# Preparation and Nuclear Magnetic Resonance Spectra of Symmetrical Spin Systems containing Phosphorus: Bis(fluorophosphinothioyl) Sulphides

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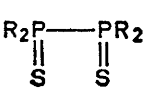
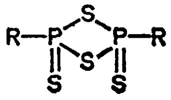
The reaction of phenyltetrafluorophosphoranes with cyclodiphospha(v)thianes affords a convenient route to bis(fluorophosphinothioyl) sulphides, $[RFP(:S)]_2S$. Proton, $^{19}F$, and $^{31}P$ n.m.r. spectra were recorded for the compounds with R = Me, Et, and Ph, each of which exists as a mixture of (±)- and *meso*-forms. The analysis of the spectra of these symmetrical spin systems is discussed. Heteronuclear double-resonance assisted the spectral analyses greatly. The coupling constants, including many signs, are reported and discussed. The values of $J_{PF}$, $J_{PP}$, and $J_{FF}$ are appreciably different for the two stereoisomers of a given compound.

PHOSPHORUS–SULPHUR compounds containing a P–P or P–S–P linkage are relatively rare. Known examples include the phosphorus sulphides, diphosphine disulphides (I),[1] and cyclodiphosphathianes (II).[2] Derivatives containing fluorine bonded to phosphorus are much rarer, only $(F_2P)_2S$,[3,4] $F_2P{\cdot}S{\cdot}P(:S)F_2$,[5] and $[F_2P(:S)]_2S$ [6] having been reported. In the hope of preparing further derivatives, we have treated several compounds of types (I) and (II) with fluorophosphoranes, $RPF_4$ and $R_2PF_3$, and investigated the products by n.m.r. spectroscopy.


(I)


(II)

Phenyltetrafluorophosphorane, $PhPF_4$, was treated with a number of diphosphine disulphides, $R_4P_2S_2$ (R = Me, Et, or Ph). In all cases the principal products obtained were $PhPF_2$, $(PhP)_5$, $PhPSF_2$, and $R_2PSF$, all of which could be readily identified by their $^{19}F$ and/or $^{31}P$ n.m.r. spectra. The amounts of $(PhP)_5$ and $PhPSF_2$ were dependent on the ratio of the reactants employed, formation of $PhPSF_2$ being favoured when an excess of phosphorane was present, $(PhP)_5$ being more readily formed when an excess of diphosphine disulphide was used. In the reaction of an excess of $PhPF_4$ with $Me_4P_2S_2$, $Me_2PF_3$ was also obtained.

These observations can be explained by the following reaction scheme. The first reaction is a reduction of the $PhPF_4$ to $PhPF_2$. The $PhPF_2$ then reacts further with

$$PhPF_4 + R_4P_2S_2 \longrightarrow PhPF_2 + 2R_2PSF \qquad (1)$$

the diphosphine disulphide, according to either of two possible reactions (2) and (3). Reaction (2) will occur

$$2PhPF_2 + R_4P_2S_2 \longrightarrow 2PhPSF_2 + R_4P_2 \qquad (2)$$

or

$$PhPF_2 + R_4P_2S_2 \longrightarrow (PhP)_n + 2R_2PSF \qquad (3)$$

more readily when an excess of $PhPF_4$ is used, reaction (3) more readily with an excess of diphosphine disulphide. An analogous reaction to (3) has been reported for $PhPCl_2$.[7] The diphosphine, $R_4P_2$, formed from reaction (2) may then react further with $PhPF_4$ according to (4).

$$3PhPF_4 + R_4P_2 \longrightarrow 3PhPF_2 + 2R_2PF_3 \qquad (4)$$

Reactions with $Ph_2PF_3$ proceeded basically in a similar fashion. The analogous reactions to (1), (2), and (3) are then (5), (6), and (7). An alternative reaction in this

$$Ph_2PF_3 + R_4P_2S_2 \longrightarrow Ph_2PF + 2R_2PSF \qquad (5)$$

$$2Ph_2PF + R_4P_2S_2 \longrightarrow 2Ph_2PSF + R_4P_2 \qquad (6)$$

$$2Ph_2PF + R_4P_2S_2 \longrightarrow Ph_4P_2 + 2R_2PSF \qquad (7)$$

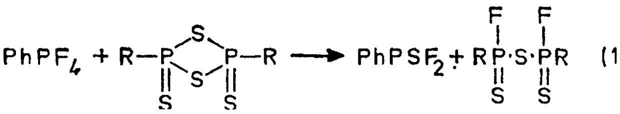
case however is the disproportionation of $Ph_2PF$,[8] which is known to occur readily according to (8). The

$$3Ph_2PF \longrightarrow Ph_4P_2 + Ph_2PF_3 \qquad (8)$$

observation of $R_2PSF$ and $Ph_2PSF$ in the reaction products is evidence that reactions (5) and (6) are occurring, though the observation of $Ph_4P_2$ could be explained by either reaction (7) or (8). Since $Et_4P_2$ but not $Et_2PF_3$ was observed in the reaction of $Ph_2PF_3$ with $Et_4P_2S_2$ the possibility of a reaction (9) analogous to reaction (4) may be ruled out.

$$3Ph_2PF_3 + R_4P_2 \longrightarrow 3Ph_2PF + 2R_2PF_3 \qquad (9)$$

The reaction of phenyltetrafluorophosphorane with cyclodiphosphathianes (II) proceeded smoothly according to (10) to give examples of the new class of compounds bis(fluorophosphinothioyl) sulphides, (III), in yields of *ca.* 60%. While this work was in progress the synthesis of these compounds was also reported by


(10)

(II) a; R = Me
b; R = Et
c; R = Ph

(III) a; R = Me
b; R = Et
c; R = Ph

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[1] A. H. Cowley, *Chem. Rev.*, 1966, **66**, 617.

