discussions with Professor P. W. R. Corfield concerning the vector calculations.

Registry No. $C_2H_5(C_6H_5)_2PO$, 1733-57-9; $(CH_3)_2C_6H_5PS$, 1707-00-2; $(CH_3)_2C_6F_5PS$, 19100-54-0; $CH_3(C_6H_5)_2PS$, 13639-74-2; $C_2H_5(C_6H_5)_2PS$, 1017-98-7; $[(CH_3)_2N](C_6H_5)_2PS$, 17513-68-7; $[(CH_3)_2N]_3PS$, 3732-82-9; $(CH_3O)_3PS$, 152-18-1; $[(CH_3)_2N](C_6H_5)_2PSe$, 23486-86-4; F_3PO, 13478-20-1; F_2HPO, 14939-34-5; Cl_3PO, 10025-87-3; $CH_3C(CH_2O)_3PO$, 1449-89-4; $(C_6H_5)_3PO$, 791-28-6; $(CH_3)_3PO$, 676-96-0; F_3PS, 2404-52-6; Cl_3PS, 3982-91-0; $CH_3C(CH_2O)_3PS$, 3196-56-3; $(C_6H_5)_3PS$, 3878-45-3; $(CH_3)_3PS$, 2404-55-9; $(C_6H_5)_3PSe$, 3878-44-2; $(C_6H_5)_3AsO$, 1153-05-5; $(CH_3)_3AsO$, 4964-14-1; $(C_6H_5)_3AsS$, 3937-40-4; $(CH_3)_3AsS$, 26386-93-6.

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Electronic Structures of Phosphorus Pentafluoride and Tetrafluorophosphorane

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Ab initio LCAO-MO-SCF calculations were carried out on the PF_5 and PF_4H molecules, employing moderately small gaussian basis sets. Using the resulting wave functions, it was found that the molecular orbitals of these two molecules are readily interrelated with respect to their detailed electron density distributions. A further such interrelationship was carried out between the molecular orbitals of PF_5 and those of the PF_3 and OPF_3 molecules.

Introduction

According to the standard valence-bond picture used by chemists, it is necessary to employ d atomic orbitals (the sp^3d hybrid[1]) to describe pentacoordinate phosphorus. However, it has been known[2] for a number of years that such structures may alternatively be described using only s and p atomic orbitals, and this approach has been delineated in a recent semiempirical study.[2b] In the study reported herein, we have carried out *ab initio* calculations of the wave functions of the PF_5 and PF_4H molecules using a small number of s and p functions in the basis set. Further calculations were made by adding to these s and p functions sufficient d functions so that adequate d character was allotted to the phosphorus atom to permit the d atomic orbitals to participate in the basic σ structure of the molecular orbitals in addition to allowing charge feedback to the phosphorus and polarization of its s and p orbitals. The resulting wave functions were employed to evaluate the similarity between the orbitals of PF_5 and PF_4H. A further inquiry was made into the possible interrelationships of the PF_5 molecular orbitals with those of the related compounds OPF_3 and OPF_2H, the orbitals of which have previously been correlated[3] with each other and with the orbitals of PF_3 and PF_2H. After this paper had been completed, another *ab initio* study of phosphorus pentafluoride appeared in the literature.[4]

Calculational Details

The bond distances in the PF_5 molecule of D_{3h} symmetry were taken to be 1.534 Å for the equatorial fluorine atoms and 1.577 Å for the axial, as determined by electron diffraction.[5] For the PF_4H molecule with the hydrogen in the equatorial position to give C_{2v} symmetry, the following geometry based on microwave spectroscopy[6] was employed: $P\text{-}F_{eq} = 1.550$ Å, $P\text{-}F_{ax} = 1.594$ Å, $P\text{-}H = 1.360$ Å, $\angle F_{eq}PH = 124°$, $\angle F_{ax}PH = 90°$. The *ab initio* calculations were carried out with an atom-optimized uncontracted gaussian basis set using nine s- and five p-type exponents to describe the phosphorus atom,[7] five s- and two p-type for each fluorine,[8] and three s-type for the hydrogen;[7] *i.e.*, the PF_5 molecule without d orbitals was described in a (95/52) and the PF_4H in a (95/52/3) basis set. These basis sets were expanded to (952/52) for PF_5 and (952/52/3) for PF_4H, using exponents[9] of 0.27 and 1.55 for the added pair of spherically harmonic fivefold sets of d functions. Note that the (52) description of fluorine was employed even though it was recognized to be only marginally adequate for such an electrophilic atom. Since 10 individual functions were added to a set of only 24 such functions by going from a (95) to a (952) basis set for the phosphorus, the d orbitals placed on this atom may possibly substitute for a paucity of s and p character in the molecule.

The SCF calculations were carried out using an uncontracted basis set with the program POLYATOM.[10] The electron densities were first calculated[11] and then converted into computer-made three-dimensional cross-sectional plots by a subsidiary program.[12] The Mulliken populations were separately calculated[13] for each molecular orbital with respect to (a) all of the individual gaussian basis functions, (b) the basis functions of each symmetry, and (c) the atomic centers.

