

Signs and Temperature Dependence of the Coupling Constants in F_2PPF_2 , F_2PSPF_2 , and $MeN(PF_2)_2$

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Abstract: The signs of all the coupling constants in F_2PPF_2 , F_2PSPF_2 , and $MeN(PF_2)_2$ have been determined. The sign of the $^1J_{PP}$ in F_2PPF_2 , -230 Hz, is opposite to that predicted by published theoretical studies. The geminal $^2J_{PP}$ increases from $+274$ Hz at $+39^\circ$ to $+392$ Hz at $+120^\circ$ in F_2PSPF_2 , but only increases from $+432$ Hz at $+31^\circ$ to $+442$ Hz at -70° in $MeN(PF_2)_2$. The different behavior in these two compounds is attributed to a less rigid P-S-P backbone compared to the P-N-P backbone.

The compound μ -thio-bis(difluorophosphine), F_2PSPF_2 , was first prepared by Bokerman,² who reported a complex nmr spectrum for the species. We have completed a thorough analysis of the ^{19}F nmr spectrum in terms of an $XX'AA'X''X'''$ spin system.³⁻⁵ The analysis included "spin-tickling" experiments⁶ to establish the signs of all the coupling constants and the discovery of a unique temperature variation of the geminal PP coupling constant.⁷

The temperature dependence of the nmr spectrum of F_2PSPF_2 prompted a reinvestigation of the spectra of μ -oxo-bis(difluorophosphine), F_2POPF_2 ,⁸ and methylaminobis(difluorophosphine), $MeN(PF_2)_2$.⁹

Recent calculations of the sign of the one bond PP coupling constant^{10,11} encouraged the authors to reinvestigate the nmr spectrum of diphosphorus tetrafluoride, F_2PPF_2 .¹² Heteronuclear spin-tickling yielded the signs of all the coupling constants and the temperature dependence of the spectrum was studied.

Experimental Section

The F_2PSPF_2 , F_2PPF_2 , F_2POPF_2 , and $MeN(PF_2)_2$ were synthesized according to known procedures.^{2,8,13} The first two compounds were obtained in pure form. Spectra were normally taken at 0° or lower to minimize decomposition of the first three compounds. The F_2POPF_2 was contaminated by about 20% PF_3 . It was not possible to separate $MeN(PF_2)_2$ completely from the petroleum ether used in the preparation. The data were obtained from a sample 37, 36, and 27 mol % in $MeN(PF_2)_2$, petroleum ether, and $CFCl_3$, respectively.

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(2) In the original characterization of F_2PSPF_2 (G. N. Bokerman, Ph.D. Thesis, University of Michigan, 1968), the structure $F_2PP(=S)F_2$ was eliminated in favor of F_2PSPF_2 by ir and Raman spectroscopy.

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(9) J. F. Nixon, *J. Chem. Soc.*, **A**, 1087 (1969).

(10) E. G. Finer and R. K. Harris, *Chem. Commun.*, 110 (1968).

(11) (a) A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, **91**, 1913, 1917 (1969); (b) A. H. Cowley, W. D. White, and M. C. Damasco, *ibid.*, **91**, 1922 (1969).

(12) F. A. Johnson and R. W. Rudolph, *J. Chem. Phys.*, **47**, 5449 (1967).

(13) J. F. Nixon, *J. Chem. Soc.*, **A**, 2689 (1968).

High resolution frequency sweep fluorine spectra were taken at 94.08 MHz using a Varian HA-100 nmr spectrometer and a Varian V4341 temperature controller. The temperature controller was calibrated with a thermocouple and temperatures are accurate only to $\pm 3^\circ$. Spectra were taken at several different concentrations in $CFCl_3$ using the solvent resonance for the lock signal. The strong line in the low field half of each spectrum provided the lock signal in neat samples used for the variable temperature and heteronuclear decoupling experiments. A very weak rf field was used for the lock, and no homonuclear double resonance perturbations were observed. In order to obtain accurate high resolution spectra, nonlinearities in the recorder sweep frequency were corrected by counting the sweep frequency to ± 0.01 Hz (using the 10-K period average of the Hewlett-Packard 5521A counter) about 1 Hz before and 1 Hz after the peak under consideration. The General Radio 1164-A frequency synthesizer served as a very stable lock frequency. The transition frequency is given as the difference between the sweep frequency necessary for resonance and the lock frequency. The 1.6-Hz $^4J_{HF}$ coupling in $MeN(PF_2)_2$ results in considerable overlap of the ^{19}F lines. Accurate high resolution spectra of the P_2F_4 subspectrum were obtained by decoupling the methyl group using the frequency synthesizer, a Hewlett-Packard 10534A doubler, and a Hewlett-Packard 230A power amplifier. The 100-MHz decoupling frequency was fed to the Varian V4333 probe using the double tuning network of Charles and McFarlane.¹⁴