[2] E. Fluck and H. Binder, *Z. anorg. Chem.*, 1967, **354**, 113.

[3] G. N. Bokerman, Ph.D. Thesis, University of Michigan, 1968.

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

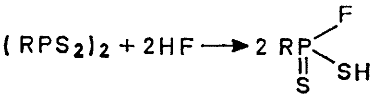
[5] R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Comm.*, 1969, 424.

[6] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1970, **9**, 379.

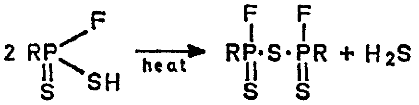
[7] L. Maier, *Chem. Ber.*, 1961, **94**, 3051.

[8] C. Brown, M. Murray, and R. Schmutzler, *J. Chem. Soc.* (*C*), 1970, 878.

Roesky[9] who used a two-stage synthesis according to reactions (11) and (12), with overall yields of only 4%.



$$(RPS_2)_2 + 2HF \longrightarrow 2\,RP(S)(F)SH \qquad (11)$$



$$2\,RP(S)(F)SH \xrightarrow{heat} RP(S)(F)\cdot S\cdot P(S)(F)R + H_2S \qquad (12)$$

The methyl and ethyl derivatives (IIIa) and (IIIb) are distillable liquids with a characteristic smell, and could be obtained analytically pure. The phenyl derivative (IIIc) underwent considerable decomposition on distillation at *ca.* 150°/0·1 mmHg and could only be characterised by n.m.r. spectroscopy in a mixture with impurities, principally $PhPSF_2$.

Since the compounds of type (III) contain two asymmetric phosphorus atoms they should exist as two stereoisomers which may be referred to as (±)- and *meso*-forms. The presence of both isomers (in roughly equal amounts) is shown clearly by the n.m.r. spectra, and could be confirmed by gas chromatography, though we were unable to separate the isomers. We have studied the n.m.r. spectra of the mixtures, and will refer to the two isomers as A and B, defining isomer A as the one with the smaller magnitude of $^1J_{PF}$ (solvent effects are, we feel, more likely to reverse the order of chemical shifts than of coupling constants). An assignment of A and B to (±)- and *meso*-forms was not possible.

TABLE 1

$^{19}F$ and $^{31}P$ Nuclear spin parameters for compounds of the type $[RFP(S)]_2S$ [a]

| | (IIIa; R = Me) [c] | | (IIIb; R = Et) [d] | | (IIIc; R = Ph) [e] | |
|---|---|---|---|---|---|---|
| | Isomer A | Isomer B | Isomer A | Isomer B | Isomer A | Isomer B |
| $\phi_F$* | +41·59 | +42·08 | +49·21 | +49·67 | +48·76 | +48·70 |
| $\delta_P$ | −102·27 | −100·96 | −113·63 | −112·37 | −100 [f] | |
| $^1J_{PF}$ [b] | −1119·0 | −1124·2 | −1137·8 | −1141·0 | −1128·6 | −1131·2 |
| $^3J_{PF}$ | −2·1 | −5·8 | −2·8 ± 0·5 | −4·0 ± 0·5 | −4·4 | −4·4 |
| $\lvert ^2J_{PP}\rvert$ [g] | 13·2 ± 0·1 | 18·4 ± 0·2 | 14·0 ± 0·5 | 17·7 ± 0·5 | 14·2 ± 0·3 | 13·9 ± 0·3 |
| $\lvert ^4J_{FF}\rvert$ [g] | 9·2 ± 0·1 | 5·6 ± 0·2 | 8·8 ± 0·5 | 5·5 ± 0·5 | 6·8 ± 0·1 | 8·2 ± 0·2 |

[a] Chemical shifts $\phi_F$* and $\delta_P$ are in p.p.m. from the resonances of $CCl_3F$ and 85% $H_3PO_4$ respectively. They are positive when the sample signal is at lower frequency than the reference signal. Coupling constants are in Hz. Values of $^1J_{PF}$ and $^3J_{PF}$ are accurate to ±0·5 Hz and ±0·1 Hz respectively except where stated. [b] Assumed to be negative. [c] $\delta_P$ From $^{31}P$-{$^1H$} spectra at 36·43 MHz. Other data from $^{19}F$-{$^1H$} spectra at 94·075 MHz. [d] $\phi_F$* From $^{19}F$ spectra at 56·44 MHz. Other data from $^{31}P$-{$^1H$} spectra at 36·43 MHz. [e] $\delta_P$ From $^{31}P$ spectra at 24·29 MHz. Other data from $^{19}F$-{$^1H$} spectra at 94·075 MHz. [f] Isomers not resolved. [g] $\lvert ^2J_{PP}\rvert$ and $\lvert ^4J_{FF}\rvert$ are not distinguished by the spectral analysis.

Roesky[9] gives the following approximate parameters: (IIIa) $\phi_F* = +40·5$, $^1J_{PF} = 1129$ (±10%); (IIIb) $\phi_F* = +48·1$, $^1J_{PF} = 1146$ (±10%).

The stable conformations of compounds of type (III) are unknown. It might be argued that the S=P–S–P=S chain will be planar and *trans*, since this allows some electron delocalisation. Moreover 1,3-interactions between the remaining substituents will be less than in the corresponding cases of substituted propanes because of the size of the intervening sulphur atom in (III). However a skew form (or a *cis*-form) cannot be ruled out.

