taining three or four imide groups per ring when the compounds are washed during the acid extraction.

The catalytic activity of the type A complexes requires a thorough reexamination, and such is currently under way in our laboratory.

B. Type B Complexes.—In a study by Drinkard and Bailar,[2] it was assumed that the products of reaction B were phthalocyanine derivatives containing peripheral carboxylic acid functional groups exclusively. The structures of the products were deduced by reference to an elemental analysis chart similar to that used in this work. However, metal analyses were not reported, and the infrared spectra were not examined.

Present attempts to prepare these compounds have resulted in products which have C, H, and N analyses in the ranges previously reported, and colors similar to those reported, but the copper analyses of the products are all grossly low (see Experimental Section). Furthermore, the infrared spectra and solubility behavior of the compounds do not bear out the assumption that only acid groups are present. On the contrary, the spectra very much resemble the spectrum of pyromellitimide (Figure 3), and the complete insolubility of the products in water and in organic solvents is in contrast to the ready solubility of the octa-acid type A derivatives. Our efforts to purify these compounds by solvent or acid extraction techniques were not successful; the compounds apparently contain an organic impurity which is as insoluble as the metal complex.

However, hydrolysis of the products in hot 50% KOH destroys the organic impurity and allows one to obtain water-soluble derivatives. Infrared spectra of the type B hydrolysis products show that only carboxylic acid functional groups are present, and elemental analyses of the compounds (Table V) identify them as oligomeric phthalocyanine derivatives with carboxylic acid functional groups at the peripheral sites (see Experimental Section for empirical formulas).

Table VIII shows the C:N, C:M, and N:M ratios for some type B hydrolysis products. Comparison of the C:N ratios of these samples with those in Table Ia indicates that sample **1**-B is a monomer, **2**-B is a dimer, **3**-B is a tetramer, and **4**-B is a pentamer. However, the C:M and N:M ratios show that the metal content of the compounds, except for **2**-B, is low.

TABLE VIII

PERTINENT RATIOS FOR VARIOUS TYPE B HYDROLYSIS PRODUCTS

	1-B	**2**-B	**3**-B	**4**-B
C/N	4.83	4.37	3.97	4.08
C/M	42.02	32.23	38.5	40.2
N/M	8.7	7.4	9.65	12.1

The excellent agreement of the C, H, and N analyses for these complexes leads us to conclude that they are quite pure and are not mixtures of oligomers. Therefore, it is thought that the low metal content is due to "unfilled" phthalocyanine sites within the oligomeric chains, or possibly to methodological problems in the analysis of these very stable molecules.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Nuclear Magnetic Resonance Spectra of Some Oxygen-, Sulfur-, and Nitrogen-Bridged Diphosphorus Tetrafluoride Compounds

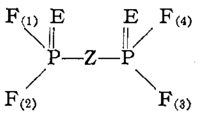
BY T. L. CHARLTON AND R. G. CAVELL*

Received June 25, 1971

The nmr spectra of bridged tetrafluorodiphosphorus molecules of the types $F_2P(E)ZP(E)F_2$ [E = O, S; Z = O, S, NCH_3, NH] have been analyzed in terms of an XX′X″X‴AA′ spin system which allows all possible couplings to be nonzero. The coupling constants for all of the compounds at 33° are reported. The compound $(SPF_2)_2O$ shows a relatively substantial variation of the $^2J_{PP}$ coupling constant with temperature whereas $(OPF_2)_2O$ and $(PF_2)_2O$ show little or no change of this coupling with temperature. The remaining molecules show intermediate $^2J_{PP}$ variations with temperature. Signs and assignments of coupling constants are discussed.

Introduction

There has been considerable recent interest in the nmr spectra of tetrafluorodiphosphorus molecules of the general type



I

(where E = O, S, or nothing and Z = O, S, NCH_3) containing either pentavalent[1] or trivalent[2,3] phosphorus and also in the mixed-valence compounds[4,5] containing phosphorus in both trivalent and pentavalent states. The symmetric molecules in the above list constitute AA′XX′X″X‴ systems, the solutions for which have been given by Lynden-Bell.[6] When $J_{XX'}$ approximates zero, reasonably good estimates of the spectral parameters can be obtained by using (*e.g.*, the initial

(1) W. E. Hill, D. W. A. Sharp, and C. B. Colburn, *J. Chem. Phys.*, **50**, 612 (1969).

(2) R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, **92**, 1195 (1970).

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

(4) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **8**, 2436 (1969). An error in the conversion of ^{31}P chemical shifts to the P_4O_6 reference has led to erroneous values of this parameter quoted in Table III (p 2437) of this paper. Correct chemical shifts are as follows: $F_2P(S)SPF_2$ (−40°), P(V) +38.2, P(III) −78.0; $F_2P(O)OPF_2$ (−10°), P(V) +148, P(III) +8.0 ppm *vs.* P_4O_6. Coupling constants remain as originally quoted.[4]

(5) D. D. DesMarteau, *J. Amer. Chem. Soc.*, **91**, 621 (1969).

(6) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961); *Mol. Phys.*, **6**, 601 (1963).

study of $(F_2P)_2O)$[7] the approximate $AA'X_2X'_2$ expressions given by Harris.[8,9] The possibility of significant F–F couplings in these systems suggests that the complete expressions should be used. We report herein the results of nmr studies on a series of pentavalent bridged tetrafluorodiphosphorus compounds which we have recently synthesized.[10] New nmr results are given for $(SPF_2)_2S$ and the nitrogen-bridged molecules [Z = NH (as the $(CH_3)_3N$ adduct) and NCH_3 and E = O and S in the above formula], and in addition the temperature dependence of the nmr spectra of $(SPF_2)_2O$ and $(OPF_2)_2O$ (previously reported to be invariant[1]) is given. Special interest in these systems is provided by the recently reported[2] pronounced temperature variation of $^2J_{PP}$ coupling[11] in the spectrum of F_2PSPF_2. Previous results on $(SPF_2)_2O$[1] and $(OPF_2)_2O$[1] and $(F_2P)_2O$[2,7] are substantiated.

Experimental Section

Compounds were prepared as described elsewhere.[10] Fluorine spectra were determined with a Varian A-56/60 at 56.4 MHz or Varian HA-100 operating at 94.1 MHz with essentially similar resolution except in the case of the compound $(SPF_2)_2S$ for which very good resolution was obtained eventually at 94.1 MHz. The compounds were studied as 5% solutions in 5-mm o.d. sample tubes. Phosphorus spectra were measured at 40.5 MHz on the Varian HA-100 instrument generally as neat liquids in 5-mm o.d. sample tubes containing a P_4O_6 capillary for lock and reference. Low-temperature spectra were measured using the Varian temperature controllers provided with the instruments and calibrated by direct measurement of the temperature of methanol in similar sample tubes in the probes by means of an immersed thermocouple for a range of temperature dial settings over the region of interest. Some difficulty was experienced with the temperature-dependent studies as a result of the difference in behavior of the two temperature controllers used so that quoted temperatures are reliable to ±5°. Low-temperature ^{31}P spectra were measured using a PBr_3 capillary as external reference to −40° at which point the reference froze and the lock was lost.

