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Structure and Bonding in CH_3PF_4 and $(CH_3)_2PF_3$. An Electron Diffraction Study[1a]

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The molecules CH_3PF_4 and $(CH_3)_2PF_3$ were found to be distorted trigonal bipyramids with methyl groups occupying equatorial positions and with axial P–F bonds longer than equatorial. The principal structural parameters observed for CH_3PF_4 were $r_g(PF)_{eq} = 1.543 \pm 0.004$ Å., $r_g(PF)_{ax} = 1.612 \pm 0.004$ Å., $r_g(PC) = 1.780 \pm 0.005$ Å., $r_g(CH) = 1.099 \pm 0.031$ Å., $\angle F_{ax}PC = 91.8 \pm 0.4°$, and $\angle F_{eq}PC = 122.2 \pm 0.9°$. For $(CH_3)_2PF_3$ the parameters were $r_g(PF)_{eq} = 1.553 \pm 0.006$ Å., $r_g(PF)_{ax} = 1.643 \pm 0.003$ Å., $r_g(PC) = 1.798 \pm 0.004$ Å., $r_g(CH) = 1.107 \pm 0.012$ Å., $\angle F_{ax}PF_{eq} = 89.9 \pm 0.3°$, and $\angle F_{eq}PC = 118.0 \pm 0.8°$. Root-mean-square amplitudes of vibration were also determined. The molecules show a striking similarity to their analogs SF_4 and ClF_3. The stereochemistry and bonding trends are found to be in good qualitative agreement with a bonding formulation proposed by Rundle which neglects d orbitals.

Introduction

The organo-substituted phosphorus(V) fluorides are a recently synthesized group of substances[2a] for which structural data are just beginning to become available. Bonding theories for phosphorus(V) compounds are in a state of flux with various sp^3d hybridization,[2b] steric, electron-pair repulsion,[3] π-bonding,[4] and molecular orbital[5] descriptions receiving attention. Until very recently[6,7] the picture has been confused by misleading structural information reported for certain prototype molecules in the series. It seemed worthwhile, then, to determine the structures of gas molecules of two of the simpler compounds, CH_3PF_4 and $(CH_3)_2PF_3$, to help clarify the situation.

Nuclear magnetic resonance and infrared studies of a series of phosphoranes have been made by Muetterties, *et al.*[7,8] The individual spectra for CH_3PF_4 and $(CH_3)_2PF_3$ by themselves did not yield definitive stereochemical conclusions. Nevertheless, a comparison of coupling constants, chemical shifts, and stretching frequencies of these two molecules with corresponding data for the other members of the series showed that the phosphoranes are trigonal bipyramids with alkyl groups in equatorial sites. An infrared investigation of CH_3PF_4 by Downs and Schmutzler,[9] performed concurrently with the present investigation, provided support for a structure in which the methyl group assumes an equatorial position in a trigonal bipyramidal framework. The microwave spectrum of CH_3PF_4 obtained by Cornwell and Cohen revealed that the molecule is an asymmetric top and hence cannot be either a tetragonal pyramid or an axially substituted bipyramid.[10]

Our electron diffraction study confirms the stereochemistry of CH_3PF_4 and also provides the detailed molecular structures of both CH_3PF_4 and $(CH_3)_2PF_3$. The stereochemistry and bond lengths are found to fit nicely into bonding theories proposed by Rundle[5] and Gillespie.[3]

Experimental

Samples of the compounds were provided through the courtesy of Drs. R. Schmutzler and E. L. Muetterties of E. I. du Pont de Nemours and Co. The purity of the samples was checked by infrared spectroscopy using a Beckman I.R. 7 spectrometer, but no impurities were detected. Diffraction patterns of 40-kv. electrons were recorded on Kodak process plates masked by an r^3 rotating sector. Experimental procedures followed those previously described.[11] All handling of the gas was carried on in stainless steel containers. Data were obtained from 11- and 21-cm. camera distances, using 3.5–9-sec. exposure times and 12–20-mm. sample pressures with a beam current of 0.6 μa.

Analysis of the data was done with the aid of an IBM 7074 computer by procedures similar to those described elsewhere.[12] It included the conversion of experimental intensities to an $M(s)$ function representing the ratio of molecular intensity to atomic intensity. A radial distribution curve, $f(r)$, was computed from $M(s)$ and compared with a synthetic $f(r)$ by means of a least-squares procedure employing geometric constraints to ensure geometric self-consistency.[13] Small corrections were made for "Bastiansen–Morino shrinkage effects."[14] Also included in the

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[1] (a) This work was performed under contract with the Atomic Energy Commission. Contribution No. 1745. Numerical electron intensity data have been deposited as Document No. 8581 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $2.50 for photoprints, or $1.75 for 35-mm. microfilms. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. (b) Author to whom correspondence concerning reprints should be addressed at the Department of Chemistry, University of Michigan, Ann Arbor, Mich.

