# Electronic Structure of $PH_5$ and Intramolecular Ligand Exchange in Phosphoranes. Model Studies[1]

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**Abstract:** The electronic structure and bonding in the hypothetical $PH_5$ are examined by nonempirical molecular orbital calculations. Computations on a model system derived from $PH_5$ are used to discuss the stereochemistry and intramolecular ligand exchange processes of phosphoranes. On the basis of calculations on $PH_5$, it is suggested that the lowest frequency fundamental of trigonal–bipyramidal phosphoranes corresponds to the equatorial in-plane bending motion.

Pentacoordinate compounds of phosphorus, in which the ligands are aryl groups or highly electronegative groups, are well known,[3] and some fluorohydrides of phosphorus have been prepared.[4–6] However, the parent compound, $PH_5$, has not been observed. It is thought that the high H–H bond energy, coupled with the low electronegativity of H, precludes its formation.[7]

Until now, theoretical investigations of pentacoordinate phosphorus appear to have been restricted to semiempirical (EHMO,[8–11] modified EHMO,[12] CNDO/2,[13] VESCF-MO[14]) calculations on $PF_5$,[8,12–14] $PH_5$,[8,10] pentaoxyphosphoranes,[11] and the series $PF_nCl_{(5-n)}$, $0 \leq n \leq 5$.[9]

We have carried out nonempirical LCAO–MO–SCF (Hartree–Fock) calculations on $PH_5$ and model systems derived from $PH_5$ in order to probe, with a minimal amount of experimental input, the electronic structure of phosphorus with an "expanded valence shell" and to explore the nature of the polytopal rearrangements that these compounds can undergo. A moderately large basis set of Gaussian-type functions (Gtf)[15] was used. The calculations were performed with and without a single set of d-type functions. No geometry search was attempted.[18] The bulk of the calculations were performed on two standard geometries: a trigonal bipyramid of $D_{3h}$ symmetry (P–$H_{ax}$ = 1.5076 Å, P–$H_{eq}$ = 1.4023 Å) and a tetragonal pyramid of $C_{4v}$ symmetry (P–$H_{ap}$ = 1.4023 Å, P–$H_{bas}$ = 1.455 Å and $H_{ap}PH_{bas}$ = 103° 57′). The bond length in the $D_{3h}$ structure was chosen by considering the P–H bond length in planar $PH_3$[20] and the relative axial and equatorial bond lengths in $PCl_5$.[21] The $C_{4v}$ structure represents a halfway point for conversion of one $D_{3h}$ structure to another by pseudorotation *via* the Berry mechanism, which appears to be the favored route.[8,22] As a reference, calculations using the present basis set were also performed on $PH_3$[20,23] in two geometries: a planar structure of symmetry $D_{3h}$ (P–H = 1.4023 Å) and a pyramidal structure of symmetry $C_{3v}$ (P–H = 1.4206 Å, HPH = 93.5°).

## Phosphorane, $PH_5$

**(a) The Role of d-Type Functions.** The computed total energies and molecular orbital energies of $PH_3$ and $PH_5$ are presented in Table I. Inspection of Table I reveals that the d-type functions make a significant contribution to the total energy of each species and that they influence the orbital energies of $PH_5$ more than of $PH_3$. However, the computed results for each species are qualitatively unaffected by the presence of the d-type functions. The energy of the highest occupied orbital (MO 10) of $PH_5$, which has d symmetry

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(2) NATO Postdoctoral Fellow, National Research Council of Canada. Address correspondence to the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada.

(3) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966).

(4) B. Blaser and K. H. Worms, *Angew. Chem.*, 73, 76 (1961).

(5) R. R. Holmes and R. N. Storey, *Inorg. Chem.*, **5**, 2146 (1966).

(6) P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, 89, 2017 (1967).

(7) W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, New York, N. Y., 1965, p 153.

(8) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, in press.

(9) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 3255 (1966).

(10) K. Issleib and W. Gründler, *Theor. Chim. Acta*, 8, 70 (1967).

(11) D. B. Boyd, *J. Amer. Chem. Soc.*, 91, 1200 (1969).

(12) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, 22, 231 (1968).

(13) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 47, 158 (1967).

(14) R. D. Brown and J. B. Peel, *Aust. J. Chem.*, 21, 2605, 2617 (1968).