Table I

Theoretical and Approximate Expressions for Some Frequencies in the X Spectrum of an $AA'XX'X''X'''$ System

Theoretical Expressions for Weak Lines in the X Half-Spectrum[a]

Exact frequency	Approximate frequency
$\nu_X + (N + H) \pm [L^2 + (N + H)^2]^{1/2}$	$\nu_X + (N + H) \pm L$
$\nu_X + (N - H) \pm [L^2 + (N - H)^2]^{1/2}$	$\nu_X + (N - H) \pm L$
$\nu_X + (M - H) \pm [L^2 + (M - H)^2]^{1/2}$	$\nu_X + (M - H) \pm L$
$\nu_X + (M + H) \pm [L^2 + (M + H)^2]^{1/2}$	$\nu_X + (M + H) \pm L$

Approximate Separations of Weak Lines in the X Half-Spectrum

$J_{AA'}$
$(J_{XX'}(\text{cis}) + J_{XX'}(\text{trans}))$
$J_{AA'} \pm (J_{XX'}(\text{cis}) + J_{XX'}(\text{trans}))$
$J_{AA'} \pm (J_{XX'}(\text{cis}) - J_{XX'}(\text{trans}))$

[a] From ref 6. $H = {}^1/_2J_{AA'}$, $N = {}^1/_2(J_{XX'}(\text{cis}) + J_{XX'}(\text{trans}))$, $M = {}^1/_2(J_{XX'}(\text{cis}) - J_{XX'}(\text{trans}))$, and $L = {}^1/_2(J_{AX} - J_{A'X})$.

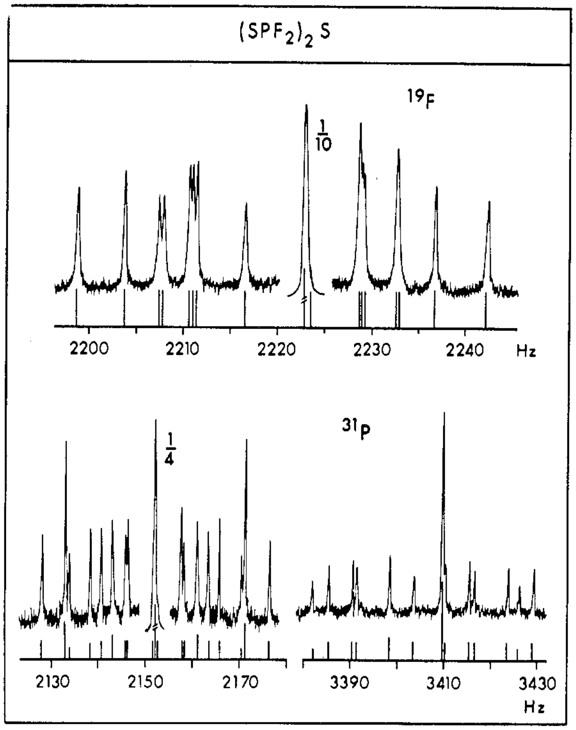


Figure 1.—Observed and calculated (stick diagram) ^{19}F (94.1 MHz) and ^{31}P (40.5 MHz) spectra of $(SPF_2)_2S$ at 33°. Only the high-field half of the ^{19}F spectrum and the high-field third and the central multiplet of the ^{31}P spectrum are illustrated. Numerical values shown are chemical shifts from the reference compounds (P_4O_6 for ^{31}P and CCl_3F for ^{19}F) with positive values indicating resonance to high field of the reference.

Results

Analyses of Spectra.—Although the fluorine nuclei and the phosphorus nuclei form chemically equivalent groups in the symmetric molecules represented by I, the differences in coupling between any one nucleus and chemically equivalent but magnetically nonequivalent nuclei in the molecule provide a second-order nmr spectrum. In the present case all of the fluorine spectra feature a strong doublet with a separation of $N = {}^1/_2({}^1J_{PF} + {}^3J_{PF})$ centered on the fluorine chemical shift (ν_F), and the phosphorus spectra show a 1:2:1 triplet of strong lines with the same separation centered on the phosphorus chemical shift (ν_P).[6] In the NCH_3-bridged compounds these groups of lines are further split into 1:3:3:1 quartets as the result of coupling to equivalent CH_3 protons. The remaining weak lines in both the ^{19}F and ^{31}P spectra are also symmetrically displaced about ν_F and ν_P such that a set of eight lines occurs twice in the fluorine spectrum and four times in the phosphorus spectrum.[6] From these lines all spectral parameters of the system can be obtained. The theoretical[6] line positions for a fluorine spectrum are given in Table I. Since most of the ^{19}F half-spectra extend over a very limited frequency range (10–40 Hz), the remaining coupling constants to nondirectly bound atoms are small relative to $^1J_{PF}$, and, consequently, simplified expressions (Table I) can be used to extract initial estimates of the coupling constants. Refinement was achieved by adjusting the values assigned to the coupling constants, computing the exact spectra using the program NSPECT III,[12] and comparing the computed spectra with the observed ^{31}P and ^{19}F spectra until the best agreement was obtained. Observed and calculated spectra are illustrated in Figures 1–4 and experimental and computed transition frequencies are listed in Tables II–IV. Excellent

---

[7] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966).

[8] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[9] R. K. Harris and C. M. Woodman, *Mol. Phys.* **10**, 437 (1966).

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

[11] The notation for coupling constants is due to J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

[12] J. S. Martin and G. R. DeMare, University of Alberta, personal communication.

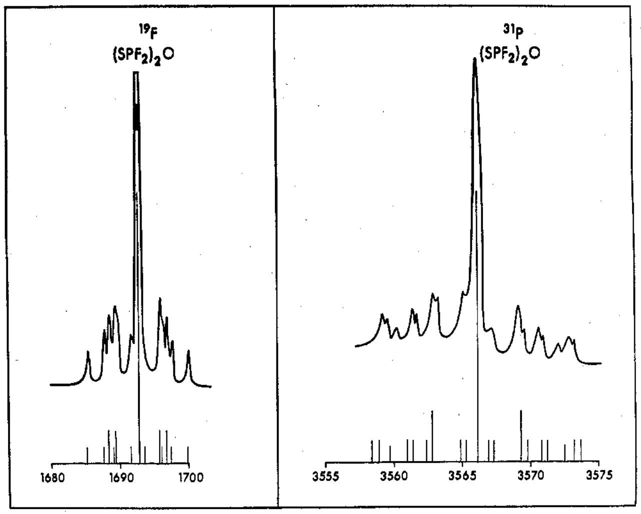


Figure 2.—The low-field half of the ^{19}F (56.4 MHz) spectrum and the central multiplet of the ^{31}P (40.5 MHz) spectrum of (SPF$_2$)$_2$O at 33°. Calculated spectra are represented by the stick diagram below each observed trace, and the numerical values are chemical shifts (Hz) to high field of the CCl$_3$F or P$_4$O$_6$ references, respectively.

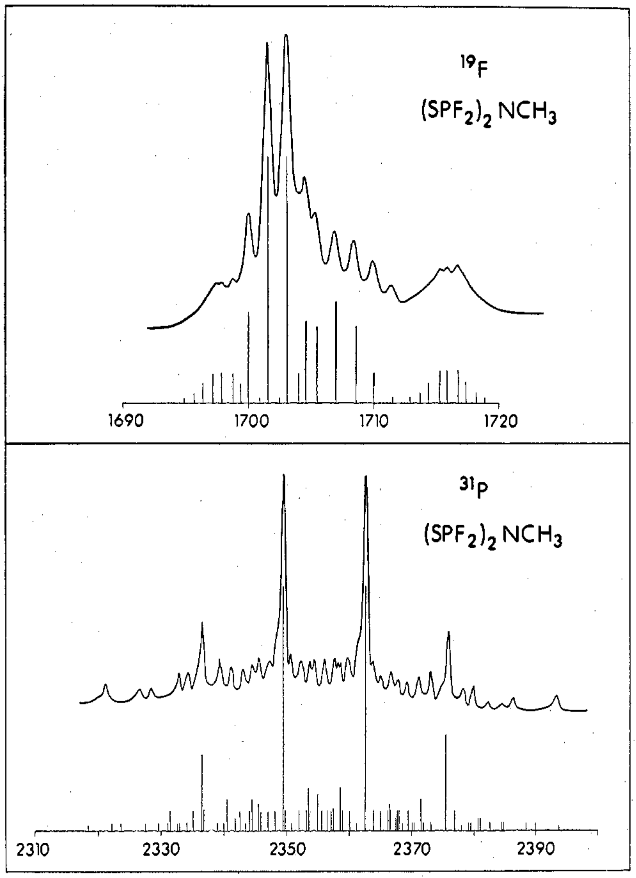


Figure 3.—Observed and calculated (stick diagram) ^{19}F (56.4 MHz) and ^{31}P (40.5 MHz) spectra of (SPF$_2$)$_2$NCH$_3$ at 33°. Only the low-field half of the fluorine spectrum and the central component of the ^{31}P triplet are illustrated. Numerical values are chemical shifts (Hz) to high field of the reference compounds CCl$_3$F and P$_4$O$_6$, respectively.