Heteronuclear spin-tickling was performed on neat samples of F_2PPF_2 and F_2PSPF_2 at -1° in order to determine the relative signs of the coupling constants. The frequency synthesizer was used here as a source of the P decoupling frequencies; its output was fed directly to the double-tuned Varian probe. Optimum decoupling frequencies of the seven low frequency and three high frequency ^{31}P lines were readily determined to ± 0.2 Hz from the symmetry of the progressive or regressive doublet being observed.⁶ Corrections for the frequency drifts of the two separate oscillators were made by monitoring the frequency necessary for optimum decoupling of the lowest frequency peak in the P spectrum.

Results

Because of magnetic inequivalence, the P_2F_4 nuclei in the four compounds studied constitute $XX'AA'X''X'''$ spin systems; the analysis and details of the X (^{19}F) part of spectra of this type have been discussed in detail previously.³⁻⁵ The fluorine spectrum consists of two strong lines, which constitute 50% of the total intensity, separated by $N = ^1J_{PP} + ^2J_{PP}$. There are 32 other peaks, each of approximately equal intensity, or $1/16$ th the intensity of the strong lines. The spectrum is symmetric about its midpoint.

F_2PPF_2 . The upfield half of the fluorine spectrum of F_2PPF_2 at -1° and -101° is shown in Figure 1. Doublets 1-2, 5-6, 11-12, and 15-16 in the -1° spectrum were not resolved in the earlier analysis of the

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Table I. Coupling Constants^a of F₂PPF₂ in the Neat Liquid at Several Temperatures and as a Function of Concentration in CFC1₃ at -1°^b

Temp, °C	-101	-81	-44	-1	-1	-1
Concentration ^b	100	100	100	100	25	5
¹ J _{PF}	-1191.1	-1191.4	-1193.0	-1194.1	-1192.9	-1192.2
¹ J _{PP}	-230.3	-230.0	-229.2	-228.6	-227.1	-226.5
² J _{PF}	+64.0	+64.3	+65.4	+65.8	+66.8	+67.2
² J _{FF}	+278	+276	+282	+277	+276	+279
³ J _{FF}	+37.40	+37.06	+35.79	+34.99	+35.84	+36.25
³ J _{FF'}	-5.92	-5.26	-3.13	-1.70	-2.15	-2.39

^a In Hz. The probable errors are less than 0.02 Hz except for ²J_{FF}; the error in the latter is about 10 Hz. ^b Concentrations are in mol %. The chemical shift upfield from CFC1₃ is 114.0 ppm for the solutions at -1°.

spectrum of this compound.¹² This doublet separation is approximately equal to the smaller vicinal J_{FF} and markedly increases as the temperature is lowered.

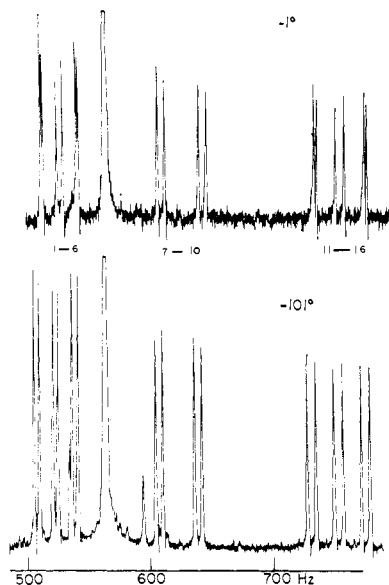


Figure 1. Upfield half-spectra of F₂PPF₂ at -1° and -101°. The peak at 564 Hz comprises 50% of the intensity of the half-spectrum; spinning side bands are evident on this peak at -101°. The other 16 lines in the half-spectrum are numbered and occur in groups 1-6, 7-10, and 11-16.