(15) Veillard's[16] 12s 9p Gaussian basis set for P was contracted as follows: (1 2 3 4 5 6)(7 8)(9)(10)(11) (12)/(1 2 3)(4 5 6) (7)(8 9).[16] A single set of d-type functions with exponent 0.45 was added. Fink and Allen's[17] 5s Gaussian basis set for H was contracted as follows: (4,1).

(16) A. Veillard, *Theor. Chim. Acta*, 12, 405 (1968).

(17) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 46, 2261 (1967).

(18) It has been shown (see, for instance, ref 19 and 20) that for a sufficiently large basis set, the LCAO–MO–SCF (Hartree–Fock) procedure will yield the correct (experimental) geometry. Therefore, if determination of molecular geometry is not a prime consideration, a tedious and expensive geometry search can be avoided by assuming the experimental geometry without violating the claim to the nonempirical nature of the computations. In the instance that the experimental geometry is not known, as in the present case, similar results may be realized by assuming a standard or reasonable geometry.

(19) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, 52, 4133 (1970).

(20) J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969).

(21) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11, 1 (1958).

(22) (a) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960); (b) R. R. Holmes and Sr. R. M. Deiters, *J. Amer. Chem. Soc.*, 90, 5021 (1968); (c) E. L. Muetterties, *ibid.*, 91, 4115 (1969); (d) G. M. Whitesides and H. L. Mitchell, *ibid.*, 91, 5384 (1969); (e) see, however, P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 10, 687 (1971).

(23) For several recent *ab initio* studies of $PH_3$, see (a) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967); (b) S. Rothenberg, R. H. Young, and H. F. Schaeffer, III, *J. Amer. Chem. Soc.*, 92, 3243 (1970); (c) J. Demuynck and A. Veillard, *Chem. Commun.*, 873 (1970); (d) I. H. Hillier and V. R. Saunders, *ibid.*, 316 (1970).

**Table I.** Total and Molecular Orbital Energies (Hartrees)[a] for PH$_3$ and PH$_5$

| | | PH$_3$ | | | | | | PH$_5$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_{3v}$ | | | $D_{3h}$ | | | $D_{3h}$ | | | $C_{4v}$ | |
| MO | | no dGtf | dGtf | | no dGtf | dGtf | | no dGtf | dGtf | | no dGtf | dGtf |
| | | −342.39955[b] | −342.45021[b] | | −342.35019[b] | −342.38544[b] | | −343.39140[b] | −343.49327[b] | | −343.38410[b] | −343.48711[b] |
| 1 | $1a_1$ | −79.9784 | −79.9628 | $1a_1'$ | −79.9555 | −79.9493 | $1a_1'$ | −80.0681 | −80.0336 | $1a_1$ | −80.0691 | −80.0342 |
| 2 | $2a_1$ | −7.5079 | −7.4884 | $2a_1'$ | −7.4860 | −7.4763 | $2a_1'$ | −7.5915 | −7.5468 | $2a_1$ | −7.5916 | −7.5465 |
| 3 | $1e$ | −5.4095 | −5.3908 | $1e_1'$ | −5.3924 | −5.3823 | $1e_1'$ | −5.4966 | −5.4534 | $3a_1$ | −5.4970 | −5.4543 |
| 4 | $1e$ | −5.4095 | −5.3908 | $1e_1'$ | −5.3924 | −5.3823 | $1e_1'$ | −5.4966 | −5.4534 | $1e$ | −5.4955 | −5.4509 |
| 5 | $3a_1$ | −5.4070 | −5.3893 | $1a_2''$ | −5.3870 | −5.3797 | $1a_2''$ | −5.4942 | −5.4501 | $1e$ | −5.4955 | −5.4509 |
| 6 | $4a_1$ | −0.8855 | −0.8599 | $3a_1'$ | −0.8568 | −0.8478 | $3a_1'$ | −0.9478 | −0.9088 | $4a_1$ | −0.9459 | −0.9063 |
| 7 | $2e$ | −0.5270 | −0.5236 | $2e_1'$ | −0.5601 | −0.5629 | $2e_1'$ | −0.6007 | −0.5837 | $2e$ | −0.5991 | −0.5771 |
| 8 | $2e$ | −0.5270 | −0.5236 | $2e_1'$ | −0.5601 | −0.5629 | $2e_1'$ | −0.6007 | −0.5837 | $2e$ | −0.5991 | −0.5771 |
| 9 | $5a_1$ | −0.3923 | −0.3910 | $2a_2''$ | −0.3093 | −0.2993 | $2a_2''$ | −0.5841 | −0.5607 | $5a_1$ | −0.5789 | −0.5641 |
| 10 | $3e$ | +0.1964 | +0.2010 | $4a_1'$ | +0.1699 | +0.1734 | $4a_1'$ | −0.2962 | −0.3228 | $1b_1$ | −0.2965 | −0.3234 |
| 11 | $3e$ | +0.1964 | +0.2010 | $3e_1'$ | +0.2566 | +0.2554 | $3e_1'$ | +0.2184 | +0.2338 | $6a_1$ | +0.1559 | +0.1731 |

[a] 1 hartree = 627.7 kcal/mol. [b] Total energy.

