mole) of borane in tetrahydrofuran. The addition was performed at −20 to −25° (NaAlH₄ crystallizes from solution at −28°) during a 5-min period. A white precipitate formed which was filtered at −20° and dried under vacuum immediately.

Anal. Na, 17.9; Al, 19.5; B, 9.87; gas evolution, 49.6 mmoles/g.

Tetrahydrofuran was removed from the filtrate by vacuum distillation at −20°, producing a white solid.

Anal. Al, 1.60 g; Na, 0.153 g; B, 0.04 g; gas evolution, 102.3 mmoles.

This analysis corresponds to a mixture of 1.0 g of AlH₃, 0.14 g of NaBH₄, and 0.11 g of NaAlH₄. Part of the original precipitated solids was extracted with benzene. The benzene filtrate had the following analysis.

Anal. Na, 0.0014 g; Al, 0.141 g; B, none; gas evolution, 13.1 mmoles.

These analyses show that aluminum hydride was extracted from the precipitated solids. The insoluble solids from the benzene extraction were completely soluble in diglyme. Infrared analysis of the diglyme solution provided a spectrum which was identical with the spectrum of NaBH₄ in diglyme; no Al–H band was present. The original product before extraction decomposed rapidly at 80°, depositing aluminum metal.

Reaction of NaAlH₄ with Triethylamine Borane. To a solution of 5.4 g (0.1 mole) of NaAlH₄ in 100 ml of tetrahydrofuran was added 11.5 g (0.1 mole) of triethylamine borane in 100 ml of tetrahydrofuran. No reaction was apparent at room temperature. The solution was allowed to reflux for 8 hr, during which time a white solid precipitated. The solid (3.5 g, 0.093 mole) was identified as pure NaBH₄ by infrared analysis in diglyme. Infrared

analysis of the filtrate showed the product to be AlH₃NEt₃. These products were produced in essentially quantitative yield.

Reaction of LiH with HAl(BH₄)·Et₂O. To 7.9 g (0.06 mole) of HAl(BH₄)₂·Et₂O in 100 ml of diethyl ether was added slowly 0.5 g (0.06 mole) of LiH slurried in 100 ml of diethyl ether. The reaction was exothermic, causing the ether to reflux. All of the LiH appeared to dissolve. The ether solvent was removed under vacuum and the residue was extracted with benzene. Infrared analysis of the benzene filtrate produced a spectrum identical with that of H₂AlBH₄·Et₂O. Extraction of the remaining solid with diethyl ether, followed by infrared analysis of the resulting solution, showed the solid to be pure LiBH₄.

Reaction of LiH with Al(BH₄)₃·Et₂O. To 9.1 g (0.062 mole) of Al(BH₄)₃·Et₂O in 100 ml of diethyl ether was added 2.0 g (0.25 mole) of LiH in 50 ml of diethyl ether. The reaction was exothermic. It appeared that all of the LiH went into solution during the first half of the addition, but not all the added LiH dissolved during the last half of the addition. The small amount of insoluble solid was filtered. The amount was too small to analyze, and the solid was thought to be LiH. Infrared analysis of the filtrate showed the product to be a 3:1 mixture of LiBH₄ and LiAlH₄. Strong bands were present at 4.5 (LiBH₄) and 5.9 μ (LiAlH₄). There were no bands characteristic of HAlBH₄ type compounds.

Bonding in Phosphorus(V) Chlorofluorides[1]

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Abstract: We have considered the bonding in the phosphorus(V) chlorofluorides (PCl₅₋ₙFₙ, $n = 0$–5) as examples of trigonal bipyramidal molecules. It is observed that axial bonds are longer than equatorial bonds and that fluorine occupies axial sites in preference to equatorial ones. Hückel-type molecular orbital calculations were carried out. Stabilization of certain isomers occurs as a result of σ bonding and is not due to more favorable π bonding or d-orbital participation although both are present to some extent. It appears that the equatorial phosphorus orbitals are more electronegative than the axial orbitals because the phosphorus s orbital is concentrated in the equatorial orbitals. This gives rise to equatorial bonds which are stronger than axial bonds. In the absence of steric hindrance electropositive (electronegative) substituents prefer electronegative (electropositive) phosphorus orbitals giving rise to the observed isomers.