[2] (a) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964); (b) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961).

[3] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); *J. Am. Chem Soc.*, **85**, 4672 (1963).

[4] R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964).

[5] R. E. Rundle, *Acta Cryst.*, **14**, 585 (1961); *Rec. Chem. Progr.*, **23**, 195 (1962); *J. Am. Chem. Soc.*, **85**, 112 (1963); *Survey Progr. Chem.*, **1**, 81 (1963).

[6] (a) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965); (b) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

[7] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[8] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

[9] A. J. Downs and R. Schmutzler, "Stereochemistry of Fluorophosphoranes. I. The Vibrational Spectrum and Molecular Structure of Methyltetrafluorophosphorane, CH_3PF_4" (to be published).

[10] C. D. Cornwell and E. A. Cohen, private communication, 1964.

[11] L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.*, **25**, 569 (1959).

[12] R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

[13] L. S. Bartell and T. L. Boates, to be published.

[14] O. Bastiansen and M. Traetteberg, *Acta Cryst.*, **13**, 1108 (1960); Y. Morino, *ibid.*, **13**, 1107 (1960); Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, *J. Chem. Phys.*, **36**, 1109 (1962).

analysis were corrections for scattering by planetary electrons,[15] the failure of the Born approximation,[16] and Fourier integral termination errors.[17] The value of b used in the damping function in the radial distribution function was 0.00142.

Amplitudes of vibration were determined as usual except in the case of the two bonded P–F distances which were too close together to be resolved easily. Amplitudes for the axial and equatorial distances were determined with the aid of the auxiliary constraint derived from Badger's rule[18]

$$(l_2/l_1) = [(r_2 - \delta)/(r_1 - \delta)]^{3/4}$$

For CH_3PF_4 the observed 0.07 Å. difference between axial and equatorial distances implied a shift of 0.003 Å. in amplitude. The 0.09 Å. difference in $(CH_3)_2PF_3$ indicated a shift of 0.004 Å. in amplitude. The values for the amplitudes were found, accordingly, by requiring the shift $[l(\text{ax}) - l(\text{eq})]$ to have the appropriate value in the least-squares analyses.

Results

CH_3PF_4.—The intensity values leveled through division by theoretical atomic intensities and corrected for the higher sensitivity of plates at the edges are given in Figure 1. Intensities were found to have an index of resolution of 1.00 ± 0.05. The experimental radial distribution curve is shown in Figure 2.

In order to determine whether the structure of CH_3PF_4 is a trigonal bipyramid or a tetragonal pyramid, comparisons were made of theoretical and experimental $f(r)$ curves for both configurations. The methyl group was placed in the axial and in the equatorial positions of a trigonal bipyramid (models 1 and 2, respectively, of Figure 3) and in the axial and basal positions of the tetragonal pyramid (models 3 and 4 of Figure 3). The theoretical $f(r)$ curve for model 1 gave a very poor comparison with the experimental curve in the central region. No peak appeared in the 2.9 Å. region, whereas a very strong peak appeared in the 2.5 Å. region.

If it is assumed for model 3 that all P–F distances are equal there are only three nonbonded distances in addition to the inconspicuous hydrogen contributions. Since the experimental distribution curve in Figure 2 exhibits four major nonbonded peaks, the nominally C_{4v} tetragonal pyramidal model can be excluded.

Poor fits to the experimental curve were shown by theoretical $f(r)$ curves for model 4 when the configuration represented a distinct tetragonal pyramid, *i.e.*, when the angles γ, δ, and ϵ were nearly equal and greater than 90°. If, however, the angle ϵ is decreased to about 90° and γ and δ are taken to be about 120°, model 4 reduces to model 2.

Theoretical and experimental $f(r)$ curves agreed extremely well for model 2. It was therefore concluded that CH_3PF_4 is a trigonal bipyramid with the methyl group occupying an equatorial site. The structural results for this model are reported in Table I.

$(CH_3)_2PF_3$.—The leveled intensity values are given in Figure 4 and the radial distribution curve is illustrated in Figure 5. An index of resolution of 1.03 ± 0.05 was obtained.

