mode[40] is favored by some experimental data (longer axial bonds, lower stretching force constants)[41] and computed results (lower bond overlap populations, e.g., Table II) which indicate that the axial bonds are weaker than the equatorial bonds. On the other hand, the lowest frequency fundamental has been assigned, by others,[39b,42] to the equatorial in-plane bending mode.

By computing the energy change of PH_5 due to small

(40) (a) H. H. Claassen and H. Selig, J. Chem. Phys., **44**, 4039 (1966); (b) L. C. Hoskins and R. C. Lord, ibid., **46**, 2402 (1967); (c) R. R. Holmes, ibid., **46**, 3724, 3730 (1967); (d) J. E. Griffiths, ibid., **49**, 1307 (1968).
(41) S. B. Pierce and C. D. Cornwell, ibid., **48**, 2118 (1968).
(42) (a) G. Nagarajan, Indian J. Pure Appl. Phys., **2**, 278 (1964); (b) J. K. Wilmshurst and H. J. Bernstein, J. Chem. Phys., **27**, 661 (1957); (c) R. R. Holmes and J. A. Golen, Inorg. Chem., **9**, 1596 (1970); (d) L. S. Bartell, ibid., **9**, 1594 (1970).

displacements from D_{3h} symmetry along the directions for pure axial and pure equatorial bending modes, force constants were obtained for these motions. The results are shown in Figure 7. The force constant $(=(\partial^2 E/\partial\theta_i^2)/R_{eq}^2)$ for axial bending ($i = 1$) is computed to be 1.94 mdyn/Å and that for equatorial in-plane bending ($i = 2$) is calculated to be 0.539 mdyn/Å. The conclusion for this system, at least, is clear cut. The axial bending mode has a force constant that is 3.6 times as large as that for the equatorial in-plane bending mode. Thus it is easier to vary the 120° equatorial angle than the 180° axial angle. This result suggests that the lowest frequency fundamental in trigonal-bipyramidal molecules ought to be assigned to the equatorial in-plane bending motion.

Semiempirical Molecular Orbital Calculations. Pseudorotation in Phosphorus Pentafluoride[1]

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Abstract: Semiempirical molecular orbital calculations have been performed for PF_3, PF_5, PH_3, and PH_5. The calculations for PF_5 include a variety of distances and angles of interest in the theory of pseudorotation. The computational method includes all valence electrons and neighbor atom potentials. Electronic structures of the phosphorus fluoride and hydrides show a very limited resemblance. The barrier to pseudorotation in the Berry mechanism is in good agreement with experiment.

Phosphorus pentafluoride holds special interest as a simple molecule for which the classical octet rule of electronic structure encounters serious difficulties. The possible role of 3d atomic orbitals on phosphorus and plausible mechanism of substitution and rearrangement can be studied in detail with techniques presently available. The present semiempirical all-valence electron calculations can be compared with the predictions of various schemes devised for interpretation and, in the near future perhaps, with chemically accurate calculations from first principles. The calculation method makes extensive use of observed and calculated data but incorporates no parameters adjusted to reproduce any molecular data or calculational results. Thus it constitutes a bona fide approximate prediction of molecular data from atomic data and computation rather than just a procedure for interpolation, extrapolation, and speculation. This method accurately predicts the ionization potentials of the valence molecular orbitals of sulfur hexafluoride[2a] and carbon tetrafluoride.[2b]

PH_5, a molecule as yet unreported, can be compared profitably with the familiar PH_3, PF_3, and PF_5. Despite the possibility that PH_5 may never be observed, its

computational study[3] is a step toward determining the extent to which H can be substituted for F in calculations for metal complexes containing substituted phosphine ligands.

In five- or six-atom ring compounds of pentavalent phosphorus, the ring ligands are constrained to occupy one axial and one equatorial position in a trigonal bipyramid. Restrictions on isomerization can be explained by the mechanism of pseudorotation which interchanges pairs of axial and equatorial ligands.[4] It is amenable to analysis with the present method with confidence because the relevant movements are primarily angle variations.

Calculations for PF_5 have been carried out by van der Voorn and Drago,[5] who considered a series of pentahalides, but only in the trigonal bipyramid geometry, and by Berry, Tamres, Ballhausen, and Johansen[6] who concluded from their lack of success in estimating the barrier to pseudorotation in PF_5 that their method was too simple to be quantitatively accurate.

Procedure

Molecular Orbital Method. We regard the semiempirical molecular orbital procedure as an LCAO–MO

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(1) Based on a thesis submitted by J. B. Florey in fulfillment of the requirements for a B.S. degree with honors in chemistry.
(2) (a) L. C. Cusachs and D. J. Miller in "Trends in Sulfur Research," T. Wiewiorowski and D. J. Miller, Ed., American Chemical Society, Washington, D. C., 1971, in press; (b) J. H. Corrington, H. S. Aldrich, C. W. McCurdy, and L. C. Cusachs, Int. J. Quantum Chem., **5S**, 307 (1971).
(3) K. Issleib and W. Gründler, Theor. Chim. Acta, **8**, 70 (1967).
(4) R. S. Berry, J. Chem. Phys., **32**, 933 (1960); R. R. Holmes and R. M. Deuters, J. Amer. Chem. Soc., **90**, 5021 (1968).
(5) P. C. van der Voorn and R. S. Drago, ibid., **88**, 3255 (1966).
(6) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, Acta Chem. Scand., **22**, 231 (1968).