The group V elements (excluding nitrogen) form many five-coordinate compounds. If one thinks of lone pairs as occupying positions in the coordination sphere, this coordination number is also found for some elements of groups VI and VII. The most common geometry for these compounds is the trigonal bipyramid in which necessarily the two axial positions are different from the three equatorial positions. This is evident in PCl₅ where the axial bonds are found to be longer than the equatorial bonds.[2] When all five substitutents are not the same, geometrical isomerism is possible.

In an early electron-diffraction study of PF₃Cl₂, it was found that all three fluorine atoms are in equatorial

positions.[3] Recent F¹⁹ nmr,[4,5] infrared and Raman,[6] nuclear quadrupole resonance,[7] and dipole moment[8] investigations of pentacoordinated alkylphosphorus(V) fluorides and phosphorus(V) chlorofluorides show that the stable isomers are those with the more electronegative substituent occupying axial positions.

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

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

(6) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, 41, 863 (1964).

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

(8) R. R. Holmes and R. P. Carter, Jr., Abstracts, Inorganic Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(1) Abstracted in part from the Ph.D. thesis of P. C. Van Der Voorn, University of Illinois, 1965.

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

Muetterties, *et al.*,[4] suggested that electropositive alkyl groups occupy equatorial positions because of maximum s character in the equatorial phosphorus hybrid orbitals. Holmes[7,9] suggested that in PF_3Cl_2 a further gain in stabilization energy may result from the presence of greater axial P–F π bonding compared to equatorial P–F π bonding.

Several approximate treatments of the bonding in PCl_5 have attempted to explain the unequal bond distances. Gillespie[10] has proposed a model based solely on electron-pair repulsions. Craig, *et al.*,[11] showed that the maximum overlap of a substituent orbital with an equatorial orbital of the central atom occurs at a smaller internuclear distance than for an axial orbital. Cotton used the magnitude of the overlap integrals as a criterion in calculating relative bond strengths in PF_5 and PCl_5. It was found that the axial bonds are weaker than the equatorial bonds for those hybridizations of phosphorus in which most of the s character is located in the plane.[12]

In the models[11,12] based on overlap considerations, it was assumed that at least one d orbital was of low enough energy to participate in the bonding. In calculations[13] on polyhalogens and polyhalide ions the correct geometrical isomers were predicted without the use of d orbitals. Similar bonding has been proposed for the axial three-atom system in trigonal bipyramidal molecules such as PF_5, PCl_5,[14] and adducts of trimethyltin chloride with bases such as N,N-dimethylacetamide.[15]

We report here the results of extended Hückel calculations[16–18] on the phosphorus chlorofluorides and compare them with the predictions from some of the more approximate treatments. The results of the extended calculation give the correct isomer for all of the known chlorofluorides of phosphorus(V) and present some interesting insights concerning bonding in these compounds. A possible explanation of why fluorine occupies apical positions in these compounds is also presented.

Calculations and Results

All possible trigonal bipyramidal and two tetragonal pyramidal isomers have been considered. In PF_4Cl, recently prepared by Carter and Holmes,[19] the single chlorine can occupy either an equatorial or an axial position, or the molecule may have C_{4v} symmetry, as pictured in IA, B, and D, respectively.

(9) R. R. Holmes, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p 116.

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(13) E. E. Havinga and E. H. Wiebenga, *Rec. Trav. Chim.*, **78**, 724 (1959); E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961), and references contained therein.

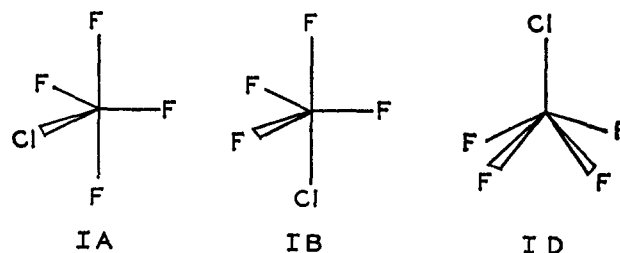(14) R. E. Rundle, *Record Chem. Progr.*, **23**, 195 (1962).