*Spectral Analysis*.—The full spin systems of the compounds (III) are complex, and the spectra are further complicated by the presence of the two isomers, so it proved essential to remove the effects of the protons from the spectra by $^{19}F$-{$^1H$} or $^{31}P$-{$^1H$} double resonance. Such decoupling leaves an $[AM]_2$ spin system in each case ($A \equiv {}^{31}P$ and $M \equiv {}^{19}F$). The properties of this spin system are well known and require little comment. The A and the M parts are identical in appearance. Each part is symmetrical about its centre. The magnitudes of all the coupling constants can be obtained by direct measurement of the spectra, but some ambiguities remain: (*a*) the only relative signs that are obtained are those of the two (A,M) coupling constants, $J_{AM}$ and $J'_{AM}$, and (*b*) no distinction can be made between $J_{AA}$ and $J_{MM}$. In principle all the relative signs could be found by A-{M} or M-{A} multiple resonance, but because proton decoupling was also required this would need heteronuclear triple resonance (which we were unable to perform with our instruments). Figure 1 shows the $^{19}F$ single resonance and $^{19}F$-{$^1H$} double resonance spectra of compound (IIIc). The spectra are dominated by the large values of $\lvert ^1J_{PF}\rvert$. The assignment of lines to the two isomers is straightforward because the values of $J_{FF}$ and $J_{PP}$ differ significantly. Three of the weaker lines are obscured by the stronger lines, but this does not prevent a complete analysis being achieved. The spectra of the two isomers are better separated for compounds (IIIa) and (IIIb). The results of the spectral analyses are given in Table 1.

In the cases of compounds (IIIb) and (IIIc) the proton spectra were not completely analysed: (IIIc) gave a complex band in the aromatic region around $\delta_H = +7·57$ p.p.m., while (IIIb) shows resonances at $\delta_H = 1·36$ p.p.m. due to $CH_3$ protons (with $\lvert ^3J_{PH}\rvert = 27·5$ Hz and $\lvert ^3J_{HH}\rvert = 7·5$ Hz). The $CH_2$ region for (IIIb) is very complex and only an approximate chemical shift ($\delta_H = 2·65$ p.p.m.) was noted. The case of (IIIa) proved to be more amenable to a full treatment. The spectra of the two isomers overlapped considerably, but the use of benzene as a solvent produced a sufficient relative chemical shift that analysis became feasible. Figure 2 shows the $^1H$ spectrum of the solution used for analysis.

[9] H. W. Roesky, *Chem. Ber.*, 1968, **101**, 3679.

Information was first obtained from $^{19}F\text{-}\{^1H\}$ double resonance spectra, as described above. Then $^1H\text{-}\{^{31}P\}$ and $^1H\text{-}\{^{19}F\}$ experiments were attempted. These were not so successful as the $^{19}F\text{-}\{^1H\}$ work because of the large region of frequency over which irradiation was necessary (due to the large value of $|^1J_{PF}|$). The results are shown in Figure 3. In principle, the decoupled spectra are of the $[MX_3]_2$ and $[AX_3]_2$ type for $^1H\text{-}\{^{31}P\}$ and $^1H\text{-}\{^{19}F\}$ double resonance respectively ($X \equiv {}^1H$).

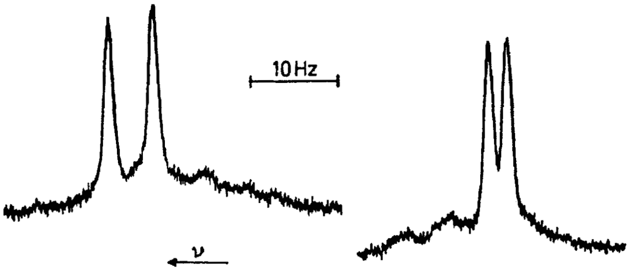


FIGURE 1a 94·075 MHz $^{19}F$ Room-temperature single-resonance n.m.r. spectrum of $\mathrm{PhPF(:S){\cdot}S{\cdot}PF(:S)Ph}$, (IIIc) (both isomers). The partial spectrum to the left is the high-frequency region; the part at the right is the low-frequency region. The two regions are separated by *ca.* $|^1J_{PF}| \approx 1100$ Hz

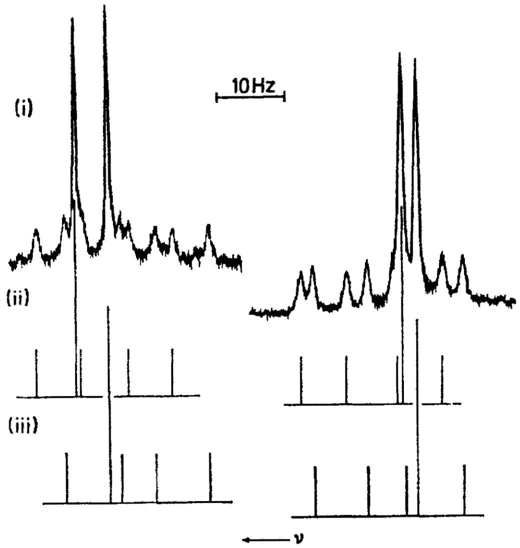


FIGURE 1b Observed and computed proton-decoupled 94·075 MHz $^{19}F$ spectrum of $\mathrm{PhPF(:S){\cdot}S{\cdot}PF(:S)Ph}$, (IIIc). (i) Full observed spectrum, high and low frequency regions; (ii) Computed spectrum of isomer B; (iii) computed spectrum of isomer A

Since coupling between protons on different methyl groups is over six chemical bonds it is probably negligible, *i.e.* $J_{XX} = 0$ may be assumed. The characteristics of spectra of this type are well-known;[10] the principal feature of the X region of an $[AX_3]_2$ spectrum with $J_{XX} = 0$ is a strong doublet of separation $|N_{AX}| = |J_{AX} + J'_{AX}|$. Such splittings for the two isomers can be readily picked out in Figure 3. There is ambiguity of pairing the strong lines, but an assumption that values of $N$ for the two isomers would be close proved to be correct.