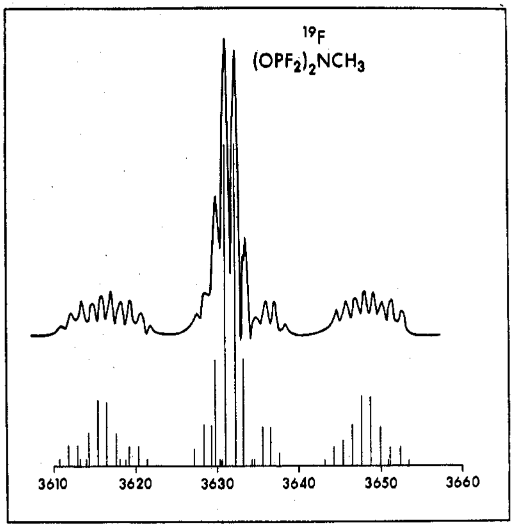


Figure 4.—Observed and calculated (stick diagram) low-field half of the ^{19}F spectrum of (OPF$_2$)$_2$NCH$_3$ at 56.4 MHz and 33°. The numerical values are chemical shifts (Hz) to high field of CCl$_3$F.

TABLE II

OBSERVED AND CALCULATED ^{19}F TRANSITION FREQUENCIES OF (SPF$_2$)$_2$S[a]

Obsd	Calcd	Obsd	Calcd
2241.9	2242.1	989.9	989.6
2236.4	2236.7	984.8	984.5
	2232.9	981.1	980.8
2232.4	2232.6	980.7	980.5
2229.0	2229.3	977.9	977.6
	2228.9	977.6	977.3
2228.5	2228.7	977.1	976.9
2222.9	2222.5	971.9	971.7
2222.6	2222.9[b]	965.6	965.3[b]
2216.3	2216.6		964.8
2211.1	2211.4	959.6	959.5
2210.7	2211.0	959.3	959.3
2210.4	2210.6		958.9
2207.6	2207.8	955.8	955.6
2207.1	2207.4		955.3
2203.4	2203.7	951.8	951.5
2198.4	2198.6	946.4	946.1

[a] At 94.1 MHz. [b] Calculated intensity of 32 units; all other lines have calculated transition intensities of approximately 2 units.

agreement between observed and calculated ^{19}F spectra was obtained. The agreement for ^{31}P spectra was, however, not as good for reasons which are discussed below. Significant deviations between observed and calculated spectra were observed if the geminal F–F coupling constant was assigned a value of 50 Hz or less. Provided, however, that this minimum value was exceeded, the spectra were generally insensitive to the magnitude and sign of the geminal F–F coupling constant. A value of 200 Hz was arbitrarily assigned to $^2J_{FF}$(gem) for all compounds. The derived values of the coupling constants for all molecules at 33° are collected in Table V.

An attempt was made to establish signs of the coupling constants where possible. The relative signs of $^1J_{PF}$ and $^3J_{PF}$ are given by the position of the weak lines relative to the strong lines in each half-spectrum. If the centers of the weak lines lie outside the strong lines, then $|^1J_{PF} - {}^3J_{PF}| > |^1J_{PF} + {}^3J_{PF}|$, and therefore $^1J_{PF}$ and $^3J_{PF}$ must be of opposite[6] sign. Since heteronuclear double resonance experiments[13-16] have

---

(13) D. L. Vanderhart, H. S. Gutowsky, and T. C. Farrar, *J. Chem. Phys.*, **50**, 1058 (1969).

(14) S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Amer. Chem. Soc.*, **89**, 4544 (1967).

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

(16) R. B. Johannesen, *J. Chem. Phys.*, **47**, 3088 (1967).

TABLE III

OBSERVED AND CALCULATED TRANSITION FREQUENCIES, ^{19}F SPECTRA[a]

$(SPF_2)_2O$

obs.	calc.
1685.3	1685.2
1687.7	1687.7
1688.4	1688.4
1689.4	1689.1
	1689.4
1691.6	1691.6
1692.8	1692.8
1693.7	1693.6
1695.8	1695.8
	1696.1
1696.8	1696.8
1697.6	1697.5
1699.9	1700.0
2856.5	2856.4
2859.0	2858.9
2859.6	2859.6
2860.4	2860.3
	2860.6
	2862.8
2863.6	2863.6
2864.8	2864.8
2866.9	2867.0
	2867.3
2868.0	2868.0
2868.8	2868.7
2871.0	2871.3

$(OPF_2)_2NH \cdot (CH_3)_3N$

obs.	calc.
3522.5	3522.2
	3527.3
	3527.6
3528.4	3528.2
	3528.4
3534.0	3533.8
3574.3	3573.5
	3574.6
3584.9	3584.0
	3585.1
3594.8	3594.8
3619.4	3619.0
	3623.0
	3623.4
3623.9	3623.8
	3624.1
3628.2	3628.4
4482.0	4481.6
	4485.8
	4486.0
	4486.4
4486.7	4486.5
	4486.8
4491.1	4491.1
4515.2	4515.2
4525.4	4524.8
	4525.8
4535.8	4535.2
	4536.3
4577.0	4576.3
	4581.4
	4581.6
4582.6	4582.2
	4582.5
4588.6	4587.9

$(OPF_2)_2NCH_3$

obs.	calc.
3610.7	3610.7
3611.9	3611.8
3613.2	3612.9
	3613.2
3614.5	3614.0
	3614.3
3615.6	3615.4
3616.8	3616.5
3618.1	3617.7
	3618.1
3619.1	3618.8
	3619.2
3620.4	3620.3
3621.6	3621.4
3627.3	3627.2
3628.4	3628.3
3629.7	3629.3
	3629.8
	3630.3
3630.9	3630.6
	3630.9
3632.1	3632.0
3633.1	3633.1
3634.5	3634.2
	3634.5
3635.8	3635.5
3636.9	3636.5
3738.1	3637.6
	3643.1
3644.2	3644.2
3645.6	3645.3
3646.7	3646.5
3647.8	3647.6
3648.9	3648.7
3650.0	3649.9
3651.1	3650.9
	3651.1
3652.5	3652.3
	3653.4
	4650.7
4651.6	4651.8
4653.0	4652.8
	4653.0
4654.2	4654.1
4655.2	4655.2
4656.3	4656.3
4657.4	4657.4
	4657.7
4658.6	4658.5
	4658.7
4659.9	4659.8
	4660.9
4666.2	4666.2
4667.3	4667.3
4668.5	4668.4
4669.7	4669.6
4671.0	4670.8
4672.1	4671.9
4673.2	4673.0
	4673.4
4674.3	4674.1
	4674.5
4675.6	4675.6
4676.9	4676.7
	4682.7
4683.7	4683.7
4684.9	4684.9
	4685.2
4686.3	4686.1
4687.4	4687.3
4688.6	4688.4
4689.7	4689.6
	4690.1
4690.9	4690.7
	4691.2
4692.3	4692.3
	4693.4