Approximate values of the coupling constants were determined following the procedures of Harris and Lynden-Bell.³⁻⁵ The signs of ¹J_{PF} and ²J_{PF} are opposite since the strong line in the upfield half-spectrum is downfield from the quartet (see Figure 1)^{3,4} The relative signs of the three FF coupling constants were determined by least-squares iteration on the frequencies of the peaks in the upfield fluorine half-spectrum using the LAOCOON3 computer program.¹⁵ In the -1° spectrum the rms error between the observed and calculated transitions was 0.03 Hz for the ²J_{FF} and ³J_{FF} signs given in Table I, and was greater than 0.44 Hz for the other three combinations of signs of the vicinal ³J_{FF} relative to the geminal ²J_{FF}. Spectra were then calculated using LAOCOON3 for the four possible sign combinations of J_{PP} and the FF coupling constants relative to a negative one-bond J_{FF}.¹⁶⁻¹⁸ Comparison of the

(15) A. A. Bothner-By and S. Castellano, Quantum Chemistry Program Exchange, No. 111, Indiana University, Bloomington, Ind. The program was modified to print out the energy levels of the transitions; details of this modification are available from R. A. Newmark.

experimental heteronuclear spin-tickling results with the calculated spectra showed that J_{PP} was negative and the larger vicinal J_{FF} positive. The spin-tickling pattern also verified that the two vicinal J_{FF} were of opposite sign, but the pattern was independent of the sign of the geminal J_{FF}. Spectra were taken at four different temperatures and at two concentrations in CFC1₃. The coupling constants are given in Table I. The rms error between the 17 upfield observed and calculated transition frequencies was less than 0.1 Hz.

F₂PSPF₂. The upfield half of the fluorine spectrum at -1° and -100° is shown in Figure 2. The ²J_{PP} is

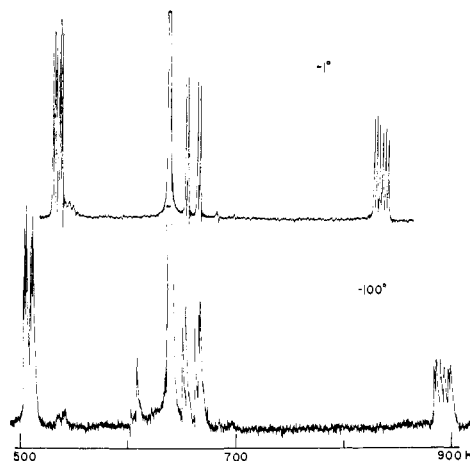


Figure 2. Upfield half-spectra of F₂PSPF₂ at -1° and -100°. At -100°, spinning side bands are evident on the strongest peak. The very small peaks at ~530 Hz are attributed to an unidentified impurity.

given by the difference between the average frequency of the low field and high field sextets in the half-spectrum. As the temperature is lowered these sextets move much further away from the strong peak. The analysis was similar to that employed for F₂PPF₂. However, calculated spectra were insensitive to the sign of ²J_{FF} because of the smaller values of the FF couplings in the compound. The signs of the couplings are given in Table II.

Spectra were taken between +31° and -120°, and at several concentrations in CFC1₃. The rms error between the observed and calculated transition frequencies was less than 0.1 Hz for concentrations greater than

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(17) R. R. Dean and W. McFarlane, *Chem. Commun.*, 840 (1967).

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Table II. Coupling Constants^a of F₂PSPF₂

Temp, °C	-120	-70	-42	-1	-1	-1	-1	-1	+31
Concn ^b	100	100	100	100	90	20	4	1	9
¹ J _{PF}	-1305.2	-1305.5	-1306.3	-1307.0	-1307.0	-1306.3	-1306.7	-1306.6	-1307.3
² J _{PP}	+392.9	+360.7	+334.5	+302.2	+300.8	+298.3	+300.0	+299.5	+274.1
³ J _{FF}	c	c	125	100	120	125	c	c	141
³ J _{PF}	+33.8	+32.3	+31.3	+30.1	+30.1	+30.3	+30.5	+30.5	+29.5
⁴ J _{FF}	+10.5	+9.7	+9.45	+8.86	+8.86	+8.79	+8.78	+8.6	8.41
⁴ J _{FF'}	+1.4	+1.8	+1.75	+2.12	+2.13	+2.12	+2.12	+2.0	2.42