**Table II.** Population Analysis of PH$_3$ and PH$_5$

| | | PH$_3$ | | | | PH$_5$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_{3v}$ | | $D_{3h}$ | | | $D_{3h}$ | | | $C_{4v}$ | |
| | | no dGtf | dGtf | no dGtf | dGtf | | no dGtf | dGtf | | no dGtf | dGtf |
| Atomic populations | P | 15.008 | 15.217 | 15.240 | 15.548 | P | 14.706 | 14.979 | P | 14.738 | 14.998 |
| | H | 0.997 | 0.928 | 0.920 | 0.847 | $H_{ax}$ | 1.167 | 1.106 | $H_{ap}$ | 0.932 | 0.905 |
| | | | | | | $H_{eq}$ | 0.987 | 0.936 | $H_{bas}$ | 1.082 | 1.024 |
| Bond overlap populations | P–H | 0.667 | 0.718 | 0.729 | 0.752 | P–$H_{ax}$ | 0.482 | 0.633 | P–$H_{ap}$ | 0.720 | 0.772 |
| | | | | | | P–$H_{eq}$ | 0.662 | 0.745 | P–$H_{bas}$ | 0.555 | 0.682 |

in both $D_{3h}$ and $C_{4v}$ geometries, is not affected more than any of the other orbitals save MO 1 and MO 2. Neither is the ordering of the orbital energies altered by inclusion of d-type functions.

The nodal structure of the highest occupied molecular orbital of the $D_{3h}$ geometry (see Figure 1) precludes appreciable contribution to this orbital from s-type functions on phosphorus. The symmetry of this orbital ($a_1'$) excludes contributions from p-type functions on phosphorus.[24] The symmetry of the highest occupied orbital of the $C_{4v}$ geometry has $b_1$ symmetry and therefore excludes contributions from both s- and p-type functions.[24] As a consequence of nodal and symmetry restrictions, the d-type functions of phosphorus, if they are present in the basis set, are the only functions on this center that contribute to these molecular orbitals. It is important to realize, however, that the presence or absence of the d-type functions in the basis set plays no part in determining the symmetry or nodal structure of the highest occupied molecular orbitals of the two geometries.

Mulliken population analyses of PH$_3$ and PH$_5$ are shown in Table II. Introduction of d-type functions has the effect, possibly due to the Mulliken population analysis scheme, of attributing more of the electron pool to the central atom of each molecule,[25] as well as increasing the bond overlap populations. In addition, the separation of charges is lessened between equatorial and axial positions of the $D_{3h}$ structure of PH$_5$ and between apical and basal positions of the $C_{4v}$ structure.

We conclude that introduction of d-type functions into the basis set serves only to overcome some inadequacies in the basis set and that no greater significance should be attached to them.[26] Hereafter, the discussion will refer only to the results obtained using the complete s, p, d basis set, unless we state otherwise.

**(b) The Electronic Structure of PH$_5$.** The highest occupied molecular orbitals of PH$_3$ and PH$_5$ are depicted in Figure 1 as combinations of atomic orbitals. The innermost molecular orbitals of PH$_3$ and PH$_5$ which are not shown are essentially localized to phosphorus and may be considered to be the 1s, 2s, and 2p atomic orbitals of the heavy atom. The molecular orbitals shown in Figure 1 may be characterized simply as s-like (nodeless), p-like (having a single node), and d-like (having two nodal surfaces). The highest occupied molecular orbital of PH$_5$, which is d-like, is nonbonding if d-type functions are omitted from the basis set but *is* bonding if d-type functions are included since only these functions on phosphorus are of the required symmetry for effective overlap. In the latter case the highest occupied molecular orbital of PH$_5$ contributes 0.133 and 0.046 electron to the bond overlap populations of P–$H_{ax}$ and P–$H_{eq}$, respectively, of the $D_{3h}$ structure and 0.103 electron to the bond overlap population of P–$H_{bas}$ of the $C_{4v}$ structure.