Results and Discussion

Overall Properties of PF_5 and PF_4H. The total energy and

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(1) G. E. Kimball, *J. Chem. Phys.*, 8, 188 (1940).

(2) (a) R. E. Rundle, *Surv. Progr. Chem.*, 1, 81 (1963); (b) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 3047 (1972), and references therein.

(3) I. Absar and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 94, 6294 (1972).

(4) A. Strich and A. Veillard, *J. Amer. Chem. Soc.*, 95, 5574 (1973).

(5) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 4, 1775 (1965).

(6) S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, 48, 2118 (1968).

(7) J.-B. Robert, H. Marsmann, L. J. Schaad, and J. R. Van Wazer, *Phosphorus*, 2, 11 (1972).

(8) D. R. Whitman and C. J. Hornbach, *J. Chem. Phys.*, 51, 398 (1969).

(9) I. Absar and J. R. Van Wazer, *Chem. Phys. Lett.*, 11, 310 (1971).

(10) A version of POLYATOM which was updated by A. J. Duke at McMaster University, Hamilton, Ontario, Canada (*cf.* A. J. Duke and R. F. W. Bader, *Chem. Phys. Lett.*, 10, 631 (1971)).

(11) W. E. Palke, A program for calculating electron densities, later modified by T. H. Dunning and H. Marsmann.

(12) D. L. Nelson, "Perspective Plotting of Two-Dimensional Assays—PLOT3D," Department of Physics and Astronomy, University of Maryland, College Park, Md.

(13) I. Absar, Program MULPOP, Vanderbilt University, 1972.

Table I. Overall Properties Calculated for the PF_5 and PF_4H Molecules

	PF_5		PF_4H	
Property	No d	With d	No d	With d
Total energy, au	−832.50	−832.94	−734.61	−735.01
	(−837.63)	(−837.84)[a]		
Kinetic energy, au	+824.18	+822.30	+728.05	+726.47
Potential energy (electronic), au	−2066.20	−2064.76	−1765.79	−1764.61
Viral ratio	−2.010	−2.013	−2.009	−2.012
Mulliken charges, e				
Phosphorus	+2.25	+1.45	+1.84	+0.97
	(+2.67)	(+2.12)		
Axial fluorine	−0.46	−0.31	−0.46	−0.31
	(−0.57)	(−0.46)		
Equatorial fluorine	−0.44	−0.28	−0.44	−0.28
	(−0.51)	(−0.40)		
Hydrogen			−0.03	+0.20
Overlap populations, e				
$P\text{-}F_{ax}$	0.27	0.49	0.24	0.49
	(0.37)	(0.56)		
$P\text{-}F_{eq}$	0.23	0.47	0.26	0.49
	(0.39)	(0.61)		
P-H			0.57	0.77
Atomic orbital occupations, e				
Axial fluorine 2s	1.99	2.03	1.99	2.03
		(1.90)		
$2p_\sigma$	1.59	1.60	1.59	1.60
		(1.62)		
$2p_\pi$	3.88	3.68	3.88	3.68
		(3.88)		
Equatorial fluorine 2s	2.00	2.04	1.99	2.04
		(1.94)		
$2p_\sigma$	1.61	1.59	1.61	1.59
		(1.94)		
$2p_\pi$	3.83	3.65	3.84	3.65
		(3.50)		
Phosphorus 3s	0.95	0.84	1.09	1.01
		(0.74)		
3p	1.80	1.58	2.07	1.93
		(1.46)		
3d	0.00	1.13	0.00	1.09
		(0.64)		
Hydrogen 2s			1.03	0.80

[a] Values in parentheses are taken from ref 4.

its breakdown into the kinetic and potential terms is presented in Table I for phosphorus pentafluoride and tetrafluorophosphorane,[14] with and without d functions being included in the basis set. Note that the inclusion of the d orbitals only lowered the total energy by 0.08 au/bond as compared to 0.09 for PF_3,[15] 0.14 for OPF_3,[16] and 0.02 for PH_3[7] in rather similar basis sets. These numbers suggest that adding d character to the phosphorus of PF_5 leads to polarization along with the usual extensive charge feedback associated with P-F bonding but not a drastic reorganization of the σ structure of the molecule.

