

involves a small charge transfer from the chlorine  $3p_{\sigma}$  atomic orbitals to the Cu  $3d_{x^2-y^2}$  (half-filled) and  $4s$ ,  $4p_x$ , and  $4p_y$  (empty) orbitals.

From independent SCF calculations, the lowest excitations are found to be d-d excitations followed by ligand to metal charge-transfer excitations, a result unexpected on the basis of the sequence of energy orbitals. The assignment from our calculation for both the d-d excitations  ${}^2B_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^2E_g(d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$ , and the charge-transfer excitations are in qualitative agreement with the experimental evidence from the polarized spectrum and magnetic circular dichroism for complex halides of Pd and Pt.

Finally, the  $T_d$  structure is computed to be more stable than the  $D_{4h}$  structure by 18 kcal/mol. However, it is found by energy minimization with respect to the Cl-Cu-Cl angle that the most stable configuration of the  $\text{CuCl}_4^{2-}$  ion corresponds to a flattened  $D_{2d}$  structure, with a value of  $120^\circ$  for the Cl-Cu-Cl angle close to the experimental value of  $124^\circ$  in  $\text{Cs}_2\text{CuCl}_4$ . The distortion with respect to an ideal  $T_d$  geometry appears as an

intrinsic property of the  $\text{CuCl}_4^{2-}$  ion, not as a consequence of packing effects.

The wave function which we have reported for the ground state of the  $\text{CuCl}_4^{2-}$  ion in the  $D_{4h}$  structure is somewhat different from the ones obtained previously from semiempirical calculations by other authors. It should be emphasized that these semiempirical wave functions were used in conjunction with either Koopmans' theorem or with the assumption that the excitation energies may be represented as a difference of orbital energies. We have made the calculation at one level more sophisticated (independent SCF calculations for the ionized and excited states). The good agreement with experimental properties achieved for the electronic spectrum, the hyperfine interaction, and the equilibrium configuration gives some confidence in the reported wave functions.

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## Electronic Structure of Phosphorus Pentafluoride and Polytopal Rearrangement in Phosphoranes

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**Abstract:** The electronic structure of  $\text{PF}_5$  is discussed through *ab initio* LCAO-MO-SCF calculations with a medium size basis set. It is shown that d functions on the phosphorus atom play a significant role through  $d_{\pi}$ - $p_{\pi}$  bonding. Computed energy differences between the  $D_{3h}$ ,  $C_{4v}$ , and  $C_2$  structures support Berry's pseudorotation mechanism as the mechanism of ligand interchange for  $\text{PF}_5$  and seem to rule out the mechanism of turnstile rotation. The ease of ligand exchange in substituted phosphoranes  $\text{PR}_n\text{F}_{(5-n)}$  is discussed in terms of the computed energy differences between the trigonal bipyramid (TBP) and the square pyramid (SP) together with the energy differences between the TBP isomeric structures. The slow exchange limit found experimentally for the amino- and thiotetrafluorophosphoranes is accounted for by a relatively high barrier to Berry's pseudorotation. The corresponding barriers to rotation around the P-N or the P-S bond are computed, and it is found that the rotation process around the P-N bond is coupled to the inversion process at the N atom.

Stereochemical nonrigidity is common in five-coordinate chemistry and has been extensively studied for pentacoordinate compounds of phosphorus.<sup>1,2</sup> The Berry mechanism, which accounts for most experimental observations relating to intramolecular rearrangements of phosphoranes, has been initially proposed for the  $\text{PF}_5$  molecule.<sup>3</sup> Other mechanisms have been proposed since.<sup>4</sup> It has been pointed out that information concerning the mechanism is usually inferential, although the corresponding potential surfaces can be obtained from nonempirical quantum mechanical calculations.<sup>5</sup>

Quantum mechanical *ab initio* calculations have been

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fairly successful in the prediction of the stereochemistry for small molecules and in the calculation of rotation and inversion barriers.<sup>6</sup> However, there has been no attempt so far to investigate nonrigid structures through *ab initio* quantum mechanical calculations, except for model studies by Rauk, *et al.*, of the intramolecular ligand exchange in phosphoranes.<sup>7</sup> Only semiempirical calculations have been reported for  $\text{PF}_5$ , with some controversy regarding the importance of d orbitals in the bonding.<sup>8-12</sup> We report here non-

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empirical LCAO-MO-SCF calculations first on  $\text{PF}_5$  in order to assess the nature of the bonding in this molecule and next on a series of phosphoranes in order to investigate the energetics and the stereochemistry of polytopal rearrangements for these molecules.