$(SPF_2)_2NCH_3$

obs.	calc.
	1694.9
	1695.7
	1696.4
1697.4	1697.3
1697.9	1697.9
1698.7	1698.8
	1699.4
1700.0	1700.1
	1701.0
1701.5	1701.5
	1702.5
1703.0	1703.1
	1704.0
1704.4	1704.5
1705.4	1705.5
1706.9	1707.0
1708.4	1708.5
1709.9	1710.0
1711.4	1711.5
	1712.9
	1713.7
	1714.4
1715.4	1715.3
1715.9	1715.9
1716.7	1716.7
	1717.4
	1718.2
	1718.9
	2823.5
	2824.1
	2825.0
2825.7	2825.6
2826.5	2826.5
2827.1	2827.1
	2828.0
	2828.6
	2829.5
2830.9	2830.9
2832.4	2832.4
2834.0	2833.9
2835.5	2835.4
2837.1	2836.9
2837.9	2837.8
	2838.4
2839.4	2839.3
2839.9	2839.9
	2840.8
	2841.5
	2842.1
2842.4	2842.3
	2843.0
2843.8	2843.6
2844.7	2844.5
2845.3	2845.1
	2846.0
	2846.6
	2847.4

$(SPF_2)_2NH \cdot (CH_3)_3N$

obs.	calc.
1274.5	1274.5
	1279.8
1280.0	1280.0
	1280.8
	1281.1
1286.4	1286.3
1316.1	1315.7
	1316.5
1327.0	1326.7
	1327.5
1335.2	1335.2
1353.6	1353.4
1358.0	1358.0
	1358.1
1359.4	1358.9
	1359.1
1363.4	1363.6
2347.5	2347.8
2352.0	2352.3
	2352.5
2353.5	2353.3
	2353.4
2357.6	2358.0
2376.2	2376.2
2383.8	2383.8
	2384.6
2395.0	2394.8
	2395.7
2425.3	2425.1
	2430.3
2430.6	2430.6
	2431.4
	2431.6
2436.9	2436.9

$(PF_2)_2O$

obs.	calc.
1383.4	1383.5
1385.7	1385.8
	1386.3
1386.9	1386.9
	1387.5
	1388.2
1390.5	1390.3
	1391.0
1391.6	1391.6
	1392.2
1392.7	1392.7
1395.2	1394.9
1403.7	1403.7
2745.1	2745.0
2754.1	2753.9
2756.4	2756.1
	2756.6
	2757.2
2757.7	2757.8
	2758.5
	2760.6
	2761.3
2762.1	2761.9
	2762.5
2762.9	2762.9
2765.2	2765.3

$(OPF_2)_2O$

obs.	calc.
4040.5	4040.6
4042.7	4042.7
4043.3	4043.2
	4045.4
4046.0	4046.0
5098.1	5098.0
	5098.7
5100.8	5100.7
5101.4	5101.2
5103.4	5103.5

[a] Spectra determined at 56.4 MHz on 5% CCl_3F solutions. The numerical values are chemical shifts in hertz relative to CCl_3F; positive values are to high field of the standard.

shown that the absolute sign of $^1J_{PF}$ in phosphorus fluorides is negative, we have assumed a negative sign for all of the $^1J_{PF}$ coupling constants in the present series of compounds. The sign of $^3J_{PF}$ is taken relative to the negative sign of $^1J_{PF}$.

In some favorable cases, an estimation of the sign of $^2J_{PP}$ relative to that of $^4J_{FF}$ and $^4J'_{FF}$ could be obtained by calculating the combination of these signs which best fitted the ^{31}P spectrum.[6] Since only a small number of lines in the ^{31}P spectrum are affected by the relative combination of these signs, cases in which $^2J_{PP}$ is small (such as in $(OPF_2)_2O$) or those in which the ^{31}P spectra were poorly resolved (as in the nitrogen-bridged compounds) did not give unambiguous indications of the relative signs.

A "spin-tickling" experiment on $(SPF_2)_2O$ indicated that $^4J_{FF}$ and $^4J'_{FF}$ have the same sign in this compound. Since the relative signs of $^2J_{PP}$ and the $^4J_{FF}$, $^4J'_{FF}$ combination appeared to be opposite in the case of the oxygen- and sulfur-bridged compounds, choosing a negative sign for $^2J_{PP}$ in agreement with the observed sign of $^2J_{PP}$ in the pyrophosphite anion[17] suggests that both of the long-range $^4J_{FF}$ coupling constants are positive in the oxygen- and sulfur-bridged compounds. The most satisfactory interpretation of the spectra of all of the nitrogen-bridged compounds considered here is obtained if a positive sign is chosen for both $^2J_{PP}$ and the pair of $^4J_{FF}$ coupling constants. The positive $^2J_{PNP}$ sign is then in agreement with the positive sign assigned to the analogous $^2J_{PNP}$ coupling constant in phosphonitrilic compounds[18] although the difference in

---

(17) W. McFarlane, *J. Chem. Soc. A*, 1715 (1968).

(18) (a) F. Heatley and S. M. Todd, *ibid.*, 1152 (1966); (b) M. L. Heffernan and R. F. M. White, *J. Chem. Soc.*, 1382 (1961).

TABLE IV

OBSERVED AND CALCULATED TRANSITION FREQUENCIES, ^{31}P SPECTRA[a]

$(SPF_2)_2O$

obs.	calc.
2388.6	2387.6
2390.7	2390.2
2391.4	2390.7
2392.3	2391.6
	2392.7
2394.5	2394.1
2395.3	2395.3
2395.8	2396.1
2396.2	2397.1
2398.5	2398.6
2399.1	2399.1
2400.1	2400.0
2402.2	2402.3
	3558.4
3559.1	3558.9
3559.4	3559.7
3560.1	3561.0
3561.3	3561.4
3561.6	3562.4
3562.8	3562.8
3563.1	3562.9
3565.1	3564.9
	3565.3
3566.1	3566.1
3566.9	3566.9
	3567.3
3569.0	3569.3
3569.4	3569.8
3570.5	3570.8
3570.9	3571.2
3572.0	3572.5
3572.7	3573.2
3573.1	3573.7
4730.3	4729.8
4732.5	4732.2
4733.4	4733.1
4734.0	4733.6
4736.1	4735.1
	4736.1
4736.9	4736.9
4738.0	4738.1
	4739.5
4740.3	4740.6
4741.2	4741.5
4741.8	4742.0
4744.2	4744.6

$(OPF_2)_2O$

obs.	calc.
5093.4	5093.3
5095.2	5095.3
5097.7	5097.9
5098.4	5098.4
5098.8	5098.9
5100.5	5100.7
5100.9	5100.9
	5101.1
5101.4	5101.6
5103.1	5102.9
	5103.5
5103.9	5104.0
	5104.2
6149.9	6150.4
6150.3	6150.9
6150.9	6151.0
6152.2	6152.7
6152.8	6153.2
6153.2	6153.6
6154.9	6155.5
6156.1	6156.1
	6156.3
	6156.8
6157.9	6158.6
6158.5	6158.7
6159.2	6159.1
	6159.5
6160.5	6161.2
6161.2	6161.4
	6161.9
7207.9	7208.2
	7208.4
7208.8	7208.8
	7209.3
7210.6	7210.7
7210.9	7211.0
	7211.2
7211.4	7211.3
	7211.5
7213.3	7213.4
7213.8	7213.9
	7214.4
7216.6	7216.9
7218.7	7218.9

$(SPF_2)_2S$

obs.	calc.
875.2	875.3
878.1	878.5
880.6	880.8
887.4	887.6
888.5	888.7
893.7	894.0
894.3	894.5
900.6	900.8
905.7	905.9
	906.1
912.4	912.7
913.2	913.7
918.4	918.7
921.7	921.3
2128.0	2127.8
2133.1	2132.9
2133.8	2133.8
2138.4	2138.3
2140.6	2140.6
2143.0	2143.0
2145.8	2145.8
2146.3	2146.2
	2151.6
2152.1	2152.1
	2152.6
2157.9	2157.9
2158.4	2158.4
2161.2	2161.2
2163.6	2163.6
2165.8	2165.9
2170.5	2170.4
2171.2	2171.3
2176.2	2176.4
3382.5	3382.3
3385.8	3385.5
3390.8	3390.5
3391.8	3391.4
3398.5	3398.2
	3398.3
3403.6	3403.4
3409.9	3409.7
3410.4	3410.2
3415.7	3415.5
3416.8	3416.6
3423.7	3423.4
3426.2	3425.7
3429.0	3428.9