The overall results from the Mulliken analysis[17] of electronic populations are presented in Table I from which it can be seen that, for both of the molecules, allowing d orbitals considerably reduced the charge difference between the phosphorus and the fluorine atoms while nearly doubling the overlap populations. Note that, for both the axial and equatorial fluorine atoms in either molecule, these calculations show a decrease in charge (*ca.* 0.15 e/atom) upon allowing d character. They also indicate that, for the PF_5 molecule, more charge is donated from each fluorine atom (calcd: 0.17 e from each F_{ax} and 0.20 e from each F_{eq}) to the phosphorus by the process of $p_\pi \rightarrow d_\pi$ feedback than the observed overall feedback (0.15 e/F). This difference is attributable to the opposing σ-bond charge transfer from the phosphorus to the fluorine, upon allowing d character to the molecule. A further interesting result of the calculations without d functions is that the $P\text{-}F_{eq}$ overlap population for the π system lying within the equatorial plane is larger (calcd: 0.10 e) than that for the $P\text{-}F_{eq}$ π system perpendicular to this plane (0.06 e). These values indicate that, for an equatorial substituent bearing lone-pair electrons, the preferred orientation would be the one having the maximum lone-pair density in the equatorial plane. Furthermore, feedback of π electrons through $d_\pi \rightarrow p_\pi$ bonding is more effective from a F lone pair in the equatorial plane (calcd: 0.11 e transferred from F to P) as compared to that from the perpendicular lone pairs (0.09), indicating that d orbitals serve only to further the tendency observed in the (sp) calculation. Experimental evidence in-

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(14) Since the results of another *ab initio* calculation[4] (using a somewhat larger basis set) are available on PF_5, we have tried to confine the discussion in this paper to those features of our calculation which are thought to be qualitatively independent of the size of a reasonably well-balanced basis set and hence generally correct for the SCF approximation. For both PF_5 and PF_4H, the valence orbitals are highly delocalized and many of them do not differ much in energy. Hence, it would seem that any discussion involving the partitioning of energy or of electronic charge on the basis of either our wave function or that of Strich and Veillard[4] will have only qualitative significance. Therefore, the reader should be concerned with trends rather than with numerical values. In this paper, we have attempted to confine the discussion to qualitative findings which would presumably not be essentially different if a similar analysis were to be carried out on a well-balanced basis set at the Hartree-Fock limit.

(15) I. Absar and J. R. Van Wazer, unpublished results.

(16) I. Absar and J. R. Van Wazer, *J. Phys. Chem.*, 75, 1360 (1971).

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

dicates that the preferred orientation is as suggested for amino phosphoranes,[18] 2,2,2-triisopropoxy-4,5-(2′,2″-biphenyleno)-1,3,2-dioxaphospholene,[19] and thiotetrafluorophosphoranes.[20]

An interesting effect shown in Table I is that the hydrogen atom of the PF_4H molecules loses electrons to the phosphorus upon allowing d character to the latter. In the phosphine molecule,[7] PH_3, there is only a little charge transfer between the phosphorus and hydrogen, whether or not d orbitals are allowed to the kinds of basis sets employed here. On the other hand, about the same amount of transfer of electrons from the hydrogen to the phosphorus upon including d functions has been found[3] for the molecules OPF_2H and PF_2H as for PF_4H. This charge transfer from the hydrogen to phosphorus reduces the high positive charge of the latter atom through the incorporation of d character into the H-P σ structure. Note in Table I that this is accompanied by a considerable increase in the P-H overlap population.

The small number of gaussian functions allotted to each fluorine atom in the basis set used here may well cause the absolute values of the atomic charges given in Table I to be too small. This effect is undoubtedly enhanced by the use of two d exponents on the phosphorus which will tend to enhance the disparity between the description of the phosphorus and the fluorine atoms. The deficiency in the fluorine description has led to a smaller P-F overlap population when the fluorine is equatorial as compared to when it is in the axial position. At the Hartree-Fock limit, we would expect the opposite to be true.

If the addition of d character to the phosphorus had led to a redistribution of the electrons which would be equivalent to the sp^3d valence-bond description of either PF_5 or PF_4H, there would have been an appreciable increase in the contribution of the phosphorus d functions of a_1' symmetry (*i.e.*, d_{z^2} for the case where the axial fluorine atoms of PF_5 lie on the z coordinate axis) to the overlap population of the P-F_{ax} bond. However, the change in this particular contribution to the P-F_{ax} overlap population was calculated to be −0.028 e/bond for PF_5 and +0.005 for PF_4H. If allowing d orbitals to the phosphorus had indeed induced effective d participation in the σ bonding, we estimate that this particular d contribution to the P-F_{ax} overlap population should be about the same as the original (sp) σ contribution to this bond, which was calculated to be 0.15 e without d functions.