(15) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964).

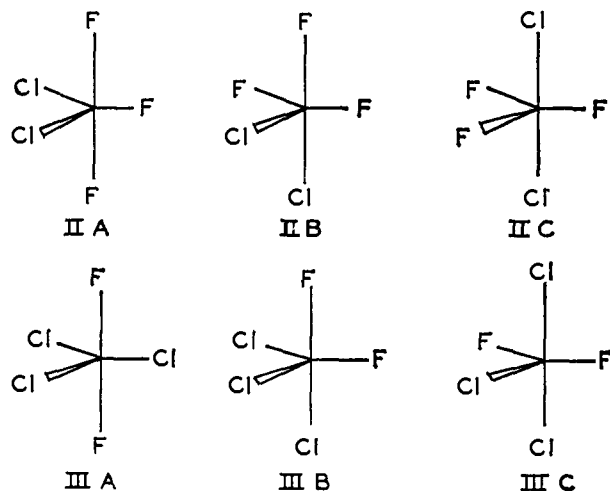(16) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962).

(17) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

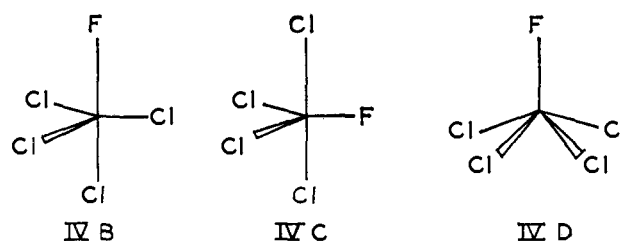(18) L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, **38**, 1607 (1963).

(19) R. P. Carter, Jr., and R. R. Holmes, *Inorg. Chem.*, **4**, 738 (1965).

IA   IB   ID

In PF_3Cl_2 and PF_2Cl_3 there are three possible isomers IIA, B, and C, and IIIA, B, and C, respectively,

IIA   IIB   IIC

IIIA   IIIB   IIIC

and finally in $PFCl_4$ there are again three possible isomers, IVB, C, and D.

IVB   IVC   IVD

The stable isomers are IIA, IIIB, and IVB; the stable isomer for PF_4Cl has not yet been determined.

The P–F bond lengths were taken as 1.55 A, the average experimentally determined distance in PF_5.[20] In the extended Hückel calculations, the P–Cl bond lengths were taken as 2.04 A for equatorial and 2.19 A for axial bonds. Ideal bond angles were assumed, *i.e.*, 120° equatorial bond angles and 90° angles between axial and equatorial bonds.

Overlap Integrals. In a manner analogous to the method of Cotton[12] in his study of PF_5 and PCl_5, we have examined the importance of the overlap integrals in the phosphorus(V) chlorofluorides. We assumed sp^2 equatorial and pd axial hybrid orbitals for phosphorus. For the halogens, s and p orbitals were considered as well as sp hybrids which were determined by maximizing the overlap integral as a function of s and p character.

An "orbital-deficient" model was considered in which the phosphorus d orbital is omitted. It is assumed that four phosphorus orbitals suffice to describe the bonding, three of them forming sp^2 equatorial

(20) K. W. Hansen and L. S. Bartell, *ibid.*, **4**, 1775 (1965).

hybrid oribtals and the p_z orbital extending over both axial halogens in a three-center bond.

Orbital exponents were calculated according to Slater's rules[21] (see Table I) and the overlap integrals were obtained from the literature.[12,22-24]

Table I. Parameters for Neutral Atoms

Atom	Slater exponents s,p	d	Coulomb integrals s	p	d
F	2.60	...	−38.24	−20.86	...
P	1.60	1.00	−20.20	−12.49	−5.00
Cl	2.033	...	−24.03	−15.03	

Use of the calculated value (0.33) of the exponent for the phosphorus d orbital leads to very small overlap integrals; with a larger value, d-orbital participation is increased.[11,25] An arbitrary value of 1.00 gives overlap integrals almost as large as those between phosphorus p and halogen p orbitals. The results are tabulated in Table II.