**Electronic Structure of  $\text{PF}_5$ .** We have carried out *ab initio* LCAO-MO-SCF calculations with a (10,6,-1/8,4) basis set of Gaussian functions,<sup>13,14</sup> contracted to [6,4,1/4,2]. The exponent of the d-type function was optimized for the  $D_{3h}$  structure with the experimental geometry<sup>15</sup> to a value of 0.57. The same value was kept for the other structures.

Geometry optimization was performed for the two structures  $D_{3h}$  and  $C_{4v}$ . For the trigonal bipyramidal (TBP) structure, equatorial and axial P-F bond lengths were found respectively equal to 1.542 and 1.571 Å. in excellent agreement with experimental values of 1.534 and 1.577 Å.<sup>15</sup> Our calculation reproduces well the slight difference of bond length associated with the axial and equatorial positions. The optimized bond lengths for the square pyramid (SP) structure are 1.514 Å for the apical position and 1.561 Å for the basal positions. There is not much experimental evidence regarding the bond lengths in  $C_{4v}$  structures except in transition metal complexes. In  $\text{BrF}_5$ , the experimental bond length is indeed shorter for the apical F (1.68 Å) than for the basal F atoms (1.75–1.82 Å).<sup>16</sup> Optimization of the angle  $F_{\text{apical}}\text{-P-F}_{\text{basal}}$  in the  $C_{4v}$  structure yields a value of 101.34°. This should be compared with the value of 99.8° obtained by Hoffmann, *et al.*, through an extended Hückel calculation<sup>8</sup> and the value of 105° from a CNDO calculation by Gillespie, *et al.*<sup>9</sup>

The nature of the bonding in  $\text{PX}_5$  molecules has been discussed by many authors, and extensive references may be found in ref 8. MO wave functions have been reported either for the parent compound  $\text{PH}_5$ ,<sup>7,8</sup> or for  $\text{PF}_5$  itself.<sup>8-12</sup> The points which have been discussed at length deal with (I) a qualitative understanding of the bonding either in terms of fully delocalized molecular orbitals or electron-rich three-center bonding, (II) the role and importance of d-type functions in this bonding, (III) the difference in bonding between the equatorial and axial positions, and (IV) the interaction between  $\pi$ -electron donors and acceptors and the framework  $\sigma$  orbitals or the phosphorus 3d orbitals. The conclusions reached previously can be summarized as follows. (I) The bonding in  $\text{PH}_5$  ( $D_{3h}$  or  $C_{4v}$ ) has been discussed in terms of a set of five valence molecular orbitals.<sup>7,8</sup> These are, in order of increasing energies, one nodeless orbital ( $a_1'$  or  $a_1$ ), three orbitals with one node ( $e' + a_2''$  or  $e + a_1$ ), and one orbital with two nodes ( $a_1'$  or  $b_1$ ). The  $a_1'$  or  $b_1$  orbital is a high-lying nonbonding orbital separated by a large gap from the other bonding orbitals, with the phosphorus contribution to this MO practically limited to d-type functions as a consequence of symmetry and nodal restrictions (the

*ab initio* calculation led to a small interversion of the  $a_2''$  and  $e'$  orbitals<sup>7</sup>). The sequence of orbital levels in  $\text{PF}_5$  has been discussed by Berry, *et al.*, on the basis of an extended Hückel calculation<sup>10</sup> (*cf.* below). (II) Different conclusions have been reached regarding the role of the phosphorus 3d orbitals. For  $\text{PH}_5$  Hoffmann concluded that only the nonbonding orbital is significantly stabilized by the introduction of 3d orbitals.<sup>8</sup> This stabilization is also apparent in the *ab initio* calculation, but it is accompanied by a destabilization of the same order of magnitude for all the other orbitals.<sup>7</sup> Musher has pointed that this is a rather general trend which is also found in  $\text{SF}_6$  and  $\text{ClO}_4^-$ .<sup>17</sup> d orbitals have been found to play an important role when back-bonding is associated with electronegative ligands<sup>18-25</sup> and, on this basis, they may play a larger role in  $\text{PF}_5$  than in  $\text{PH}_5$ . From the results of extended Hückel calculations<sup>8,10</sup> it was concluded that d orbitals make only minor contributions to the bonding. However, according to a CNDO calculation, the inclusion of sulfur or phosphorus 3d orbitals in  $\text{SF}_6$  or  $\text{PF}_5$  results in a considerable back-donation of  $\pi$  electrons onto the central atom.<sup>26</sup> (III) The difference in the bonding between the axial and equatorial ligands has been ascribed chiefly to the fact that the equatorial orbitals lie deeper than the axial orbitals containing the same sort of atomic orbital composition, with the phosphorus 3s character greater in equatorial bonds as a consequence.<sup>10,11</sup> All calculations have agreed that the axial bonds should be weaker, with the corresponding ligand more negative and this independently of the effect of d orbitals.<sup>7-11</sup> (IV) The importance of  $\pi$  back-bonding in  $\text{PF}_5$  has been recognized by Santry and Segal<sup>26</sup> and  $\pi$  bonding was predicted to be greater in the equatorial positions for a series of phosphorus(V) chlorofluorides.<sup>11</sup> Hoffmann, *et al.*, have given a very careful examination to the interaction of  $\pi$ -electron donors in phosphoranes.<sup>8</sup> The following conclusions were reached on the basis of model calculations. (I) If 3d orbitals are not important, interactions between donor orbitals and framework  $\sigma$  orbitals are stronger for axial than for equatorial substitution. (II) In an equatorial site, the interaction is stronger for a donor orbital perpendicular to the equatorial plane. (III) The difference between axial and equatorial interactions is dominated by the interaction with the framework  $\sigma$  orbitals rather than the 3d orbitals. (IV) Equatorial p-d  $\pi$  bonding is more efficient than axial p-d  $\pi$  bonding.