The atomic orbital occupations presented in Table I show that, upon the addition of phosphorus 3d character to either the PF_4 or the PF_4H molecule in this description, there is a small diminution in the occupation of the phosphorus 3s and 3p atomic orbitals with small changes also occurring in the 2s and 2p σ orbitals of the axial and equatorial fluorine atoms. The biggest changes in atomic orbital occupations of the substituent atoms are found in the drop of 0.2 e in the $2p_\pi$ orbitals of each fluorine of PF_5 or PF_4H, as well as in the 1s orbital of the PF_4H hydrogen. This diminution in the occupancy of the fluorine $2p_\pi$ atomic orbitals shows that much of the charge feedback from fluorine to phosphorus upon allowing d character to the latter may be found in $p_\pi \rightarrow d_\pi$ bonding. According to these atomic orbital occupations, essentially all of the potential 2s and 2p charge-carrying capacity of the fluorine atoms has been utilized in the filled valence-shell molecular orbitals of PF_5 or PF_4H so that any appreciable amount of charge on the fluorine in the higher orbitals (virtual orbitals) must involve 3s or 3p atomic orbitals. On the other hand, a considerable amount of phosphorus 3s and some 3p charge-carrying capacity is left to the phosphorus for utilization in the higher P-F σ^* molecular orbitals of both molecules.

Table II. Molecular Orbitals of Phosphorus Pentafluoride

			Dominant character			
	Orbital energies, au		F-P bonding		F lone pair	
Orbital	Ref 4	This work	Loc[a]	Type[b]	Loc[a]	Type[c]
$2e''$	−0.665	−0.592	Ax	[p-d]	All	n_π
$6e'$	−0.684	−0.602	Ax	[p_π-p_π]	Ax	n_π
$5a_2''$	−0.695	−0.611	Ax	p_σ-p_σ	Ax	n_σ
					Eq	n_π
$8a_1'$	−0.709	−0.645	Ax	p_σ-d_σ	Ax	n_σ
			Eq	[p_σ-d_σ]	Eq	[n_σ]
$1a_2'$	−0.722	−0.643	None		Eq	n_π
$5e'$	−0.763	−0.700	Eq	p_π-d_π	Eq	n_π
				p_σ-d_σ	Eq	n_σ
$1e''$	−0.804	−0.736	Ax	$(p_\pi$-$d_\pi)^2$	Eq	n_π
			Eq	p_π-d_π	Ax	[n_π]
$4a_2''$	−0.852	−0.791	Ax	p_σ-p_σ	Ax	n_σ
			Eq	p_π-p_π	Eq	n_π
$4e'$	−0.858	−0.798	Ax	p_π-p_π	Eq	n_σ
			Eq	p_σ-p_σ		
$7a_1'$	−0.971	−0.919	All	p_σ-s_σ	All	n_σ
$6a_1'$	−1.635	−1.566	All	[$(s_\sigma$-$d_\sigma)^*$]		
$3a_2''$	−1.672	−1.594	Ax	s_σ-p_σ		
$3e'$	−1.712	−1.649	Eq	s_σ-p_σ		
$5a_1'$	−1.782	−1.725	All	s_σ-s_σ		

[a] For each orbital of A symmetry or each E pair, the three equatorial positions, Eq, are mutual, equivalent and the two axial positions, Ax, are also equivalent to each other. [b] The notation s_σ-p_σ means that the fluorine 2s atomic orbital is involved in σ bonding with the phosphorus 3p. The superscript 2 in the notation $(p_\pi$-$p_\pi)^2$ means that there is a pair of mutually perpendicular π orbitals making up the specified F-P bond. Brackets indicate lesser importance. [c] n_σ corresponds to the lone-pair charge lying on the F-P bond axis and n_π to a pair of equal lone-pair charges lying on opposite sides of this bond axis.

Valence Molecular Orbitals of PF_5. The orbital energies obtained for the valence orbitals of PF_5 in this work and in ref 4 are compared in Table II, from which it can be seen that our calculated valence-orbital energies are consistently about 2 eV less energetic than those of Strich and Viellard. Table II also shows the dominant character of each of the PF_5 valence orbitals with respect to P-F bonding and the fluorine lone pairs. For additional information concerning the PF_5 valence orbitals, the reader should turn to ref 4.

The nodal structure in the valence region (exclusive of the nodes and antinodes of these orbitals in the core region) are shown in Figure 1 for the 20 valence-shell orbitals of phosphorus pentafluoride. For this molecule, the five more stable valence orbitals (which involve fluorine s character, see Table II) exhibit valence-region nodal structures of the same general shape that would be found for one s, three p,

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(18) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, 8, 1097 (1967); V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, 10, 142 (1969); M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, 10, 1113 (1969); J. J. Harris and B. Rudner, *J. Org. Chem.*, 33, 1392 (1968); J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, 10, 1538 (1971).

(19) (a) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Amer. Chem. Soc.*, 86, 4394 (1964); F. Ramirez and N. B. Desai, *ibid.*, 82, 2652 (1960); 85, 3252 (1963); F. Ramirez, *Bull. Soc. Chim. Fr.*, 113 (1970); (b) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, 87, 127 (1965); W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, 89, 2268 (1967); R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, 89, 2272 (1967). See also D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Amer. Chem. Soc.*, 91, 5243 (1969).

(20) S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968); *J. Chem. Soc. A*, 1049 (1970).