^a In Hz. The probable errors are less than 0.1 Hz in the 1% solution, and less than 0.02 Hz in the other solutions except for ³J_{FF}; the error in the latter is about 30 Hz. ^b Concentrations are in mol % in CFCl₃. Chemical shifts are 65.3, 65.0, 64.9, and 64.9 ppm upfield from CFCl₃ for 90%, 20%, 4%, and 1% solutions, respectively. The chemical shift of the 90% solution increases from 64.7 at 31° to 65.0 at -1°, 65.3 at -40°, and 65.5 at -70°. ^c 125 Hz assumed for ³J_{FF}.

Table III. Coupling Constants^a of MeN(PF₂)₂

Temp, °C	+30 ^b	+30	+1	-24	-70
¹ J _{PF}	1264	-1263.1	-1263.1	-1262.5	-1262.0
² J _{PP}	437	+433.0	+438.4	+441.4	+442.7
² J _{FF}	0	39	28	28	32
³ J _{PF}	47	+42.2	+41.9	+41.7	+41.4
⁴ J _{FF}	11.7	+11.87	+11.83	+11.94	+11.93
⁴ J _{FF'}	1.7	+3.01	+3.00	+3.03	+3.06
⁴ J _{HF}	1.6	1.51	1.45	1.34	1.44
δ ^c	74.6	74.58	74.69	74.76	74.89

^a In Hz. The probable errors are less than 0.02 Hz, except for ²J_{FF}; the error in the latter is about 4 Hz. ³J_{HP} is approximately twice ⁴J_{HP} at all temperatures, and could not be determined more accurately because of overlap of lines in the proton spectrum. ^b References 9 and 13. ^c Chemical shifts are in ppm upfield from CFCl₃.

15%. The coupling constants are given in Table II. The temperature dependence of ²J_{PP} in a 9 mol % solution of F₂PSPF₂ in CFCl₃ was identical to that observed in the neat solutions. Since ²J_{PP} changes about 1 Hz/°C, and the reproducibility of the temperature controller is no better than ±3° for different samples on different days, the values for ²J_{PP} given in Table II are independent of the concentration within the experimental error.

MeN(PF₂)₂. Each of the normal 34 lines in the X portion of the XX'AA'X'X''' spin system is split into a quartet, ⁴J_{HF} = 1.6 Hz, due to coupling to the methyl protons. Decoupling the methyl group simplifies the fluorine spectrum and makes it possible to accurately determine the frequencies of the 17 peaks in the upfield half-spectrum; the spectrum is essentially identical with the spectrum of F₂PSPF₂ in Figure 2 under these conditions. The results at several temperatures are given in Table III, and compared to the earlier results of Nixon^{9,13} on this compound. The temperature dependence of ⁴J_{HF} was determined from observations of the two very strong ¹⁹F resonances, and the proton spectrum was taken to determine ³J_{HP}. In the heteronuclear decoupling experiments the ¹⁴N quadrupole moment made it impossible to decouple individual ³¹P lines because the lines in the ³¹P spectrum were broadened to a width of about 100 Hz. Since the seven low frequency ³¹P lines are over 300 Hz away from any other ³¹P transitions, it was possible to decouple simultaneously all seven low (or high) frequency transitions and observe which of the 17 upfield quartets in the high field ¹⁹F half-spectrum were perturbed. Calculated P₂F₄ subspectra showed that ²J_{PP} had to be opposite in sign to ¹J_{PF} and the same sign as the larger ⁴J_{FF} in order to reproduce the experimental decoupling results. The best fit of the ¹⁹F transition frequencies required

that the two ⁴J_{FF} have the same sign. Thus, the signs in this molecule are the same as those found in F₂PSPF₂.

The geminal FF coupling clearly decreases in this series of compounds from 275 Hz in F₂PPF₂ to 125 Hz in F₂PSPF₂ and to about 35 Hz in the MeN(PF₂)₂. The separation of lines 3 and 4 and of lines 13 and 14 (see Figure 1) is a moderately sensitive function of this parameter, and it can be determined to an accuracy of about 10% if the transition frequencies are known to 0.03 Hz. Large percentage changes in geminal couplings are well known for ²J_{HH} due to variation in the hybridization about carbon,¹⁹ and changes in the hybridization about phosphorus are probably responsible for the variation of ²J_{FF}.