Table II. Total Bond Strengths as Sums of Overlap Integrals

		Halogen s orbitals	Halogen p orbitals	Halogen sp hybrids	Halogen p orbitals, no d orbitals
PF₄Cl	IA	2.490	1.369	2.899	1.451
	IB	2.523	1.329	2.863	1.372
PF₃Cl₂	IIA	2.437	1.556	2.977	1.638
	IIC	2.503	1.476	2.905	1.480
PF₂Cl₃	IIIA	2.384	1.743	3.055	1.825
	IIIC	2.450	1.663	2.983	1.667
PFCl₄	IVB	2.364	1.890	3.097	1.933
	IVC	2.397	1.850	3.061	1.854

Molecular Orbital Calculations. We have carried out three types of Hückel mo calculations: (1) simple Hückel calculations, (2) Hückel calculations on the σ-bond system only, (3) extended Hückel calculations including both σ and π bonding.

Simple Hückel Calculations. These calculations, analogous to those carried out by Havinga and Wiebenga,[13] are essentially an extension of the usual Hückel calculations on organic molecules.[26]

In the first column of Table III, we have presented the results for calculations in which the Coulomb integrals for equatorial and axial phosphorus orbitals were given the same value of α and those for chlorine and fluorine were assigned values of $\alpha + \beta$ and $\alpha + 2\beta$, respectively. The calculations were repeated for the case where the phosphorus equatorial hybrid orbitals are more electronegative than the axial p_z orbital by assigning $\alpha + \beta$ and α to the equatorial and axial

phosphorus orbitals, respectively. The results are presented in columns a and b, respectively.

Table III. Total Energies of Phosphorus(V) Chlorofluorides (ev)

		Simple Hückel (−10α) a	b	Σ Hückel	Extd Hückel No d orbitals	Extd Hückel With d orbitals
PF₅		23.95β	25.17β	−279.2	−988.9	−994.8
PF₄Cl	IA	22.36β	23.94β	−267.8	−932.1	−938.9
	IIB	22.09β	23.31β	−264.0	−930.1	−937.6
	IID				−932.3	−938.5
PF₃Cl₂	IIA	20.76β	22.70β	−255.4	−875.1	−882.3
	IIB	20.50β	22.08β	−251.8	−873.5	−881.1
	IIC	20.48β	21.72β	−247.4	−872.4	−880.0
PF₂Cl₃	IIIA	19.17β	21.46β	−241.2	−817.8	−824.8
	IIIB	18.90β	20.84β	−237.4	−816.2	−823.7
	IIIC	18.89β	20.47β	−233.6	−815.1	−822.7
PFCl₄	IVB	17.31β	19.60β	−255.2	−758.6	−765.3
	IVC	17.30β	19.24β	−221.2	−757.5	−746.4
	IVD				−756.9	−763.3
PCl₅		15.71β	18.00β	−206.8	−699.5	−705.1

Hückel Calculations on the σ Systems. In these calculations both overlap integrals and electronegativities were taken into account. The Coulomb integrals for neutral atoms were approximated as valence state ionization potentials (vsip), calculated by Hinze and Jaffé,[27] and are tabulated in Table I. The off-diagonal elements of the H matrix were calculated from[28]

$$H_{ij} = KS_{ij}(H_{ii} + H_{jj})/2; \quad K = 2.0 \quad (1)$$

where H_{ii} is the negative of the vsip of an electron in the ith orbital and S_{ij} is the overlap integral between the ith and jth orbitals. The hybridization of phosphorus was the same as in the orbital-deficient model and that of the substituents was estimated as previously reported.[29]

As in the ω technique,[26] the Coulomb integrals were adjusted for the partial charges according to

$$H_{ii} = H_{ii}^0 - Kq_i \quad (2)$$

where H_{ii}^0 and H_{ii} are the Coulomb integrals for neutral and charged atoms, respectively, and K equals 2.00 ev per ionic charge. The new Coulomb integrals were used for a next calculation in which new charges were calculated. This procedure was repeated until self-consistency was achieved for every atom to within a charge of 0.01. The total energies are tabulated in Table III.

