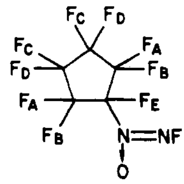

area		ϕ	
4	F_A	-120.76	$J = 264$ Hz
	F_B	-130.25	
4	F_C	-124.1	$J = 253$ Hz
	F_D	-129.0	
1	F_E	-149.7 (s)	
1	F_F	$+58.4$ (br s)	

Reactions of Heptafluoronitrosocyclobutane with N_2F_4 in Metal. Into a 75-mL stainless-steel Hoke cylinder fitted with a stainless-steel Hoke valve were added 4 mmol of $\overline{\mathrm{CF_2CF_2CF_2C}}\mathrm{FNO}$ and 8 mmol of N_2F_4. The cylinder was allowed to warm to and remain at room temperature for 12 h. After it was heated for 3 h at 45 °C, spectroscopic examination of the products obtained after trap-to-trap distillation showed that (heptafluorocyclobutyl)difluoramine is formed in about 30% yield. In a similar reaction between nonafluoronitrosocyclopentane and N_2F_4, (nonafluorocyclopentyl)difluoramine was found in about 30% yield.

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Registry No. I, 2261-41-8; II, 91816-92-1; III, 91816-93-2; IV, 91816-94-3; V, 91816-95-4; VI, 91816-96-5; VII, 91816-97-6; VIII, 91816-98-7; IX, 91816-99-8; X, 91817-00-4; $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CFCF{=}CF_2$, 685-63-2; N_2F_4, 10036-47-2; hexafluorocyclobutene, 697-11-0; octafluorocyclopentene, 559-40-0.

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Molecular Structure of Diaminotrifluorophosphorane, $PF_3(NH_2)_2$, in the Gas Phase

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The gas-phase molecular structure of $PF_3(NH_2)_2$ at 50 °C has been determined by electron diffraction. The heavy-atom skeleton is a trigonal bipyramid of C_{2v} symmetry with the nitrogen atoms occupying equatorial sites. The N–P–N angle is larger than the other equatorial angles, and the axial P–F bonds are bent slightly toward the equatorial fluorine atom. The planes of the $-NH_2$ groups are perpendicular to the equatorial plane of the molecule. There is no evidence for nonplanarity of the $-PNH_2$ groups, but small deviations from planarity cannot be excluded. Values of the principal structural parameters with estimated 2σ uncertainties (obtained after taking the effects of vibrational averaging into account) are $\langle r_g(\text{P–Y})\rangle$ (weighted average phosphorus bond length) = 1.616 (4) Å, $\Delta r_g(\text{P–N,F}_e)$ (difference in equatorial bond lengths) = 0.088 (22) Å, $\Delta r_g(\text{P–F}_a\text{,F}_e)$ = 0.060 (8) Å, $r_g(\text{P–F}_e)$ = 1.560 (10) Å, $r_g(\text{P–N})$ = 1.648 (13) Å, $r_g(\text{P–F}_a)$ = 1.619 (7) Å, $r_g(\text{N–H})$ = 1.033 (10) Å, $\angle\text{N–P–F}_e$ = 116.3 (5)°, $\angle\text{F}_a\text{–P–F}_e$ = 89.5 (9)°, and $\angle$P–N–H = 119.8 (22)°. A rough value for the twofold torsional barrier of the $-NH_2$ groups, obtained from the torsional amplitude, is 13 kcal·mol^{-1}, in good agreement with NMR measurements. $PF_3(NH_2)_2$ is discussed with the aid of comparison to the structures of other fluorophosphoranes.

Introduction

Pentacoordinate phosphorus compounds play an important role in the development and understanding of main-group stereochemistry. Thus, the structure, vibrational force field, and internal dynamics of PF_5 have been extensively investigated both experimentally and theoretically,[2] and much elegant work has been recently done on complex phosphoranes with cyclic substituents,[3] which have structures ranging from distorted trigonal bipyramidal to square pyramidal. It is surprising, therefore, that relatively little precise structural information is available for simple phosphoranes. Derivatives of PF_5, for example, offer sensitive tests of the usefulness of bonding theories, be they as simple as VSEPR[4] or as involved as ab initio calculations, for description and prediction of structural variation in these rather flexible molecules.

We have recently begun a series of studies of the gas-phase structure of phosphoranes that is planned to include halides, amines, and hydrides. This article presents our results for diaminofluorophosphorane.

Experimental Section

A sample of $PF_3(NH_2)_2$ was prepared as follows.