pseudopotential approximation.[7] In such a procedure, atomic orbitals are used to generate overlap and various energy integrals. A single Slater-type orbital is not sufficiently flexible to be satisfactory for both types of integral, so the explicit orbitals of this work are used only for the calculation of overlap integrals. These overlap-matched orbitals are determined to reproduce two center overlap integrals calculated with accurate Hartree–Fock atomic orbitals. The energy integrals are required in constructing the effective Hamiltonian matrix, $\mathcal{H}$, whose diagonal elements take the form

$$H_{ii} = -A_i - B_i q^{\text{atom}} + \text{NAP} \qquad (1)$$

where A_i is the valence state ionization potential of atomic orbital ϕ_i double occupied in the neutral free atom, and B_i is the change in ionization potential with unit change in the net charge on the atom on which it is located, q^{atom}. The neighbor atom potential, NAP, contains both nuclear attraction and electron repulsion integrals which are expressed as functions of the internuclear distance and an effective orbital radius, $1/RI = \langle i|1/r|i\rangle$. For the lighter elements A and B can be obtained from atomic energy level data, but for heavier atoms these must be deduced from atomic calculations. Since the B_i obtained from atomic data appear to be simply proportional to $1/RI$, the same relationship can be assumed when B values are otherwise not available. In some of the calculations reported below the B_i were taken from valence state data, but others compute B from RI.

Data from free atoms are not adequate to characterize extravalent orbitals, such as the 3d of phosphorus, in molecules, for which descriptions must be obtained by methods open to serious question. Fortunately for this study the results obtained with the 3d functions included in the calculation were not very sensitive to the exact values of the parameters defining the 3d orbitals. The atomic data used are collected in Table I.

Table I. Atomic Orbital Parameters[a]

Atom	Orbital	n-STO	z[b]	A[c]	B[c]	RI
P	3s	3	1.81	18.0	8.9	1.45
	3p	2	1.08	10.6	8.9	1.75
	3d	3	1.40	1.9	6.2	2.14
F	2s	2	2.50	39.0	16.2	0.70
	2p	1	1.38	18.2	16.2	0.79
H	1s	1	1.20	11.6	10.0	0.80

[a] The STO are in the form of a radial function, $r^{n-1}[\exp(-zr)]$, multiplied by a spherical harmonic. The RI are derived from the calculations by C. Froese [*J. Chem. Phys.*, **45**, 1417 (1966)] who kindly made available values of $\langle 1/r \rangle$ prior to publication. Values of these parameters for hydrogen are all heuristic estimates. [b] L. C. Cusachs and J. H. Corrington in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. Wiberg, Ed., Yale University Press, New Haven, Conn., 1969. [c] L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, 160 (1965); L. C. Cusachs, K. W. Reynolds, and D. Barnard, *ibid.*, **44**, 835 (1966).

Off-diagonal H matrix elements were obtained by a generalization of the approximation suggested by Cusachs and Cusachs.[7] This operation involves factoring a term that transforms like an overlap integral under

rotation of the coordinate system in which the atoms are located into the product of terms whose rotational properties are less transparent. To ensure that the molecular properties be independent of the orientation of the arbitrary master or absolute coordinate system chosen, certain precautions in this approximation are necessary. Writing the general off-diagonal element as in eq 2 we have in the first term a product

$$H_{ij} = (\hat{H}_{ii} + \hat{H}_{jj})S_{ij}(2 - |\hat{S}_{ij}|) + \text{NAP}_{ij} \qquad (2)$$

of diagonal elements of H and what appears to be a quadratic in overlap integrals. Since the neighbor atom potential in (1) above depends on the orientation of atomic orbitals with respect to other atoms, the H_{ii} in a set of otherwise equivalent p or d orbitals generally will not be identical. For the H_{ij} approximation, and for this purpose only, the H_{ii} of such a set of orbitals with common n and l quantum numbers are averaged over orientation. The second factor contains a term ambiguously written as $S_{ij}(2 - |\hat{S}_{ij}|)$. Both for ensuring rotational invariance and because the underlying approximation is derived on its assumption, this factor is computed in the local diatomic coordinates used for computing overlap integrals and subsequently rotated (treated as a single term transforming as an overlap integral) to the molecular coordinate system. Once the H matrix is constructed, it may be subjected to arbitrary nonsingular transformations if hybrid or other special atomic orbitals are preferred for interpretation. The off-diagonal contribution from the neighbor atom potential, NAP_{ij}, connects members of a set of p or d orbitals on the same atom, in which case the first term must vanish. Only the first term is present for pairs of orbitals on different atoms. The simplification of the two center electron repulsion integrals and the precautions taken to preserve rotational invariance are described in detail elsewhere.[2b]

This method retains all overlap integrals. The overlap matrix, S, is diagonalized and the transformation matrix, $D = S^{-1/2}$, constructed for transforming H to the Löwdin basis[8] for diagonalization. The atomic orbital populations used to compute a net charge on the atoms in (1) and in the NAP are defined in the Löwdin basis, so that the repetitive process in iteration is the construction of the H matrix, its transformation to the orthogonal basis, DHD, diagonalization, and the computation of atomic orbital populations and atom charges. After convergence the coefficients in the ordinary nonorthogonal basis are obtained by multiplication by the same transformation matrix.

Iteration to charge self-consistency employed a complex system of automatic variable damping, quadratic averaging, and Hartree extrapolation to expedite convergence. For PF_5 in various conformations, convergence was typically achieved by the fifth full cycle, each cycle requiring two diagonalizations of the H matrix.

