in a one-electron-transfer process whereas oxygen bonding is a necessary and sufficient condition for two-electron transfer. Since each vanadium(IV) can transfer *only* one electron, we suggest that only the chlorine-bonded species would result in the formation of vanadium(V). We also wish to suggest that at high vanadium concentrations an additional term second order in vanadium(IV) would become important and this species would involve the oxygen-bonded complex.

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Microwave Spectrum, Structure, Dipole Moment, and Nuclear Quadrupole Coupling Constants of Cyanodifluorophosphine[1]

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The microwave spectra of the ground and some excited vibrational states of PF_2CN, $PF_2{}^{13}CN$, and $PF_2C^{15}N$ have been analyzed. From the moments of inertia, structural parameters have been derived as follows: $d(PF) = 1.566 \pm 0.007$ Å, $d(PC) = 1.815 \pm 0.005$ Å, $d(CN) = 1.157 \pm 0.003$ Å, $\angle FPF = 99.2 \pm 0.2°$, $\angle FPC = 96.9 \pm 0.2°$, and $\angle PCN = 171.2 \pm 0.8°$. The tilt of the CN group is away from the fluorine atoms. The nitrogen quadrupole coupling constants are $\chi_{aa} = -4.66 \pm 0.12$ MHz, $\chi_{bb} = 5.08 \pm 1.0$ MHz, and $\chi_{cc} = -0.42 \pm 1.0$ MHz. The dipole moments are $\mu_a = 2.03 \pm 0.01$ D, $\mu_c = 1.27 \pm 0.03$ D, and $\mu = 2.39 \pm 0.02$ D.

Introduction

An investigation of the microwave spectrum of cyanodifluorophosphine, PF_2CN, was undertaken as a result of the current interest in the structure and bonding in substituted fluorophosphines.[2] Of particular interest in this study were the PC bond distance and the PCN angle. The results of a determination of the crystal structure of phosphorus tricyanide, $P(CN)_3$, by X-ray diffraction[3] indicated that the average PCN angle is about 171 ± 3°, rather than the 180° that would be predicted by simple bonding theory. It has been suggested that this nonlinearity is due to the close packing in the crystal lattice and that it would not occur in the free molecule.[4]

Experimental Section

Samples of PF_2CN, $PF_2{}^{13}CN$, and $PF_2C^{15}N$ were prepared by the interaction of PF_2I with CuCN as reported by Rudolph, *et al.*[5] For the ^{13}C and ^{15}N species, the corresponding cuprous cyanides were obtained from appropriately enriched KCN by the use of the procedure of Barber.[6] The enriched samples contained 15% $PF_2{}^{13}CN$ and 25% $PF_2C^{15}N$, respectively. All samples were purified by trap-to-trap distillation, and their presence was confirmed by mass spectroscopy. In each case, the mass spectrum also revealed the presence of PF_2I as the major impurity, apparently because PF_2CN and PF_2I have about the same volatility.[5] Although PF_2I has a fairly rich spectrum, its interference in the study of the spectrum of PF_2CN has been minimal.

The spectra, all taken at Dry Ice temperature, were obtained with conventional Stark-modulated spectrometers of our own construction and a Hewlett-Packard R8460A MRR spectrometer. The uncertainty in the observed frequencies reported here is ±0.10 MHz.

Spectra.—The spectrum of PF_2CN was initially calculated by assuming a pyramidal structure and a plane of symmetry. The assignment of the normal species was based on the characteristic Stark effect of the three *a*-type $J = 1 \rightarrow 2$ transitions. Spectra for the isotopic species were assigned in the same fashion. The frequencies of the observed transitions in the ground vibrational state of the three isotopic species are listed in Table I, and the corresponding rotational parameters are given in Table II. Transitions belonging to excited states of the lowest frequency vibrational mode of the three isotopic species were also observed and fit and are given in Table III; the corresponding rotational parameters are in Table IV. At Dry Ice temperature the ratio of the intensity of a transition in the first excited state to that of a corresponding transition in the ground state is approximately