We have reported in Tables I and II the sequence of energy levels and the orbital population analysis for the  $D_{3h}$  structure. The description<sup>7,8</sup> for the bonding in  $\text{PH}_5$  appears to be equally valid to describe the bonding in  $\text{PF}_5$ , provided that one recognizes the existence of

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**Table I.** Molecular Orbital Energies for the  $D_{3h}$  Structure of  $PF_5$  (in au)

	No d functions	With d functions	$\Delta^a$
2e''	-0.681	-0.665	+0.016
6e'	-0.702	-0.684	+0.018
5a <sub>2</sub> ''	-0.714	-0.695	+0.019
8a <sub>1</sub> '	-0.686	-0.709	-0.023
1a <sub>2</sub> '	-0.743	-0.722	+0.021
5e'	-0.765	-0.763	+0.002
1e''	-0.807	-0.804	+0.003
4a <sub>2</sub> ''	-0.870	-0.852	+0.018
4e'	-0.877	-0.858	+0.019
7a <sub>1</sub> '	-1.004	-0.974	+0.030
6a <sub>1</sub> '	-1.650	-1.635	+0.015
3a <sub>2</sub> ''	-1.696	-1.672	+0.024
3e'	-1.735	-1.712	+0.023
5a <sub>1</sub> '	-1.815	-1.782	+0.033
2a <sub>2</sub> ''	-5.786	-5.692	+0.094
2e'	-5.787	-5.694	+0.093
4a <sub>1</sub> '	-7.883	-7.788	+0.095
3a <sub>1</sub> '	-26.338	-26.328	+0.010
1a <sub>2</sub> ''	-26.338	-26.328	+0.010
1e'	-26.394	-26.378	+0.016
2a <sub>1</sub> '	-26.394	-26.378	+0.016
1a <sub>1</sub> '	-80.352	-80.270	+0.082

<sup>a</sup> Difference of columns 2 and 3.

effect on the phosphorus inner shells) and most of the valence orbitals with the exception of the 1e'' and 5e' orbitals which are not affected and of the 8a<sub>1</sub>' orbital which is stabilized. This is a situation slightly different from the one in PH<sub>5</sub> (with all the orbitals destabilized except the 4a<sub>1</sub>')<sup>8</sup> but similar to the one in SF<sub>6</sub>.<sup>17, 27-30</sup> These three orbitals 8a<sub>1</sub>', 1e'', and 5e' are indeed the ones with the largest participation of d functions (*cf.* in Table II the populations of the d functions in these orbitals). In PH<sub>5</sub> the role of d functions was limited to  $\sigma$  bonding, essentially through the 4a<sub>1</sub>' orbital, with a corresponding transfer of electron density from the hydrogens to the phosphorus (about the same for the axial and equatorial hydrogens) and a simultaneous increase (somewhat larger for the axial bonds) in the bond overlap populations.<sup>7,8</sup> In the extended Hückel calculation, the corresponding transfer of electron density is approximately 0.6 electron,<sup>8</sup> while the *ab initio* calculation gave a more conservative value of 0.27 electron.<sup>7</sup> The same  $\sigma$ -bonding is found in the 8a<sub>1</sub>' orbital (and to a smaller extent in the 6a<sub>1</sub>' and 3e' orbitals) but additional  $\pi$  back-bonding is operative through the orbitals 5e' and 1e''. As a result, the