The method described above was first incorporated into the computer program GIVNAP to permit testing the Corrington neighbor atom potential[9] in polyatomic molecules. When its practical utility became clear, the program was rewritten to increase computational efficiency, incorporate improvements, and facilitate

(7) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967); L. C. Cusachs, *Spectrosc. Lett.*, **3**, 7 (1970); K. S. Wheelock, H. B. Jonassen, and L. C. Cusachs, *Int. J. Quantum Chem.*, **4S**, 209 (1971).

(8) P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).
(9) J. H. Corrington, Dissertation, Tulane University, 1968.

Table II. Charge and Population Analysis for PF_3 and PH_3[a]

Orbital set		—PF$_3$—			—PH$_3$—	
		3s/3p	3s/3p/3d		3s/3p	3s/3p/3d
Atom charge						
Löwdin	P	1.350	0.889	P	0.211	0.109
	F	−0.450	−0.296	H	−0.070	−0.036
Mulliken	P	1.697	2.084	P	0.224	0.109
	F	−0.566	−0.695	H	−0.075	−0.122
Overlap population						
	P–F	0.339	0.225	P–H	0.754	0.718
	Total	0.882	0.552	Total	2.143	2.022
Overlap energy						
	P–F	−11.881	−7.713	P–H	−14.484	−14.079
	Total	−29.970	−16.316	Total	−40.479	−38.861

[a] Column headings indicate the phosphorus orbitals employed. Since the three hydrogens or fluorines are equivalent, only the unique values are given. The total overlap population and total overlap energies are not three times the P–F or P–H value because of ligand–ligand interactions, normally of opposite sign.

Table III. Charge and Population Analysis PF_5 and PH_5[a]

Orbitals		—PF$_5$—			—PH$_5$—	
		3s/3p	3s/3p/3d		3s/3p	3s/3p/3d
Atom charge						
Löwdin	P	2.440	1.717	P	0.882	0.420
	F$_A$	−0.583	−0.451	H$_A$	−0.298	−0.153
	F$_E$	−0.426	−0.273	H$_A$	−0.076	−0.038
Mulliken	P	2.856	3.423	P	0.661	0.892
	F$_A$	−0.639	−0.708	H	−0.267	−0.265
	F$_E$	−0.526	−0.670	H	−0.043	−0.210
Overlap population						
	P–F$_A$	0.405	0.327	P–H$_A$	0.570	0.711
	P–F$_E$	0.497	0.338	P–H$_E$	0.693	0.725
	Total	1.727	1.171	Total	2.611	3.130
Overlap Energy						
	P–F$_A$	−14.821	−11.285	P–H$_A$	−11.480	−13.058
	P–F$_E$	−19.393	−13.051	P–H$_E$	−14.588	−14.915
	Total	−62.674	−38.754	Total	−52.355	−59.448

[a] The quantities displayed have the same meaning as in Table II, except that there are now axial ligands, F_A, H_A, which are not equivalent to the equatorial ones, F_E, H_E.

further extension to the calculation of molecular electronic spectra. The revised program, ARCANA, includes an approximate valence total energy. This total energy is defined as that quadratic functional of the atomic orbital populations whose minimization leads to the secular equation solved.

Molecular Geometries. In addition to specifying the atomic orbitals and the core charges of the atoms, the position of each atom is supplied to the computer programs as the Cartesian coordinates in an arbitrary master coordinate system, usually called the absolute coordinate system. Since PH_3 and PF_3 are of secondary interest to this study, no special efforts were made to obtain high precision coordinates for them. The PH_3 coordinates are those used for a number of years in course exercises and correspond to distances and angles from a structure determination. However, for PF_3 the angles are tetrahedral rather than 104°. Previous studies of barrier problems in this laboratory[10] have shown that the gross features of bonding should not be seriously affected by this angle difference. For PH_5, the hydrogen position was constrained to be proportionately equivalent to the fluorine positions in PF_5 (1.71 Å axial, 1.52 Å equatorial) on the assumption that the P–H bond lengths in PF_5 change from those in PH_3 (1.42 Å) in proportion to the changes in P–F distance going from PF_3 (1.54 Å) to PF_5. The same proportionality assumption was used in the

(10) B. L. Trus, Honors Thesis, Tulane University, 1968.

calculations where one atom was pulled away from its equilibrium position.[10a] Results are summarized in Tables II and III.

Rather than attempt to compute the full many-dimensional potential surface in the pseudorotation calculations, the nuclear path was simplified by assuming that the P–F distance of the four moving ligands varied sinusoidally toward the arithmetic mean of the normal axial and equatorial P–F distances, 1.615 Å, as the molecule approaches the square-pyramid midpoint of the conversion. This process can be described by an angle for which the range 0–15° brings the trigonal bipyramid to a square pyramid, and the range 15–30° completes the interchange of the two axial and two of the former equatorial fluorines. In a second series of calculations an axial ligand was progressively removed from PF_5 and PH_5, respectively, and the reorganization analyzed. These results appear in Table IV. Several structures of lower symmetry were also examined in an inconclusive search for a minimum energy path for the process $PX_5 \rightleftharpoons PX_4^+ + X^-$.

Estimation of the Barrier

The barrier to changes in molecular shape is simply the difference between the energies of the two con-

(10a) NOTE ADDED IN PROOF: The accepted P–F axial distance in PF_5 is 1.58 Å, rather than the 1.71 Å used here. Repeating the trigonal-bipyramid and square-pyramid calculations with this distance produced no significant change in barrier energetics or bonding indices.