$(PF_2)_2O$

obs.	calc.
-1307.5	-1307.2
	-1306.0
-1303.7	-1303.8
-1299.4	-1299.2
-1296.0	-1297.0
-1295.1	-1295.8
-1293.0	-1292.7
-1289.7	-1289.9
-1288.7	-1288.7
	-1288.1
	-1285.9
-1285.4	-1285.3
-1284.4	-1284.1
-1281.1	-1281.3
-1272.3	-1272.5
48.7	48.5
51.7	51.4
52.7	52.6
	53.2
	55.4
56.0	56.0
56.9	57.2
60.1	60.0
61.5	62.0
65.2	65.4
68.8	68.8
72.6	72.2
76.2	75.6
77.7	77.6
80.9	80.4
81.9	81.6
	82.2
85.2	84.4
	85.0
86.2	86.2
89.5	89.1
1410.3	1410.1
1418.9	1418.9
1422.2	1421.7
1423.1	1422.9
	1423.5
1426.4	1425.7
	1426.3
1427.4	1427.5
1430.7	1430.4
1433.6	1433.4
1434.2	1434.6
1437.1	1436.8
1441.6	1441.4
	1443.6
1445.3	1444.8

$(OPF_2)_2NH \cdot (CH_3)_3N$

obs.	calc.
4134	4138.7
4147	4149.2
	4154.5
4161	4159.1
	4164.5
4167	4165.1
	4170.6
4230	4231.6
	4239.7
4241	4244.9
4252	4255.4
	4255.6
	4260.2
	4260.6
	4265.1
	5079.4
	5084.8
5085	5085.4
	5090.9
	5118.4
	5122.9
	5123.3
5126	5127.9
	5141.4
	5146.6
5152	5151.9
	5157.1
	5162.4
5177	5176.1
	5180.7
	5181.1
	5185.6
	5212.9
5217	5218.5
	5219.0
	5224.5
	6038.7
6040	6043.2
	6043.6
	6048.3
6055	6058.8
	6064.1
6067	6072.4
	6133.4
6136	6139.0
	6139.5
	6145.0
6152	6149.3
	6154.5
6163	6165.0

$(SPF_2)_2NH \cdot (CH_3)_3N$

obs.	calc.
1445.7	1446.4
1456.2	1457.4
1461.8	1462.9
1463.9	1465.1
1468.7	1470.4
1471.2	1471.7
1475.7	1476.9
1525.7	1525.8
1530.5	1530.0
1535.9	1535.5
1544.3	1544.0
1546.5	1546.8
1548.6	1548.6
1550.5	1549.7
1554.5	1554.2
2505.6	2506.1
2510.5	2511.4
2512.9	2512.7
2517.9	2517.6
2538.4	2538.4
2542.2	2542.9
2544.5	2544.0
2548.7	2548.6
2556.1	2555.8
2561.8	2561.3
2566.8	2566.8
2572.4	2572.3
2578.1	2577.8
2586.0	2585.0
2590.1	2589.6
2592.1	2590.7
2596.2	2595.2
2617.1	2615.7
2621.7	2620.9
2623.9	2622.2
2629.0	2627.5
3578.8	3579.4
3583.0	3583.9
3585.2	3585.0
3587.0	3587.0
3589.2	3589.6
3597.7	3598.0
3603.3	3603.5
3607.8	3607.8
3657.7	3656.7
3662.3	3662.0
3664.7	3663.2
3669.3	3668.5
3671.5	3670.7
3677.1	3676.2
3688.4	3687.2

$(SPF_2)_2NCH_3$

obs.	calc.	obs.	calc.	obs.	calc.
	1190.8		2318.5		3447.7
1192.5	1193.6	2321.2	2322.2		3455.2
	1195.1		2323.7	3459.5	3460.0
1198.0	1198.3	2326.5	2327.6		3460.7
1198.9	1198.8	2328.3	2329.6	3463.1	3461.4
	1201.2		2331.1	3464.3	3464.2
1201.9	1202.7		2331.5		3465.7
1202.9	1203.8		2332.6	3467.5	3467.4
	1204.2	2332.8	2332.9		3468.3
1205.5	1205.7	2334.3	2334.1		3468.9
	1206.6		2335.2		3470.4
	1207.3	2336.5	2336.5	3472.2	3471.9
	1208.1	2339.3	2339.0		3473.0
1209.1	1208.8		2340.1		3473.7
1210.5	1211.3		2340.5	3474.4	3474.4
1211.8	1211.8	2341.2	2341.7	3475.8	3474.7
	1213.1		2342.0	3477.1	3477.2
1214.9	1214.2	2343.0	2342.6		3477.9
1215.8	1215.7		2343.5		3478.7
1216.9	1216.8		2344.1		3479.5
	1217.2	2344.4	2344.5	3480.7	3480.4
	1217.8	2345.6	2345.6		3481.3
1218.5	1218.7		2345.9		3481.9
	1219.6	2347.3	2347.1	3482.2	3482.2
	1220.3		2348.2	3483.2	3483.4
	1221.1	2349.5	2349.5	3484.2	3484.9
1221.9	1221.8		2349.7	3485.2	3486.0
1223.5	1224.3	2350.5	2350.9		3486.7
1224.9	1224.8		2352.0	3487.8	3487.4
	1225.3	2353.2	2353.2	3488.5	3487.7
	1226.1	2353.6	2353.5	3490.1	3490.2
1227.0	1227.2	2354.3	2354.7		3491.0
1227.9	1228.7		2355.0	3491.6	3491.7
1229.2	1229.8		2355.6		3492.5
1230.0	1230.2	2356.1	2356.5	3493.4	3493.4
	1230.8		2357.1		3494.3
1231.5	1231.7	2357.7	2357.4	3495.1	3494.9
	1232.6	2358.1	2358.6		3495.2
	1233.3	2358.6	2358.9	3496.4	3496.4
	1234.1	2359.7	2360.1	3497.3	3497.9
1235.1	1234.8		2361.2		3499.0
1236.6	1237.3	2362.6	2362.5	3500.5	3500.4
1238.0	1237.7	2363.6	2363.9	3501.5	3500.7
	1238.3	2365.1	2365.0	3502.9	3503.2
	1239.1		2366.2		3504.0
1240.2	1240.2	2366.6	2366.5		3504.7
	1241.7		2367.5		3505.5
	1243.2	2367.7	2367.7	3506.8	3506.4
	1243.8		2368.0		3507.9
1244.8	1244.7	2369.2	2368.6		3508.2
	1246.3		2369.5	3509.3	3509.4
1248.3	1247.8		2370.1	3510.4	3510.9
1249.7	1250.6		2370.4	3513.5	3513.3
	1251.3	2371.2	2371.5	3514.5	3513.7
1253.5	1252.1		2371.9		3516.9
	1256.8	2373.0	2373.1		3518.5
	1264.3	2375.8	2375.5	3520.1	3521.1
			2376.9		
		2378.2	2378.0		
			2379.1		
		2379.8	2379.5		
			2380.5		
			2380.7		
			2381.0		
		2382.4	2382.5		
		2384.3	2384.5		
		2386.3	2388.4		
			2389.9		
		2393.0	2393.5		