F₂POPF₂. The ¹⁹F nmr spectrum of F₂POPF₂ was originally interpreted in terms of an X₂AA'X'₂ spin system and ²J_{PP} was found to be 4 Hz.⁸ A reinvestigation of the spectrum showed incipient resolution of broad shoulders on several peaks. However, attempts to determine the other coupling constants and the sign of the ²J_{PP} were unsuccessful. The ¹⁹F spectrum of the neat liquid was slightly temperature dependent. The width of the multiplet showed ²J_{PP} was less than 10 Hz at -100°.

Discussion

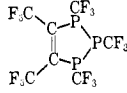
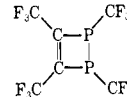
The absolute sign of the one-bond PF coupling constant has been shown to be negative from chemical shift anisotropy arguments in BaFPO₃¹⁶ and from the relative sign arguments of Dean and McFarlane¹⁷ and of Manatt, *et al.*¹⁸ All the signs determined in this study have been related to the ¹J_{PF} and are therefore also absolute signs.

F₂PPF₂. The experimental value of ¹J_{PP} in F₂PPF₂, -320 Hz, is opposite to the sign predicted from Finer

(19) A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 195 (1965).

and Harris' qualitative extension of the theory of Pople and Santry.¹⁰ It is also opposite in sign to the values of +217 Hz in the *gauche* rotamer and +707 Hz in the *trans* rotamer, calculated by Cowley and White using a parameterized LCAO-SCF MO theory including overlap.¹¹ The known directly bonded ³¹P(III)–³¹P(III) coupling constants range from 100 to 400 Hz in magnitude, excluding the $^1J_{PP} = 55$ Hz for the highly strained 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphosphacyclobutene (Table IV). In this class of coupling constants

Table IV. Coupling Constants between Directly Bonded Phosphorus Nuclei

Compound	$^1J_{PP}$	Ref
LiEtPP(C ₆ H ₅)Et	396 ^a	<i>b</i>
P(PF ₂) ₃	323 ^a	<i>c</i>
Et ₂ PP(C ₆ H ₁₁) ₂	282 ^a	<i>d</i>
(CF ₃) ₂ PPMe ₂	–256	<i>e</i>
F ₂ PPF ₂	–230	This work
(C ₆ H ₅) ₂ PP(C ₆ H ₁₁) ₂	224 ^a	<i>d</i>
	220 ^a	<i>f</i>
F ₂ PPH ₂	211 ^a	<i>g</i>
Me ₂ PPMe ₂	–179.7	<i>h</i>
H ₂ PPH ₂	–108	<i>i</i>
	55 ^a	<i>f</i>

^a Signs have not been determined. ^b E. Fluck and K. Issleib, *Z. Anorg. Chem.*, **339**, 274 (1965). ^c D. Solan and P. L. Timms, *Chem. Commun.*, 1540 (1968). ^d E. Fluck and K. Issleib, *Chem. Ber.*, **98**, 2674 (1965). ^e Reference 18. ^f W. Mahler, *J. Amer. Chem. Soc.*, **86**, 2306 (1964). ^g R. W. Rudolph and H. W. Schiller, *ibid.*, **90**, 3581 (1968). ^h E. G. Finer and R. K. Harris, *Mol. Phys.*, **13**, 65 (1967). ⁱ Reference 5.

those signs which have been determined are negative, despite large degrees of variance in the P substituents. Thus, it would appear that all such $^1J_{PP}$ values are negative. On the other hand, Finer and Harris have observed a positive $^1J_{PP}$ in the diphosphite anion [HP₂O₃]³⁻.¹⁰ Thus, since directly bonded P^V–P^V couplings vary from low to high values,¹⁰ it seems likely that the $^1J_{PP}$ in these species may have either sign.

Since the magnitudes of $^1J_{PP}$ for the two staggered forms of P₂F₄ calculated by Cowley and White¹¹ differ by about 500 Hz, a marked dependence of $^1J_{PP}$ on the rotameric form of the molecule is implied. No substantial temperature variation in the P–P coupling was observed, but the relatively large change in the vicinal coupling and absence of any substantial temperature dependence of the geminal and one-bond coupling constants suggests that more than one rotamer might contribute to the observed spectrum. In the latter case the temperature dependence would be attributed to changes in population of the two staggered forms of the molecule, the *gauche* and *trans* rotamers. However, without knowledge of the intrinsic temperature dependence of the vicinal FF coupling constants, it is not possible to attempt to fit the observed temperature dependence to couplings in the individual rotamers.^{20, 21}

(20) R. J. Abraham and L. Cavelli, *Mol. Phys.*, **9**, 67 (1965).