Table IV. Changes in Indices with Stretch for PF_5 and $PH_5{}^a$

Orbitals		PF₅ 3s/3p	3s/3p/3d		PH₅ 3s/3p	3s/3p/3d
Atom charges						
Löwdin	P	−0.097	−0.060	P	−0.100	−0.002
	F_S	−0.076	−0.113	H_S	−0.065	−0.071
	F_A	−0.008	+0.008	H_A	+0.052	+0.015
	F_E	+0.056	+0.046	H_E	+0.038	+0.019
Mulliken	P	−0.150	−0.249	P	−0.093	−0.074
	F_S	−0.027	+0.060	H_S	−0.062	−0.025
	F_A	+0.010	+0.014	H_A	+0.051	+0.021
	F_E	+0.056	+0.060	H_E	+0.035	+0.025
Overlap population						
	$P–F_S$	−0.109	+0.012	$P–H_S$	−0.138	−0.160
	$P–F_A$	−0.003	+0.020	$P–H_A$	+0.016	−0.008
	$P–F_E$	+0.026	+0.057	$P–H_E$	+0.007	−0.002
	Total	+0.099	+0.312		+0.058	−0.080
Overlap energy						
	$P–F_S$	+5.094	+1.754	$P–H_S$	+2.810	+3.269
	$P–F_A$	−0.109	−0.771	$P–H_A$	−0.562	−0.151
	$P–F_E$	−0.447	−2.199	$P–H_E$	−0.454	−0.342
	Total	−5.130	−10.692		−2.882	−0.254

^{a} Changes in indices with stretch of one axial ligand, F_S of H_S, with remaining axial and equatorial ligands fixed. The axial fluorine went from 1.71 to 2.16 Å, the stretched hydrogen from 1.480 to 1.864 Å.

formations of the molecule as long as the electron configuration does not change. If the electronic configuration, i.e., assignment of electrons to molecular orbitals, changes then it is necessary to decide whether molecular orbital configuration is conserved or not.[11] The calculation of barrier energies in ab initio methods is well defined if handicapped in practice by the desired result being obtained as the small difference between very large numbers. Semiempirical calculations are able to make part of the cancellation occur before the energies are computed by invoking the separation of inner cores supposed constant through the entire process. While the valence electrons have little effect on the cores, this little effect may well be large compared with barrier energies so that we can at best hope that it will be insensitive to molecular shape. With the ARCANA program we have an approximate total energy that gives the correct bond angle for SO_2, as well as the sums of occupied orbital energies at the beginning and at charge self-consistency. With the earlier program we have only these orbital energy sums and wish to decide whether the iterated or uniterated orbital energy sum may be expected to give the best prediction of bond angles. There is a paradox here, for the uniterated orbital energy sum often gives quite accurate bond angles but poor ionization potentials, while the charge self-consistent orbital energies for SF_6, SO_2, and CF_4, previously cited, have a probable error of about 0.5 eV as ionization potentials, yet are unreliable as indices of bond angle.

The semiempirical calculation logically may be started in any one of three ways: (a) use only the A_i terms of eq 1 in the first cycle, or (b) use the full expression (1) but with atomic orbital populations for the free atoms, i.e., including penetration via the NAP, or (c) attempting to guess a set of orbital populations close to the self-consistent ones. Corrington[12] has noted that in many cases convergence is much more rapid with choice (a) than with (b) which in turn is about as good as what we are able to do with (c). We find

(11) L. C. Cusachs, M. Krieger, and C. W. McCurdy, Int. J. Quantum Chem., 3S, 67 (1969).
(12) J. H. Corrington, private communication.

quite generally that the orbital energy sum of the first cycle using the A_i alone tends to be more reliable as an index of bond angle than either (b) or the final self-consistent one.

The total energy from ARCANA is the sum of four terms

$$E_T = OES + CORE - ER2 - ER1 \qquad (3)$$

the orbital energy sum, the core–core repulsion, the two-center electron repulsion, and the one-center electron repulsion. The last term, ER1, is large but rather insensitive to changes in molecular shape, varying slowly, usually in the sense opposite to ER2. Thus for angle variation the interesting terms of the correction to the orbital energy sum come from the CORE and ER2 terms, of like magnitude and opposite sign. The choice (a) of starting potential implies retention of only short range forces. For a model AB_2 molecule, we examine the asymptotic form of the correction term for the B–B interaction in the Appendix, finding that the variation in the ER2 term does indeed more closely follow that of CORE in case (a) than at self-consistency if there is appreciable charge transfer. It is possible to go somewhat further, assuming that charge transfer is insensitive to angle, finding that the OES should overestimate the angle if the direction is A^+B^- and underestimate if it is A^-B^+.

Particularly for large molecules, there is a further source of error coming from the iteration process itself. Starting from option (a), the numerical precision of the orbital energies of the first cycle relative to the A_i is limited only by the errors of the matrix diagonalization process, which can usually be satisfactorily controlled. In the charge self-consistent calculation, some convergence tolerance must be accepted which may further affect the orbital energy sum and calculated total energy.