A correlation diagram for the highest occupied molecular orbitals of PH$_3$ and PH$_5$ is shown in Figure 2.

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(24) By way of illustration, carbon 1s and 2s orbitals are excluded, on symmetry grounds, from participating in the $t_2$ molecular orbitals of methane. For the same reason, 2p atomic orbitals cannot contribute to the molecular orbitals of $a_1$ symmetry.

(25) The Mulliken population analysis partitions electronic change among the centers according to the prescription

$$p_A = 2\sum_k\left(\sum_i C_{ik}^2 + \sum_i\sum_j C_{ik}C_{jk}S_{ij}\right)$$

where $p_A$ is the electron population of center A, $k$ sums over occupied molecular orbitals, $i$ sums over all functions on center A, $j$ sums over all functions not on center A, $C_{ik}$ is the coefficient of the $i$th basis function in the $k$th molecular orbital, and $S_{ij}$ is the overlap integral between the $i$th and $j$th basis functions. Thus, although introduction of the d-type functions centered on phosphorus serves mainly to improve the electronic description of the bonding region (the radial maximum of the d-type functions occurs at 0.79 Å), additional charge is attributed to phosphorus due to the $C_{ik}^2$ terms in the above equation.

(26) See also (a) C. A. Coulson, *Nature* (*London*), 221, 1106 (1969), and (b) M. A. Ratner and J. R. Sabin, *J. Amer. Chem. Soc.*, 93, 3542 (1971).

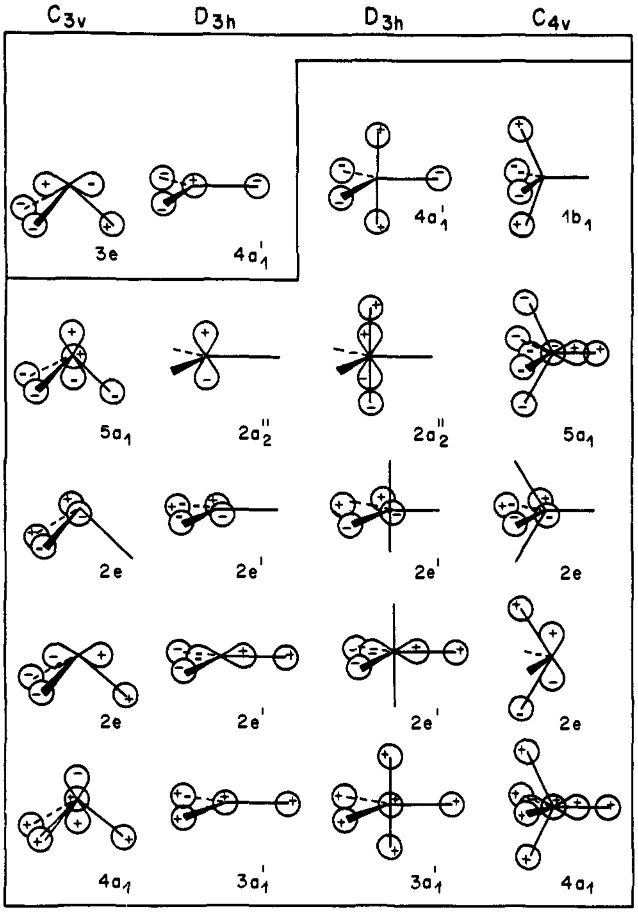

Figure 1. The symmetries of the higher occupied orbitals of $PH_3$ and $PH_5$.

The left half of Figure 2 represents a correlation diagram for pyramidal inversion of $PH_3$, which requires 40.7 kcal/mol. The right side of this figure represents a correlation diagram for pseudorotation, by the Berry mechanism, of $PH_5$, which requires 3.9 kcal/mol. It is strikingly apparent from Figure 2 and Table I that a relatively small perturbation of the molecular orbital energy levels occurs when the geometry of $PH_5$ is deformed from $D_{3h}$ to $C_{4v}$, *i.e.*, in the process of pseudorotation. The data in Table II add additional support to the suggestion that a much smaller amount of electron redistribution is required during pseudorotation than during pyramidal inversion. This, in part, explains the low barrier which is in accord with experimentally observed rapid intramolecular ligand exchange as in $PF_5$ (barrier reported to be 7.5–7.7 kcal/mol).[22b,27]