TABLE I

FREQUENCIES[a] OF GROUND STATE ROTATIONAL TRANSITIONS FOR ISOTOPIC SPECIES OF PF_2CN

Transition	PF_2CN	$PF_2{}^{13}CN$	$PF_2C^{15}N$
$1_{01} \rightarrow 2_{02}$	11,613.94 (0.14)[b]	11,506.42 (−0.35)	11,239.05 (−0.18)
$1_{11} \rightarrow 2_{12}$	11,024.66 (0.24)	10,926.68 (0.16)	10,682.31 (0.07)
$1_{10} \rightarrow 2_{11}$	12,349.86 (0.37)	12,227.12 (−0.01)	11,921.86 (0.15)
$2_{02} \rightarrow 3_{03}$	17,243.59 (0.04)	17,090.54 (0.27)	16,706.15 (0.03)
$2_{12} \rightarrow 3_{13}$	16,493.14 (−0.04)	16,348.22 (0.09)	15,985.41 (−0.54)
$2_{21} \rightarrow 3_{22}$	17,530.81 (0.38)	17,365.71 (0.49)	16,953.06 (0.10)
$2_{11} \rightarrow 3_{12}$	18,475.52 (−0.19)	18,294.43 (0.14)	17,841.27 (0.11)
$2_{20} \rightarrow 3_{21}$	17,817.57 (0.25)	17,640.21 (0.01)	17,200.09 (0.29)
$3_{03} \rightarrow 4_{04}$	22,690.52 (0.11)	22,497.01 (−0.16)	22,011.64 (−0.08)
$3_{13} \rightarrow 4_{14}$	21,916.52 (−0.04)	21,726.45 (0.37)	21,250.61 (0.52)
$3_{31} \rightarrow 4_{32}$	23,506.02 (−0.17)	23,279.85 (−0.76)	22,717.95 (−0.39)
$3_{12} \rightarrow 4_{13}$	24,536.53 (0.09)	24,299.32 (0.31)	23,704.95 (−0.28)
$4_{04} \rightarrow 5_{05}$	27,963.57 (−0.25)	27,733.79 (−0.27)	27,156.52 (−0.02)
$4_{22} \rightarrow 5_{23}$	30,305.97 (−0.27)	29,992.32 (−0.10)	29,212.32 (−0.02)
$4_{14} \rightarrow 5_{15}$	27,289.35 (−0.26)	27,055.18 (−0.16)	
$4_{13} \rightarrow 5_{14}$	30,498.12 (−0.02)	30,209.53 (0.05)	29,486.35 (0.22)
$0_{00} \rightarrow 1_{10}$	10,656.72 (0.08)		
$1_{01} \rightarrow 2_{11}$	17,162.57 (−0.08)		

[a] Uncertainty in observed frequencies is ±0.10 MHz. [b] Numbers in parentheses are differences between observed and calculated values of the frequencies. Rotational parameters are in Table II.

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[1] (a) Supported in part by grants from the National Science Foundation. (b) Presented at the 161st National Meeting of the American Chemical Society, Los Angles, Calif., March 1971.

[2] (a) R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **90**, 1705 (1968); (b) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *ibid.*, **93**, 6772 (1971); (c) A. H. Brittain, J. E. Smith, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 33 (1972); (d) R. L. Kuczkowski, H. W. Schiller, and R. W. Rudolph, *ibid.*, **10**, 2505 (1971); (e) Y. Morino, K. Kuchitsu, and T. Moritano, *ibid.*, **8**, 867 (1969).

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TABLE II

GROUND STATE ROTATIONAL PARAMETERS OF PF_2CN, $PF_2{}^{13}CN$, AND $PF_2C^{15}N$

Parameter	PF_2CN	$PF_2{}^{13}CN$	$PF_2C^{15}N$
A^a	7403.63 ± 0.27	7404.41 ± 2.8	7400.31 ± 2.5
B	3253.01 ± 0.04	3219.36 ± 0.07	3135.36 ± 0.06
C	2590.47 ± 0.04	2569.06 ± 0.07	2515.63 ± 0.06
$I_a{}^b$	68.2606	68.2534	68.2911
I_b	155.3565	156.9804	161.1858
I_c	195.0905	196.7167	200.8948
$P_{aa}{}^c$	141.0932	142.7219	146.8947
P_{bb}	53.9973	53.9948	54.0000
P_{cc}	14.2633	14.2586	14.2911
κ	−0.724697	−0.731022	−0.746253

[a] In MHz. [b] In u Å²; conversion factor: 505,376 MHz u Å². [c] In u Å²; $P_{aa} = (I_b + I_c - I_a)/2$, etc.