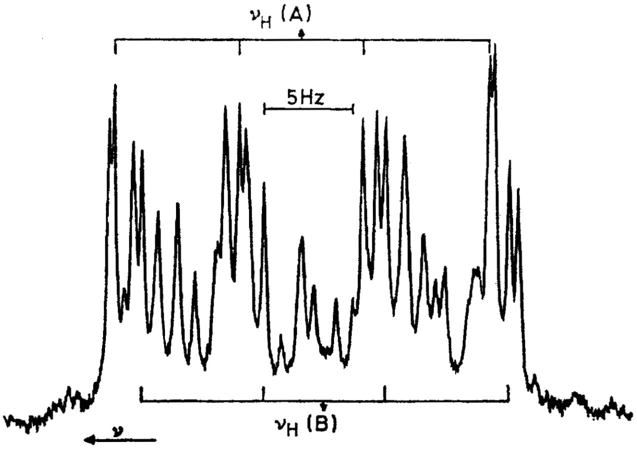


FIGURE 2 100 MHz $^1H$ n.m.r. spectrum of $\mathrm{MePF(:S){\cdot}S{\cdot}PF(:S)Me}$, (IIIa) showing the $N$ doublet lines for each isomer

More accurate values of $|N_{AX}|$ and $|N_{MX}|$ could then be obtained from the single resonance $^1H$ spectrum (Figure 2). The full spin system for each isomer is $[AMX_3]_2$; the spectra of some similar systems have already been discussed by Mann.[11] * Use of the 'X approximation'

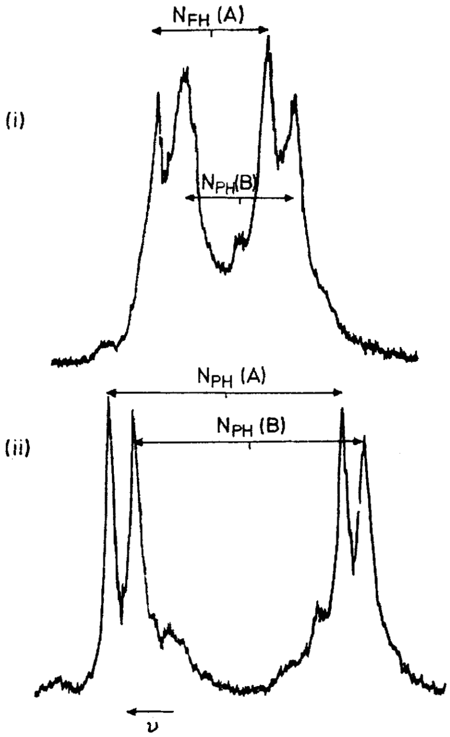


FIGURE 3 Double resonance spectra of $\mathrm{MePF(:S){\cdot}S{\cdot}PF(:S)Me}$, (IIIa) recorded at 100 MHz. (i) $^1H\text{-}\{^{31}P\}$ Spectrum. (ii) $^1H\text{-}\{^{19}F\}$ Spectrum. The $N$ doublets for the two isomers are indicated in each case. Noise decoupling was used, the noise bandwidth being 135 Hz

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* The cases described here are more amenable to extensive factorization than that studied by Mann.[11] He examined an $[AMX_{18}]_2$ case with $|L_{AM}| \gg |J_{MM}|$, but $|J_{AA}|$ was actually larger than $|L_{AM}|$, whereas for our compounds $|J_{AM}| \gg$ all other coupling constants.

[10] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[11] B. E. Mann, *J. Chem. Soc.* (*A*), 1970, 3050.

shows that there will be four lines showing splittings $|N_{AX}|$ and $|N_{MX}|$ each having $\frac{1}{16}$th of the total X intensity for the isomer. These arise from spin states in which the two A nuclei have the same spin component and the two M nuclei have the same spin component. These intense lines are indicated in Figure 2. Advantage may then be taken of the fact that $|{}^1J_{PF}|$ is large. This means that there is no mixing between spin states in which the AAMM spins are αβαβ, βαβα, βααβ, and αββα. The first two of these spin states give X lines separated by $|L_{AX} + L_{MX}|$ where $L_{AX} = J_{AX} - J'_{AX}$ and $L_{MX} = J_{MX} - J'_{MX}$. The other two spin states give X lines separated by $|L_{AX} - L_{MX}|$. These lines will also contain $\frac{1}{16}$th of the total X intensity each. Since it is anticipated that ${}^4J_{PH}$ and ${}^5J_{FH}$ will be small the four lines of separation $|L_{AX} + L_{MX}|$ and $|L_{AX} - L_{MX}|$ must be sought close to the lines of separation $|N_{AX}|$ and $|N_{MX}|$. There will, in fact, be some ambiguity between the '*N* lines' and the '*L* lines' but at this point it is best to compute the whole X spectrum for the various cases and see which corresponds to reality (computer iteration was not used). Explicit expressions can, in fact, be given for the remaining lines (there will be $[ax_3]_2$ and $[mx_3]_2$ subspectra) and these can be used as checks. Figure 4 shows computed proton spectra for the two isomers of (IIIa). The $^{19}F$ spectra were also computed, and the high frequency half is compared with the observed spectrum in Figure 5. The agreement is good, though not perfect. The parameters are given in Tables 1 and 2.