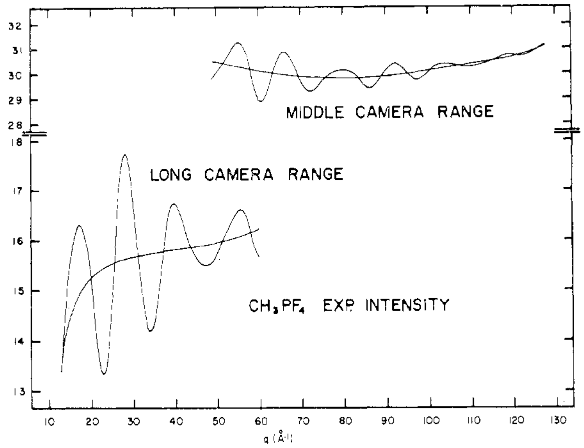

Figure 1.—A plot of the experimental intensity and background functions for CH_3PF_4; 21- and 11-cm. camera distances.

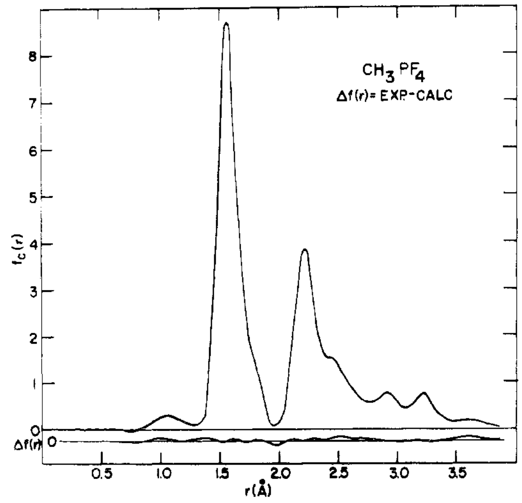

Figure 2.—A plot of the experimental radial distribution function for CH_3PF_4. The lower curve is a plot of the difference between the experimental and calculated radial distribution functions.

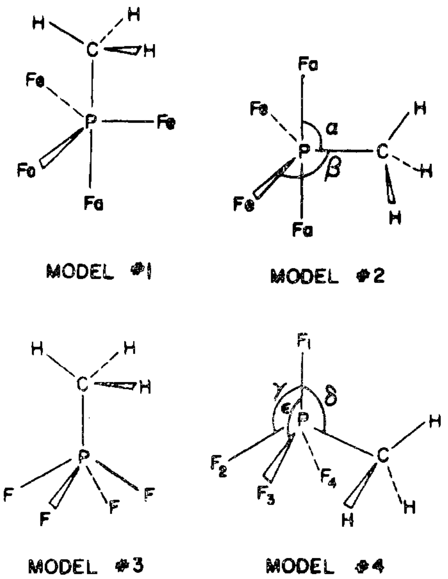

Figure 3.—Possible structures for CH_3PF_4.

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[15] L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

[16] V. Schomaker and R. Glauber, *Nature*, **170**, 291 (1952).

[17] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).

[18] L. S. Bartell and B. L. Carroll, *ibid.*, **42**, 1135 (1965).

TABLE I

ELECTRON DIFFRACTION RESULTS FOR THE STRUCTURE OF CH_3PF_4

	r_g, Å.	$\sigma(r)$, Å.	l_g, Å.	$\sigma(l)$, Å.
P-F (mean dist.)	1.577	$\pm 0.000_9$		
$P\text{-}F_{eq}$	1.543	$\pm 0.003_7$	0.039	±0.001
$P\text{-}F_{ax}$	1.612	$\pm 0.003_5$	0.042	±0.001
P-C	1.780	$\pm 0.004_6$	0.048	±0.006
C-H	1.099	±0.031	0.100	±0.024

$\angle F_{ax}PC = 91.8 \pm 0.4°$

$\angle F_{eq}PC = 122.2 \pm 0.9°$

$\Delta r = (P\text{-}F_{ax}) - (P\text{-}F_{eq}) = 0.069 \pm 0.007$ Å.

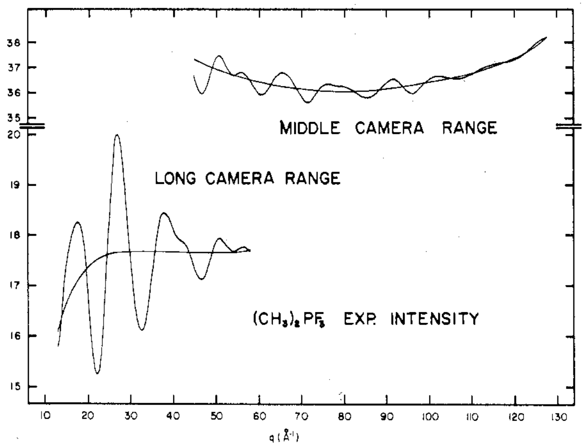

Figure 4.—A plot of the experimental intensity and background functions for $(CH_3)_2PF_3$; 21- and 11-cm. camera distances.