To a 1-L Pyrex round-bottomed flask equipped with a cold finger and a Kontes Teflon stopcock was added 15 mmol of PF_5. Anhydrous NH_3 (45 mmol) was added very slowly to the flask by maintaining a slightly higher pressure of NH_3 in the vacuum line than the pressure of PF_5 in the flask. The reaction was rapid and exothermic. A dense cloud formed immediately on contact. After all of the NH_3 was added, the mixture was kept at 25 °C for 0.25 h and then condensed in the cold finger at −196 °C. As the contents were allowed to warm slowly to 25 °C the volatile material was caused to move under dynamic vacuum into and through a trap cooled to −45 °C. The pure compound, $PF_3(NH_2)_2$ (40%), was retained in this trap. Prior to reaction the entire vacuum system and reaction vessel had been carefully dried. The purity of $PF_3(NH_2)_2$ was confirmed by infrared and ^{19}F and ^{31}P NMR spectral measurements. These spectra agreed with those in the literature.[5]

Diffraction photographs were made in the Oregon State apparatus under the following conditions: r^3 sector; nozzle-tip temperature, 50 °C; bulk sample temperature, 45–55 °C; plates, 8 × 10 in. Kodak projector slide medium contrast; development, 10 min in D-19 diluted 1:1; nominal nozzle-to-plate distances, 75 and 30 cm; exposure times, 150–300 s; nominal electron wavelengths, 0.057 Å (calibrated from CO_2 with r_a(CO) = 1.1646 Å, r(O·O) = 2.3244 Å); number of plates

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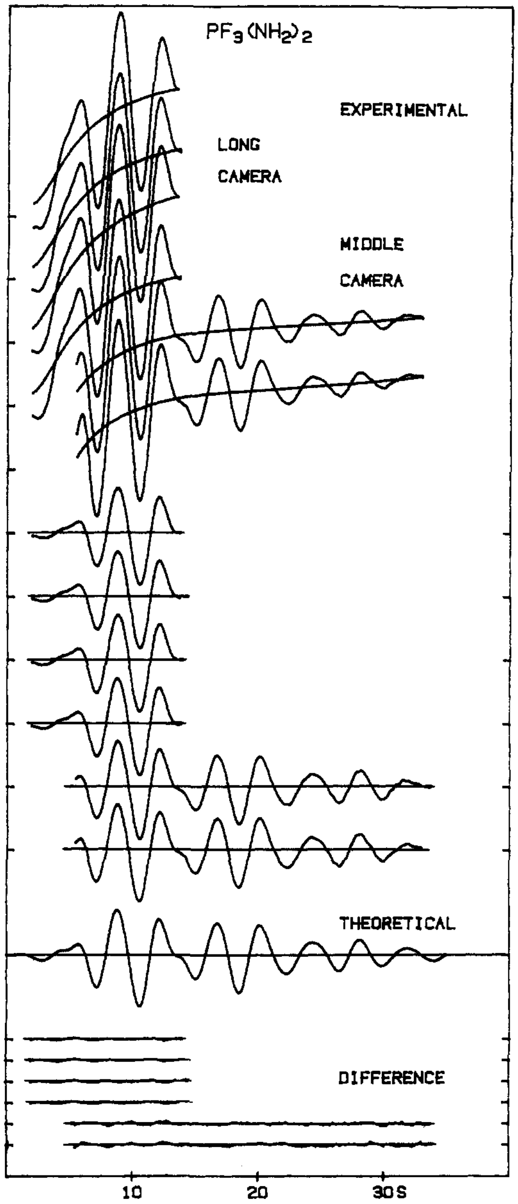

Figure 1. Intensity curves. Individual s^4I_t curves magnified 5× to reveal their features better are shown superimposed on their backgrounds. The theoretical curve is for the model of Table II.

used, four from the longer and two from the shorter distance; ranges of data, $2.00 \leq s \leq 13.50$ Å^{-1} and $5.50 \leq s \leq 33.00$ Å^{-1} at intervals $\Delta S = 0.25$ Å^{-1}. The mass spectrum of the sample, continuously monitored by a spectrometer attached to the diffraction chamber, was unchanged during the experiments. Procedures for deduction of the total scattered intensities ($s^4(I_t(s))$), removal of backgrounds, and generation of average molecular intensities ($s(I_m(s))$) are described elsewhere.[6,7] Electron-scattering amplitudes for our experimental conditions were interpolated[7] from literature values.[8] Figure 1 shows plots of the data. The data themselves are available from the OSU authors.