TABLE III

FREQUENCIES[a] OF TRANSITIONS IN VIBRATIONALLY EXCITED STATES FOR ISOTOPIC SPECIES OF PF_2CN

Transition	PF_2CN $v = 1$	PF_2CN $v = 2$	$PF_2{}^{13}CN$ $v = 1$	$PF_2C^{15}N$ $v = 1$
$1_{11} \rightarrow 2_{12}$	11,042.56 (0.12)[b]	11,060.01 (0.02)		
$2_{12} \rightarrow 3_{13}$	16,519.15 (−0.25)	16,543.55 (−0.02)		
$4_{04} \rightarrow 5_{05}$	27,994.15 (0.08)	28,024.25 (0.00)	27,763.05 (−0.01)	27,189.44
$4_{13} \rightarrow 5_{14}$	30,580.61 (0.30)		30,289.70 (−0.07)	29,569.60
$4_{23} \rightarrow 5_{24}$	29,120.48 (−0.14)			28,180.40
$4_{14} \rightarrow 5_{15}$	27,325.53 (0.00)	27,361.33 (0.00)		
$4_{22} \rightarrow 5_{23}$	30,413.52 (0.06)		30,099.39 (0.01)	
$5_{14} \rightarrow 6_{15}$			36,070.49 (0.05)	

[a] Uncertainties in the observed frequencies are ±0.10 MHz. [b] Numbers in parentheses are observed minus calculated frequencies. Rotational parameters are in Table IV.

TABLE IV

ROTATIONAL PARAMETERS FOR THE VIBRATIONALLY EXCITED STATES OF PF_2CN, $PF_2{}^{13}CN$, AND $PF_2C^{15}N$

Parameter	PF_2CN $v = 1$	PF_2CN $v = 2$	$PF_2{}^{13}CN$ $v = 1$	$PF_2C^{15}N$ $v = 1$
A^a	7377.22	7351.27	7367.08	7387.22
B	3265.50	3275.45	3231.60	3147.72
C	2592.40	2594.85	2571.04	2517.31
$I_a{}^b$	68.5049	68.7467	68.5992	68.4122
I_b	154.7624	154.2919	156.3856	160.5528
I_c	194.9455	194.7614	196.5648	200.7603
$P_{aa}{}^c$	140.6015	140.1533	142.1756	146.4505
P_{bb}	54.3440	54.6087	54.3892	54.3098
P_{cc}	14.1609	14.1386	14.2101	14.1023
κ	−0.718653	−0.713815	−0.724539	−0.741098

[a] In MHz. Uncertainty in rotational constants is ±5 MHz for *A;* ±0.10 MHz for *B* and *C*. [b] In u Å²; conversion factor: 505,376 MHz u Å². [c] In u Å²; $P_{aa} = (I_b + I_c - I_a)/2$, etc.

0.4. Thus, the energy separation is about 125 cm⁻¹. The assignment of the infrared spectrum of this compound is incomplete.[5] The frequencies of two modes (the rocking and out-of-plane wagging motion of the PF_2 group) are believed to lie below 200 cm⁻¹. By analogy with PF_2NH_2,[2b] PF_2Cl, and PF_2Br[7] the lowest frequency mode observed in the microwave spectrum is probably the out-of-plane wagging motion of the PF_2 group. In addition, rotational transitions arising from molecules in the first excited state of a second mode were also observed in the microwave spectrum but not assigned. The relative intensity of these transitions is intermediate between those of the first and the second excited states of the lowest fundamental.

Molecular Structure.—In PF_2CN there are five atoms, and hence a total of 15 atomic coordinates is needed to fix the structure. As a result of the plane of symmetry, the *b* coordinates of the P, C, and N atoms are zero and the *b* coordinate of one fluorine atom is the negative of that of the other. Also, the *a* and *c* coordinates of the two fluorine atoms are the same. To fix the nine nonzero coordinates there are three moments of inertia of the normal species, two moments of inertia for each of the labeled species, two first-moment relations, $\Sigma m_i a_i = 0$ and $\Sigma m_i c_i = 0$, and the product-of-inertia relation, $\Sigma m_i a_i c_i = 0$. Thus, there are ten pieces of information from which to determine nine coordinates.