Analysis of Results

In addition to the orbital energies described above, the computer programs provide orbital energies and populations in the Löwdin basis at each cycle of iteration. At convergence it is possible to request a Mulli-

Table V. Comparison of Trigonal-Bipyramid and Square-Pyramid PF₅[a]

Run	1	2	3	4
Shape	T-B	S-P	T-B	S-P
Basis	s/p	s/p	s/p/d	s/p/d
OES–NONAP	−933.0835	−932.5019	−939.4202	−938.9607
OES–NON	−1022.4587	−1020.0825	−1025.3618	−1023.0821
VE–NON	−3743.0910	−3742.4465	−3745.9941	−3745.4461
ER2–NON	2884.4785	2886.8946	2884.4785	2886.8946
CES–IT	−943.0248	−940.0192	−975.5018	−969.8559
VE–IT	−3760.7527	−3760.1867	−3730.1367	−3729.7692
ER1–IT	3072.0900	3068.9620	2957.6956	2957.3902
ER2–IT	2708.8203	2714.0724	2760.3599	2766.3599
Q_P^L–NON	3.466	3.481	2.633	2.648
Q_P^L–IT	2.513	2.497	1.718	1.715
Q_P^M–IT	2.945	2.916	3.422	3.392
CORE	2963.1824	2963.8668	2963.1824	2963.8668
TOP	1.659	1.627	1.177	1.159
TOE	−59.664	−57.705	−38.052	−37.388

[a] T-B, trigonal bipyramid; S-P, square pyramid; OES, orbital energy sum; NON, noniterative, but with NAP assuming free atom populations; VE, valence total energy; ER2, two-center valence electron repulsion; Q_P^L, net charge on phosphorus atom, computed in Löwdin basis; Q_P^M, net charge on phosphorus atom, from Mulliken gross population; CORE, core repulsion, scaled to ²/₃ with electron interaction as described in ref 2; TOP, total overlap population; TOE, total overlap energy. The ER1–NON, one-center electron repulsion, noniterative, was 2799.3362 for all four runs.

ken population analysis and an overlap energy analysis, differing from the population analysis in that the final H matrix elements are used rather than the S matrix in computing overlap quantities. The Löwdin and Mulliken bases analysis has been described by Davidson.[13] None of these quantities has absolute significance but within common assumptions about the basis atomic orbitals they permit an economical description of changes in electronic structure and bonding when distances or angles are varied.

Table II displays the bonding indices for PF₃ and PH₃, both with and without 3d orbitals on the phosphorus atom. Table III provides similar data for PF₅ and PH₅ in the assumed normal geometries. PF₅ and PH₅ were further compared by a series of calculations in which one axial ligand was progressively drawn away, in steps of 0.15 Å for PH₅ and 0.128 Å for PH₅. Tables similar to Table III for each point are contained in the thesis.[14] Changes in the quantities displayed were essentially linear over the three increments of stretch, and Table IV contains the changes from the original values of Table III. The orbital energy sum, unlike the bonding indices, first became less negative, then, at the final step, more negative again. While it is well known that the single configuration molecular orbital description is adequate for describing complete dissociation, the small changes of distance considered did not provoke crossing of filled and empty molecular orbitals. If a filled orbital and an empty orbital change places in the calculation, the indices show an abrupt jump. When this exchange occurs in the course of iteration, the effect is most conspicuous, usually leading to catastrophic failure of the run. Since the bonding indices varied linearly, the values of Table IV would only be reduced proportionately by reducing the nuclear displacement, so all qualitative conclusions remain unchanged. The secondary drop in orbital energy sum on stretch was much less marked in the calculations including the 3d orbital, so this basis was selected for the pseudorotation calculations, since the computer time available was insufficient for both series of calculations. In going from the normal to the square-pyramid geome-

try, the overlap population decreased smoothly by 0.025 and the overlap energy increased, became less negative, by 0.868 eV. The orbital energy sum, in the noniterative state, option (a), predicts a barrier of 0.46 eV or 10.6 kcal. This is remarkably close to the mean of the ARCANA valence energy differences, 0.57 for s/p orbitals only, 0.37 eV with 3d orbitals included. The orbital energy sum with NAP, but no iteration, is less successful, predicting 1.39 eV in the s/p basis and 2.28 eV with the 3d orbitals. As expected the iterated orbital energy sum is rather poor, predicting barriers of 2.13 and 5.65 eV, as can be deduced from the data in Table V. The experimental data, cited in ref 4, do not establish a unique value for the barrier to pseudorotation, but the failure of low-temperature nmr studies to resolve separate axial and equatorial fluorines which are distinct in the microwave spectrum establishes rough bounds suggesting a barrier of the order of 9–10 kcal.

Table VI. Orbital Energies of PF₅ in Square Pyramid[a]

ARCANA		NISEMO	BTBJ	
s/p	s/p/d	s/p	s/p/d	
15.26 a₂	15.77	16.16 a₂	16.61 a₂	
16.34 e	16.85	16.26 b₁	16.80 b₁	
16.37 b₁	16.89	16.84 e	16.94 e₁	
17.02 b₁	17.50	17.27 a₁	17.06 a₁	
17.13 e	17.67	17.32 e	17.56 e	
17.93 a₁	18.45	17.46 b₁	17.96 b₁	
18.78 e	19.31	18.69 e	19.75 e	
18.88 b₂	19.55	19.36 e	20.87 b₂	
20.62 e	21.03	19.55 a₁	20.91 e	
21.02 a₁	21.20	19.77 b₂	21.07 a₁	
23.38 a₁	23.53	20.08 a₁	23.35 a₁	
36.56 b₁	37.66	38.04 b₁	46.51 e	
37.88 e	38.57	38.88 a₁	47.15 a₁	
39.25 a₁	40.33	39.05 e	47.76 b₁	
42.84 a₁	42.92	40.30 a₁	51.43 a₁	

[a] The abbreviations are the same as those of Table VII.

We believe that our method overestimates the importance of the 3d orbitals of phosphorus and that the best estimate we can offer from these calculations is 0.5 eV. The ionization potentials of PF₅ have not been reported, but by comparison with those of SF₆, CF₄, and SO₂, we can expect the values of Table VI to have probable errors of about 0.5 eV.

(13) E. R. Davidson, *J. Chem. Phys.*, **46**, 3320 (1967).
(14) J. B. Florey, Honors Thesis, Tulane University, 1970.