Extended Hückel Calculations. In the extended Hückel[16-18] calculations, all π- and σ-bonding interactions are included and we can determine how the inclusion of d orbitals affects the difference in energy between the geometrical isomers. *No assumptions have to be made about hybridization.*

The Coulomb integrals were approximated as above and the H matrix was calculated according to

$$H_{ij} = KS_{ij}(H_{ii}H_{jj})^{1/2}; \quad K = 1.75 \quad (3)$$

The use of the same constant for σ and π interactions leads to an underestimate of π bonding relative to σ bonding.[18] This is shown where attempts are made to

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(24) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 354 (1954).
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(27) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(28) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).
(29) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

Table IV

	Without 3d orbitals				With 3d orbitals			
	ax P–F	eq P–F	ax P–Cl	eq P–Cl	ax P–F	eq P–F	ax P–Cl	eq P–Cl
PF₅	0.435	0.470	...	...	0.486	0.527	...	...
PF₄Cl A	0.387	0.448	...	0.684	0.380	0.431	...	1.082
PF₃Cl₂ A	0.339	0.426	...	0.680	0.269	0.331	...	1.028
PF₂Cl₃ A	0.290	...	...	0.677	0.158	...	...	0.985
PFCl₄ B	0.265	...	0.432	0.660	0.071	...	0.700	0.920
PCl₅	...	...	0.416	0.647	...	...	0.658	0.855

Overlap populations in P–X bonds

reproduce Hartree–Fock results by means of the extended Hückel method. For small molecules, it was found that a larger value for K should be used for π than for σ interactions.[30]

The calculations were carried out using a program obtained from Hoffmann, which calculates the overlap matrix from the cartesian coordinates of the atoms and the orbital exponents, sets up the H matrix, solves the secular equation, and finally carries out a Mulliken population analysis.[31]

Consider a normalized molecular orbital as a linear combination of atomic orbitals

$$\psi = c_i\phi_i + c_j\phi_j$$

Upon squaring the wave function and integrating over all space, the following breakdown of the electron density in the molecular orbital is obtained

$$N = Nc_i^2 + 2Nc_ic_jS_{ij} + Nc_j^2 \qquad (4)$$

where N is the number of electrons in the molecular orbital (usually $N = 2$), Nc_i^2 and Nc_j^2 are the net atomic populations, and $2Nc_ic_jS_{ij}$ is the overlap population. The gross atomic population equals the net atomic population plus one-half of the overlap populations. From this the net charge on an atom can be calculated by summing over all occupied molecular orbitals. The overlap population has been proposed[31] as a measure of bond strength and positive and negative overlap populations correspond to bonding and antibonding interactions, respectively.

Modifications were made in Hoffmann's program to allow adjustment of the Coulomb integrals as described above (eq 2). The Slater exponents were adjusted according to

$$\mu_i = \mu_i^0 + \frac{0.35q_i}{n^*} \qquad (5)$$

where μ_i^0 and μ_i are the exponents for orbitals on the neutral and charged atom, respectively. This is merely an extension of Slater's rules, where n^* is the effective principal quantum number.[21] These adjusted parameters are used in an iterative procedure until self-consistent charges are obtained. The energies are tabulated in Table III, and the overlap populations in Table IV.

Hybridization. In order to obtain a qualitative idea of the phosphorus hybridization, we have considered the overlap populations,[31] in particular those involving the phosphorus 3s orbital. Only that part of the phosphorus 3s orbital is considered which is contained

in the overlap populations; the remaining part is included in the net atomic population. If $n(i, j)$ is the overlap population between orbitals i and j, and X_i denotes the substituent atom, then the extent to which the phosphorus 3s overlap populations are involved in the total overlap population in the bond to X_i is given by

$$\frac{n(\text{P 3s, } X_i \text{ s}) + n(\text{P 3s, } X_i \text{ p})}{\sum_{\substack{\text{all} \\ \text{bonds}}}[(n\text{P 3s, } X_i \text{ s}) + n(\text{P 3s, } X_i \text{ p})]} \qquad (6)$$

Thus, if this were a perfect criterion for hybridization, and the phosphorus in PF₅ were sp² hybridized in the equatorial bond and pd hybridized in the axial bonds, the ratio would be one-third for any equatorial bond and zero for either axial bond. The results for the phosphorus halides are tabulated in Table V both without and with P 3d orbitals.