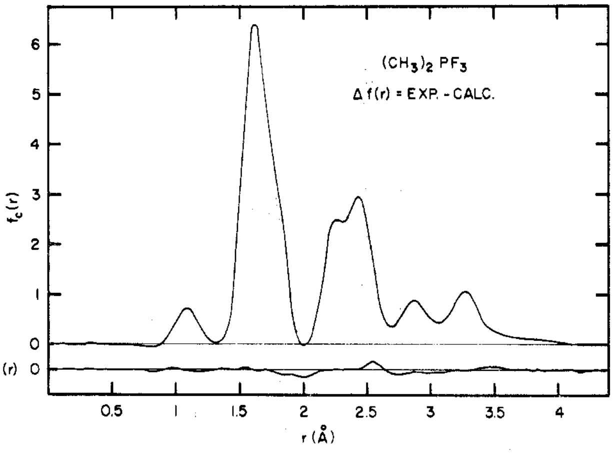

Figure 5.—A plot of the experimental radial distribution function for $(CH_3)_2PF_3$. The lower curve is a plot of the difference between the experimental and calculated radial distribution functions.

The various models assumed to be possible for the structure of $(CH_3)_2PF_3$ are shown in Figure 6. Model 1 would have only three major nonbonded distances in the radial distribution curve. This is in contrast to the four major nonbonded peaks in the experimental curve in Figure 5. Model 1 was therefore rejected.

Models 2 and 6 were eliminated because of the poor agreement between the experimental and theoretical curves in the region from 2.0 to 4.0 Å. This mismatch is shown in Figure 7.

The theoretical radial distribution curve for model 5 compares favorably with the experimental. Upon refining to a close fit between theoretical and experimental curves, however, this model reduces to model 3 with $\delta \approx 120°$, $\epsilon \approx 90°$. The same is true for model 4 when $\delta = \phi \approx 120°$ and $\epsilon \approx 90°$. There is a form of

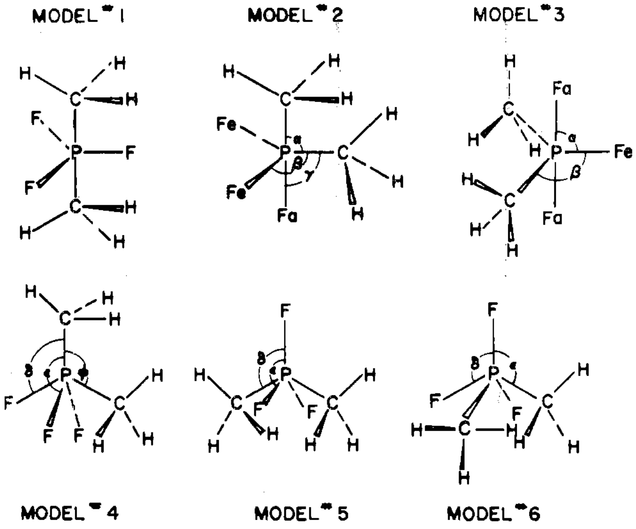

Figure 6.—Possible structures for $(CH_3)_2PF_3$.