Although the phosphorus atom in $PH_3$ is computed to have a negative charge,[28] the phosphorus atom in $PH_5$ has a small net positive charge. As in $PH_3$, the equatorial protons of the $D_{3h}$ structure of $PH_5$ and the apical proton of the $C_{4v}$ structure are more positive than the phosphorus.[29] The axial and basal protons of the two structures thus have net negative charges. This result suggests that axial orbitals of a trigonal bipyramid are more electropositive than equatorial orbitals and provides the first justification, on a nonempirical basis, of the empirical deductions of Muetterties and coworkers and of several independent semiempirical results[8,9,30,31] that bonding to electronegative substituents in the axial positions is favored in the $D_{3h}$ structure. On the basis of the population analysis of the $C_{4v}$ structure one might also expect that pseudorotation would be easiest by way of tetragonal-pyramidal structures that have an electropositive substituent in the apical position. We pursue this question further in a later section.

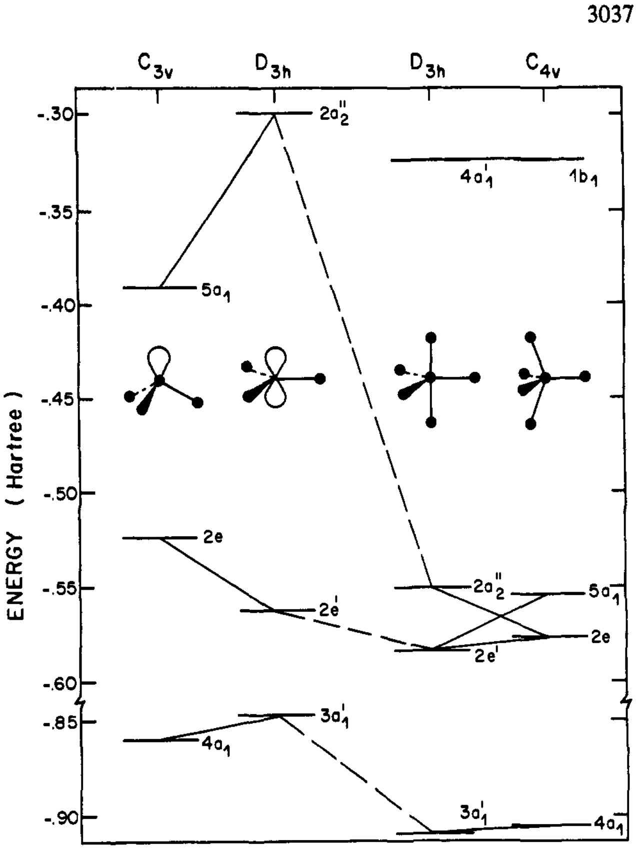

Figure 2. Correlation diagrams for pyramidal inversion ($C_{3v} \rightarrow D_{3h}$) of $PH_3$ and for pseudorotation ($D_{3h} \rightarrow C_{4v}$) of $PH_5$.

**(c) The Stability of $PH_5$.** The calculated total energy of $PH_5$ in the more stable $D_{3h}$ structure is $-343.49327$ Hartrees. The energy calculated using the same basis set for $H_2$ is $-1.12436$ hartree. For $PH_3$ it is $-342.45021$ hartrees, which is only slightly higher than the lowest energy yet reported for $PH_3$, $-342.4603$.[23b] The heat of formation, $\Delta H$, for the reaction $H_2 + PH_3 \rightarrow PH_5$ is calculated to be $-343.49327 - (-342.45021) - (-1.12436) = 0.0813$ hartree ($\Delta H = 51.0$ kcal/mol), neglecting vibrational, rotational, and translational energies. It has been shown[19,32] that correlation energy is approximately conserved in reactions involving only closed shell reactants and products. Thus $PH_5$ is predicted to be thermodynamically unstable relative to $PH_3$ and $H_2$ by approximately 51 kcal/mol. This fact alone, however, does not preclude its existence. It is possible that the low ionization poten-

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(27) R. R. Holmes, Sr. R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, 8, 2612 (1969).

(28) The opposite result was recently obtained using a somewhat extended basis set.[23b]

(29) In the absence of d-type functions the opposite is true; the phosphorus of $PH_5$ is more positive than the equatorial protons of the $D_{3h}$ structure.