The nine coordinates were determined in two ways. An approximate "r_0" structure was obtained by the method of least squares by fitting the seven moments of inertia of the three species, the first-moment relations, and the product of inertia. A Kraitchman (Kr) structure was obtained by using the Kraitchman equations[8] to obtain the *a* and *c* coordinates of the C and N atoms, followed by fitting the remaining coordinates to the second moments of the normal species, the first-moment relations, and the product of inertia. The Kraitchman equations used were those which assume an *ac* plane of symmetry and do not require a value for the moment of inertia, I_a. The *a* moments were omitted because they are less precise than the *b* and *c* moments. Solution of the Kraitchman equation gave an imaginary value for the *c* coordinate of the carbon atom. Therefore, this coordinate was set equal to zero in the Kr structure. The coordinates for the r_0 and Kr structures are compared in Table V and the corresponding bond distances and bond angles are shown in Table VI. Except for the *c* coordinates of the carbon and nitrogen atoms, which have a large uncertainty in both cases, the two structures are quite comparable.

TABLE V

CARTESIAN COORDINATES[a] IN THE PRINCIPAL AXIS SYSTEM OF PF_2CN

Atom	Method	*a*	*b*	*c*
P	r_0	−0.4532 ± 0.0034	0.00	0.5288 ± 0.0029
	Kr	−0.4565 ± 0.0034	0.00	0.5290 ± 0.0029
F	r_0	−0.9283 ± 0.0017	±1.1921 ± 0.0013	−0.3703 ± 0.0041
	Kr	−0.9265 ± 0.0016	±1.1921 ± 0.0013	−0.3707 ± 0.0041
C	r_0	1.2793 ± 0.0012	0.00	0.0023 + 0.0079[b]
	Kr	1.2798 ± 0.0012	0.00	0.0000 ± 0.0076[b]
N	r_0	2.4250 ± 0.0006	0.00	−0.1670 ± 0.0098
	Kr	2.4252 ± 0.0006	0.00	−0.1634 ± 0.0093

[a] In Å. The uncertainties in the coordinates include an experimental contribution and a vibration–rotation contribution estimated to be $\delta q = 0.0015/q$. [b] The uncertainty in this coordinate was estimated from $\delta c_{\mathrm{carbon}} = 2\{\Sigma(m_i \delta c_i)^2\}^{1/2}/m_{\mathrm{carbon}}$.

TABLE VI

STRUCTURAL PARAMETERS OF PF_2CN

Parameter[a]	r_0	Kr
P—F	1.567 ± 0.007	1.566 ± 0.007
P—C	1.811 ± 0.005	1.815 ± 0.005
C≡N	1.158 ± 0.003	1.157 ± 0.003
∠FPF	99.1 ± 0.2	99.2 ± 0.2
∠FPC	97.1 ± 0.2	96.9 ± 0.2
∠PCN	171.5 ± 0.8	171.2 ± 0.8

[a] Bond distances in ångströms and bond angles in degrees.

To examine the effect of the large uncertainty in the *c* coordinates of the carbon and nitrogen atoms on the overall structural parameters, a series of r_0 structures were calculated by fixing the carbon *c* coordinate at values from −0.006 to 0.010 and fitting the remaining coordinates. The resulting variations in the structural parameters were within the uncertainties listed. Thus, for

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(7) A. Muller, B. Krebs, B. Vizi, and S. J. Cyvin, *J. Mol. Struct.*, **2**, 149 (1968), and references therein.

(8) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

example, the nonlinear PCN angle does not appear to be merely a result of uncertainty in the coordinates.

In comparison with other substituted difluorophosphines, the P–F distance and FPF angle appear to be normal, whereas the P–C bond length and PCN angle were unexpected. The P–C bond length (1.810 Å) is significantly shorter than the sum of the covalent bond radii (1.87 Å), and the nonlinearity of the PCN angle is apparently independent of physical state.

Recently, the structure of PF_2CN has been determined by electron diffraction.[9] Two of the bond distances reported (PF = 1.568 ± 0.003 Å and CN = 1.165 ± 0.005 Å) agree within experimental error with the values reported here. The third distance reported (PC = 1.792 ± 0.009 Å) and the two angles (FPC 98.3 ± 0.3° and FPF = 97.9 ± 0.3°) differ from the microwave results by more than the sum of the uncertainties. Part of the difference may be due to the different definitions of the parameters and part may be due to the fact that the PCN angle was assumed to be 180° in the analysis of the electron diffraction data, whereas we have shown the angle to be 171°. It is difficult to estimate the effect of this assumption on the electron diffraction results, but it is certain to have a larger effect on the angles than on the distances.