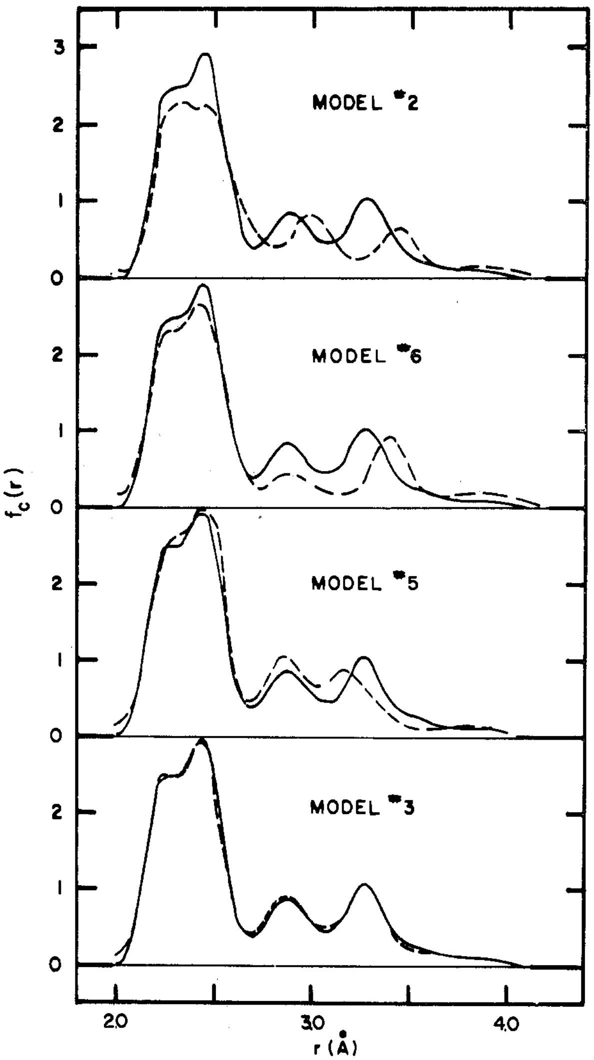

Figure 7.—Comparison of theoretical and experimental radial distribution curves for models 2, 6, 5, and 3.

models 4 and 5 which does not reduce to model 3. It is impossible to refine this form, however, to within two times the standard deviation possible for model 3. The best fit obtainable without sacrificing geometric consistency is shown in Figure 7. It was also noted that the amplitudes of vibration for the F···F nonbonded distances are unreasonable for this form when compared with corresponding values found in CH_3PF_4 and PF_5. Models 4 and 5 were therefore considered inappropriate except in the limiting form equivalent to model 3.

The theoretical radial distribution curve for model 3 agrees satisfactorily with the experimental curve. This trigonal bipyramidal model with the methyl groups in equatorial sites was therefore considered to represent the configuration of $(CH_3)_2PF_3$. Table II shows the refined structural results.

Table II

Electron Diffraction Results for the Structure $(CH_3)_2PF_3$

	r_g, Å.	$\sigma(r)$, Å.	l_g, Å.	$\sigma(l)$, Å.
P–F (mean dist.)	1.614	$\pm 0.001_3$		
$P–F_{eq}$	1.553	$\pm 0.005_8$	0.039	±0.003
$P–F_{ax}$	1.643	$\pm 0.002_9$	0.043	±0.003
P–C	1.798	$\pm 0.004_1$	0.046	±0.007
C–H	1.107	±0.012	0.070	±0.010

$\angle F_{ax}PF_{eq} = 89.9 \pm 0.3°$

$\angle F_{eq}PC_{ax} = 118.0 \pm 0.8°$

$\Delta r = (P–F_{ax}) - (P–F_{eq}) = 0.090 \pm 0.008$ Å.

In neither of the molecules studied was it possible to characterize the internal rotations of the methyl groups. The C_{2v} structure found for CH_3PF_4 can possess, at lowest, a 6-fold barrier to rotation. Since 6-fold barriers studied to date have been small ($\approx$10 cal./mole[19]) it is probable that the rotation in CH_3PF_4 is virtually free. The symmetry of $(CH_3)_2PF_3$ does not exclude a 3-fold component in the barrier potential. Nevertheless, substitution of a fluorine by a methyl on going from CH_3PF_4 to $(CH_3)_2PF_3$ would probably not hinder the methyl rotation in the latter compound seriously at room temperature.

Discussion

Observed structural features in the gaseous molecules $(CH_3)_nPF_{5-n}$ may be summarized as follows: (A) The molecules are trigonal bipyramids or distorted trigonal bipyramids. (B) CH_3 groups occupy equatorial sites. (C) Axial P–F bonds are longer than their equatorial counterparts. (D) The split $[r(PF)_{ax} - r(PF)_{eq}]$ increases as the number of CH_3 substituents increases. (E) Both P–F and P–C bond lengths decrease as the number of F atoms increases. (F) Methyl substitution leads to distortions of the bipyramidal framework in which P–F bonds are bent away from CH_3 groups. Several of these features were anticipated by Muetterties, *et al.*,[7,8] on the basis of infrared and n.m.r. studies. It is to be noted that structural features