$(OPF_2)_2NCH_3$

obs.	calc.
	4061.5
4061.0	4062.5
	4064.1
	4066.1
4067.5	4066.4
	4068.9
	4072.4
4071.5	4073.4
	4075.0
4077.0	4077.0
	4077.3
	4079.8
4081.5	4080.8
	4083.3
	4084.3
	4085.9
	4087.9
	4088.2
	4090.7
4092.0	4091.6
	4093.9
	4094.3
	4095.1
	4096.4
	4096.8
	4098.4
	4098.9
	4099.1
	4101.0
	4101.8
4103.0	4102.5
	4104.9
	4106.0
4107.5	4107.3
	4109.3
	4111.9
4113.5	4112.9
	4113.4
	4115.8
4118.5	4118.2
	4120.2
4123.0	4122.8
	4123.7
	4126.7
4129.0	4129.1
	4131.0
	4131.2
	4133.6
	4134.6

obs.	calc.
5100.5	5101.6
	5102.5
	5104.0
	5105.1
5106.0	5106.0
	5107.3
	5108.5
	5109.9
5111.5	5112.4
	5113.4
	5114.7
	5116.0
5117.5	5117.0
	5118.2
	5119.4
	5120.8
5121.5	5121.6
	5123.3
	5124.3
	5125.3
	5125.8
	5126.9
	5127.9
	5129.0
	5130.3
	5131.7
5132.5	5132.5
	5133.5
	5134.2
	5135.1
	5136.2
	5136.7
	5137.6
	5138.3
	5138.8
	5139.7
	5140.1
	5141.0
	5142.6
5143.5	5143.4
	5144.4
	5145.9
	5147.0
	5148.3
	5149.2
	5150.5
	5151.8
	5152.8
5154.5	5154.3
	5155.3
	5156.8
5158.5	5157.9
	5159.2
	5160.1
	5161.4
	5162.6
5164.5	5163.7
	5166.1
	5167.7
5169.5	5168.8
	5170.1
	5171.1
	5172.2
	5173.6
5175.0	5174.6

obs.	calc.
	6141.4
	6142.5
	6145.0
6146.5	6147.1
	6142.4
	6152.2
6154.5	6153.4
	6155.9
6158.5	6157.9
	6160.4
	6162.7
6163.5	6163.2
	6164.3
	6166.7
6169.0	6168.8
	6169.9
	6171.2
6174.0	6173.6
	6174.3
	6175.3
	6177.1
	6177.7
	6179.3
	6179.8
	6180.8
	6181.9
	6182.1
6185.0	6184.5
	6185.4
	6188.0
	6190.2
	6191.6
	6192.8
6195.0	6195.3
	6196.3
6199.0	6198.9
	6201.1
	6202.5
6205.5	6203.7
	6207.2
	6209.8
	6212.0
	6213.5
6218.0	6214.6

[a] Spectra determined at 40.5 MHz on neat liquid samples. The numerical values are chemical shifts in hertz relative to a capillary of P_4O_6; positive values are to high field of the standard.

phosphorus coordination in the two systems might negate this comparison.

There would appear to be no evidence to support the preservation of a unique sign for $^2J_{PP}$ in all of these compounds. In fact, the most consistent rationalization of the data obtained herein suggests that the signs of the $^4J_{FF}$ coupling constants should be taken to be consistently positive while $^2J_{PP}$ is permitted to take both negative and positive values. This provides the best explanation for the variations of $^2J_{PP}$ coupling constants in the spectrum of $(SPF_2)_2O$ with temperature because the long-range $^4J_{FF}$ coupling constants, which

TABLE V

NMR PARAMETERS OF BRIDGED DIPHOSPHORUS TETRAFLUORIDE COMPOUNDS[a]

	Chemical shifts[b]			Coupling constants						
Compound	ϕ	Δ	τ	${}^1J_{PF}$[c]	${}^3J_{PF}$[e]	${}^4J_{FF}$	${}^4J'_{FF}$[d]	${}^2J_{PP}$[e]	${}^3J_{PH}$[f]	${}^4J_{FH}$[f]
$(PF_2)_2O$[g]	36.8	1.7	. . .	−1355.8	14.5	4.0	2.8	(−) 4.7	. . .	. . .
$(OPF_2)_2O$[h]	81.1	152.3	. . .	−1055.1	3.0	2.7	2.4	(−) 0.5	. . .	. . .
$(SPF_2)_2O$[h]	40.3	88.3	. . .	−1171.0	0.2	3.9	2.5	(−) 8.4	. . .	. . .
$(SPF_2)_2S$	17.0	53.1	. . .	−1254.7	−3.0	12.9	5.3	(−) 25.1	. . .	. . .
$(OPF_2)_2NCH_3$	73.6	127.1	6.51	−1040.2	−0.9	4.7	2.5	(+) 32.2	10.9	1.1
$(SPF_2)_2NCH_3$	40.2	58.3	6.48	−1133.1	−4.7	10.5	7.5	(+) 1.5	13.0	1.5
$(OPF_2)_2NH \cdot (CH_3)_3N$	71.9	127.4	6.90	−937.0	16.6	5.5	5.0	(+) 95.7	. . .	. . .
$(SPF_2)_2NH \cdot (CH_3)_3N$	32.9	66.1	6.70	−1055.3	14.3	6.1	4.9	(+) 78.1	. . .	. . .

[a] Temperature of measurement +33°. [b] τ *vs.* TMS (τ = 10.0), ϕ, ppm, *vs.* CCl_3F. Δ, ppm, *vs.* P_4O_6. Positive ϕ and Δ values indicate resonances to high field of the reference. [c] Sign assumed negative (see text). [d] Spin tickling experiments suggest a positive sign for this coupling. [e] Tentative sign values only as deduced from spectral interpretation. Dubious values are enclosed in parentheses (see text). [f] Signs not deduced. [g] Results are in essential agreement with those of ref 2 and 7. [h] Results are in essential agreement with those of ref 1.

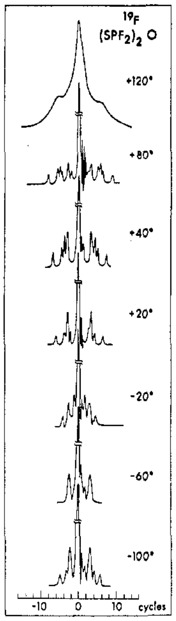


Figure 5.—Temperature dependence of the ^{19}F nmr spectrum (56.4 MHz) of μ-oxo-bis(thiophosphoryl difluoride). The low temperature spectra (+40 to −110°) were obtained on 5% solutions in CCl_3F while those at +80 and +100° were obtained on neat liquid samples. The spectra are shown relative to the position of the strong central peak of the low-field half of the spectrum.

do not change greatly in magnitude with temperature, then maintain a constant (positive) sign.

The spectra of the amine adducts $(EPF_2)_2NH \cdot (CH_3)_3N$ (E = O, S) were broad and poorly resolved probably as a result of the viscous nature of the neat liquid. Broadening could also arise from the nitrogen quadrupole moment[19] or from dissociation of the adduct into its molecular constituents

$$(EPF_2)_2NH \cdot (CH_3)_3N \rightleftharpoons (EPF_2)_2NH + (CH_3)_3N$$

or into ions

$$(EPF_2)_2NH \cdot (CH_3)_3N \rightleftharpoons (CH_3)_3NH^+ + (EPF_2)_2N^-$$

but present information does not permit an evaluation of the relative importance of these processes.

The proton spectra of the NCH_3-bridged compounds were essentially first order showing a triplet of quintets from which $^3J_{HP}$ and $^4J_{HF}$ were readily extracted. The first-order spectral behavior appears to be the result of relatively unrestricted rotation about the C–N bond giving averaged values for coupling. The relative signs of $^3J_{HP}$ and $^4J_{HF}$ were not determined.