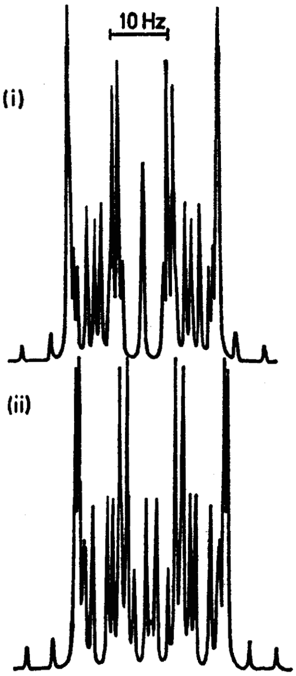

FIGURE 4 Computed $^1H$ n.m.r. spectra for $MePF(:S){\cdot}S{\cdot}PF(:S)Me$, (IIIa). (i) Isomer A. (ii) Isomer B. The spectra are correctly offset to correspond to the observed spectrum (see Figure 2.)

The signs of the coupling constants are only obtained by this analysis in pairs—${}^1J_{PF}$ *vs.* ${}^3J_{PF}$, ${}^2J_{PH}$ *vs.* ${}^4J_{PH}$, and ${}^3J_{FH}$ *vs.* ${}^5J_{FH}$. The signs of ${}^1J_{PF}$, ${}^2J_{P(V)H}$, and ${}^3J_{FH}$ are normally negative, negative, and positive respectively. We have confirmed these relative signs for compound (IIIa) by $^1H$-$\{^{19}F\}$ and $^1H$-$\{^{31}P\}$ selective decoupling experiments, so that Tables 1 and 2 give absolute signs (relying only on, say, the sign of ${}^1J_{PF}$). The signs of $J_{PP}$ and $J_{FF}$ remain unknown. In principle there is also ambiguity as to the assignment of the coupling constants within the pairs, *e.g.* one cannot distinguish between ${}^3J_{FH}$ and ${}^5J_{FH}$. However, comparison with literature values for related molecules leaves doubt only in the cases of $J_{PP}$ and $J_{FF}$. In this instance we tentatively assign $J_{PP}$ the larger magnitude on the grounds that the values of $J_{FF}$ are then very similar to those for $F_2PSPF_2$[4] and $F_2P(S)SPF_2$.[5]

TABLE 2

$^1H$ N.m.r. parameters for bis[fluoro(methyl)phosphinothioyl] sulphide [a]

| | Isomer A | Isomer B |
|---|---|---|
| $\delta$ | +2·097 | +2·083 |
| ${}^2J_{PH}$ | −14·5 | −14·5 |
| ${}^4J_{PH}$ | +0·5 | +0·75 |
| ${}^3J_{FH}$ | +6·7 | +6·6 |
| ${}^5J_{FH}$ | +0·25 | +0·3 |

[a] $\delta_H$ Is in p.p.m. from the resonance of tetramethylsilane (TMS), positive when the TMS line is at the lower frequency. Coupling constants are in Hz. All values are ±0·1 Hz.

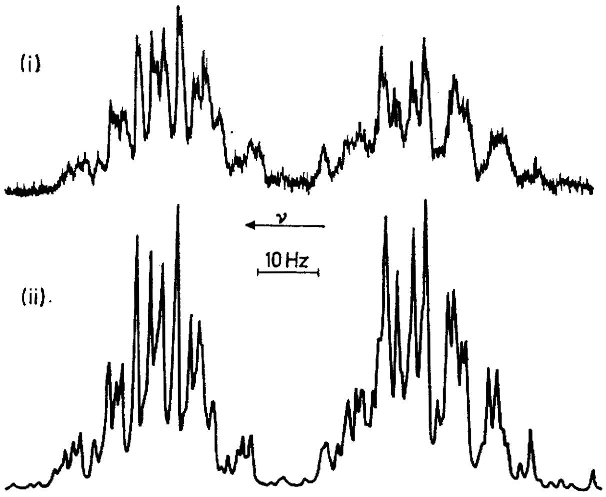

FIGURE 5 High frequency region of the 94·075 MHz $^{19}F$ spectrum for $MePF(:S){\cdot}S{\cdot}PF(:S)Me$, (IIIa). The band due to isomer A is to high frequency of that due to isomer B. (i) Observed spectrum. (ii) Computed spectrum

## EXPERIMENTAL

The fluorophosphoranes used in the present work were prepared by the reaction of halogenophosphines with arsenic or antimony trifluoride as described in the literature.[12] Diphosphine disulphides were prepared by the reaction of Grignard reagents with $PSCl_3$,[1] and dithiophosphonic acid anhydrides by the reaction of $H_2S$ with thiophosphonic acid dichlorides.[13] Reactions of phosphoranes with P–S compounds were carried out by refluxing the reactants in an

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[12] R. Schmutzler, *Inorg. Synth.*, 1967, **9**, 63.

[13] Houben-Weyl, 'Methoden der Organischen Chemie,' Georg Thieme Verlag, Stuttgart, 1963, vol. XII/1, p. 615.