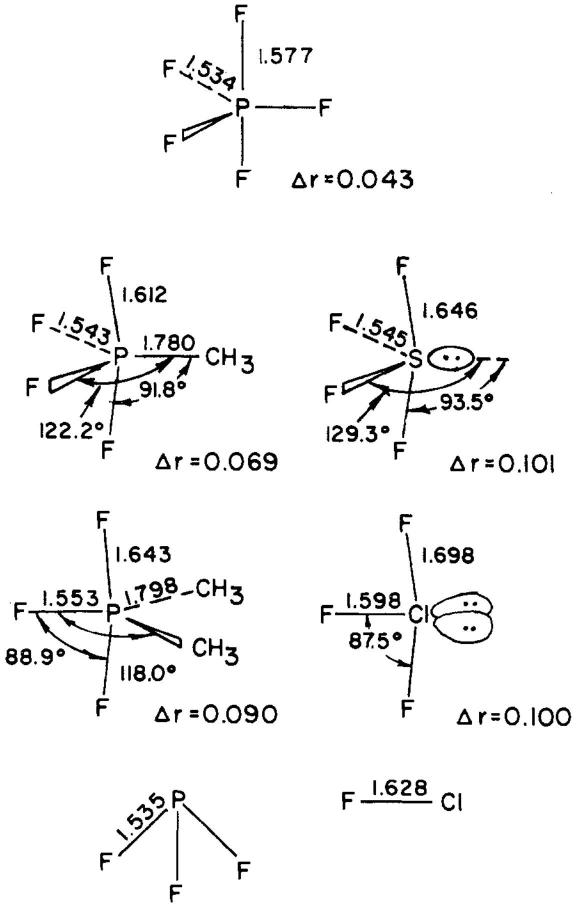

Figure 8.—Structures of the fluophosphoranes and related molecules. The symbol Δr represents the difference between lengths of axial and equatorial bonds to F atoms.

in the series PF_5, CH_3PF_4, and $(CH_3)_2PF_3$ bear a striking similarity to those in the series PF_5, SF_4, and ClF_3. This is illustrated in the diagrams of Figure 8.

Conclusion (A) above is consistent with virtually all evidence on analogous group V compounds except for pentaphenylantimony, which exists as tetragonal pyramids in the solid state.[20]

Trend (E) seems to be related to the shortening observed in many other molecules when fluorine substitution increases. For example, the C–F bond length decreases from 1.43 ± 0.02 to 1.323 ± 0.005 Å. in the series from $(CH_3)_3CF$ to F_3CF,[21] and similar shifts have been reported for N–F and other bonds. The most commonly cited rationalizations invoke a shrinking of the radius of the central atom as the highly electronegative fluorides are added,[22] a "double-bond, no-bond resonance,"[23] or hybridization changes.[24] The shrinking of bonds to atoms other than F as F substitution increases has often been reported, but it seems not to be as general or as large.

The deformations noted in conclusion (F) are easily

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(19) R. E. Naylor, Jr., and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1057 (1957); E. Tannenbaum, R. Myers, and W. Gwinn, *ibid.*, **25**, 42 (1956); K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **75**, 2219 (1953).

(20) P. J. Wheatley and G. Wittig, *Proc. Chem. Soc.*, 251 (1962); P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964).

(21) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958); L. E. Sutton, "Tables of Internuclear Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(22) A. Burawoy, *Trans. Faraday Soc.*, **40**, 537 (1944).

(23) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(24) H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).

accounted for by a steric model inasmuch as carbon has a larger van der Waals radius in comparison with its bond radius than does fluorine. It is unwise to attach great physical significance to this simple argument because more subtle forces may be at play. This possibility is suggested by the similarity between the deformations in the fluorophosphoranes and in SF_4 and ClF_3 where the latter molecules possess lone pairs instead of methyl groups. To discuss steric properties of lone pairs as if they were ligands is a rather great extrapolation.

Perhaps the most interesting results are (B) through (D) because of their direct relation to various bonding theories in the literature. The present results are not easy to predict on the basis of the once popular sp^3d hybridization model.[2b] Although this model provides a ready source for five covalent bonds, it is subject to certain theoretical criticisms[5,25] and gives little basis for prediction until it is "calibrated" in terms of known structures. A more appealing bonding scheme is that proposed by Havinga and Wiebenga to describe interhalogen complexes.[25] The scheme was extended by Rundle to cover more general molecules, including phosphorus(V) complexes and rare gas compounds.[5] The virtues of this scheme lie in its simplicity and the directness with which qualitative predictions can be made. In contrast to the sp^3d model, the Rundle molecular orbital model neglects d orbitals altogether in the first approximation. It pictures axial bonds as three-center, four-electron bonds constructed principally from p orbitals and possessing individual bond orders of roughly $^1/_2$. Natural consequences of Rundle's scheme are that axial bonds are more polar than equatorial bonds, that axial bonds tend to be longer than equatorial bonds, and that the more electronegative substituents go preferentially to the axial sites.[26] It was envisioned that the above consequences were dictated by the overriding influence of p orbitals but that d orbitals probably stabilize the resulting bonds somewhat, especially through π interactions. Rundle confidently predicted[27] shortly before his death that, contrary to published results, PF_5 would be found to have longer axial than equatorial bonds and that the chlorines in PF_3Cl_2 would be found in equatorial, not axial, positions. Both predictions have proven to be correct.[6-8] It is now acknowledged, at least in applications to rare gas compounds, that Rundle's model is the most appropriate of the simple bonding descriptions available today.[28]