The calculation by Berry, *et al.*,[6] was somewhat similar to the noniterative first cycle with option (a). Most notable differences are (1) they used the same distance for axial and equatorial P–F bonds, 1.57 Å, (2) they used the geometric mean H_{ij} approximation, and (3) their d orbitals were taken from excited state calculations for free atoms rather than for the molecular environment. The averages of our axial and equatorial overlap integrals between P and F atoms are quite close to theirs, so that the choice of atomic orbital representations is probably not the cause of the difference. As can be observed in Table VII there are several differences in

Table VII. Orbital Energies of PF_5 in Trigonal Bipyramid

—————ARCANA—————			—BTBJ[a]—		—NISEMO[b]—	
s/p		s/p/d	s/p/d		s/p	
14.94	e''	15.62	15.87	e'	16.57	a₂''
15.30	e'	16.01	16.65	a₁'	16.64	a₁'
15.90	a₁'	16.52	16.87	e''	16.64	e''
16.00	a₂''	16.55	17.22	a₂''	17.16	e'
18.42	a₂'	19.29	18.17	a₂'	17.60	a₂'
19.12	e'	19.93	18.32	e'	17.85	e'
19.24	e''	20.15	20.55	e''	19.37	e''
20.21	a₂''	20.81	20.61	a₂''	19.40	e'
21.51	e'	22.01	21.65	e'	19.52	a₂''
23.62	a₁'	23.94	23.25	a₁'	20.07	a₁'
35.63	a₁'	36.72	46.51	a₂''	38.18	a₁'
36.03	a₂''	36.75	47.37	e'	38.91	e'
39.58	e'	40.87	49.49	a₁'	39.07	a₂''
43.14	a₁'	43.44	51.59	a₁'	40.22	a₁''

[a] BRBJ calculations of Berry, Tamres, Ballhausen, and Johansen, *Acta Chem. Scand.*, **22**, 231 (1968). We have converted the energy units from thousands of reciprocal centimeters to electron volts. [b] NISEMO noniterative semiempirical molecular orbital method, calculation with our H_{ij} approximation but only the A term or VSIP as H_{ii}. From this beginning, ARCANA converges to the results of the first column. ARCANA obtained the same ordering with and without 3d orbitals on phosphorus.

the order of energies of the occupied molecular orbitals, of the present PF_5 calculations and those of Berry, *et al.* Since our method gives reliable orderings for SF_6 and CF_4 where more highly parametrized semiempirical methods fail, we are confident that the ARCANA level orderings will ultimately be found correct. The reason why Berry, *et al.*, did not obtain a satisfactory barrier is not apparent in Table VII, since our noniterative (NISEMO) calculation presented for comparison is also significantly different in ordering from the self-consistent results of ARCANA which include neighbor atom potentials. The most striking difference in the orbital energies is that the calculations of Berry, *et al.*, separate the molecular orbitals built up primarily from fluorine 2s oribtals from the rest to a much greater extent than ours, either iterative or noniterative. This is known[15] to be a consequence of the choice of the geometric mean H_{ij} approximation which we believe to be somewhat less realistic than the one we have employed. The simplest way of determining the utility of the procedure of Berry, *et al.*, would be to compare results for SF_6 and CF_4 with ours.[2] Because of the special choice of coordinates employed by them, it would require a major programming effort for us to attempt to duplicate their procedure. The most time consuming part of our calculations is working out the symmetry labels for the molecular orbitals.

(15) L. C. Cusachs, "Sur l'approximation de Wolfsberg et Helmholz," Technical Report, Battelle Memorial Institute, Geneva, 1963.

Discussion

The pattern of results in the present calculations is familiar in the following respects: (1) augmentation of the basis set shows a migration of charge toward the atom whose number of orbitals is increased in the Löwdin definition of charge, but frequently the reverse in the Mulliken gross populations; (2) the orbital energy is useful for angle but not for distance variation; (3) total overlap population and total overlap energy are frequently better than orbital energy sum, as suggested by Kaufman,[16] but bond distance predictions deteriorate seriously with polarity. When Rydberg orbitals, such as the 4s of sulfur[17] or the 5p of rhodium,[18] are included in the calculation, we encounter a variety of maxima and minima in the bonding indices on distance variation. It is not yet possible to decide whether any of these extrema have special significance.

The phosphorus fluorides are sufficiently polar that the overlap population and overlap energy describe only the covalent component of the bonding. This may vary in the opposite sense to the polar or Madelung-type stabilization.[19] This conclusion is supported by the modest changes in the PH_5 calculation on variation of the basis set and on stretching a bond, as indicated in Table IV.

Only a very modest similarity between the hydrides and fluorides of phosphorus appears. Most notable, the phosphorus atom of PF_5 drops consistently in charge on stretching an axial ligand, while the PH_5 phosphorus is little changed. Calculations for ammonia and ammine complexes of AgI show a similar rearrangement, the nitrogen not changing greatly in charge, with donation from the hydrogen through the nitrogen to the silver ion. In contrast, it was found[2a] that addition of an oxygen to H_2S, taken as a model for $(CH_3)_2S$, leading to H_2SO in the geometry of $(CH_3)_2SO$, produced almost no effect on the H–S bond, further unchanged in going to H_2SO_2. This does not seem to be an artifact of the semiempirical method for it is also found in a series of *ab initio* calculations for this series of molecules.[20]

The irregular behavior of the overlap population and overlap energy on addition of the 3d orbitals is similar to that encountered in a variety of sulfur compounds. In all of these compounds there are more electrons than tightly held valence atomic orbitals, so the higher filled molecular orbitals are predominantly antibonding. The 3d orbitals contribute to these antibonding orbitals and to the empty molecular orbitals essential to a realistic description of the electronic spectra. The large overlap integrals involving 3d orbitals accumulate large negative contributions to the overlap population while the coefficients of these atomic orbitals in the filled molecular orbitals remain extremely small. The molecular orbital method employed assumes relations among kinetic and potential terms[7] that are hardly likely to be satisfied for the 3d orbitals of phosphorus in these molecules. The effect on the bonding indices

(16) J. J. Kaufman, *Int. J. Quantum Chem.*, **1S**, 485 (1967).