atmosphere of dry nitrogen for 2—3 h. A typical example is the reaction of $PhPF_4$ with $Me_4P_2S_2$: 6·2 g (0·033 mol) of $Me_4P_2S_2$ were heated with 18·4 g (0·1 mol) of $PhPF_4$ to reflux for 3 h. The diphosphine disulphide dissolved, and on cooling a small amount of solid separated which was identified as $(PhP)_5$ by $^1H$ and $^{31}P$ n.m.r. ($\delta_P = +4·0$ p.p.m. *cf.* lit.[14] $\delta_P = +4·6$ p.p.m.). The $^{19}F$ n.m.r. spectrum of the liquid showed signals due to $PhPSF_2$ (doublet: $\phi_F{}^* = 47·0$ p.p.m., $|J_{PF}| = 1156$ Hz, *cf.* lit.[15] $\phi_F{}^* = 46·1$ p.p.m., $|J_{PF}| = 1140$ Hz), $PhPF_4$ (doublet: $\phi_F{}^* = 55·0$ p.p.m., $|J_{PF}| = 981$ Hz, *cf.* lit.[16] $\phi_F{}^* = 53·9$ p.p.m., $|J_{PF}| = 963$ Hz), $Me_2PSF$ (doublet of septets: $\phi_F{}^* = 76·5$ p.p.m., $|J_{PF}| = 992$ Hz, *cf.* lit.[15] $\phi_F{}^* = +75·7$ p.p.m, $|J_{PF}| = 985$ Hz), and $PhPF_2$ (doublet: $\phi_F{}^* = 92·5$ p.p.m., $|J_{PF}| = 1184$ Hz, *cf.* lit.[17] $\phi_F{}^* = 92·3$ p.p.m., $|J_{PF}| = 1173$ Hz). Distillation of the liquid at atmospheric pressure yielded two fractions, the first boiling at 60°, the second at 120—140°. The first was confirmed as $Me_2PF_3$ by its $^1H$ n.m.r. spectrum (broad doublet: $\delta_H = +1·76$ p.p.m., $|J_{PH}| = 16·2$ Hz, *cf.* lit.[16,18] b.p. 63°, $\delta_H = +1·76$ p.p.m., $|J_{PH}| = 17·0$ Hz. The effects of (F,H) coupling are lost due to intermolecular exchange processes [19,20]). The second fraction was confirmed as $PhPF_4$ and $Me_2PSF$ by its $^{19}F$ n.m.r. spectrum.

Other reactions were carried out similarly, and all n.m.r. data agreed well with literature values. For $Et_2PSF$, obtained from the reactions of $PhPF_4$ and $Ph_2PF_3$ with $Et_4P_2S_2$, $^{19}F$ n.m.r. values have not been published previously. The values we obtained were: doublet of quintets, $\phi_F{}^* = 93·4$ p.p.m., $|J_{PF}| = 1020$ Hz, $|J_{FH}| = 6·6$ Hz.

*Preparation of Compounds* (III).—*P,P'*-Dimethylcyclodiphospha(v)thiane (IIa) (22 g, 0·1 mol) and phenyltetrafluorophosphorane (28 g, 0·15 mol) were heated to reflux for 2 h. The resulting clear liquid was fractionally distilled, yielding a mixture of $PhPF_4$ and $PhPSF_2$ as the more volatile fraction, and 13·3 g (59%) of (IIIa), b.p. 88—90°/2 mm. (Found: C, 10·9; H, 2·8; F, 16·5; P, 25·7. $C_2H_6F_2P_2S_3$ requires C, 10·6; H, 2·7; F, 16·8; P, 27·4%).

Compounds (IIIb) and (IIIc) were prepared similarly from $PhPF_4$ with (IIb) and (IIc) respectively. The yield for (IIIb) is 44·1%; b.p. 75°/0·05 mmHg (Found: P, 24·8, 24·6; S, 37·5, 37·2. $C_4H_{10}F_2P_2S_3$ requires P, 24·4; S, 37·8%). Compound (IIIc) was not obtained pure, so no analyses were carried out.

Initial $^1H$, $^{19}F$, and $^{31}P$ n.m.r. spectra were run at 60, 56·4, and 24·3 MHz respectively on a Perkin-Elmer R10 spectrometer,* using 5 mm O.D. tubes for the $^1H$ and $^{19}F$ spectra and 8 mm tubes for the $^{31}P$ spectra.

$^{31}P$-{$^1H$} Spectra for compounds (IIIa) and (IIIb) were obtained at 36·43 MHz using a Bruker HFX spectrometer from a solution in $C_6F_6$, the $^{19}F$ signal of which was used for field-frequency locking.

The $^1H$ n.m.r. parameters given in Table 2 for compound (IIIa) were obtained from 100 MHz spectra using a Varian HA 100 spectrometer. The parameters for (IIIa) and (IIIc) in Table 1 (except $\delta_P$) were obtained from $^{19}F$ spectra at 94·075 MHz using the same spectrometer. In all these cases the frequency sweep mode was used and the spectra were calibrated with a Hewlett–Packard HP 5212A Frequency Counter to correct for recorder chart non-linearity. Several spectra were averaged to obtain the results for each case. The measured spectra were recorded at sweep scale 1 Hz cm$^{-1}$ and sweep rate 0·02 Hz s$^{-1}$. The probe temperature was *ca.* 35 °C. The heteronuclear double-resonance experiments were carried out using a double-tuned probe described earlier.[21] The decoupling frequencies were audio-frequency noise-modulated using a Hewlett–Packard Noise Generator (model HP 3722 A). The noise band-widths were 135 Hz for the $^1H$-{$^{19}F$} and $^1H$-{$^{31}P$} experiments on (IIIa), 35 Hz for the $^{19}F$-{$^1H$} work on (IIIa) and 13·5 Hz for the analogous work on (IIIc).

The 100 MHz proton resonance spectra of (IIIa) and (IIIc) were obtained from concentrated solutions in $C_6D_6$ with a little tetramethylsilane (TMS) to provide a signal for field/frequency locking purposes. The 94·075 MHz $^{19}F$ spectra of (IIIa) and (IIIc) were obtained from concentrated solutions in $C_6D_6$ with a little $CFCl_3$ for locking. It was assumed in obtaining the coupling constants of Table 2 that the (P,F), (F,F), and (P,P) coupling constants of (IIIa) were unaffected by the slight difference in solution conditions of the two samples used. The samples of (IIIa) and (IIIc) were degassed by the freeze-pump-thaw cycle method and sealed under vacuum into 5 mm O.D. Pyrex tubes.

