). Data for (XII) and for $P_3N_3Cl_5NMe_2$ (49·7 Hz) [8] may be used to estimate reduction factors for the replacement of F by NMe_2; these are found to be 0·63 for a directly-bonded substituent and 0·97 for substitution at the uninvolved phosphorus. The four reduction factors obtained suffice to correlate all our other results (excluding the brominated compounds) for $^2J_{PP}$ reasonably well, plus those reported [5,42] for $P_3N_3F_5NMe_2$ and *cis*-$P_3N_3Cl_4(NMe_2)_2$. A similar treatment involving phenyl groups reduces but does not eliminate the discrepancies reported by Allen,[4] so clearly the substituent effects cannot be entirely treated as transferable reduction factors when there is multiple substitution. The geometric effects discussed above under (ii) also, of course, complicate the pattern. The use of empirical reduction factors, if valid, may be related to *s*-electron participation in bonding (and hence to electronegativity) and its influence on the contact contribution to coupling in the manner discussed by Finer [40] for his substituent parameters. The reduction factor for directly-bonded substituents incorporates effects at *both* the phosphorus nuclei involved in the coupling, as does the reduction factor for substituents bonded to the uninvolved phosphorus.

Conclusions.—It has proved feasible to obtain reasonably accurate n.m.r. parameters from iterative computer-fitting of n.m.r. spectra for a range of fluorinated cyclotriphosphazatrienes with complex spin systems. The parameters (in particular the coupling constants) obtained here do show marked structural dependencies. Such parameters should prove to be valuable aids to structure assignments in future. The parameter $^4J_{FF}$ is especially sensitive to the *cis*- or *trans*-orientation of the relevant P–F bonds.

EXPERIMENTAL

Details of the preparation and separation of these compounds, together with some preliminary n.m.r. data, have been discussed earlier.[2,3] Several spectrometers were used in this work. The ^{19}F spectra of the mixed halides (I)—(VIII) were recorded at 94·075 MHz using a Varian HA100 spectrometer, modified for extended locking using a Hewlett–Packard 3310 A voltage-controlled function generator as sweep oscillator in conjunction with a Muirhead decade oscillator for generation of sidebands. The internal field-frequency locking resonance was provided by $CFCl_3$ which was also the solvent and the reference compound. The $^{19}F-\{^1H\}$noise-decoupled spectra of (IX), (XI), and (XII) were also obtained using a Varian HA100 spectrometer with a double-tuned network,[43] a Schlumberger 3005 frequency synthesizer, and a Hewlett–Packard noise generator. The ^{19}F signal of C_6F_6 was employed for field/frequency locking purposes. For the HA100 ^{19}F spectra the chart paper was calibrated at intervals, in order to correct for recorder non-linearity. The $^{31}P-\{^{14}N\}$ spectra of (IV)—(VI) and the $^{31}P-\{^1H\}$ spectra of (IX), (XI), and (XII) were obtained at 40·5 MHz using a Varian XL100 spectrometer, with the ^2H signal of C_6D_6 providing a field/frequency lock. The ^{14}N frequency was supplied by a Schlumberger frequency synthesizer, but the ^1H noise-decoupling experiment used the gyrocode arrangement of the spectrometer. The $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ spectra of (X) were recorded using a Bruker spectrometer operating at 84·67 MHz for ^{19}F and 36·43 MHz for ^{31}P. Field/frequency locking was achieved using the ^{19}F signal of internal C_6F_6.

The ^{19}F spectra were recorded at a sweep rate of *ca.* 0·5 Hz s^{-1} or less on a scale of *ca.* 5 Hz cm^{-1} or less and the values of transition frequencies used in the calculations are the mean of three spectra. The conditions for the ^{31}P spectra were not, in general, so rigorous.

For the ^{19}F work on compounds (I)—(VIII) the samples and solvents were distilled into the n.m.r. tubes using a vacuum line, and the pressure then adjusted to atmospheric with dry nitrogen; the tubes were then capped, not sealed. For the ^{31}P work on (IV)—(VI), and for all the experiments on (IX)—(XII) the sample tubes were degassed using the freeze-pump-thaw technique and then sealed. Compounds (IX)—(XII) were studied in solution in CCl_4, with the appropriate substance for field/frequency locking added.

The ^{31}P chemical shifts, δ_P, of (IX)—(XII) were obtained (Table 1) with respect to 85% H_3PO_4 by measuring the resonance frequencies, converting into a field such that protons in Me_4Si resonate exactly at 100 MHz, subtracting 40,480,720 Hz [44] and converting into p.p.m. (see ref. 45). The ^{19}F chemical shifts, δ_F, are presented in Table 1 in p.p.m. with respect to the signal of $CFCl_3$. In the case of compounds (IX)—(XII) the shifts were actually measured with respect to the ^{19}F signal of C_6F_6 and converted using $\delta_F(C_6F_6) = -164·9$.[46] Both δ_P and δ_F are presented in Table 1 such that a positive sign implies the substance resonates to high frequency of the reference.

---

[42] R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 1965, 7193.

[43] J. R. Woplin, Ph.D. Thesis, University of East Anglia, 1970.

[44] M. I. M. Wazeer and E. M. McVicker, unpublished work.

[45] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 135.

[46] C. H. Dungan and J. R. Van Wazer, 'Compilation of Reported ^{19}F N.M.R. Chemical Shifts,' Wiley–Interscience, 1970.

The magnetic field at which the HA100 and XL100 spectrometers operated for compounds (IX), (XI), and (XII) differed slightly (equivalent ^1H frequencies differ by *ca.* 60 kHz). However, discrepancies in transition frequencies in our ^{31}P and ^{19}F spectra consequent on this variation were smaller than the experimental error in measuring spectra. Hence the line positions from the two spectra (^{31}P and ^{19}F) were used together in the computer iteration, without any correction for the field difference. Computation of all the spectra was carried out using the computer program LACX [except for (XII), when UEANMR was used], plus a plotting routine which assigns to each line a Lorentzian shape of a specified width (common to each transition of a given spectrum). The standard errors for the coupling constants (from the computer fitting), given in Table 1, probably represent minimum estimates.

We are grateful to the University of Braunschweig for the opportunity to obtain the n.m.r. spectra of (X), to Dr. B. Green for providing samples of compounds (IX)—(XII), and to Drs. M. Kinns and K. M. Worvill for assistance with computation. We thank Mr. P. W. Haylett (East Anglia) and Mr. A. Healy (Nottingham) for assistance in recording the spectra. One of us (M. I. M. W.) acknowledges with thanks the receipt of a scholarship from the Commonwealth Scholarship Commission in the U.K.

[4/1560 *Received, 29th July,* 1974]