Structure Determination

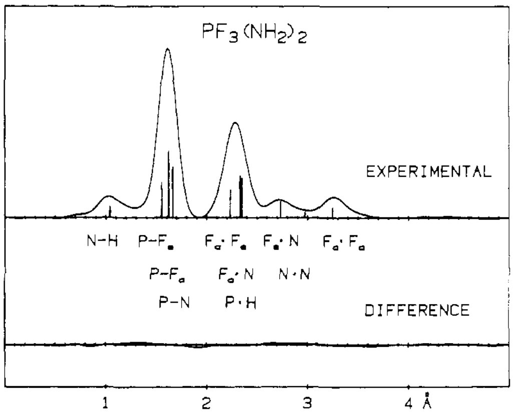

Figure 2. Radial distribution curve. The vertical bars indicate the positions and weight of the torsion-insensitive distances. The difference curve corresponds to use of the theoretical curve for the model of Table II. The value of the convergence coefficient B was 0.0025.

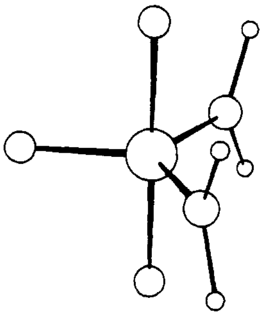

Figure 3. Diagram of the structure.

Although preliminary experimental radial distribution curves (the final one is shown in Figure 2) indicated that the molecule had the shape of a distorted trigonal bipyramid, neither the sites of the two types of ligands nor the structural details of the $-NH_2$ groups were apparent. Since the axial positions in pentacoordinate phosphorus compounds are usually occupied by the more electronegative atoms, our initial refinements were based on C_{2v}-symmetry models with the $-NH_2$ groups in equatorial positions (Figure 3). The PNH_2 groups were at first assumed to be planar and to eclipse the axial P–F bonds. In later refinements axial dispositions of the $-NH_2$ groups as well as their possible nonplanarity and rotational properties were investigated. (The NMR spectra[5,9] of $PF_3(NH_2)_2$ are consistent with planar $-NH_2$ groups, or with rapidly inverting hydrogens in a pyramidal arrangement, and with relatively rapid rotation about the P–N bonds.[9]

The seven parameters needed to specify the initial models of C_{2v} symmetry were chosen as r(N–H), $\langle r(\text{P–N,F})\rangle = [2r(\text{P–N}) + 2r(\text{P–F}_a) + r(\text{P–F}_e)]/5$, $\Delta r(\text{P–N,F}) = r(\text{P–N}) - r(\text{P–F}_e)$, $\Delta r(\text{P–F}_a\text{,F}_e) = r(\text{P–F}_a) - r(\text{P–F}_e)$, $\angle$P–N–H, $\angle$N–P–F$_e$, and $\angle$F$_a$–P–F$_e$. The unresolved character of the principal peaks of the radial distribution function made it impossible to refine the vibrational amplitudes for all the interatomic distances as independent vibrational parameters. As is usual in such cases, some of the amplitudes were formed into groups that were refined with a single group parameter. Calculations based on the force field described below showed that differences between members of a group could be ignored. The groups are evident from Table II.

It was decided to define the structure in terms of the geometrically consistent r_α-type parameters, which required calculation of the $r_a - r_\alpha$ corrections. A crude vibrational force field sufficient for this purpose and for the estimation of amplitude differences within amplitude groups was deduced as follows. A partial IR spectrum for $PF_3(NH_2)_2$ has been reported,[5] but it has not been assigned. By analogy with the spectra of PF_5[10,11] and $PF_2H(NH_2)_2$,[12] we assigned the following skeletal stretching frequencies: 968, 790, and (unob-

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Table I. Values of Structure-Defining Parameters for $PF_3(NH_2)_2$

parameter	r_α/Å[a]	parameter[b]	$\angle_\alpha$/deg[a]
r(N–H)	1.033 (10)	∠P–N–H	119.8 (22)
⟨r(P–N,F)⟩[c]	1.616 (4)	∠N–P–F_e	116.3 (5)
Δr(P–N,F_e)[c]	0.088 (22)	∠F_a–P–F_e	89.5 (9)
Δr(P–F_a,F_e)[c]	0.060 (8)	$\sigma(\phi)$[d]	8.9 (11)
		$R^e = 0.041$	