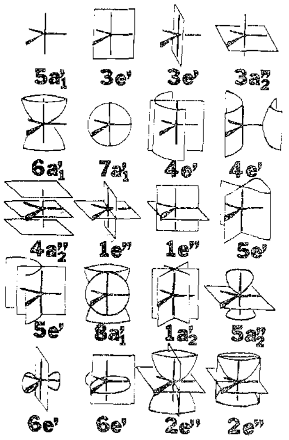

Figure 1. Sketches of the nodal surfaces of the valence-shell molecular orbitals of phosphorus pentafluoride.

and one d atomic orbitals of the central phosphorus atom. The hour-glass shape for the nodal structure of molecular orbital $6a_1'$ is indicated by an absence of P-F bonding and negative overlap between any axial and any equatorial fluorine atom, along with the presence of insignificantly small positive overlap between the three equatorial fluorines and also between the pair of axial fluorine atoms. Thus, the group of the five more stable valence-shell molecular orbitals of PF_5 bear a close formal relationship to an sp^3d phosphorus hybrid.

Note that the single essentially spherical outer-nodal surface of orbital $7a_1$ passes through each of the five fluorine nuclei and is consistent with all P-F bonds exhibiting p_σ-s_σ character. Also, for example, the nodal structure for orbital $4a_2''$ corresponds to two pancake-shaped lumps of charge lying between the phosphorus and axial fluorine atoms above and below the equatorial plane. This structure, of course, is consistent with and follows from the p_σ-p_σ bonding between the axial fluorines and the phosphorus and the p_π-p_π bonding between the equatorial fluorines and the phosphorus, as well as being in accord with the n_σ character for the axial and n_π for the equatorial lone-pair charges (see Table II). Numerous relations can be adduced between the nodal structures shown in Figure 1. For example, there is the development of the nodal structure in the series of orbitals $6a_1'$, $8a_1'$, $5a_2''$, and $6e'$. Orbital $8a_1'$ follows from $6a_1'$ by the addition of an approximately spherical nodal surface while the orbital trio consisting of the $5a_2''$ and 6e molecular orbitals result from the addition of a nodal plane. This sequence, of course, parallels the development in the series of atomic orbitals 1s, 2s, $2p_x$, $2p_y$, and $2p_z$.

Valence Molecular Orbitals of PF_4H. Orbital energies and Mulliken population data are given for the 17 valence-shell molecular orbitals of PF_4H in Table III where these data are compared with those obtained on the PF_5 (values in italics) molecule in an equivalent basis set. For the PF_4H molecule, there are four valence-shell molecular orbitals which are considerably more stable than the remaining ones, as was the case for five of the valence-shell orbitals of PF_5. These more stable valence orbitals of PF_4H involve the 2s atomic orbitals of the fluorine atoms. From perusal of Tables II and III it is clear that certain of the valence-shell molecular orbitals of the PF_4H molecule can be correlated with those of the PF_5 molecule with respect to orbital populations and bonding characteristics. By comparing electron density plots for both the equatorial and axial planes of the valence-shell molecular orbitals of PF_4H with the equivalent plots for the orbitals of PF_5, it was apparent that an electron density correlation between the valence-shell molecular orbitals of this pair of molecules could be clearly established; and, for most of the orbitals thus correlated, the detailed similarity in electron density distribution was striking.

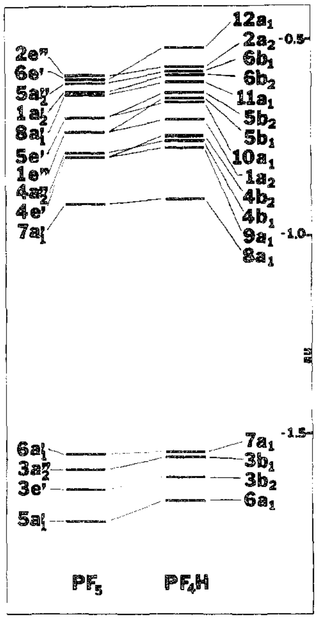

Figure 2. A correlation plot for the valence molecular orbitals of phosphorus pentafluoride and tetrafluorophosphorane, based on similarities in detailed electron density distributions.

The correlation plot resulting from this analysis is presented as Figure 2. Note that this electron density correlation is different from the usual Mulliken correlation[21] based on symmetry. If a Mulliken correlation is carried out for the reaction $PF_5 + H \rightarrow PF_4H + F$ while consistently maintaining C_{2v} symmetry throughout the entire course of the reaction, it is found that orbital $7a_1$ of PF_4H must correlate with the appropriate $3e'$ orbital of PF_5, even though the axial fluorine atoms of the $3e'$ orbital of the PF_5 molecule exhibit essentially no electron density while the axial fluorine atoms of orbital $7a_1$ of PF_4H have a population of 0.74 e/atom, as shown in Table III. The matching of orbital $7a_1$ of PF_4H with $6a_1'$ of PF_5 based on electron density distributions is not only consistent with the Mulliken population analysis (0.76 e/atom for orbital $6a_1'$ of PF_5) but also shows detailed interorbital agreement with respect to the 2s character of the contributing axial fluorine orbitals and the considerable polarization of these orbitals.