Rundle's scheme is qualitatively in accord with the findings of the present research and it provides a convenient framework for discussing the trends observed. It does not, however, lead to an unequivocal prediction of magnitudes. The uncertainty results from the unknown involvement in bonding of the valence shell s orbital of the central atom. In many cases Rundle found it useful to apply Pauling's equation[29]

$$D(n) = D(1) - 0.60 \log n \tag{1}$$

for lengths D of bonds with bond number n. An extreme value for the split, $[r(\mathrm{PF})_{\mathrm{ax}} - r(\mathrm{PF})_{\mathrm{eq}}]$, would seem to be $\sim$0.18 Å. This value is obtained from eq. 1 if it is assumed that axial bonds utilize only p orbitals and that equatorial bonds make full use of the 3s orbital so that $n_{\mathrm{ax}} = {}^1/_2$ and $n_{\mathrm{eq}} = 1$. Such an apportionment of s character exclusively to the equatorial bonds is arbitrary and improbable. Moreover, the cost of promoting a 3s electron in order to use the 3s orbital in bonding is high enough to make the bonding role of the 3s orbital less important than that of the 3p orbitals.[28a,30]

If it is assumed that each bond shares the 3s orbital equally, the corresponding maximum bond numbers of $n_{\mathrm{ax}} = {}^1/_2 + {}^1/_5$ and $n_{\mathrm{eq}} = {}^2/_3 + {}^1/_5$ imply a split of 0.056 Å. If the 3s orbital is neglected altogether, the calculated split becomes 0.075 Å.

The above range of values may be compared with experimental splits of 0.15 ± 0.06 Å. for PCl_5[31] and 0.043 ± 0.008 Å. for PF_5.[6a] The fact that bonds in PX_3 (with n presumably unity) and equatorial bonds in PX_5 (with n_{eq} presumably somewhat less than unity) are very similar in length despite an apparently different bond number appears somewhat inconsistent. This discrepancy may be rationalized on the basis of trend (E) or, perhaps, in terms of d orbital involvement, but it is unfruitful here to add speculative corrections to simplified models.

An explanation of the increase of the split $[r(\mathrm{PF})_{\mathrm{ax}} - r(\mathrm{PF})_{\mathrm{eq}}]$ with increased methyl substitution is suggested by the similarities in the series portrayed in Figure 8. The molecules SF_4 and ClF_3 exhibit a split, 0.10 Å., which is twice as large as that in PF_5. In SF_4 and ClF_3 it is reasonable to expect the lone pairs to utilize the lion's share of the 3s orbital. If d orbitals are neglected this leaves bond numbers of $n_{\mathrm{eq}} = 1$ and $n_{\mathrm{ax}} = {}^1/_2$, consistent with a larger split than in PF_5. Linnett[32] and Bent[24] have argued that the s character of bonds decreases as the electronegativity of the ligand increases. In comparison with P–F, a P–C bond orbital would then have a greater s character and resemble a lone pair orbital. Accordingly, the molecules CH_3PF_4 and $(CH_3)_2PF_3$ would tend to emulate SF_4 and ClF_3. An alternative steric model is also consistent with observed splits but seems ruled out by the smallness of the angular deformations observed.

The simple electron-pair repulsion model of Gillespie and Nyholm, as augmented by Gillespie,[3] is qualitatively in very close accord with the structural results,

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(25) E. E. Havinga and E. H. Wiebenga, *Rec. trav. chim. Pays-Bas*, **78**, 724 (1959); E. H. Wiebenga, E. E. Havinga, and K. H. Boswick, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

(26) In the case of phosphoranes experimental observations were presented by Muetterties, *et al.*,[7,8] which led the authors, independently, to very similar conclusions.

(27) R. E. Rundle, private communication, 1963.

(28) (a) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964); (b) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

(29) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 255.