Table V. Distribution of P 3s Character in Overlap Populations

	Without 3d orbitals				With 3d orbitals			
	ax P–F	eq P–F	ax P–Cl	eq P–Cl	ax P–F	eq P–F	ax P–Cl	eq P–Cl
PF₅	19.4	20.4	...	...	20.2	19.8	...	...
PF₄Cl A	15.6	20.5	...	27.7	18.4	19.1	...	25.0
PF₃Cl₂ A	16.7	20.2	...	27.9	16.5	18.4	...	24.3
PF₂Cl₃ A	8.5	...	...	27.7	14.5	...	...	23.6
PFCl₄ B	10.6	...	10.6	26.3	13.4	...	14.6	24.0
PCl₅	...	...	11.7	25.5	...	...	13.1	24.6

% s character per P–X bond

Discussion

Square-Pyramidal Isomers. The concern here is primarily with the bonding in trigonal bipyrimidal molecules, but the isomers of PF₄Cl (ID) and PFCl₄ (IVD) of C_{4v} symmetry have been considered briefly. Calculations were carried out with ClPF bond angles of 80, 90, and 100°. For PFCl₄, the trigonal bipyramidal structure IVB has the lowest energy, but for PF₄Cl, the tetragonal pyramid with a bond angle of 100° is lower in energy than the trigonal bipyramid. Its structure has not yet been determined, but it is expected to be a distorted trigonal bipyramid, the structure found for CH₃PF₄;[32] in a similar compound, (C₂H₅)₂NPF₄, there are two different fluorine environments which give nmr signals of equal intensities.[5] It is not surprising that the extended Hückel method fails when two widely differing geometries such as the trigonal bipyramid and the tetragonal pyramid are compared.

(30) P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **52**, 890 (1965).

(31) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

(32) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).

At higher temperatures, the fluorines in PF_3Cl_2 become equivalent;[5,7] a tetragonal pyramid has been postulated as a possible transition state. Any attempt to calculate an energy of activation is hampered by lack of information about bond angles and distances in the transition state.

Overlap Integrals. With the sum of the overlap integrals as a measure of the total bond strength, the correct isomer is calculated to be of lowest energy when halogen p or sp hybrid orbitals are used (Table II). It is unlikely that the halogens use pure s orbitals since these are of considerably lower energy than the halogen p orbitals and phosphorus orbitals (Table I). Favorable overlap certainly contributes to the stability of certain isomers.

Russian investigators[33] have carried out calculations on a variety of isomers of several geometries, including the trigonal bipyramid. They assumed bond strengths to be proportional to the projections of the angular parts of the atomic orbitals. This is the same criterion proposed originally by Pauling and Sherman[34] and shown to be inadequate by Coulson.[35] Cotton[12] has shown that this criterion leads to unreasonable predictions for the relative bond strengths of the axial and equatorial bonds in PF_5 and PCl_5. The Russian workers[33] predict D_{3h} symmetry for both PF_3Cl_2 and PF_3Br_2, which have been shown to have C_{2v} symmetry.[4,6,7] It seems fortuitous that some of the isomers they treated are predicted correctly.