It is worth noting that the three uncorrelated molecular orbitals of the PF_5 molecule [one each of the $2e''$, $6e'$, and $3e'$ sets (or, according to the Mulliken scheme, $6a_1'$ instead of $3e'$)] correspond respectively to occupation of two 2p and the one 2s atomic orbital of an equatorial fluorine atom. These orbitals correspond to the three unshared pairs of electrons of the PF_5 fluorine atom which was substituted by a hydrogen to obtain the PF_4H molecule.

As can be seen in Table III, the P-H bonding in PF_4H is concentrated in orbitals $12a_1$, $10a_1$, and $9a_1$, which are P-H (p_σ-s_σ), and in orbital $8a_1$, which is P-H (s_σ-s_σ). This comes about because of the relatively high energy of the hydrogen 1s atomic orbital with respect to the fluorine atomic orbitals and the fact that these four molecular orbitals are the only ones exhibiting nodal-plane orientation which allows density on both the hydrogen and the phosphorus as well as orientation of the constitutent phosphorus

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(21) R. S. Mulliken, *Rev. Mod. Phys.*, 4, 1 (1932).

Table III. Valence-Shell Molecular Orbitals of Tetrafluorophosphorane and Phosphorus Pentafluoride[a]

		Gross atomic pop[b]				Overlap pop[b]		
Orbital	Energy[b]	P	F_a	F_e	H	$P-F_a$	$P-F_3$	P-H
$2a_2$	−0.572	0.020	0.612	0.378	0.000	0.037	−0.027	0.000
$2e''$	*−0.592*	*0.035*	*1.242*	*0.494*		*0.036*	*0.081*	
$12a_1'$	−0.520	0.307	0.625	0.018	0.407	−0.041	−0.002	0.337
$6e'$[c]	*−0.602*	*0.020*	*1.657*	*0.222*		*0.050*	*−0.041*	
$6b_1$	−0.580	0.016	0.547	0.444	0.000	0.028	−0.020	0.000
$5a_2''$	*−0.611*	*0.012*	*0.430*	*0.376*		*0.022*	*−0.013*	
$6b_2$	−0.581	0.012	0.786	0.208	0.000	0.024	−0.025	0.000
$1a_2'$	*−0.643*	*0.000*	*0.000*	*0.667*		*0.000*	*0.000*	
$11a_1$	−0.608	0.148	0.690	0.205	0.062	0.056	−0.001	0.034
$8a_1'$	*−0.645*	*0.139*	*0.627*	*0.202*		*0.053*	*0.007*	
$5b_2$	−0.635	0.085	0.017	0.941	0.000	0.003	0.043	0.000
$10a_1$	−0.659	0.293	0.098	0.737	0.036	0.011	0.106	0.049
$5e'$	*−0.700*	*0.461*	*0.000*	*1.179*		*0.000*	*0.162*	
$5b_1$	−0.656	0.248	0.746	0.131	0.000	0.115	0.012	0.000
$1a_2$	−0.703	0.292	0.292	0.562	0.000	0.079	0.100	0.000
$1e''$	*−0.736*	*0.621*	*0.566*	*0.749*		*0.161*	*0.147*	
$4b_1$	−0.756	0.417	0.446	0.346	0.000	−0.010	0.097	0.000
$4a_2''$	*−0.791*	*0.423*	*0.435*	*0.236*		*−0.046*	*0.070*	
$4b_2$	−0.754	0.398	0.124	0.677	0.000	0.042	0.019	0.000
$9a_1$	−0.771	0.693	0.165	0.417	0.143	0.056	0.066	0.171
$4e'$	*−0.798*	*0.871*	*0.216*	*0.899*		*0.082*	*0.066*	
$8a_1$	−0.908	0.760	0.253	0.298	0.143	−0.008	0.012	0.168
$7a_1'$	*−0.919*	*0.559*	*0.222*	*0.333*		*0.002*	*0.014*	
$7a_1$	−1.551	−0.042	0.741	0.279	0.002	−0.036	−0.019	0.001
$6a_1'$	*−1.566*	*−0.074*	*0.762*	*0.184*		*−0.053*	*−0.020*	
$3b_1$	−1.567	0.130	0.934	0.002	0.000	0.106	0.001	0.000
$3a_2''$	*−1.594*	*0.135*	*0.929*	*0.002*		*0.109*	*0.001*	
$3b_2$	−1.614	0.378	0.001	0.980	0.000	0.000	0.026	0.000
$3e'$	*−1.649*	*0.080*	*0.002*	*1.305*		*0.001*	*0.035*	
$6a_1$	−1.673	0.223	0.232	0.651	0.010	0.036	0.105	0.006
$5a_1'$	*−1.725*	*0.272*	*0.222*	*0.427*		*0.044*	*0.085*	

[a] The data for phosphorus pentafluoride are shown in italics. [b] Energies are reported in atomic units (1 au = 27.211 eV). Populations are given in electron per atom or bond. [c] Entries for the population analysis of e′ and e″ orbitals refer to the sum of both members in the degenerate set.