The computations for compound (IIIa) were carried out on an Atlas computer using the computer program UEA NMR BASIC, which incorporates magnetic equivalence factoring, and its associated plotting routine MRPLOT.

## DISCUSSION

Table 2 shows that the $^1H$ parameters differ only slightly for the two isomers of compound (IIIa). Since the differences between the isomers are long-range [*i.e.* the local grouping MeFP(S)–S is the same for both] it is expected that $^2J_{PH}$ and $^3J_{FH}$ would be insensitive to the isomeric change; $^4J_{PH}$ and $^5J_{FH}$ should be more sensitive, but their magnitudes are so small that the observed differences are not of great significance.

The differences in the parameters of Table 1 are more pronounced. It is clear that $^1J_{PF}$, $^3J_{PF}$, $^2J_{PP}$, and $^4J_{FF}$ are very sensitive to the fine details of molecular constitution and should be of future importance in structural chemistry. Unfortunately understanding of the factors affecting these parameters is not yet good enough to permit us to use them to any great extent in predicting structure. Some comments, however, may be of use:

(a) The differences are more marked for (IIIa) and (IIIb) than for (IIIc). It is possible that the presence of the phenyl group increases the PSP angle somewhat and hence reduces the importance of long-range effects.

(b) The differences are not consistent between (IIIa), (IIIb), and (IIIc). Thus, although isomer A is defined as the one with smaller $|^1J_{PF}|$ in each case, it has the

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* We have reason to believe that this spectrometer was giving values for $\phi_F{}^*$, $\delta_F$, and $|J_{PF}|$ which were consistently too high; the agreement of our approximate results (given above) with literature values is therefore considered to be reasonable.

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larger $|^4J_{FF}|$ for (IIIa) and (IIIb) but the smaller $|^4J_{FF}|$ for (IIIc).

(c) It is possible that a contributory factor to $^4J_{FF}$ is the 'through space' mechanism. If so, and if the values of $^4J_{FF}$ are positive, then isomer A of (IIIa) and (IIIb) and isomer B of (IIIc) are presumably the *meso*-forms. However the differences between the magnitudes of $^4J_{FF}$ are only of the same order as the differences observed for varying situations where through-space effects are highly unlikely, as for the isomers of $(MeF_2PNMe)_2$.[22]

(d) It must be recalled that the signs and assignments of the $^2J_{PP}$ and $^4J_{FF}$ are, in principle, uncertain. Thus it is possible that changeovers occur.

(e) Whatever the isomer assignments it seems clear that there are either several rotamers (for internal rotation about the P–S bonds) of very nearly equal energy and rapidly interconverting, or else there is one stable rotamer for each isomer. This follows from the fact that the spectra change very little as the temperature is varied [we examined $^1H$ spectra of (IIIa) from +10 to +75 °C, and $^{19}F$ spectra of (IIIc) over the range +35 to +75 °C]. We favour the existence of one stable rotamer for each isomer.

Because few structurally similar compounds are known, there is little n.m.r. data in the literature for direct comparison. However, Table 3, which gives some data relevant to the 'local' MePF(S)-group, indicates that our compounds are normal in their 'local' parameters. There is clearly a substituent electronegativity effect on $^2J_{PH}$, and also on $^1J_{PF}$. Figure 6 shows a plot of $|^1J_{PF}|$ *vs.* substituent electronegativity for compounds of the type XYPF(S). Previous treatments of the effect of substituent parameters on $^1J_{PF}$ have been given by Mavel[31] and by Fluck and Heckmann.[32] Mavel's work was restricted to three-co-ordinate phosphorus compounds, while Fluck and Heckmann only discussed derivatives of fluorophosphoric acids and did not relate their empirical increments to electronegativities.

TABLE 3

N.m.r. parameters for compounds containing the MePF(:S)-group

| MePF(S)Y<br>Y | $\delta_H$ | $\lvert ^2J_{PH}\rvert$ | $\lvert ^3J_{FH}\rvert$ | $\lvert ^1J_{PF}\rvert$ | Ref. |
|---|---|---|---|---|---|
| SPF(S)Me | +2·097<br>+2·083 | 14·5<br>14·5 | 6·7<br>6·6 | 1119·0<br>1124·2 | This work |
| SH | +2·50 | 14·6 | 7·5 | 1107 | 9 |
| F | +2·30 | 16·5 | 6·5 | 1148 | 9 |
| $NMe_2$ | *a* | 12 | 6·2 | 1046 | 15 |
| SEt | *a* | 14·3 | 6·4 | 1093 | 15 |
| Me | +2·02 | 13·7 | 7·8 | 985 | 15, 23 |

[a] Not known.

It can be seen from Figure 6 that when X and Y belong to the first row of the Periodic Table decrease of electronegativity decreases $|^1J_{PF}|$, though there appears to be a separate correlation when either X or Y is carbon. This anomaly for carbon is also apparent from an attempt to apply the additivity rules found by Fluck and Heckmann to the carbon compounds, where they fail completely (*e.g.* in the series $F_3PS$, $MeF_2PS$, $Me_2FPS$). Since OMe and $NMe_2$ compounds were used for Figure 6, it might be better to have data for $CMe_3$ (rather than $CH_3$) substituents, but these are in general not available. Data for $Me(Bu^t)P(S)F$ and $(Bu^t)_2P(S)F$[33] indicate that the anomaly for carbon would be increased by the use of $Bu^t$ compounds. In any case, for X = F and Y = halogen, decrease of electronegativity increases $|^1J_{PF}|$ so perhaps size of substituent is also important. These two types of trend are also apparent when X = S, Y = first-row element (as for our compounds). There is, perhaps, again an anomaly when Y = C. Our results for $^1J_{PF}$ fall within the range of those published for X = S, Y = $CH_3$ (see Table 3). As far as the general trends for $^1J_{PF}$ are concerned, if Bent's mechanism is important here, the more electronegative substituents should cause there to be more *s*-character in the P–F bond; this appears to increase $|^1J_{PF}|$, *i.e.* to decrease