**Table II.** Population Analysis for the Valence Orbitals of  $PF_5$  ( $D_{3h}$  Structure)

	P					F <sub>1</sub> <sup>a</sup>				F <sub>2</sub> <sup>b</sup>				F <sub>4</sub> <sup>c</sup>			
	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>	d	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>
2e''									0.49				0.12				0.64
2e''													0.36				0.64
6e'			0.02					0.07			0.08	0.04					0.83
6e'		0.02						0.14			0.01	0.08					0.83
5a <sub>2</sub> ''				0.08					0.40				0.40				0.36
8a <sub>1</sub> '					0.19			0.20			0.05	0.15		0.02			0.58
1a <sub>2</sub> '								0.67			0.50	0.17					
5e'		0.05			0.09			0.28			0.75	0.04					
5e'			0.05		0.09			0.95			0.04	0.41					
1e''					0.08				0.82				0.21			0.34	
1e''					0.08								0.62			0.34	
4a <sub>2</sub> ''				0.28					0.23				0.23				0.45
4e'		0.33				0.07	0.66			0.02	0.02	0.30				0.13	
4e'			0.33					0.20		0.06	0.30	0.25				0.13	
7a <sub>1</sub> '	0.50					0.06	0.27			0.06	0.07	0.20		0.06			0.19
6a <sub>1</sub> '					0.05	0.19				0.19				0.67			
3a <sub>2</sub> ''				0.10										0.92			0.02
3e'		0.10			0.03	1.22	0.03			0.30							
3e'			0.10		0.03					0.92		0.02					
5a <sub>1</sub> '	0.24					0.40	0.02			0.40		0.02		0.23			0.02

<sup>a</sup> Equatorial ligand on the x axis. <sup>b</sup> Equatorial ligand. <sup>c</sup> Axial ligand on the z axis.

three sets of valence molecular orbitals. The first set, which includes the levels 5a<sub>1</sub>', 3e', 3a<sub>2</sub>'', and 6a<sub>1</sub>', is built essentially from the 2s atomic orbitals of the F atoms. The second set includes the orbitals 7a<sub>1</sub>', 4e', 4a<sub>2</sub>'', and 8a<sub>1</sub>' and corresponds to the levels 3a<sub>1</sub>', 2e', 2a<sub>2</sub>'', and 4a<sub>1</sub>' of PH<sub>5</sub>,<sup>7,8</sup> with the 2p $\sigma$  atomic orbitals of the F atoms now playing the role of the H 1s orbitals. Again one finds a large energy gap between the 8a<sub>1</sub>' orbital and the other orbitals of the same set. The last set includes the levels from 1e'' to 2e'' (8a<sub>1</sub>' excluded) and corresponds to the lone pairs of the fluorine atoms. The sequence of energy levels in the extended Hückel calculation<sup>10</sup> was not very different from the one reported here (interventions occur for the four highest occupied levels).

We have also reported in Table I the orbital energies in the absence of d functions. The introduction of d functions destabilize the inner shells (with a marked

charge transfer into the phosphorus d functions is 0.55 electron, a value much higher than the one in PH<sub>5</sub>.<sup>31</sup> The same conclusions may be reached from an analysis of the P-F overlap population (Table III). The 8a<sub>1</sub>' orbital exhibits the expected increase in the P-F<sub>ax</sub> overlap population upon introduction of the d orbitals

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**Table III.** P-F Overlap Populations ( $D_{3h}$  Structure)

	P-F <sub>eq</sub>		P-F <sub>ax</sub>	
	No d functions	With d functions	No d functions	With d functions
2e''		-0.014		0.018
6e'	-0.011	-0.004	0.060	0.044
5a <sub>2</sub> ''	-0.006	0.021	0.009	0.022
8a <sub>1</sub> '	0.019	0.018	0.029	0.089
1a <sub>2</sub> '				
5e'	0.044	0.130	-0.010	
1e''		0.043		0.050
4a <sub>2</sub> ''	0.046	0.043	0.045	0.052
4e'	0.117	0.115	0.074	0.070
7a <sub>1</sub> '	0.052	0.059	0.028	0.037
6a <sub>1</sub> '	-0.004	0.002	0.008	0.058
3a <sub>2</sub> ''			0.074	0.071
3e'	0.062	0.123		
5a <sub>1</sub> '	0.074	0.069	0.052	0.049
Total	0.393	0.605	0.369	0.560