[a] Parenthesized quantities are estimated 2σ. [b] Values for other angles: ∠H–N–H = 120.4 (44)°, ∠N–P–N = 127.4 (10)°, ∠N–P–F_a = 90.2 (4)°. [c] See text for definition of parameters. [d] Root-mean-square torsional amplitude of NH_2 groups. Planar PNH_2 groups are assumed. Potential minimum: NH_2 groups perpendicular to equatorial plane. [e] $R = [\Sigma_i w_i(\Delta_i(s))^2/\Sigma_i w_i[s_i(I_i(s))]^2]^{1/2}$, where $\Delta(s) = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Table II. Distances (r) and Amplitudes of Vibration (l) for $PF_3(NH)_2$

	r_α/Å	r_g/Å[a]	l/Å[b]	
N–H	1.033	1.033 (10)	0.073 (10)	
P–F_e	1.556	1.560 (10)	0.053	(6)
P–N	1.644	1.648 (13)	0.053	
P–F_a	1.616	1.619 (7)	0.053	
H·H	1.792	1.792 (46)	[0.12]	
F_a·F_e	2.234	2.238 (19)	0.065	(11)
F_a·N	2.310	2.314 (9)	0.065	
P·H	2.336	2.336 (26)	0.129 (43)	
F_e·N	2.719	2.721 (11)	0.083	(8)
N·N	2.948	2.950 (22)	0.083	
F_a·F_a	3.232	3.233 (14)	0.065 (12)	
F_a·H_1[c]	2.27–2.31		[0.10]	
F_e·H[c]	3.20–3.43		[0.10]	
N·H[c]	3.42–3.63		[0.10]	
F_a·H_2[c]	3.30–363		[0.06]	

[a] Quantities in parentheses are estimated 2σ. Quantities in brackets were assumed; those shown with a brace were refined as a group. [c] Ranges of torsion-sensitive distances for $-2\sigma < \tau < +2\sigma$.

served, chiefly P–F_{ax} stretch) 600 cm^{-1} (a_1); 828 cm^{-1} (b_1); 1035 cm^{-1} (b_2). The geometry of the molecule was simplified by replacing the $-NH_2$ groups with pseudoatoms of mass 16 u located at the group center of mass. All axial–equatorial bond angles were set at 90°, and the angle between bonds to the pseudoatoms was 126.7°. The D_{3h} force field for PF_5[13] was resymmetrized to C_{2v}, and the stretching constants were adjusted to reproduce the assigned frequencies; the bending constants were left at their PF_5 values. This force field led to calculated amplitudes that differed by less than 0.0005 Å for all bonds to phosphorus, less than 0.0015 Å for the F_{ax}·F_{eq} and F_{ax}·N distances, and less than 0.0070 Å for the F_{eq}·N and N·N distances.

The refinements were carried out by least squares[14] fitting a theoretical intensity curve in the form $s(I_m(s))$ simultaneously to the curves representing the experimental data from the six plates. Vibrational averaging corrections ($r_a - r_\alpha$) calculated from the force field were applied to all distances not involving a hydrogen atom.

There were three matters of special interest: the possible presence of other isomers of $PF_3(NH_2)_2$, the rotational properties of the $-NH_2$ groups, and the possible nonplanarity of these groups. We investigated the first by refining a model with the (planar) $-NH_2$ groups in the axial positions and then including the result as a hypothetical component of a binary mixture in which the composition as well as the parameters of the C_{2v} model were defined. The result of this test was an indicated amount of the component with axial $-NH_2$ groups insignificantly different from zero. We made no similar attempt to evaluate the possible presence of the isomer with one axial and one equatorial $-NH_2$ group because of uncertainity about the structure of such species. It is likely, however, that the diffraction data could not rule out small amounts of this isomer. The questions of $-NH_2$ group rotation and planarity promised to be difficult because the answers depended on disentangling the effects of each on the distribution of weakly scattering, rotation-sensitive terms. As far as planarity is concerned, refinement of C_{2v} symmetry models incorporating nonplanar PNH_2 groups led to a sum for the angles at nitrogen equal to 359.2° with a standard deviation of more than 2°. Our data thus contain no evidence for nonplanar bonding at the nitrogen atoms. Our investigation of $-NH_2$ group rotation was based on the assumption that the groups were planar and their motion uncorrelated. It was further assumed that the rotational potential of each group could be represented by the function $V(\phi) = V_0\phi^2$. This function comprises a sum of terms correct through second order in the expansion of $V = {}^1/_2\sum V_n(1 - \cos\phi)$; it is valid when the barrier is reasonably high, as proved to be the case for $PF_3(NH_2)_2$. The minimum of the potential was taken with the $-NH_2$ angles eclipsing the two axial fluorines in accordance with tests on static models showing this conformation to give a much better fit to experiment than the one with $-NH_2$ groups in the equatorial plane. To represent the continuous distribution of molecules over the torsional coordinate, 13 angle positions or pseudoconformers corresponding to $\phi = 0, \pm\sigma/2, ..., \pm3\sigma$ were chosen and weighted according to $P(\phi) = Q^{-1}\exp(-V(\phi)/RT)$.[15] The perpendicular amplitude corrections and vibrational amplitudes assumed for the torsion-sensitive distances were modified to reflect separation of torsion. Refinement of this more elaborate, dynamic model (ignoring all H···H interactions between $-NH_2$ groups) gave about the same agreement with experiment as did the better models without inclusion of group rotations.