The absence of any correlation of the dihedral-angle dependence of vicinal FF coupling constants in ethylenes, halogenated ethanes, and fluorinated cyclobutanes and cyclobutenes²² also makes it impossible to draw any conclusions from the vicinal nmr couplings concerning whether the *gauche* or *trans* rotamer is the most stable. In particular, the 60° *gauche* and 180° *trans* $^3J_{FF}$ values in substituted ethanes are always negative and generally differ by less than 5 Hz,^{23, 24} whereas the dominant vicinal FF coupling in F₂PPF₂ is positive. However, as originally suggested on the basis of vibrational spectroscopy,^{8, 12} the *trans* rotamer probably predominates in P₂F₄.

The signs of the two vicinal $^3J_{FF}$ coupling constants are believed to be the first such signs determined in a diphosphine, but because of the symmetry of the XX'–AA'X'X''' spin system, it is not possible to assign the two vicinal couplings.

$^2J_{PP}$. The most intriguing feature of the spectral analysis is the approximately linear variation of the geminal PP coupling from +274 Hz at +31° to +393 Hz at –120° in F₂PSPF₂. The authors know of no other case in which a geminal coupling changes by anywhere near this magnitude.⁷

Since there were no appreciable changes in the spectrum down to a dilution of 1 mol % F₂PSPF₂ in CFCl₃, the effect of molecular interaction must be negligible.

The absence of a large temperature dependence of the $^2J_{PP}$ in the oxygen and nitrogen analogs provides some clues concerning a possible mechanism for the coupling in the sulfur compound.

Changes in the average PSP bond angle with temperature might cause large changes in $^2J_{PP}$ since geminal PP coupling is very sensitive to changes in the geminal bond angle, and ranges from 8 Hz for the *cis* form to over 500 Hz in the *trans* form of platinum and palladium complexes.²⁵ The PSP deformation frequency has been tentatively assigned to the 234-cm⁻¹ line in the Raman spectrum² of F₂PSPF₂. Then, in going from –120° to +30°, the population of the ground vibrational state decreases from 89% to 66% assuming a Boltzmann distribution. However, it seems very unlikely that the bond angle dependence of $^2J_{PP}$ is sufficient to account for changes of over 100 Hz in the average value of $^2J_{PP}$ over the various vibrational states, since the bond angle changes should be less than 10° and the population change in the ground state is only 23%. Also, such an effect should be important in the oxygen and nitrogen compounds, since they also have low frequency POP and PNP deformations.

The decrease of $^2J_{PP}$ with temperature in F₂PSPF₂ could reasonably be attributed to changes in the relative populations of the various rotameric forms of the molecule. The latter effect would change the average "axial" symmetry along the PSP backbone, and could cause a change in the electron correlation between the P nuclei.

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(24) S. L. Manatt and D. D. Elleman, *J. Amer. Chem. Soc.*, **84**, 1305 (1962).

(25) R. G. Goodfellow, *Chem. Commun.*, 114 (1968).

Such an effect would not be anticipated in $\text{MeN}(\text{PF}_2)_2$ if the P–N–P backbone were rigid due to nitrogen→phosphorus π bonding.⁹ Extrapolation from the well studied dimethylaminodifluorophosphine, Me_2NPF_2 , substantiates this contention of a p_π – d_π interaction enhanced by the presence of electronegative fluorine atoms. Thus, Nordman's X-ray diffraction study²⁶ has revealed C_s molecular symmetry for Me_2NPF_2 (a mirror plane containing the P–NC₂ moiety and bisecting the FPF angle). The P–N distance at 1.63 Å is in the range of P=N multiple bond distance found in phosphonitrilic derivatives.²⁷ The short bond and the planarity about nitrogen strongly suggest N→P multiple bonding in Me_2NPF_2 .

Since the sign and magnitude of $^2J_{\text{PP}}$ in F_2PSPF_2 and $\text{MeN}(\text{PF}_2)_2$ are the same, it seems reasonable to conclude that similar mechanisms are responsible for the transmission of spin–spin coupling between the phosphorus nuclei in both cases.