Discussion

Two distinct long-range F–F coupling constants ($^4J_{FF}$ and $^4J'_{FF}$) can be extracted from all spectra, but specific values cannot be associated with "trans" (*i.e.*, $F_{(1)}$–$F_{(3)}$ coupling in structure I) or "cis" (*i.e.*, $F_{(1)}$–$F_{(4)}$ coupling) $^4J_{FF}$ couplings. All of the spectra, with the exception of that of $(F_2P)_2O$, are noticeably temperature dependent, and typical behavior is illustrated in Figure 5. The results of spectral measurements at different temperatures, given in Table VI, indicate that both $^2J_{PP}$ and the long-range $^4J_{FF}$ and $^4J'_{FF}$ coupling constants are subject to considerable variation with temperature. While the rate of change of the long-range ($^4J_{FF}$) coupling constants with temperature decreases greatly with temperature, it is apparent that limiting spectra have not been achieved at the lowest temperature attained.

The temperature dependence of the spectra also accounts in part for the discrepancies between the observed and calculated ^{31}P spectra, since the majority of the ^{19}F spectra were obtained on the A-56/60 instrument operating at 40°, while all of the ^{31}P spectra were obtained on the HA-100 instrument which normally operates at a temperature of 33°. Also the ^{19}F spectra were measured on 5% solutions in CCl_3F, whereas the ^{31}P spectra were measured on neat liquids, and this difference may be responsible for part of the discrepancy. The ^{31}P spectra were, in general, calculated on the basis of the coupling constants obtained from the 40° ^{19}F solution spectra, and exact agreement with the observed ^{31}P spectra is not to be expected. The derived coupling constants are probably reliable to within ±0.2 Hz.

The results clearly indicate that the $^2J_{PP}$ coupling constant in these molecules is temperature dependent. The extent of the temperature variation depends on the specific system, with the largest temperature variation of $^2J_{PP}$ being exhibited by $(SPF_2)_2O$, assuming that the suggested sign change is authentic. This change of sign with temperature allows the preservation of a regular variation in coupling constant with temperature for the $^2J_{PP}$ and all other coupling constants in the system and therefore appears to be reasonable. Although the *relative* variation of $^2J_{PP}$ over the range +80 to −110° for $(SPF_2)_2O$ is the largest yet encountered, the small value of this coupling constant (~10 Hz) in this system makes its effect on the spec-

---

(19) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

TABLE VI

TEMPERATURE DEPENDENCE OF THE NMR PARAMETERS OF SOME BRIDGED DIPHOSPHORUS TETRAFLUORIDE COMPOUNDS

		Coupling constants, Hz[e]				
Temp, °C	ϕ, ppm	$^1J_{PF}$	$^3J_{PF}$	$^2J_{PP}$	$^4J_{FF}$	$^4J'_{FF}$
		(a) $(SPF_2)_2O$				
+80[a]	40.5	−1169.0	0.1	−10.75	3.7	2.45
+60[a]	40.5	−1169.15	0.15	−9.5	3.7	2.4
+40[a]	40.3	−1168.8	0.2	−8.05	3.95	2.4
+40[b]	40.5	−1171.0	0.2	−8.4	3.9	2.5
+20[b]	40.5	−1170.7	0.3	−6.2	3.75	2.25
0[b]	40.4	−1169.6	0.3	−4.5	3.75	2.15
−20[b]	40.3	−1170.2	0.3	−2.9	4.0	1.6
−40[b]	40.3	−1169.7	0.3	−0.5	3.7	1.7
−60[b]	40.3	−1169.8	0.3	+0.5	3.7	1.7
−80[b]	40.2	−1169.2	0.3	+2.6	4.2	1.3
−80[b,c]	40.1	−1171.4	0.4	+3.2	4.2	1.6
−100[b]	40.2	−1170.3	0.3	+5.0	3.95	1.55
−100[b,c]	40.1	−1172.2	0.4	+5.4	4.1	1.5
−114[b,c]	40.1	−1169.5	0.5	+7.0	4.2	1.5
		(b) $(SPF_2)_2S$				
+160[a]	16.3	−1251.45	−2.05	−23.4	11.5	6.9
+140[a]	16.4	−1251.05	−2.15	−23.3	11.6	6.7
+120[a]	16.5	−1252.95	−2.25	−23.7	11.8	6.45
+100[a]	16.7	−1253.15	−2.35	−24.0	12.0	6.25
+80[a]	16.7	−1255.05	−2.45	−24.2	12.1	5.9
+80[b]	16.9	−1253.2	−2.2	−23.8	11.95	5.85
+60[a]	16.8	−1255.5	−2.6	−24.45	12.3	5.65
+60[b]	16.9	−1252.7	−2.6	−24.35	12.2	5.6
+40[a]	16.8	−1256.3	−2.7	−24.85	12.5	5.2
+40[b]	17.0	−1255.4	−3.0	−25.0	12.9	5.6
+10[b]	17.0	−1257.85	−2.85	−25.6	13.5	4.65
−10[b]	17.1	−1257.55	−2.95	−25.95	13.95	4.15
−30[b]	17.1	−1260.35	−3.05	−26.7	14.6	3.85
−50[b]	17.1	−1260.2	−3.2	−27.35	15.2	3.45
−70[b]	17.1	−1263.15	−3.15	−27.8	15.65	2.95
−80[b,c]	17.0	−1261.5	−3.6	−28.9	16.6	2.8
−90[b]	17.0	−1263.0	−3.3	−28.3	16.4	2.4
−100[b,c]	16.9	−1263.3	−3.6	−29.3	16.6	2.6
−114[b,c]	16.9	−1264.0	−3.6	−29.7	16.3	3.0
		(c) $(SPF_2)_2NH\cdot(CH_3)_3N$[d]				
+40	33.6	−1047.8	13.75	83.0	6.2	5.15
+20	33.6	−1045.9	14.5	86.15	6.3	5.2
0	33.7	−1046.6	14.8	88.1	6.75	4.6
−20	33.8	−1045.3	15.15	90.4	7.0	4.45
−40	33.8	−1043.6	15.4	93.35	7.45	3.95
−50	33.8	−1042.05	15.75	95.1	7.55	3.85
		(d) $(PF_2)_2O$[b]				
+40	36.8	−1356.25	14.65	−4.8	4.1	3.0
+20	36.9	−1356.9	14.6	−5.2	3.9	2.9
0	37.0	−1354.85	14.65	−5.2	4.3	2.35
−20	37.0	−1356.05	14.95	−4.7	4.2	3.1
−40	37.0	−1354.65	15.15	−4.85	4.25	2.5
−60	37.1	−1256.15	15.35	−4.8	3.75	2.85
−80	37.2	−1354.2	15.6	−4.55	3.9	2.8

[a] Neat sample. [b] 5% sample in $CFCl_3$. [c] Values obtained at 94.1 MHz; all others at 56.4 MHz. [d] 5% sample in CH_3CN. [e] The sign of $^1J_{PF}$ is assumed to be negative (ref 13–16). All other sign assignments quoted are tentative and have been derived as described in the text.

trum much less dramatic than the effect of the 30% variation of $^2J_{PP}$ with temperature reported[2] for F_2PSPF_2, because of the much larger magnitude of $^2J_{PP}$ (∼300 Hz) in the latter case.

The nitrogen-bridged tetrafluorodiphosphine $(F_2P)_2NCH_3$ also shows[2,3] a large $^2J_{PP}$ coupling; however, the temperature variation[2] in this case was very small, amounting to less than 10 in 400 Hz. The origin of the temperature variations of these coupling constants is not clear. In view of the lack of structural and configurational parameters on these compounds, we can only speculate that the most likely origin of this behavior is an intramolecular twisting or bending motion (*i.e.*, a low-frequency vibration) which alters the orientation of the phosphorus atoms relative to each other and thus the overlap integrals between P and the bridging atom. A difficulty with this interpretation arises from the relative insensitivity of the long-range $^3J_{PF}$ and $^4J_{FF}$ coupling to changes in temperature in both the presently investigated systems and the phosphines investigated by Rudolph and Newmark.[2] This is surprising, especially in those cases where $^2J_{PP}$ exhibits very large temperature variations since it seems reasonable to expect that any intramolecular motions which have an effect on $^2J_{PP}$ would also have a pronounced effect on $^3J_{PF}$ and the $^4J_{FF}$ pair. There is, of course, no *a priori* reason to expect that one mechanism alone would account for all of the temperature variations exhibited by the system.