Nuclear Quadrupole Coupling Constants.—The interaction of the quadrupole moment of the nitrogen nucleus with the electric field gradient of the electronic charge distribution at the ^{14}N nucleus gives rise to hyperfine structure in certain transitions. An analysis of the hyperfine splittings affords a means of determining the nuclear quadrupole coupling constants. In molecules containing ^{14}N, the splittings are of the order of only 1 or 2 MHz; hence, a first-order correction to the rigid-rotor Hamiltonian should be quite adequate. For any transition this correction may be written as

$$\Delta\nu_{\text{quad}} = \Delta\alpha\chi_{aa} + \Delta\beta(\chi_{bb} - \chi_{cc})$$

where $\Delta\alpha$ and $\Delta\beta$ depend only on the inertial asymmetry parameter. The experimental splittings were fit by least squares to give values of χ_{aa} and $\chi_{bb} - \chi_{cc}$. A comparison of observed and calculated frequencies of the hyperfine components is shown in Table VII, and the resulting quadrupole parameters appear in Table VIII.

TABLE VII

FREQUENCIES[a] OF THE TRANSITIONS USED IN THE DETERMINATION OF THE NUCLEAR QUADRUPOLE CONSTANTS OF PF_2CN

Transition	F → F′	ν_{obsd}	ν_{hyp}[b]
$1_{01} \rightarrow 2_{02}$	2 → 3	11,613.94 (0.06)[c]	11,613.87 (0.06)[d]
	1 → 2	11,613.94 (0.02)	11,613.81 (0.02)
	0 → 1	11,612.52 (−0.01)	11,613.79 (−0.02)
$1_{11} \rightarrow 2_{12}$	2 → 3	11,024.66 (0.01)	11,024.44 (0.01)
	1 → 2	11,023.20 (−0.06)	11,024.36 (−0.06)
$1_{10} \rightarrow 2_{11}$	2 → 3	12,349.86 (0.01)	12,349.52 (0.01)
	1 → 2	12,348.53 (0.18)	12,349.69 (0.18)
$2_{21} \rightarrow 3_{22}$	3 → 4	17,530.81 (0.03)	17,530.48 (0.03)
	2 → 3	17,529.31 (0.02)	17,530.47 (0.02)
$8_{27} \rightarrow 8_{26}$	9 → 9	10,148.67 (−0.07)	10,148.28 (0.09)
	8 → 8	10,147.36 (0.09)	10,148.28 (0.09)

[a] In MHz. [b] ν_{hyp} = the hypothetical unsplit frequency derived by subtracting the calculated quadrupole contribution from the observed frequency. [c] Numbers in parentheses are ($\nu_{\text{obsd}} - \nu_{\text{calcd}}$). [d] Numbers in parentheses are ($\nu_{\text{hyp}} - \nu_{\text{calcd}}$).

TABLE VIII

QUADRUPOLE COUPLING CONSTANTS[a] OF PF_2CN

Principal axis system	C≡N bond-axis system
$\chi_{aa} = -4.66 \pm 0.12$ MHz	$\chi_{zz} = -4.75 \pm 1.0$ MHz
$\chi_{bb} = 5.08 \pm 1.0$ MHz	$\theta_z{}^c = 8.2°$
$\chi_{cc} = -0.42 \pm 1.0$ MHz	$\eta_{\text{bond}}{}^b = 1.14 \pm 0.22$
$\eta^b = 1.18 \pm 0.22$	

[a] $\chi_{aa} = eQ(\partial^2V/\partial a^2)_0$, etc. [b] $\eta = (\chi_{bb} - \chi_{cc})/\chi_{aa}$; $\eta_{\text{bond}} = (\chi_{xx} - \chi_{yy})/\chi_{zz}$; the b and y axes are parallel. [c] θ_z was calculated from the Kr structure, Table V.

The coupling constants in the principal quadrupolar axis system can be obtained from those in the principal inertial axis system by the following simple transformation.

$$\chi_{zz} = (\chi_{aa}\cos^2\theta_z - \chi_{cc}\sin^2\theta_z)/(\cos^2\theta_z - \sin^2\theta_z)$$

$$\chi_{xx} = (\chi_{aa}\sin^2\theta_z - \chi_{cc}\cos^2\theta_z)/(\sin^2\theta_z - \cos^2\theta_z)$$

In these equations θ_z is the angle between the z axis of the quadrupolar system and the a inertial axis, and an ac plane of symmetry is assumed. Then, χ_{yy} is equal to χ_{bb}, the out-of-plane component. By comparison with HCN[10] and CH_3CN[11] it is apparent that χ_{bond} of the CN bond of PF_2CN is essentially that expected for a CN triple bond. However, the observed asymmetry, ($\chi_{yy} - \chi_{xx}$) = 5.44 MHz, strongly suggests the presence of some perturbation to the bonding.