(30) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, pp. 80, 81.

(31) M. Rouault, *Ann. Phys.*, **14**, 78 (1940).

(32) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954).

also. Gillespie's approach accounts for certain trends in a formally different way from Rundle's. According to Rundle's model variations in polarity and bond lengths stem in a straightforward way from variations in the atomic populations and bonding characteristics of the filled molecular orbitals. In Gillespie's scheme the forms of the orbitals are ignored and the trends correlate, through considerations of geometry, with the magnitudes of repulsions between the various valence-shell electron pairs.

In summary, the stereochemistry and bonding trends in the series $(CH_3)_nPF_{5-n}$ can be qualitatively understood on the basis of Rundle's formulation which neglects d orbitals or Gillespie's approach which neglects hybridization altogether.[33] The quantitative interpretation of results, however, remains an interesting challenge.

(33) NOTE ADDED IN PROOF.—For the molecules studied in this research Rundle's and Gillespie's models give similar structural implications. In the case of XeF_6, however, Rundle's model has been widely interpreted as predicting that the molecule is a regular octahedron, whereas Gillespie's model requires that it be distorted from O_h symmetry. A preliminary analysis of electron diffraction data for XeF_6 has just been carried out in our laboratory. It shows that the molecule is indeed distorted, but that it is distorted much less than demanded by Gillespie's hypotheses. The truth seems to lie somewhere between the two simple models.

CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY
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Chemical Properties of Disulfur Decafluoride[1,2]

BY BERNARD COHEN AND ALAN G. MACDIARMID

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Disulfur decafluoride, S_2F_{10}, has been found to react with Cl_2 at approximately 150° in a borosilicate glass vessel to give almost quantitative yields of SF_5Cl. With Br_2, high yields of SF_5Br were obtained. Disulfur decafluoride also underwent reaction with BCl_3 under similar conditions to give SF_5Cl, and with NH_3 to give NSF_3. The interaction of S_2F_{10} with $(CN)_2$, Al_2Cl_6, NO, C_2H_4, and $(CH_3)_2NH$ was also investigated.

Although the chemical inertness of sulfur hexafluoride, SF_6, to a large variety of reagents is well known,[3,4] relatively little information is available concerning the chemical properties of the related compound, disulfur decafluoride, S_2F_{10}.[3] The properties of the sulfur–sulfur bond in S_2F_{10} are of particular interest, since this is the only sulfur–sulfur bond known in which both sulfur atoms exhibit a coordination number of six.

Disulfur decafluoride is less stable thermally and more reactive chemically than SF_6. It decomposes slowly in an inert container above 150° to give SF_6 and SF_4[5]; it reacts upon heating with certain olefins and benzene to give small quantities of derivatives containing the $-SF_5$ group[6] and with N_2F_4 to give SF_5NF_2.[7] When streamed with chlorine through a heated tube, trace amounts of SF_5Cl have been observed.[8] Under the influence of ultraviolet irradiation, S_2F_{10} reacts with SO_2 to give SF_5OSO_2F.[9]

In the present investigation it was found that S_2F_{10} underwent reaction with excess chlorine in a glass container at 150° during 29 hr. to give almost quantitative yields of SF_5Cl (eq. 1). Essentially no attack of the

$$S_2F_{10} + Cl_2 \longrightarrow 2SF_5Cl \tag{1}$$

glass was observed. The reaction was slow, and a heating period of less than 20 hr. resulted in incomplete consumption of the S_2F_{10}. When the heating was carried out during a period of 50 hr., some of the SF_5Cl underwent reaction with the glass reaction vessel to form SiF_4 and unidentified materials.

When S_2F_{10} was heated with bromine at 138° for 24 hr. in a glass vessel, a reaction analogous to that observed with chlorine took place, and a 77% yield of SF_5Br, based on the quantity of S_2F_{10} consumed, was obtained (eq. 2). The reaction differed markedly from

$$S_2F_{10} + Br_2 \rightleftarrows 2SF_5Br \tag{2}$$

that with chlorine in that nearly 53% of the S_2F_{10} did not react, even though an almost threefold molar excess of bromine was used. Even when the molar ratio of Br_2 to S_2F_{10} was increased to 5:1 and the temperature was raised to 150°, a large fraction of the S_2F_{10} remained unreacted. It therefore appears that the reaction is reversible and that SF_5Br partly decomposes at 135–150° to form S_2F_{10} and bromine. The reaction appears to be a useful method for the preparation of SF_5Br, which has been synthesized previously only by the very

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