We are led to speculate that $3p_\pi$ – $3d_\pi$ bonding, such as that implied for the PSP backbone, is less rigid than the $2p_\pi$ – $3d_\pi$ bonding proposed for the nitrogen homolog. It is not clear, however, whether the size of the orbitals involved in the π backbone, or alternatively,

the number of lone-pair electrons in the bridging moiety affects the rigidity.

A through-space mechanism²⁸ or a through-bond mechanism may be responsible for the transmission of the PP coupling. However, it is difficult to imagine how a through-space effect could be present in F_2PSPF_2 and not in F_2POPF_2 , where the shortness of the P–O bond relative to the P–S bond should offset any expansion of the geminal angle in the oxygen compound. Nevertheless, because of the geometry of these systems, it is reasonable to expect that through-space coupling would only be significant for $^2J_{\text{PP}}$, and thus it might explain why the percentage variations with temperature of the 3- and 4-bond couplings in F_2PSPF_2 are much less than those for $^2J_{\text{PP}}$.

Certainly, structural data on all the P–X–P systems mentioned here will be of considerable value in explaining the nmr results. Also, the preparation and investigation of $\text{F}_2\text{PP}(\text{R})\text{PF}_2$ species should provide data pertinent to the role of p_π orbital size.

Acknowledgment. The frequency synthesizer was purchased with funds from the Research Corporation and the University of Colorado Council on Creative Research. R. A. N. also acknowledges support from the National Institutes of Health, Grant GM 16264-01.

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 (27) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

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Electron Paramagnetic Resonance Studies of Phosphorus-Containing Reactive Intermediates^{1a}

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Abstract: Several novel phosphorus-containing radicals have been produced at -196° by photolytic methods and characterized by epr spectrometry. In addition to the formation of PCl_2 ($A(\text{P}) = 92$ MHz; $g = 2.018$) in neat parent PCl_3 , a secondary reaction has been observed which yields PCl_4 ($A(\text{P}) = 3398$ MHz; $A'(\text{Cl}) = 175$ MHz; $A''(\text{Cl}) = 21$ MHz; $g = 2.013$). Appropriate modification of the parent matrix by either cocondensation of inert diluent (Xe) or possibly reactive materials (PF_3 , SnCl_4) results in useful additional spectral information. Thus in $\text{PF}_3:\text{PCl}_3$ (1:10) the full anisotropy of PCl_2 is revealed ($A_{||}(\text{P}) = 753$ MHz; $A_{\perp}(\text{P}) = 78$ MHz; $A_{||}(\text{Cl}) = 41.5$ MHz; $A_{\perp}(\text{Cl}) = 0$ MHz; $g_{||} = 2.001$; $g_{\perp} = 2.021$). In contrast to neat PCl_3 , irradiation of $\text{Xe}:\text{PCl}_3$ (9:1) does not result in formation of PCl_4 , presumably from inhibition of $\text{Cl} + \text{PCl}_3 \rightarrow \text{PCl}_4$ by competitive Cl recombination. Irradiation of $\text{SnCl}_4:\text{PCl}_3$ (6:1) results in formation both of PCl_2 and PCl_4 . Several related organophosphines were also irradiated, but only with CH_3PCl_2 was evidence obtained suggesting formation of a four-coordinate radical similar to PCl_4 ($A(\text{P}) = 3015$ MHz, $g = 2.000$). In all cases, however, epr data are consistent with bond scission of the ternary phosphine to produce PCl_2 -like fragments. The above results are discussed in light of their bearing on the role of reactive intermediates in synthetic chemistry, and considerations of molecular geometric and orbital composition are presented with reference to current MO and electrostatic models.

The main group V elements form both neutral three-coordinate compounds and, with the exception of nitrogen, neutral five-coordinate compounds. Both of these types are of interest in terms of (1) their stereochemistry and (2) the nature and orbital composition

of their bonds. The simplest case of a group V atom forming both three- and five-coordinate halogen compounds is phosphorus. Several recent theoretical papers have described the bonding in five-coordinate phosphorus compounds including such aspects as d-orbital participation and the relationship between stereochemistry and relative electronegativities in the mixed halo compounds.^{2,3}

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