(a comparable increase is also observed for the 6a<sub>1</sub>' orbital).  $\pi$  back-bonding results in a similar effect on the P-F<sub>ax</sub> and P-F<sub>eq</sub> overlap populations for the 1e'' orbital, but the differential effect of d functions in the 3e' and 5e' orbitals is an increase in the P-F<sub>eq</sub> overlap populations. The net balance is an equal increase (of about 0.2) in the P-F<sub>ax</sub> and P-F<sub>eq</sub> overlap populations upon the introduction of d functions.<sup>32</sup> This is substantiated through an examination of the change in the gross atomic populations of the fluorine atoms (Table IV); upon introduction of the d functions, the same

**Table IV.** Population Analysis for PF<sub>5</sub>

		$D_{3h}$			$C_{4v}$	
		No d functions	With d functions		No d functions	With d functions
Atomic populations	P	12.33	12.88	P	12.31	12.87
	F <sub>ax</sub>	9.57	9.46	F <sub>ap</sub>	9.52	9.39
	F <sub>eq</sub>	9.51	9.40	F <sub>bas</sub>	9.54	9.43
Overlap populations	P-F <sub>ax</sub>	0.368	0.562	P-F <sub>ap</sub>	0.420	0.645
	P-F <sub>eq</sub>	0.393	0.610	P-F <sub>bas</sub>	0.380	0.576

decrease of 0.11 electron is observed in the population of the axial and equatorial ligands. With this respect, for PF<sub>5</sub> we reach a conclusion different from the one for PH<sub>5</sub>, where it was observed that the introduction of d functions lessens the separation of charges between equatorial and axial positions.<sup>7</sup>

Geometry optimization leads to a shorter equatorial bond length compared with the axial bond length for the  $D_{3h}$  structure and to a shorter apical bond length compared with the basal bond length for the  $C_{4v}$  structure. This reflects the difference in the corresponding overlap populations (Table IV) and this result is independent of the use of d functions. Calculations on PH<sub>5</sub> have predicted that the electron density should be greater on the axial hydrogens in the  $D_{3h}$  structure and on the basal hydrogens in the  $C_{4v}$  structure.<sup>7,8</sup> This has been traced to electron-rich multicenter bonding in both structures for PH<sub>5</sub><sup>7</sup> or, alternatively, to a greater participation of the P 3s orbital in the equatorial bond of PF<sub>5</sub>, a consequence of the fact that the equatorial orbitals lie deeper than the corresponding axial or-

(32) A similar trend is observed in the results of ref 11.

bitals.<sup>10,11</sup> These two explanations are not opposite but rather complementary. From Table II the phosphorus 3s orbital is involved in the molecular orbitals 5a<sub>1</sub>' and 7a<sub>1</sub>' which have more equatorial than axial character, with no participation of the 3s orbital into the orbitals 6a<sub>1</sub>' and 8a<sub>1</sub>' which have more axial than equatorial character. The difference in the electron density of the axial and equatorial fluorines should be traced indeed to these orbitals. However, the origin of the difference in the P-F overlap population, which has been ascribed also to the greater 3s character in the equatorial bonds, seems to be due to the 4e' orbital rather than to the 7a<sub>1</sub>' and 8a<sub>1</sub>' orbitals (*cf.* Table III).

**Pseudorotation and Turnstile Rotation in PF<sub>5</sub>.** The computed energy difference between the  $D_{3h}$  and  $C_{4v}$  structures represents the barrier to the classic Berry pseudorotation.<sup>3</sup> Before turning to the results, we would like to emphasize the differences between this calculation and the previous ones. Previous calculations of the barrier for Berry's mechanism in PF<sub>5</sub> have been restricted to semiempirical methods.<sup>8-10,33</sup> Some of them, like the extended Hückel method, provide a satisfactory picture but may give in some cases misleading predictions regarding small energy barriers.<sup>10</sup> In some of these methods the total energy is not well defined.<sup>33</sup> The *ab initio* calculation for PH<sub>5</sub><sup>7</sup> gave a reasonable value for the barrier but may be considered only as a model calculation for PF<sub>5</sub> (for instance the computed inversion barriers for NH<sub>3</sub> and NH<sub>2</sub>F are respectively 5.1 and 20.3 kcal/mol<sup>34</sup>). Furthermore, no consideration was given to the turnstile mechanism through a  $C_s$  structure, a possible alternative to Berry's mechanism.<sup>4</sup> Finally in all of the previous studies for PH<sub>5</sub> and PF<sub>5</sub> the bond lengths were kept constant. Careful geometry optimization has been shown to be important for the calculation of small rotation barriers.<sup>35</sup>