(30) (a) R. J. Gillespie, *Inorg. Chem.*, 5, 1634 (1966); (b) R. J. Gillespie, *J. Chem. Educ.*, 40, 295 (1963); (c) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11, 339 (1957).

(31) (a) L. S. Bartell, *Inorg. Chem.*, 5, 1635 (1966); (b) R. E. Rundle, *Surv. Progr. Chem.*, 1, 81 (1963); (c) R. E. Rundle, *Rec. Chem. Progr.*, 23, 195 (1962).

(32) L. C. Snyder, *J. Chem. Phys.*, 46, 3602 (1967).

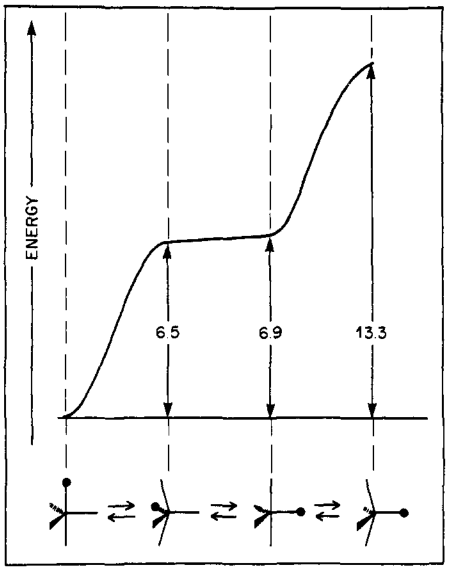

Figure 3. Potential energy curve connecting all possible trigonal-bipyramidal and tetragonal-pyramidal structures of compounds of the type $PR_4X$. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

tial, 8.8 eV (given as the negative of the energy of the highest occupied molecular orbital), contributes to the instability of $PH_5$ by rendering it susceptible to attack by Lewis acids.[8]

## Stereochemistry of Pseudorotation in Phosphoranes

**(a) The Model.** Since $PH_5$, as shown above, incorporates many of the features of stable phosphoranes, it has been used below as the basis for a model for calculating the stereochemistry of more complicated systems. Electronegativity differences between substituents are simulated by small alterations in the nuclear charge[33] of one or more of the hydrogen atoms. Specifically, a substituent more electronegative than hydrogen is simulated by changing the nuclear charge of H to +1.1. This corresponds to an approximate electronegativity of 2.9 on the Pauling scale.[34] This procedure yields a set of model substituted phosphoranes which may be characterized by $PR_nX_{(n-5)}$ where R is represented by a hydrogen atom, X is a modified hydrogen atom with a nuclear charge of 1.1, and $0 \leq n \leq 5$. The potential curves connecting all unique trigonal-bipyramidal and tetragonal-pyramidal structures of the type $PR_4X$, $PR_3X_2$, $PR_2X_3$, and $PRX_4$ are presented in Figures 3–6, respectively. In these figures X is represented by a black circle.

The shapes of the curves are determined solely by inductive electronic effects since interactions through $\pi$ orbitals of ligands are not incorporated into the model. This may not be a serious omission however, since, in actual systems, the orientation of ligands about a trigonal bipyramid is very largely correlated by relative electronegativity.[3,35,36] In addition, the steric bulk of the R and X groups of the model are negligible. Again, steric bulk effects play a minor role in determining the conformations of most stable phosphoranes.[3,35,37]

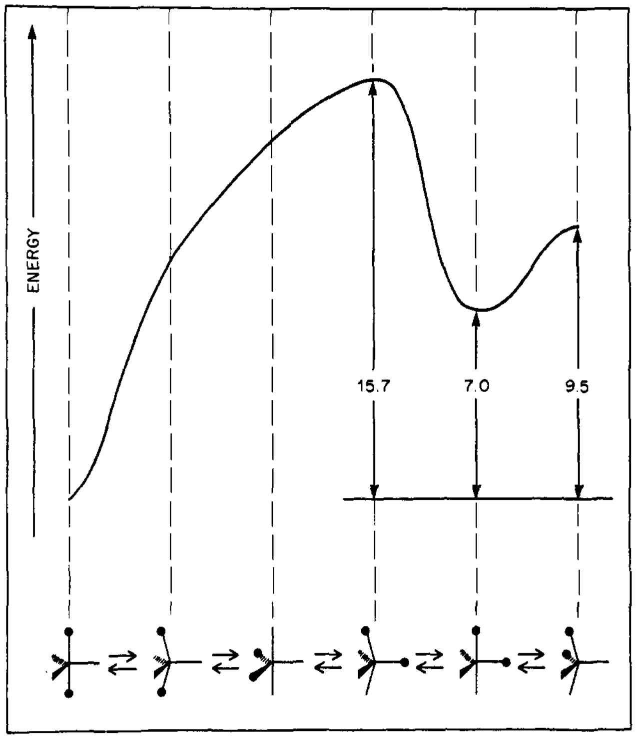

Figure 4. Potential energy curve connecting all possible trigonal-bipyramidal and tetragonal-pyramidal structures of compounds of the type $PR_3X_2$. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