Orbital-Deficient Model. The electronegativity of phosphorus orbitals appears to be an important feature in the prediction of the correct isomer. In Table III (column 2) it is seen that the first isomer in each series is calculated to be the most stable even when Coulomb integrals of equal value are assigned to axial and equatorial phosphorus orbitals. When, however, the axial orbitals are made more electronegative, the wrong isomers are predicted.[36] Since more of the phosphorus s orbital is in the equatorial bonds than in the axial bonds (see below) instead of being equally distributed among all five bonds, the much simplified orbital-deficient model is of value in explaining the preference of fluorine for axial positions. As discussed by Rundle,[14] three molecular orbitals are formed in a linear, three-center arrangement of atoms: one occupied bonding orbital involving all three centers, one occupied nonbonding orbital with most of the electron density on the two extreme centers and some on the central atom, and one empty nonbonding orbital. When the extreme atoms are identical, the nonbonding orbital involves only the extreme centers. The large amount of electron density on the extreme atoms satisfies their electronegativity and leads to a lower total energy. In view of this, the three possible linear arrangements in the phosphorus(V) chlorofluorides can be ranked in the following order of decreasing stabilization energy relative to the separated atoms: FPF > FPCl > ClPCl. In an equatorial position, no such nonbonding orbital exists. Thus, more stabilization energy is gained with the more electronegative

substituents in axial positions than in equatorial positions.

π **Bonding.** Energy differences between the most and least stable isomers become less as the extent of π bonding and d-orbital participation increases (cf. columns 3, 4, and 5, in Table III; trends rather than exact energy differences should be compared as part of the difference is due to the nature of the calculation itself). On the basis of these results, we propose that stabilization of those isomers with apical fluorines occurs through σ bonds. This does not imply that π bonding is not present, nor that d orbitals do not participate in the bonding. Holmes, et al.,[7] concluded that the difference in fluorine chemical shifts for the two fluorine environments in PF_3Cl_2 is the result of greater axial than equatorial π bonding and suggested that this could lead to a gain in stabilization energy. The magnitudes of π-bonding overlap populations indicate, however, that π bonding is greater in the equatorial positions. The discrepancy probably is the result of an oversimplification of the theory of F^{19} chemical shifts in the reported[7] interpretation.

It is interesting to point out that the inclusion of d orbitals in an extended Hückel calculation of geometrical isomers of $(CH_3)_2NSO_2N(CH_3)_2$ leads to a significant increase in energy difference. In that case, stability of one isomer is due almost completely to d-orbital interactions.[37]

Hybridization. In the extended Hückel theory, no simple hybridization scheme is assumed; phosphorus atomic orbitals are distributed according to their energies and overlap properties but always consistent with the symmetry of the molecule. The distribution of the phosphorus 3s orbital in the overlap populations was found by application of eq 6. The two most prominent features are that: (1) the P 3s character is greater in equatorial bonds, and (2) the P 3s character is concentrated in bonds to the more electropositive substituent. The former implies that the equatorial phosphorus orbitals are the more electronegative.

The results in Table V follow Bent's rules[38] saying that atomic p character concentrates in those orbitals directed toward electronegative substituents, and atomic s character in those directed toward electropositive orbitals. We can state further that based upon energy lowering, electronegative substituents prefer orbitals with large p character and electropositive substituents prefer those with large s character. The result is that of a number of possible isomers in the phosphorus chlorofluorides, the one with the largest number of axial fluorines is most stable.

Gillespie[10] has explained the difference in bond lengths in PCl_5 solely on the basis of repulsions between bonding electron pairs. In order to extend this model to predict correct isomers among the phosphorus(V) mixed halides, we would have to state that in a bond to a more electropositive substituent (a lone pair in the extreme case), the electrons are more loosely held than in a bond to an electronegative element. On the basis of Gillespie's arguments, this would place the more electropositive element in an equatorial position to mini-

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mize repulsions. However, the fact that such an electron pair is more diffuse is a direct result of the nature of the bonding. It is not possible to put these electron-pair repulsions on a semiquantitative basis, hence it is difficult to ascertain their magnitude. Although bond lengths and isomer stabilities are easily explained in terms of the σ bonding, it is quite likely that electron-pair repulsions give rise to secondary effects such as distortions from ideal geometries.