3p orbital so that a lobe is directed toward the hydrogen.

The close correspondence in electron density distribution between most of the correlated orbitals of PF_4H and PF_5 indicates little mixing of the PF_5 orbitals in constructing those of PF_4H. However, the nodal planes of the equatorial fluorine atoms in orbital $12a_1$ of PF_4H are rotated almost 90° with respect to the corresponding 6e′ orbital of PF_5, while there is also some similar rotation of the nodal planes of the equatorial fluorine atoms. Examination of the wave functions of both molecules shows that there is considerable mixing of orbital 6e′ of the PF_5 with virtual orbital 7e′ to give orbital $12a_1$ of PF_4H. Although orbital $8a_1'$ of PF_5 at an energy of −0.64 au would be thought more likely to mix with orbital 6e′ at −0.60 au than orbital 7e′ at +0.36 au, this cannot be the case in our calculations for two reasons. First, orbital $11a_1$ of PF_4H which is correlated with $8a_1'$ of PF_5 is not perturbed; and, second, orbital $2a_1$ of PF_4H exhibits $P-F_{ax}$ antibonding while 8a′ of PF_5 is $P-F_{ax}$ bonding.

There is also appreciable mixing of orbitals $5a_2''$ with 1e″ of PF_5 to give some twisting of the direction of the nodal planes of the axial fluorine atoms in orbitals $6b_1$ and $5b_1$ of PF_4H. In addition, very slight mixing of the PF_5 orbitals, 5e′ and $1a_2'$, causes a small change in orientation in the constituent 2p nodal planes of the equatorial fluorine atoms in orbitals $5b_2$ and $6b_2$ of PF_4H, as compared to the PF_5 orbitals with which they are correlated. The molecular nodal surfaces of PF_4H are generally quite similar to those of PF_5. The greatest differences in this respect for the orbitals of the PF_4H molecule, as compared to their correlated PF_5 orbitals for which the nodal surfaces are shown in Figure 1, are found for the following PF_4H orbitals: $8a_1$, $9a_1$, $5b_1$, $10a_1$, $11a_1$, $6b_1$, and $12a_1$. For orbitals $8a_1$, $9a_1$, and $11a_1$, the closure of the nodal surface through the original fluorine in the correlated PF_5 orbital disappeared when this fluorine was substituted by the hydrogen, thus allowing the resulting PF_4H nodal surface simply to continue on into space. In other words, the nodal surface of orbital $8a_1$ of PF_4H no longer has the approximately spherical shape of orbital $7a_1'$ of PF_5 but looks more like a hemispherically terminated cylinder (or perhaps a paraboloid). The remaining PF_4H orbitals, $5b_1$, $10a_1$, $6b_1$, and $12a_1$, all exhibit a bending in the nodal surface which was derived from the nodal plane passing through the phosphorus of PF_5 perpendicular to the P-F bond to the fluorine atom which was substituted by the hydrogen. The line of the bend in all cases lies in the equatorial plane of the PF_4H molecule and is perpendicular to the P-H bond axis. For orbitals $5b_1$, $10a_1$, and $12a_1$, the bending is such that the nodal surface is pulled away from the hydrogen and, for orbital $6b_1$, it is pulled toward the hydrogen.

PF_3-PF_5-OPF_3 Orbital Correlations. Even though PF_3 and OPF_3 exhibit C_{3v} symmetry, there is considerable similarity between many of their orbitals and those of the PF_5 molecule of D_{3h} symmetry. A molecular orbital correlation between these three molecules was readily made on the basis of electron density plots and is shown in Figure 3. In a prior publication[3] from this laboratory, the valence-shell molecular orbitals of PF_2H and OPF_2H were correlated with PF_3 and OPF_3, similarly to the way that the orbitals of PF_4H have been correlated with those of PF_5 in Figure 2. From this work, it is quite obvious that a correlation scheme can be set up between all molecules having fluorine and/or hydrogen substituents based on tri- through hexacoordinate phosphorus, including such compounds as the phosphoryl

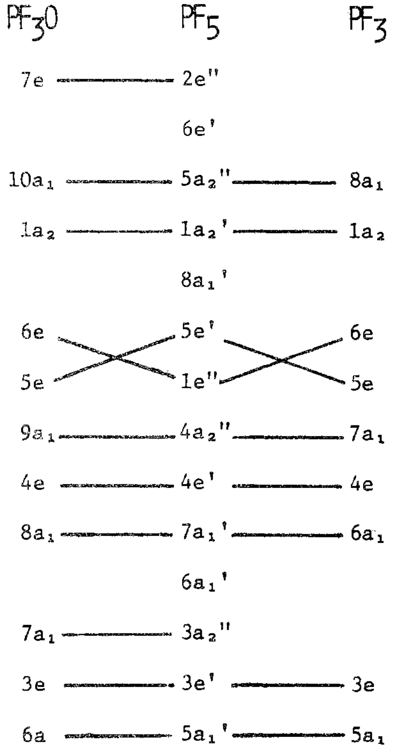

Figure 3. A correlation plot based on detailed electron density matching for the valence-shell molecular orbitals of phosphorus pentafluoride with those of phosphorus trifluoride and of phosphoryl fluoride. Note that the orbitals are listed downward in order of increasing stability but that the distance between them bears no relationship to the difference in their orbital energies.

and thiophosphoryl fluorohydrides.