Results

Table I summarizes the parameter values obtained from the structure refinements. The values themselves, with the exception of that for $\sigma(\tau)$, have been taken from the refinement of the C_{2v} model with planar PNH_2 groups perpendicular to the equatorial plane; however, the parenthesized uncertainties have been slightly expanded to encompass refinement results from the other models. The torsion-insensitive interatomic distances and their vibrational amplitudes collected in Table II are also taken from the refinement of the C_{2v} model. The ranges of values for the torsion-sensitive distances, also given in Table II, were deduced from refinements of the model with librating $-NH_2$ groups. Table III is the correlation matrix for the refined parameters of the C_{2v} model. Since both our C_{2v} and librating models gave excellent agreement with experiment, we believe the values of Tables I and II form an accurate picture of the structure of gaseous $PF_3(NH_2)_2$. At the same time it is worth noting that some of the geometrical parameters are strongly correlated with amplitude parameters that have rather large uncertainties. Examples are the difference between the P–N and P–F_e bonds (by l(P–X)) and the F_a–P–F_e angle (by $l(F_a{\cdot}F_e)$). These correlations should be kept in mind when use is made of the tabulated results. A final point concerns the possible presence of other stereoisomers linked to the major one by the phenomenon of Berry inversion.[16] Although our data contain no evidence for the presence of other isomers, amounts of a very few percent cannot be ruled out with certainty.

Discussion

It is a longstanding rule, supported by both empirical[17] and theoretical evidence,[18-20] that the axial position in pentacoordinate trigonal-bipyramidal molecules will be preferentially occupied by the more electronegative ligands. Moreover, molecular orbital calculations, both semiempirical[19] and ab

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Table III. Correlation Matrix (×100) for the C_{2v} Model of $PF_3(NH_2)_2$

parameter[a]	σ_{LS}[b]	r_1	$\langle r_2 \rangle$	Δr_3	Δr_4	$\angle_5$	$\angle_6$	$\angle_7$	l_8	l_9	l_{10}	l_{11}	l_{12}	l_{13}
1. r(N–H)	0.37	100												
2. $\langle r$(P–N,F)$\rangle$	0.055	6	100											
3. Δr(P–N,F_e)	0.77	10	57	100										
4. Δr(P–F_a,F_e)	0.29	1	−35	44	100									
5. $\angle$P–N–H	75.0	−23	−20	4	12	100								
6. $\angle$N–P–F_e	20.0	−1	12	54	45	25	100							
7. $\angle F_a$–P–F_e	32.0	7	17	22	6	−45	9	100						
8. l(N–H)	0.33	−2	−1	2	5	1	3	4	100					
9. l(P–F_e)	0.19	−8	−54	−98	−44	−5	−53	−17	<1	100				
10. $l(F_a \cdot F_e)$	0.38	1	−22	−40	−16	−49	−26	78	4	43	100			
11. l(P·H)	1.5	−2	38	19	−14	32	30	−8	7	−14	−31	100		
12. $l(F_e \cdot N)$	0.26	4	−2	−10	−6	−24	−19	4	2	11	12	−13	100	
13. $l(F_a \cdot F_a)$	0.43	−24	−11	−20	−4	−22	−12	24	4	21	35	−11	<1	100

[a] For definition of parameters see text. [b] Standard deviations (×100) from least squares. Distances (r) and amplitudes (l) are in angstroms and angles in degrees.