Dipole Moment.—The results of an analysis of Stark effect measurements on PF_2CN are shown in Table IX. As expected, the total dipole moment (2.39 D) is considerably smaller than the ~4.0 D typically obtained for organic cyanides.[12] This decrease may be attributed to partial cancellation of the CN bond moment by the PF_2 group. The dipole moment vector in PF_2CN makes an angle of about 32° with the a axis and the probable orientation is shown in Figure 1.

TABLE IX

COMPARISON OF OBSERVED AND CALCULATED STARK SHIFT SLOPES FOR PF_2CN

Transition	M	$(d\nu/dE^2)_{\text{obsd}}{}^a$	$(d\nu/dE^2)_{\text{calcd}}{}^a$
$1_{01} \rightarrow 2_{02}$	0	−22.67	−23.29
$1_{01} \rightarrow 2_{02}$	1	40.03	39.89
$2_{11} \rightarrow 3_{12}$	1	−10.61	−10.35
$2_{11} \rightarrow 3_{12}$	2	−40.33	−39.78
$2_{12} \rightarrow 3_{13}$	1	13.15	13.15
$2_{12} \rightarrow 3_{13}$	2	48.53	48.40

$\mu_a{}^2 = 4.109 \pm 0.046$ D^2 $\mu_a = 2.027 \pm 0.011$ D

$\mu_b{}^2 = 0$ (assumed) $\mu_c = 1.272 \pm 0.028$ D

$\mu_c{}^2 = 1.619 \pm 0.070$ D^2 $\mu = 2.393 \pm 0.018$ D

[a] In MHz (kV/cm)$^{-2}$; $\mu_{\text{OCS}} = 0.7152$ D assumed.

Discussion

As mentioned previously, the outstanding characteristics of the structure of PF_2CN are the short PC bond length and the nonlinear PCN arrangement. There are several electronic effects which could be used to rationalize these characteristics. The shortened PC bond is most easily explained by a delocalization of the CN π system to include the phosphorus atom. Such a delocalization could be of two types, an n–π interaction involving the lone pair of the phosphorus atom or a d–π interaction which uses the phosphorus d orbitals. Either type of interaction would give some ionic character to the PC bond (although the polarities would be different) and hence shorten it. The n–π interaction has been used before to explain the SC bond length in $S(CN)_2$.[13]

The bend of the PCN angle may be the result of the n–π interaction or a result of an electrostatic repulsion between the fluorines and the CN π system or some combination of both effects. If the n–π interaction is bonding, a bend of the π system toward the lone pair would be favored since such a bend would increase the interaction. An F–π steric repulsion would also lead to a tilt in the direction observed. Detailed quantum mechanical calculations will probably be required to quantitatively characterize the contributions of these interactions.

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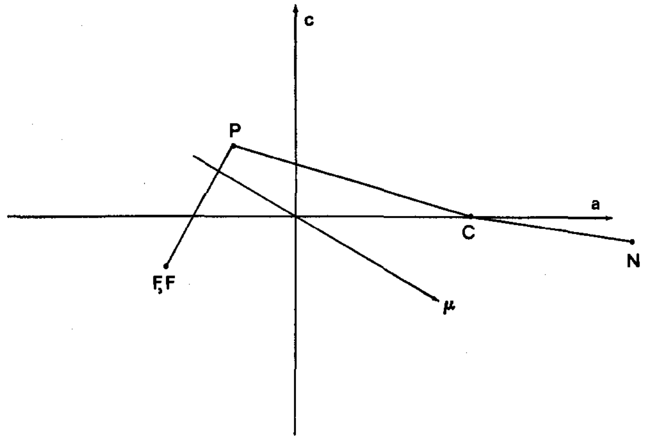

Figure 1.—A projection of PF_2CN in its *ac* plane of symmetry. The probable direction of the dipole moment is shown.