From Table V, the computed value for the barrier to

**Table V.** Total Energies (in au) for PF<sub>5</sub>

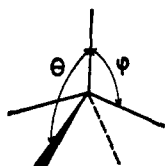
	$D_{3h}$	$C_{4v}$	$C_{2v}$	$C_s$
No d functions	-837.6313	-837.6178		
With d functions	-837.8366	-837.8289	-837.8323	-837.8077

Berry's pseudorotation is 4.8 kcal/mol. An estimate of 7.5-7.7 kcal/mol has been based on the use of a vibrational potential function<sup>36,37</sup> with a lower value of 3.8 kcal/mol reported more recently.<sup>2</sup> An upper limit of 5 kcal/mol has been placed on the basis that the barrier height cannot be estimated using the nmr line-shape method.<sup>38</sup> Our computed value is somewhat higher than the previous estimates based on CNDO (3.5 kcal/mol<sup>9</sup>) or extended Hückel (1.4 kcal/mol<sup>8</sup>) or from the *ab initio* calculation (3.9 kcal/mol for PH<sub>5</sub> and 3.5 kcal/mol for a hypothetical PX<sub>5</sub> compound with X

(33) J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, **94**, 3040 (1972).(34) J.-M. Lehn, *Top. Current Chem.*, **15**, 311 (1970).(35) A. Veillard, *Theor. Chim. Acta*, **18**, 21 (1970).(36) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, **90**, 5021 (1968).(37) R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).(38) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

more electronegative than H<sup>7</sup>). The barrier computed in the absence of d functions is raised to 8.5 kcal/mol. Thus the introduction of d functions lowers the barrier by 3.7 kcal/mol. This is reminiscent (although the trend is opposite) of the effect of d functions on the inversion barrier of ammonia which results almost solely from the differential mixing of *polarization* functions in the two structures  $C_{3v}$  and  $D_{3h}$ .<sup>39</sup> Pyramidal inversion and Berry's pseudorotation are fairly different processes, and the data of ref 7 suggest that there is comparatively less change in the wave function during pseudorotation than during pyramidal inversion. Still the effect of d functions on the pseudorotation barrier may be ascribed either to a polarization effect similar to the one in ammonia or to the participation of d orbitals (rather than d functions) to the bonding, as it emerges from the preceding discussion.<sup>40</sup> There is no way to answer this question directly for PF<sub>5</sub>. However one clue is given by the fact that d functions do not affect appreciably the barrier in PH<sub>5</sub> (the introduction of d functions decreases the barrier from 4.9 to 3.9 kcal/mol<sup>7</sup>). We tentatively conclude that the influence of d functions on the barrier in PF<sub>5</sub> should be traced to their effective participation into the bonding, not to polarization effects.

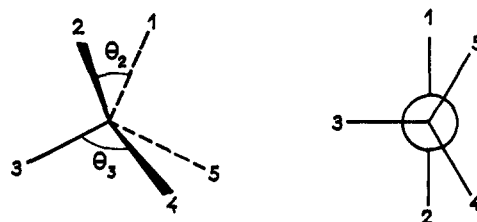
To assess more exactly the  $D_{3h}$ - $C_{4v}$  pathway corresponding to the classic Berry's mechanism, we have computed one intermediate point of  $C_{2v}$  symmetry. A  $C_{2v}$  structure is defined by five parameters, corresponding to three bond lengths and to the angles  $\theta$  and  $\varphi$ .



We have fixed the angle  $\varphi$  to a value of 96°, close to the average of its value in the  $D_{3h}$  structure (90°) and in the  $C_{4v}$  structure (101.34°). Optimization of the angle  $\theta$  gives a value of 112.1°, not very different from the average of its value in the  $D_{3h}$  structure (120°) and in the  $C_{4v}$  structure (101.34°). This substantiates the conclusion that during Berry's pseudorotation the axial and equatorial ligands move synchronously<sup>4,8</sup> (in the CNDO calculation,<sup>4</sup> the corresponding values of  $\varphi$  and  $\theta$  for one  $C_{2v}$  structure were 97.5 and 112.5°). The destabilization with respect to the  $D_{3h}$  structure is 2.6 kcal/mol, about half the barrier.