Bond Strengths. The fact that in many trigonal bipyramidal molecules axial bonds are longer than equatorial bonds suggests that the former are weaker. The same conclusion is reached on the basis of force constants determined from normal coordinate analysis in PF_5, PF_2Cl_3, and PCl_5.[39]

On the basis of overlap populations (Table IV), we find equatorial bonds in PF_5 and PCl_5 to be stronger than axial ones. The smaller difference in PF_5 compared to that in PCl_5 corresponds to the smaller difference in bond lengths: 0.02 Å in PF_5,[20] 0.15 Å in PCl_5.[2] In Table IV, the P–Cl overlap populations are nearly always larger than the P–F overlap populations, contrary to the single-bond energies of 117 and 79 kcal/mole for P–F and P–Cl bonds, respectively.[40] However, Mulliken[31] pointed out that overlap populations are a measure of the extent of covalent interaction only. Ionic contributions are certainly greater for fluorine bonds than for chlorine bonds. If the bond dissociation energies are corrected for an amount in electron volts equal to the square of the electronegativity differences on Pauling's scale,[41] the "covalent" energies are 2.02 ev for the P–F bond and 2.43 ev for the P–Cl bond, in the same order as the overlap populations. The stronger equatorial bonds are a result of the larger electronegativity of the equatorial phosphorus orbitals.

It appears (Table IV) that P–F and P–Cl bond strengths decrease in the series upon replacing fluorines with chlorines, a trend also found from the force constant determinations.[39] Ionic as well as covalent interactions must be considered. The overlap integrals between the phosphorus p orbital and fluorine are nearly constant for the series PF_5 to $PFCl_4$; those between the phosphorus s orbital and fluorine increase. The explanation must lie in the energy match of the orbitals. As fluorines are replaced by chlorines, the decrease of net charge on phosphorus and therefore the decrease of its electronegativity is greater than the increase of charge on fluorine. As a result, the energy match becomes poorer and the covalent bond energy as measured by the overlap population decreases. The variation in total bond energies is not as great as indicated by the overlap populations, however, since the ionic contributions increase in the opposite direction.

The small decrease in P–Cl overlap populations compared to P–F overlap populations is not readily attributed to any one factor. In the series PF_4Cl to PCl_5,

all P–Cl overlap integrals increase. It also appears that the energy match improves for most combinations of atomic orbitals. It is difficult, however, to draw any conclusions from the relative values of the Coulomb integrals of phosphorus and chlorine orbitals because they are close in value, and hence the value of the constant used in the charge adjustment (eq 2) has a large effect on the relative values of the Coulomb integrals. When the total overlap populations are broken down into orbital overlap populations, it is found that from PF_4Cl to PF_2Cl_3 the π-bonding overlap populations are the cause of the net decrease; from PF_2Cl_3 to PCl_5, the decrease is due to the $Pp-Cls$, $Pp-Clp$, and π-bonding overlap populations.

The electronegativity of the PF_nC_{4-n} entity to which the chlorine is bonded decreases, but it is not clear what bearing this has on the ionic contributions to the total bond energy since the electronegativity of the chlorine orbitals is similar. In either case, the difference is probably small and such ionic contributions are probably of minor importance. It is observed in Table IV that upon inclusion of phosphorus d orbitals, the rate of decrease in overlap populations in going from PF_5 to PCl_5 is even greater. This is attributed to a decrease in the d-orbital overlap populations, which is observed in spite of the fact that the overlap integrals between the phosphorus d orbitals and the halogen s orbitals increase. Overlap between the d orbitals and halogen p orbitals decreases. The decrease in overlap populations is attributed to less favorable P_d-X_p overlap and increasingly poor energy matching, which is evident from the magnitudes of the Coulomb integrals.

Conclusion. The concentration of the phosphorus s orbital in the equatorial hybrid orbitals is a direct consequence of the trigonal bipyramidal geometry. In the absence of steric hindrance electropositive (electronegative) substituents prefer electronegative (electropositive) orbitals, hence chlorines prefer equatorial, and fluorines axial, positions. In the case of five like substituents, a further consequence is that equatorial bonds are stronger than axial bonds. To a first approximation, the bonding can be described in terms of σ bonds formed by phosphorus s and p orbitals. π bonding and d-orbital participation make minor contributions. The true bonding can be pictured as in the orbital-deficient model with the phosphorus s orbital participating to a small extent in the bonding of axial substituents, and probably some d character in both axial and equatorial bonds; finally, some $p\pi-p\pi$ and $d\pi-p\pi$ bonding is probably present in all bonds.

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