**(b) $PR_4X$.** The potential curve for pseudorotation in the model system $PR_4X$ is shown in Figure 3. Only one stable isomer is predicted: a trigonal bipyramid with the electronegative substituent in an axial position.

**(c) $PR_3X_2$.** The potential curve for pseudorotation of this model system is shown in Figure 4. Of the three trigonal-bipyramidal structures of the form $PR_3X_2$, two are predicted to be stable. The structure that has both electronegative substituents in axial positions is calculated to be 7 kcal/mol more stable than that which has one of the X substituents in an equatorial site. An equilibrium mixture of the two diastereomers would have a negligible amount of the less stable isomer.

**(d) $PR_2X_3$.** The potential curve for pseudorotation of the model system $PR_2X_3$ is shown in Figure 5. As in the case of $PR_3X_2$, three trigonal-bipyramidal structures are possible. Of these, however, only one is predicted to be stable, namely that which has both axial sites occupied by X. The structure which has all equatorial sites occupied by X is calculated to represent a maximum energy configuration. There is no low energy pathway for averaging the environments of the three X substituents.

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(33) (a) T. L. Cottrell and L. E. Sutton, *Proc. Roy. Soc., Ser. A*, 207, 48 (1951); (b) A. C. Hurley, *ibid.*, 218, 333 (1953).

(34) According to the Mulliken definition, electronegativity, $\chi$, is given by $\chi = {}^1/_2(IP + EA)$. The ionization potential (IP) of a one-electron atom is equal in magnitude to the energy of the atom, which is proportional to $Z^2/2$. The electron affinity (EA) is equal to the ionization potential of the corresponding two-electron system which is estimated by Hylleraas' formula (see W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, p 290).

(35) (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).

(36) See, however, ref 8.

(37) For examples where steric bulk effects do play a dominant role, see (a) R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, 1010 (1969), and references cited therein; (b) K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, 91, 7393 (1969), and references cited therein.

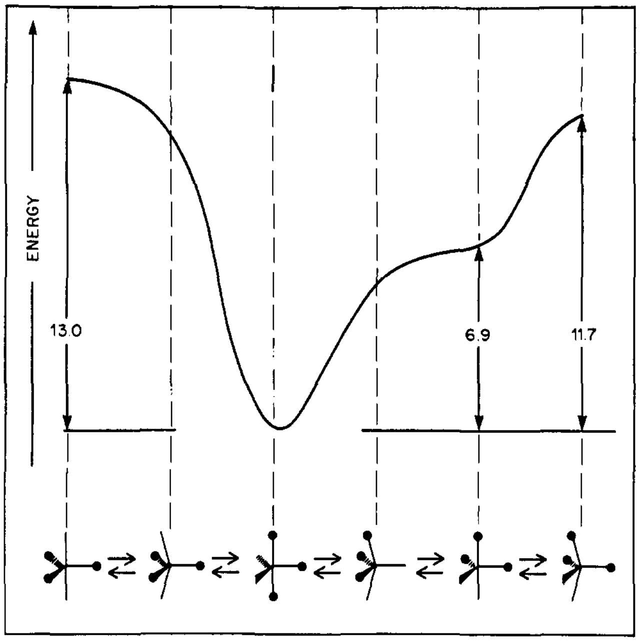

Figure 5. Potential energy curve connecting all possible trigonal-bipyramidal and tetragonal-pyramidal structures of compounds of the type $PR_2X_3$. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