An alternative to the Berry's pseudorotation (BPR) is the turnstile rotation (TR) mechanism.<sup>4</sup> This invokes a  $C_s$  structure either as a transition state or as a local minimum. From a CNDO calculation, the computed barriers for the two mechanisms were found equal to 3.5 kcal/mol for the BPR and 9.1 kcal/mol for the TR, and it was claimed that, the differences in the barriers being within the range of error of the method of calculation, exchange could occur equally well by the two mechanisms for PF<sub>5</sub>.<sup>4</sup> An extended Hückel calculation by Hoffmann, *et al.*, produced computed

barriers of 1.4 kcal/mol (BPR) and 10.0 kcal/mol (TR) and it was concluded that in a symmetrically substituted phosphorane of the PR<sub>5</sub> type, interconversion of axial and equatorial positions through a  $C_s$  transition state is unlikely.<sup>8</sup> To investigate further the possibility of the TR mechanism, we have carried out a calculation for one  $C_s$  structure. Only the angles  $\theta_2$  and  $\theta_3$



were optimized, and an idealized bond length of 1.55 Å (average value in the  $D_{3h}$  structure) was used for all five bonds. We assumed a staggered conformation.<sup>41</sup> Optimization of the angles produced the values  $\theta_2 = 85^\circ$  and  $\theta_3 = 95^\circ$  (similar values were obtained from the CNDO and extended Hückel calculations<sup>4,8</sup>). The corresponding energy reported in Table V gives a barrier of 18.1 kcal/mol for the TR mechanism. It is doubtful that further optimization would appreciably lower this value.<sup>42</sup> In agreement with the conclusion of Hoffmann, *et al.*,<sup>8</sup> this high value of the barrier seems to rule out the TR mechanism for the interconversion of PF<sub>5</sub>. It has been pointed out that even PX<sub>3</sub>Y<sub>2</sub> molecules, where a distortion from  $D_{3h}$  to  $C_s$  would be expected on the basis of electronegativity differences, retain a local trigonal-bipyramidal geometry at phosphorus.<sup>8</sup>

**The Energetics of Polytopal Rearrangement in Phosphoranes.** The relative rates of exchange in PR<sub>2</sub>F<sub>3</sub> compared with PRF<sub>4</sub> systems (with R an alkyl group) are considerably slower.<sup>2</sup> By analogy with the exchange mechanism proposed for PF<sub>5</sub> and PRF<sub>4</sub>, it has been assumed that the exchange in PR<sub>2</sub>F<sub>3</sub> proceeds through a square-pyramidal conformation. Then the difference in the relative rates of exchange can be rationalized on the basis of the electronegativity rule (the more electronegative ligands occupy the axial sites of TBP and the basal positions of SP).<sup>1</sup> The barrier height is relatively low for RPF<sub>4</sub> since, in order to exchange equatorial and axial fluorine atoms, this species need not pass through a high-energy TBP intermediate with the ligand R occupying an axial site. For the R<sub>2</sub>PF<sub>3</sub> species, on the other hand, such a high-energy intermediate would be required.<sup>1</sup> This explanation puts the emphasis on the energy differences between the possible TBP structures for a given species and ignores the energy difference between the TBP and the SP structures. This is based on the idea that substitution in PF<sub>5</sub> should not substantially alter the barrier to Berry rearrangement. In fact, it has been stated explicitly that "one might infer as a guiding principle in constructing exchange mechanisms that energy differences between isomeric trigonal bipyramids for a particular molecular formulation are appreciable while energy differences between a nonrigid trigonal bipyramid and its associated square-pyramidal conformation are

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

(40) One further possibility is that d functions serve only to overcome some inadequacies in the basis set (this may be the case with a minimal basis set<sup>19</sup>). We believe that the basis set used is extended enough to avoid this difficulty.

(41) The energy difference between the staggered and eclipsed conformations is 0.07 kcal/mol from the extended Hückel calculation.<sup>8</sup>

(42) Small variations in the P-F<sub>i</sub> bond length did not produce any appreciable change.

Table VI. Relative Stabilities of Isomeric Structures for the Various Phosphoranes (in kcal/mol)<sup>a</sup>

	PF <sub>5</sub>	PF <sub>4</sub> H	PF <sub>3</sub> H <sub>2</sub>	PH <sub>4</sub> F	PH <sub>5</sub>	PH <sub>4</sub> SH	PH <sub>3</sub> NH <sub>2</sub>	PF <sub>4</sub> NH <sub>2</sub>
SP I <sup>b</sup>	4.8	9.2	13.0	7.9	4.2	11.9	18.6, <sup>e</sup> 16.4 <sup>f</sup>	18.0 <sup>e</sup>
II <sup>c</sup>	8.5	7.5	10.2	9.6	4.8	14.9	20.4	19.8
C <sub>s</sub> <sup>b</sup>	18.1		28.3					
TBP <sup>b,d</sup>			14.6	15.8				