(17) L. C. Cusachs, D. J. Miller, and C. W. McCurdy, Jr., *Spectrosc. Lett.*, **2**, 141 (1969).

(18) L. C. Cusachs, *ibid.*, **3**, 195 (1970).

(19) C. K. Jørgensen, S. M. Horner, W. E. Hatfield, and S. Y. Tyree, Jr., *Int. J. Quantum Chem.*, **1**, 191 (1967).

(20) J. R. Van Wazer in "Trends in Sulfur Research," T. Wiewiorowski and D. J. Miller, Ed., American Chemical Society, Washington, D. C., 1971,

is exaggerated because there is no way at present to include the increase in orbital kinetic energy upon contraction of the 3d orbital from the diffuse Rydberg form of the states of the free atom in which it is occupied. While one could arbitrarily adjust the H_{ii}, it would require extensive reformulation of the calculation to separate the kinetic and potential energy terms so that the off-diagonal H matrix elements would also reflect the change in relative magnitude of these terms. The effect of taking the 3d orbital contraction into account correctly would be to deemphasize the 3d orbitals' role in the normal state of these molecules. The present calculations can safely be regarded as giving upper bounds to the effect of the d orbitals, which merely serve to introduce a better shape, or polarization, to the atomic basis. The small admixture we encounter could be significant in the dipole moments calculated for molecules of low symmetry; however, in no case so far observed do they approach the occupation expected from classical hybridization theory, which postulates dsp³ bonding orbitals for phosphorus in the trigonal bipyramid PF_5 but no extensive mixing of 3d orbitals in the trivalent compounds. The d orbital occupation in PF_5 was little greater than in PF_3, an outcome similar to (unpublished) results for sulfides, sulfoxides, sulfones, and sulfur fluorides where the 3d orbital mixing did not correlate simply with oxidation state of the sulfur. All of our results are consistent with the theory of hypervalent molecules recently proposed by Musher[21] who correctly predicted the general results of our calculations before they were begun.

As stressed by Berry, et al., the trigonal-bipyramid and square-pyramidal structures of PF_5 are very close together on the same potential surface. While their calculations considered only the extreme geometric configurations, our calculations, covering a series of small steps along a possible trajectory, showed clearly that the electronic rearrangement only involves mixing filled molecular orbitals with other filled ones and empty ones with empty ones. Even structures of low symmetry did not indicate close approach between the filled and empty molecular orbitals. This is in contrast to the pattern of levels found by Berry, et al., for BrF_5, where the trigonal-bipyramid geometry would have a degenerate pair of orbitals to be occupied by one pair of electrons. The same phenomenon would be expected for SF_4 in the tetrahedral geometry. It is not immediately apparent why SF_4 should not have at least the symmetry of the square pyramid if mere avoidance of orbital degeneracy is the primary criterion for the preferred geometry. From our calculations on PF_5 the ligand–ligand antibonding appears much more important.

Tables V–VII show how little the atomic and molecular parameters change in going from the trigonal bipyramid to the square pyramid.

Table VIII displays ligand–ligand interaction changes for PF_5. In the trigonal-bipyramid structure the axial-equatorial repulsion is important, accounting, we believe, for the longer axial bond length. In the square pyramid the axial–equatorial interaction is much reduced, but there are then more strong equatorial-equatorial interactions, the differences in the neighbor

(21) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

Table VIII. Ligand–Ligand Antibonding Interactions in PF_5^a

Pair	Calculation	Trigonal bipyramid OP	OE	Square pyramid OP	OE
F_A–F_E	s/p NON	−0.046	+1.974	−0.023	+0.979
F_E–F_E		−0.013	+0.531	−0.062	+2.675
F_A–F_E	s/p IT	−0.081	+3.509	−0.045	+2.026
F_E–F_E		−0.028	+1.291	−0.104	+4.490
F_A–F_E	s/p/d IT	−0.071	+3.222	−0.043	+2.030
F_E–F_E		−0.029	+1.386	−0.088	+3.959

^{a} F_A = axial fluorine; F_E = equatorial fluorine; other quantities also as in Tables II–V; OP = overlap population; OE, overlap energy. Positive overlap population and negative overlap energy indicate covalent bonding, the converse "nonbonded repulsion."

overlap energies roughly approximating the calculated barrier in the iterative calculation with 3d orbitals.

There are other possible mechanisms of ligand interchange corresponding to different trajectories and symmetries of the transition geometry. Since we have no accepted procedure for estimating the relation between P–F distance and angular deformations, it would require an unacceptably large number of calculations to search for other possible low-energy transition mechanisms. From the results we have obtained, we expect that many transition geometries of lower symmetry would be only slightly higher in energy, so that other monomolecular mechanisms might be observed for five-coordinate phosphorus compounds where ligand geometry or size precludes the square-pyramidal transition geometry.