It seems reasonable to expect that the long-range $^3J_{PF}$ and $^4J_{FF}$ coupling constants would be particularly sensitive to intramolecular motions, particularly if a "through-space" coupling mechanism[20-23] (which is likely to possess a very marked angular separation dependence[20]) is involved. It is possible that the relatively small variations in $^4J_{FF}$ and $^4J'_{FF}$ coupling with temperature are significant, and, although it is not possible to differentiate specific $^4J_{FF}$(cis) and $^4J_{FF}$(trans) couplings, the two $^4J_{FF}$ couplings can reasonably be considered to represent average cis and trans couplings which vary with temperature because the relative populations of the possible conformations of the molecule are controlled by the temperature of the system.

Estimations of F–F internuclear separations based on assumed bond lengths and bond angles for the bridged compounds indicate that only cis fluorines in a gauche structure may be close enough to permit a through-space interaction.[20] Because the fluorines are separated by four bonds, the difference between cis and trans coupling constants is not expected to be large despite the differences in dihedral angles. This is supported by the fact that the magnitude of $^4J_{FF}$ or $^4J'_{FF}$ in most of the bridged compounds is relatively small. It would thus appear that the increase in the larger F–F coupling constant ($^4J_{FF}$) (which can be assigned to the cis F–F coupling constant) can be attributed to a larger through-space interaction as a preferred gauche structure is adopted at lower temperatures. Similarly, the decrease in the smaller F–F coupling can be attributed to a decrease in the through-space contribution to the observed averaged value of the long-range F–F coupling constant.

Magnitudes of directly bonded P–F couplings observed in this study are in the same range as those found in similar systems.[24] The only previous reports of $^3J_{PF}$ couplings in pentavalent phosphorus compounds in addition to those reported elsewhere[1] for $(OPF_2)_2O$ and $(SPF_2)_2O$ are values of +2 Hz for $^3J_{PF}$ in $(OPFCl)_2O$,[25] +32 Hz in $(F_3PNCH_3)_2$,[9] ±11 Hz in

---

[20] L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).

[21] M. T. Rogers and J. D. Graham, *J. Amer. Chem. Soc.*, **84**, 3666 (1962).

[22] N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963).

[23] S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964).

[24] R. Schumtzler, *Advan. Fluorine Chem.*, **5**, 31 (1965), and references therein.

[25] M. M. Crutchfield, C. F. Callis, and J. R. Van Wazer, *Inorg. Chem.*, **3**, 280 (1964).

$P_3N_3Cl_5F$,[18a] and +14 Hz in $P_3N_3Cl_4F_2$.[18b] Mahler[26] reported $^3J_{PF}$ values of 20 Hz for some polyphosphine heterocycles, but no signs were given. These $^3J_{PF}$ values are comparable to all those given here. The magnitudes of $^2J_{PF}$ in the pyrophosphite anion[17] (−17 Hz) and the isohypophosphite anion[27] (±17.7 Hz) are in keeping with the values encountered for this coupling in the present study for oxygen-bridged diphosphorus systems. Likewise, the P–N–P coupling constants in the phosphonitrilic compounds $P_3N_3Cl_5F$ ($^2J_{PP} = +78.3$ Hz)[18a] and $P_3N_3Cl_4F_2$ ($^2J_{PP} = +100$ Hz)[18b] are comparable to the values observed here for the nitrogen-bridged compounds which have been formulated as trimethylamine adducts,[10] but the NCH_3-bridged compounds show very small $^2J_{PP}$ couplings. Temperature effects on the coupling constants of the above compounds have not been reported in the literature.

It appears that $^2J_{PP}$ couplings may have a wide range of values with either sign. Indeed, as the temperature studies of $(SPF_2)_2O$ indicate, $^2J_{PP}$ in a given compound may have a range of values with either sign. The signs and the range of values obtained in the present study for $^2J_{PP}$ are supported by the observation that long-range F–F coupling constants increase (that is, become more positive) if one of the intermediate atoms is nitrogen.[20] The $^2J_{PP}$ coupling in the trivalent tetrafluorodiphosphorus-bridged compounds shows a regular trend to more positive values in the order P–O–P (−4 Hz) < P–S–P [+272 Hz (at 31°)][2] < P–N–P (+437 Hz),[2,3] which could be associated with the change in hybridization of the bridge atom and its potential π-bonding ability.[28] In the system $(OPF_2)_2Z$ a similar trend is suggested by the larger coupling across nitrogen ($^2J_{PP} = +32.2$ Hz; Z = NCH_3) than across oxygen (−0.5 Hz). The sulfur-bridged member of this series has unfortunately not yet been prepared.[10] The thiophosphoryl system, $(SPF_2)_2Z$, does not follow the trend since the magnitude of $^2J_{PP}$ in $(SPF_2)_2S$ is larger than (and if the signs are correct, more *negative* than) $^2J_{PP}$ in either the oxygen-bridged or nitrogen- (Z = NCH_3) bridged molecules. A change of the quoted signs does not remove the anomalous position of the sulfur-bridged molecule. Clearly the negative sign suggested for $^2J_{PP}$ in $(SPF_2)_2S$ requires verification. Either sign for this coupling constant, however, suggests that the value of 68 Hz for $^2J_{PP}$ in the mixed-valence compound[4] $F_2P(S)SPF_2$ has a positive sign, thus placing this coupling intermediate between that of the trivalent[2] $(F_2P)_2S$ and the pentavalent $(SPF_2)_2S$ diphosphorus compounds. No $^2J_{PP}$ value has yet been reported[4,5] for $F_2P(O)OPF_2$.

The $^2J_{PP}$ coupling constants are more positive (if the given signs are correct) in each case for the oxygen-substituted compound $(OPF_2)_2Z$ than for the sulfur-substituted analog $(SPF_2)_2Z$ with the same Z. This trend can be understood as the effect of increased electron-withdrawing power of the oxygen-containing substituent leading to an increased "s" character in the bridge bonding.

The largest (and most positive) $^2J_{PP}$ coupling constants encountered in the system are those of the nitrogen-bridged "amine adduct" molecules $(EPF_2)_2NH\cdot N(CH_3)_3$ (E = O, S), assuming that the given signs are correct. These values are substantially larger and more positive than their NCH_3-bridged analogs in each case. It is not clear why these adducts should show such a large coupling across nitrogen, although it is tempting to speculate that the large values arise as a result of the formation of the $(EPF_2)_2N^-$ structure with a different geometry than that of the NCH_3-bridged analogs with perhaps an increased σ and π bonding across the bridge framework. Clearly further studies of these particular systems would be of interest.

While it seems reasonable to relate the signs and magnitudes of $^2J_{PP}$ couplings in all of the diphosphorus tetrafluoride molecules to parameters such as the P–X–P bridge angle, the nature of X (and thus its hybridization and potential π-bonding capabilities[28]), the valence of phosphorus, and the nature of the substituents on phosphorus, the range of observed $^2J_{PP}$ values is such as to resist classification. Obviously further efforts must be directed toward the fuller understanding of the origin of $^2J_{PP}$ and its relationship to the above factors before the temperature effects can be properly understood.

Acknowledgment.—We thank the National Research Council of Canada for generous financial support of this work. We also thank the National Research Council for the award of a Postgraduate Scholarship (to T. L. C.), and we would like to thank Mr. A. R. Quirt for checking some of the spectra and Dr. J. S. Martin for helpful discussions.

---

(26) W. Mahler, *J. Amer. Chem. Soc.*, **86**, 2306 (1964).
(27) R. L. Carroll and R. E. Mesmer, *Inorg. Chem.*, **6**, 1137 (1967).
(28) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).