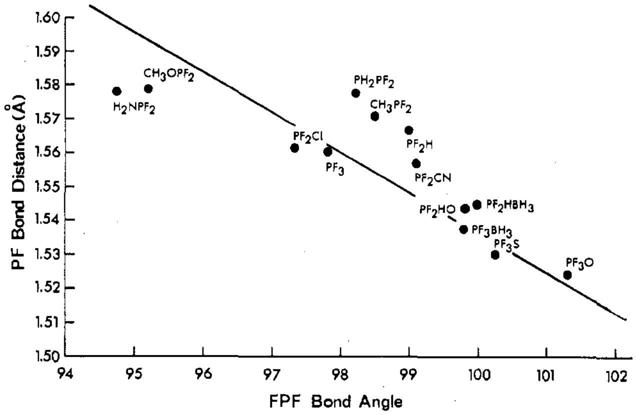

Figure 2.—Plot of PF bond distance *vs.* FPF bond angle for three- and four-coordinate difluorophosphines. The solid line joins points of constant FF distance = 2.355 Å. Data are from the papers cited in ref 2 and T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971); R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967); L. F. Centofanti and R. L. Kuczkowski, *Inorg. Chem.*, **7**, 2582 (1968); E. Codding, Ph.D. Thesis, Michigan State University, 1971.

The PF_2 geometry in PF_2CN adds further confirmation to an apparent positive correlation between the PF bond length and the FPF bond angle in compounds in which the phosphorus atom is three- or four-coordinate. The correlation, shown in Figure 2, can be rationalized by considering the interactions between bonded and nonbonded pairs of electrons. In every case involving a quadruply connected phosphorus atom, the FPF bond angle is larger and the PF bond distance is shorter than in compounds of trivalent phosphorus. This suggests that in the quadruply connected compounds the electron pairs are all effectively localized in bonds and do not repel one another as strongly as they are repelled by the nonbonded electron pair in the phosphines.

Another interesting correlation is that the longest PF bonds and smallest FPF bond angles are found in compounds in which a (p → d)π bond has been proposed.[2b] An electronic interaction of this type would increase the electron density on phosphorus which, on the basis of a simple electrostatic repulsion model, would increase the PF bond lengths and decrease the FPF angles. Where the (p → d)π interaction is less likely to occur (in PF_2H and PF_3, for example), the PF bond lengths are smaller and FPF angles are larger.[2a,e] On this basis, the fact that PF_2CN has the shortest PF bond length of any triply connected PF_2 derivative suggests that in this molecule the electronic interaction which reduces electron density on phosphorus, the p → π interaction, is more important than the π → d interaction.

There is another correlation between the PF bond distance and FPF bond angle in Figure 2. The solid line in the figure joins points for which the FF distance is constant (2.355 Å). It is apparent that, whatever the electronic interactions which are responsible for altering the PF bond distance and FPF bond angle in these compounds, the parameters are altered in such a way as to keep the FF distance nearly constant. No attempt was made to select a "best" FF distance in Figure 2; no single "best" FF distance is likely in these compounds.

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Microwave Spectrum, Structure, and Dipole Moment of Difluorocyanamide[1]

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Rotational transitions in the microwave spectrum of the ground and three excited vibrational states of NF_2CN and in the ground states of $^{15}NF_2CN$, $NF_2{}^{13}CN$, and $NF_2C^{15}N$ have been assigned. By analysis of the moments of inertia, bond distances and bond angles have been derived as follows: $d(CN) = 1.158 \pm 0.004$ Å, $d(NC) = 1.386 \pm 0.009$ Å, $d(NF) = 1.399 \pm 0.008$ Å, $\angle NCN = 173.9 \pm 2.2°$, $\angle CNF = 105.4 \pm 0.7°$, and $\angle FNF = 102.8 \pm 0.5°$. The tilt of the CN group is away from the fluorine atoms. The dipole moments are $\mu_a = 1.03 \pm 0.02$ D, $\mu_c = 0.39 \pm 0.10$ D, and $\mu = 1.10 \pm 0.02$ D.

Introduction

The question of multiple bonding in organic and inorganic chemistry is still a topic for discussion.[2] In H_2NCN it has been suggested that delocalization of the lone pair of electrons on the NH_2 group into the π-bonding system of the CN group leads to an increase in the bond angles about the NH_2 group and a shortened N–C bond. Although there has been considerable controversy about the exact geometry of the NH_2 group in NH_2CN, it is now generally accepted that in

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[2] For a recent review see L. D. Pettit, *Quart. Rev., Chem. Soc.*, **25**, 1 (1971).