Mulliken correlations were carried out for PF_5 with PF_3 and for PF_5 with OPF_3, using the following hypothetical reactions: $2F + PF_3 \rightarrow PF_5$ and $2F + OPF_3 = PF_5 + O$, maintaining C_{3v} symmetry throughout the transformation. Not surprisingly, orbitals 2e″, 8a$_1$′, and 6e′ of PF_5 were found to correlate with the 2p atomic orbitals of the fluorine atom reactants in the Mulliken scheme. Likewise, orbitals 6a$_1$′ and 3a$_2$″ of PF_5 were found to correlate with the 2s orbitals of these fluorine atoms and orbital 7a$_1$ of OPF_3 correlated with the 2s orbital of the oxygen atom product. Thus, the correlation orbitals 2e″ and 3a$_2$″ of PF_5 with 7e and 7a$_1$ of OPF_3 in our electron density scheme obviously represent the somewhat formal relationship whereby the oxygen of the OPF_3 molecule is replaced by a pair of fluorine atoms in PF_5.

The only key difference between the Mulliken correlation scheme and our scheme based on detailed electron density distributions is found in a switching of the correlation of orbitals 6e and 5e of either the PF_3 or OPF_3 molecules with orbitals 1e″ and 5e′ of PF_5. This switch simply means that mixing between the closely lying 6e and 5e orbitals of either PF_5 or OPF_3 leads to an interchange of the bonding characteristics in the Mulliken scheme. From the viewpoint of the chemist, it would seem that our correlation through electron density distributions (*i.e.*, the bonding characteristics) is more germane.

In comparing the electron density plots for the valence-shell orbitals of PF_3 and OPF_3 with those of PF_5, it was clear that the equatorial fluorine atoms of the latter molecule were closely related to the three fluorine atoms of the PF_3 and OPF_3 molecules and that the orbital of PF_3 dominated by the phosphorus lone pair transformed into the orbital dominated by P–O bonding in OPF_3 which in turn is closely related to the $P–F_{ax}$ bonding orbitals.

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Group V Boranes. I. Synthesis of Arsaboranes from Decaborane[1]

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In the presence of a base and a reducing agent, decaborane reacts with $AsCl_3$ to give $7\text{-}B_{10}H_{12}As^-$. Excess base and $AsCl_3$ produce $1,2\text{-}B_{10}H_{10}As_2$, also obtained from the reaction of purified $B_{10}H_{12}As^-$ with $AsCl_3$ in the presence of a base. Piperidine removes a boron from $1,2\text{-}B_{10}H_{10}As_2$ to produce $7,8\text{-}B_9H_{10}As_2^-$. $B_{11}H_{11}As^-$ is produced from the reaction of $B_{10}H_{12}As^-$ with triethylamine-borane at 160° or by pyrolysis of $CsB_{10}H_{12}As$. The arsenic in $B_{10}H_{12}As^-$ quaternizes with methyl iodide to give $B_{10}H_{12}AsCH_3$, which dissolves in dilute ammonia to give $B_{10}H_{11}AsCH_3^-$. Sodium in liquid ammonia removes the methyl group from $B_{10}H_{12}AsCH_3$. Decaborane and $C_6H_5AsCl_2$ in the presence of base give $B_{10}H_{11}AsC_6H_5^-$. Acidification of solutions of $B_{10}H_{11}AsC_6H_5^-$ gives $B_{10}H_{12}AsC_6H_5$.

In recent years several papers have appeared reporting borohydrides containing a group V atom in the polyhedral framework. Carboranes containing a group V atom,[2,3] as well as their transition metal complexes,[3,4] and P-substituted phosphaboranes[5,6] have been reported.

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[1] (a) Presented in part at the 162nd and 165th National Meetings of the American Chemical Society, Washington, D. C., Sept 1971, and Dallas, Tex., April 1973. (b) Taken in part from the M.S. thesis of S. S. Pao, The University of Mississippi, 1973.

[2] L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969).

[3] L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, **9**, 2175 (1970).

[4] J. L. Little, P. S. Welcher, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, **9**, 63 (1970).

[5] J. L. Little, J. T. Moran, and L. J. Todd, *J. Amer. Chem. Soc.*, **89**, 5495 (1967).