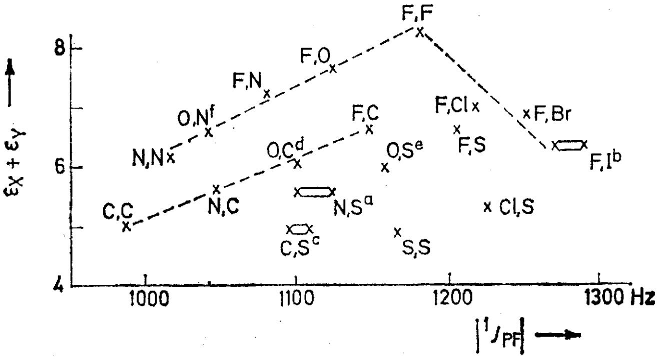

FIGURE 6 Plot of $|^1J_{PF}|$ *vs.* $\varepsilon_X + \varepsilon_Y$ for compounds of the type XYP(:S)F, where $\varepsilon_X$ and $\varepsilon_Y$ are the Allred–Rochow electronegativities[24] of the α-atom in substituents X and Y respectively. The data (where multivalent nuclei are concerned) are for substituents OMe, $NMe_2$, Me, and SMe, except where indicated below. The values are taken from refs. 9, 15, 25—30. The dashed lines show correlations. (a) Ref. 27 gives values from $^{19}F$ and $^{31}P$ resonance which differ by 23 Hz. (b) Data from refs. 26 and 30 differ by 19 Hz. (c) Data are for X = Me, Y = SEt (1093 Hz, ref. 15) and X = Me, Y = SH (1107 Hz, ref. 9). (d) This value is for X = OEt, Y = Et (ref. 15). (e) This value is for X = OMe, Y = SEt (ref. 27). (f) This value is for X = OMe, Y = $NH_2$ (1042 Hz, ref. 29). Ref. 29 also gives *J* = 1123 Hz for X = OEt, Y = $NH_2$ but this is presumably in error. The above notes indicate that not all the literature values can be accurate, and caution is needed in discussing correlations

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$^1J_{PF}$ algebraically. It is uncertain whether this effect, in terms of the Pople–Santry theory,[34] is due to increasing $\langle s_P|\delta_P|s_P\rangle$ or to changes in the mutual polarizability of $s_P$ and $s_F$ (these can act in either direction with substituent change). Since the replacements $F \rightarrow N \rightarrow O$ cause changes in $^1J_{PF}$ opposite to those for $F \rightarrow Cl \rightarrow Br \rightarrow I$ it would seem that changes in $\langle s_P|\delta_P|s_P\rangle$ are not dominant.

The parameters $^3J_{PF}$ and $^4J_{FF}$ are remarkably sensitive to molecular structure and conformation, but the origin of the effects remains obscure. Table 4 gives some relevant values from the literature. Usually $^3J_{PF}$ is positive, so our results are of particular interest because they are negative. The only other values for $^3J_{PF}$ in sulphur-bridged diphosphorus compounds are those for $F_2P{\cdot}S{\cdot}P(\dot{:}S)F_2$[5] and $F_2PSPF_2$;[4] in the latter case the coupling constant is certainly positive, but the stereochemistry about phosphorus is, of course, different for the three compounds. In the case of $F_2PSPF_2$ both $^3J_{PF}$ and $^4J_{FF}$ are temperature dependent, in contrast to the present examples. The temperature variation was attributed to changes in the relative populations of the various rotameric forms. Unless there are sign changes, values of $^4J_{FF}$ vary less than those of $^3J_{PF}$, but our results show a strong influence of stereochemistry.

TABLE 4

N.m.r. coupling constants for diphosphorus compounds [a]

| | $^3J_{PF}$ | $^4J_{FF}$ | $^2J_{PP}$ | Ref. |
|---|---|---|---|---|
| $F_2P{\cdot}S{\cdot}P(\dot{:}S)F_2$ [b] | 15·0<br>22·0 | 5·9 | 68 | 5 |
| $F_2P{\cdot}S{\cdot}PF_2$ [c] | +29·5 | +8·4<br>+2·4 | +274 | 4 |
| $F_2P{\cdot}NMe{\cdot}PF_2$ [c] | +42·2 | +11·9<br>+3·0 | +433 | 4 |
| $F_3\overline{P{\cdot}NMe{\cdot}PF_3N}Me$ | +32 | 8·7 | 210 | 35 |
| $F\overline{P{\cdot}NBu^t{\cdot}PF{\cdot}N}Bu^t$ | +25·5 | 29·0 | 92·5 | 36 |

[a] Signs are only given where known. [b] There should, in theory, be two distinct values of $^4J_{FF}$ for this compound. Only the single value quoted was given in ref. 5. [c] Room temperature parameters; however, the spectra are temperature dependent (especially $^2J_{PP}$ for $F_2P{\cdot}S{\cdot}PF_2$).

Values of $^2J_{PP}$ (see Table 4) depend very greatly on co-ordination at phosphorus. Our values are considerably less in magnitude than those for $F_2P{\cdot}S{\cdot}PF_2(S)$ and $F_2P{\cdot}S{\cdot}PF_2$, but the comparison is complicated by the presence of the relatively electropositive hydrocarbon groups for (III). The doubly-bridged compound (II; R = Me) appears to have a very low (P,P) coupling constant,[37] though lack of solubility prevents accurate measurement. Variation in PSP angle will certainly strongly influence $^2J_{PSP}$.

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