Table IV. Bond Lengths in Derivatives of PF_5[a]

compd	r(P–F_e)/Å	r(P–F_a)/Å	r(P–Y)/Å	Σn[b]	ref
PF_5[c]	1.534 (4)	1.577 (5)		7.2	27
PF_4CH_3[c]	1.543 (4)	1.612 (4)	1.780 (5)	6.6	28
$PF_3(CH_3)_2$[c]	1.553 (6)	1.643 (3)	1.798 (4)	5.9	28
$PF_2(CH_3)_3$[c]		1.685 (1)	1.813 (1)	5.2	29
PF_4CF_3[d]	1.537 (5)	1.573 (7)	1.881 (8)	6.8	30
$PF_3(CF_3)_2$[d]	1.559 (3)		1.884 (6)	6.1	30
$PF_2(CF_3)_3$[d]		1.600 (4)	1.888 (4)	5.1	30
$PF_3(NH_2)_2$[c]	1.560 (10)	1.619 (7)	1.648 (13)	6.7	this work
$PF_2H(NH_2)_2$[d]		1.643 (5)	1.640 (5)	6.2[e]	25

[a] Parenthesized uncertainties were estimated in different ways and are not necessarily comparable. [b] Phosphorus bond-order sum.[21] [c] r_g lengths. [d] r_a lengths. [e] n(P–H) = 1.0 was assumed.

initio,[21] predict that π-donor substituents such as NH_2 will be oriented with the donor orbitals in the equatorial plane in order to maximize π-orbital overlap with the central atom. Our structure for $PF_3(NH_2)_2$ agrees with these predictions in all details. The equatorially sited $-NH_2$ groups with their planes perpendicular to the equatorial plane of the molecule are linked to the phosphorus atom by bonds that have a substantial amount (ca. 43%) of double-bond character, judged[22] from their length, which is about 0.11 Å less than the sum of the covalent single-bond radii corrected for electronegativity difference.[23] The torsional amplitude of the $-NH_2$ groups, too, although very imprecisely measured by our experiment, is consistent with the high rotational barrier expected for partial double bonds: the value[24] of this barrier, V_0, corresponding to the measured amplitude is 13 kcal·mol^{-1}, in agreement with an activation energy of 11.2 kcal·mol^{-1} deduced from NMR measurements in solution.[9]

According to VSEPR theory[4] the bond angles in $PF_3(NH_2)_2$ are determined by the bond orders (double bonds occupy more space than single bonds) and by the relative electronegativities of the ligands. Since the P–N and P–F_e bonds have about the same bond order based on the bond-order–bond-length criterion,[22] the equatorial angles are determined primarily by electronegativities. The P–N bonds, then, should be sterically more demanding than the P–F_e bonds because the nitrogen atom is less electronegative than the fluorine, and the N–P–N bond angle is predicted to be increased from the nominal 120° at the expense of $\angle F_e$–P–N. Similarly, the F_a–P–N angles are predicted to be increased from 90° at the expense of $\angle F_a$–P–F_e. The experimental values agree with these predictions, although in the case of $\angle F_a$–P–N the associated uncertainty makes the result of doubtful significance. It is notable that in the case of $PF_2H(NH_2)_2$,[25] where a single bond to hydrogen replaces the (partial double) bond to the equatorial fluorine, the N–P–N angle is 2° larger and $\angle F_a$–P–N 0.1° larger than the corresponding angles in $PF_3(NH_2)_2$.

The bonding of five ligands to phosphorus implies the use of 3d orbitals by this atom. In the case of PF_5 and its derivatives the P–F bond lengths vary in a way that reflects the number and electronegativities of the remaining ligands. The variation of these distances may be accounted for as follows. The greater the effective nuclear charge on phosphorus, the smaller the energy gap between the atomic 3p and 3d orbitals and the greater the constructive mixing of these orbitals in bond formation. As the fluorine atoms in PF_5 are replaced by substituents of lower electronegativity, the effective nuclear charge on phosphorus decreases, the participation of 3d orbitals is diminished, and the P–F bond lengths increase. The effect is seen in the data for several series of PF_5 derivatives summarized in Table IV. Throughout each series both the axial and equatorial P–F bonds grow longer, the former somewhat more rapidly than the latter, while in general the bonds to the other ligands seem to be less affected. The sum of the bond orders to phosphorus thus diminishes in accordance with the diminished 3d orbital participation. In the limit of no involvement of 3d orbitals the axial bonds in pentacoordinate phosphorus compounds are most readily described in terms of "three-center" molecular orbitals[26] with axial bond orders of only $^1/_2$. The longest axial bonds in Table IV ($PF_2(CH_3)_2$) correspond to bond orders of about 0.9.

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