To investigate the possibility of a bimolecular intermediate, calculations bringing together two PF_5 monomers to a dimer with local octahedral symmetry were performed by H. S. Aldrich and S. T. Kent. A smoothly rising curve with no indication of a minimum was obtained. Relaxation of the P–F distances might reduce the barrier enough for the bimolecular mechanism to be operative, but we regard this as most unlikely. Again, we find no indications of orbital degeneracy, so the bimolecular mechanism must also be regarded as permitted by the rules of orbital symmetry conservation.

Appendix

Orbital Energy Sum and Angle Variation. Consider a triatomic molecular, B–A–B, where the angle is to be varied in search of an energy minimum using the OES as an approximation to the total energy.

The correct total energy, eq 3 of the text, is

$$E_T = OES + CORE - ER2 - ER1$$

We assume (a) the one-center part of the electron repulsion energy, ER1, varies slowly with the angle and may be taken as constant, (b) the B–B distance is great enough that asymptotic form of the two-center electron interaction integral, $1/R$, may be used in ER2. With $R = R_{B-B}$, the variable part of the correction to the OES is simply

$$E = (Z_B - p_B)^2/R$$

where Z_B is the core charge of atom B and p_B is its electronic population. It will differ from Z_B by some amount t, $p_B = Z_B + t$, and t may be positive for negative B as in CO_2 or negative for positive B as in Li_2O.

There are two interesting cases. In the first, noniterative model, the calculation uses the free atom population in the effective Hamiltonian, meaning that one of the p_B factors above is equal to Z_B. The correction varies as

$$E = (Z_B^2 - Z_B(Z_B + t))/R = -tZ_B/R$$

In the second case, iteration to self-consistency, both populations are $(Z_B + t)$, though t may be reduced typically by about 30–40%. Then the correction varies as

$$E = (Z_B^2 - (Z_B + t)^2)/R = -(2tZ_B + t^2)/R$$

In addition to suggesting that the neutral starting option may provide better angle estimates by OES, this analysis also suggests that the self-consistent values should be relatively worse when the ligands are negative.

It is clear that the most favorable case is that of little or no charge transfer, when the long distance corrections for angle variation disappear.

Molecular Orbital Theory of Pentacoordinate Phosphorus

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Abstract: The electronic structure of some idealized PH_5 geometries of D_{3h}, C_{4v}, and C_s symmetries is analyzed. Each geometry is characterized by a low-lying nodeless orbital, three singly noded orbitals close in energy, and a high-lying doubly noded nonbonding orbital. The latter orbital is the only one significantly stabilized by the inclusion of 3d orbitals in the P basis set and also determines the relative stability of substituted compounds differing in electronegativity from H. A potential surface connecting the D_{3h} and C_{4v} geometries through C_{2v} structures is constructed. It shows a small barrier for the Berry pseudorotation process. Optimum C_s structures are at higher energy than the C_{4v} geometry. An examination of substituent effects rationalizes favored apical substitution in the trigonal bipyramid and preferred basal substitution in the square pyramid by more electronegative groups. It is predicted that π acceptors will prefer axial sites in the trigonal bipyramid, π donors equatorial positions. If a substituent has a single π system and is located in the equatorial position it will prefer to have its acceptor orbital perpendicular to the equatorial plane or its donor orbital in that plane. In the square pyramid, π donors will favor the apical position, π acceptors the basal sites. The concerted fragmentation reaction $PR_5 \rightleftarrows PR_3 + R_2$ is symmetry forbidden for the least-motion axial–equatorial departure from a trigonal bipyramid, and allowed for axial–axial or equatorial–equatorial departure.

The literature is replete with theories of bonding of pentacoordinate phosphorus.[1–31] We add here a molecular orbital description which is (1) simple,

(2) covers a wide range of geometries, (3) focuses on the role of substituents, and (4) gives some further insight

(1) I. Langmuir, *J. Amer. Chem. Soc.*, **41**, 868 (1919).

(2) F. J. Garrick, *Phil. Mag.*, **14**, 914 (1932).

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

(4) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940).

(5) R. Daudel and A. Bucher, *J. Chim. Phys.*, **42**, 6 (1945); R. Daudel, A. Bucher, and H. Moureu, *C. R. Acad. Sci.*, **218**, 917 (1944).

(6) G. H. Duffey, *J. Chem. Phys.*, **17**, 196 (1949).

(7) A.-C. Tang and H.-K. Lee, *J. Chin. Chem. Soc. (Taipei)* **17**, 252 (1950).

(8) H. Siebert, *Z. Anorg. Allgem. Chem.*, **265**, 303 (1951).

(9) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(10) J. W. Linnett and C. F. Mellish, *Trans. Faraday Soc.*, **50**, 665 (1954); J. W. Linnett, "The Electronic Structure of Molecules," Methuen and Co., London, 1964, p 122.

(11) C. Duculot, *C. R. Acad Sci.*, **245**, 802 (1957).

(12) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 177, 178.

(13) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); **39**, 318 (1961); *J. Chem. Soc.*, 4672, 4679 (1963); *Inorg. Chem.*, **5**, 1634 (1966); *J. Chem. Educ.*, **40**, 295 (1963); *J. Amer. Chem. Soc.*, **85**, 4672 (1963).

(14) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961).

(15) (a) R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963); *Rec. Chem. Progr.*, **23**, 195 (1962); *Acta Crystallogr.*, **14**, 585 (1961); (b) R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963); (c) R. J. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4321 (1951).

(16) V. M. Volkov, A. A. Levin, and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **152**, 359 (1963).

(17) A. Golebiewski, *Acta Phys. Polon.*, **23**, 243 (1963).

(18) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966), and references therein;