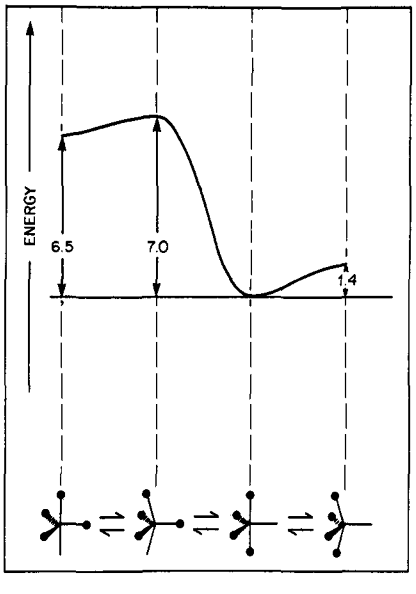

Figure 6. Potential energy curve connecting all possible trigonal-bipyramidal and tetragonal-pyramidal structures of compounds of the type $PRX_4$. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

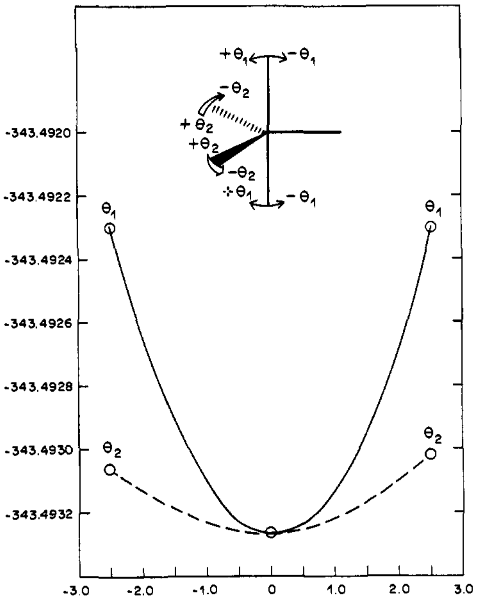

Figure 7. Energy of $PH_5$ as a function of displacements from $D_{3h}$ symmetry along directions for axial ($\pm\theta_1$) and equatorial ($\pm\theta_2$) in-plane bending modes.

(e) $PRX_4$. The potential curve for pseudorotation of this model system is shown in Figure 6. Both trigonal-bipyramidal structures represent energy minima. However, a negligible barrier hinders transformation of the less stable form with one axial X group into the thermodynamically more stable form with both axial sites occupied by electronegative substituents.

(f) $PX_5$. The $D_{3h}$ structure of the model system, where all substituents have nuclear charges of +1.1, is computed to be 3.4 kcal/mol more stable than the $C_{4v}$ structure. This value is not significantly different from the value 3.9 kcal/mol obtained for $PR_5 \equiv PH_5$.

(g) **Summary**. For all of the model phosphoranes studied, the most stable structure, without exception, is a trigonal bipyramid. All trigonal-bipyramidal structures, however, do not represent energy minima (Figures 3–5). In cases where more than one minimum does occur (Figures 4 and 6), the less stable isomer is computed to be sufficiently less stable that significant amounts would not appear in equilibrium mixtures. Although the numbers shown on the figures (Figures 3–6) refer only to the model systems and not to real phosphoranes, the values are sufficiently small that fast equilibration is expected. In every case the structure of the most stable model is the same as that observed for actual phosphoranes to which the model applies. The shapes of the curves for different structural types help explain the, perhaps surprising, lack of observed isomerism among monomeric acyclic pentacoordinate systems.[38]

## Axial *vs.* Equatorial Bending Modes in Phosphoranes

The trigonal-bipyramidal form of $PH_5$ is computed to be more stable than the tetragonal pyramid by 3.9 kcal/mol. A value of 6.3 kcal/mol has been estimated[27] for the barrier to pseudorotation of this hypothetical molecule by assuming transferability of infrared and Raman vibrational data from stable phosphoranes.[27] A further assumption regarding the assignment of the lowest frequency fundamental to the equatorial in-plane bending mode was necessary to arrive at the above number. If this fundamental were assigned to the axial bending mode, an exchange barrier of 6.9 kcal/mol is obtained.[27]

The question of the assignment of the lowest frequency fundamental is relevant to all force field studies of phosphoranes.[39] The assignment to an axial bending

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(38) See, however, E. A. Cohen and C. D. Cornwell, *Inorg. Chem.*, 7, 398 (1968), and ref 40d.

(39) For a discussion of this problem, see (a) S. J. Cyvin and J. Brunvoll, *J. Mol. Struct.*, 3, 151 (1969); (b) P. C. Van Der Voorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, 43, 3457 (1965); (c) P. Lockett, W. Fowler, and P. M. Wilt, *ibid.*, 53, 452 (1970); (d) ref 27.

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 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.

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(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).

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# 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).

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(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).