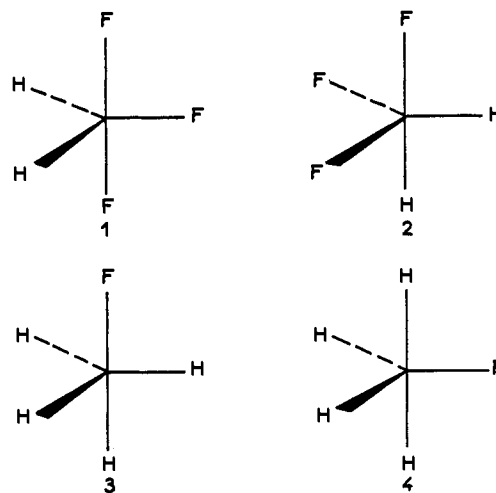
<sup>a</sup> With respect to the most stable TBP structure (the structures considered are the ones which are expected to be the most stable on the basis of the electronegativity rule or from extended Hückel calculations<sup>5</sup>). <sup>b</sup> With d functions on the P atom. <sup>c</sup> No d functions on the P atom. <sup>d</sup> See text. <sup>e</sup> No d functions and a planar structure assumed for the nitrogen atom. <sup>f</sup> With d functions on the nitrogen atom (the SP structure is found more stable with a pyramidal amino group).

relatively small.<sup>2,43</sup> Calculation of the energy differences between the TBP and SP structures for RPF<sub>4</sub> and R<sub>2</sub>PF<sub>3</sub> species should tell us if the above principle is valid (we rely on the assumption that the square pyramid is an adequate representation of the transitory exchange state).

We have reported in Table VI the energy differences between the TBP, SP, and C<sub>s</sub> structures for a variety of compounds.<sup>44</sup> We find that the energy difference between the TBP and SP structures increases regularly from PF<sub>5</sub> (4.8 kcal/mol) to PF<sub>4</sub>H (9.2 kcal/mol) and PF<sub>3</sub>H<sub>2</sub> (13.0 kcal/mol). This suggests that the energy difference between the TBP and SP structures may play a role in the exchange mechanism which is as important as the energy difference between isomeric trigonal bipyramids (the computed energy difference between the two isomeric structures 1 and 2 of PF<sub>3</sub>H<sub>2</sub> is 14.6 kcal/mol and is thus comparable to the energy difference between the TBP and SP structures). For PH<sub>4</sub>F, the energy difference of 15.8 kcal/mol between the two structures 3 and 4 is much larger than the energy difference of 7.9 kcal/mol between the TBP and SP structures and accounts indeed for the absence of intramolecular exchange in PY<sub>4</sub>F molecules.<sup>2</sup> Our results for PF<sub>3</sub>H<sub>2</sub> are in qualitative agreement with estimates by Holmes which put the energy difference between the TBP and SP structures as 3.8 kcal/mol for PF<sub>5</sub> and in the range 10–15 kcal/mol for a PF<sub>3</sub>R<sub>2</sub> compound.<sup>2</sup> Rauk, *et al.*, have investigated the stereochemistry of pseudorotation in phosphoranes through the use of a model where electronegativity differences are simulated by small alterations in the nuclear charge of one or more hydrogen atoms of PH<sub>5</sub>.<sup>7</sup> Calculations for PH<sub>5</sub> account for the substituted phosphoranes PR<sub>n</sub>X<sub>5-n</sub> where R is represented by a hydrogen atom and X is a modified hydrogen atom with a nuclear charge corresponding to an electronegativity of 2.9 on the Pauling scale (approximately the electronegativity of nitrogen or chlorine and less than the one of fluorine). With this model the energy difference between the TBP and

(43) However, this does not mean that the energy difference between the TBP and SP structures is negligible. In the same reference<sup>2</sup> this energy difference is reported as 3.8 kcal/mol for PF<sub>5</sub> and 10–15 kcal/mol for R<sub>2</sub>PF<sub>3</sub> species.

(44) In the corresponding calculations, the basis set is similar to the one for PF<sub>5</sub>: (8, 4) set contracted to [4, 2] for the first-row atoms, (10, 6) set contracted to [6, 4] for the second-row atoms P and S (with one set of d functions on the P atom), (4) set contracted to [2] for the H atom. Only idealized TBP and SP geometries were considered, with a 120° angle between the equatorial bonds in the TBP structure and an angle of 101.34° (computed value in PF<sub>5</sub>) for the X<sub>ap</sub>PY<sub>bas</sub> angle in the SP structure. P–F bond lengths were taken from the optimized geometry for PF<sub>5</sub> and P–H bond lengths from the geometry used for PH<sub>5</sub> by Rauk, *et al.*<sup>7</sup> Other bond lengths and angles were P–S, 2.09 Å; S–H, 1.33 Å; P–N, 1.70 Å; ∠PSH 94°. The structure of the amino group was taken from the experimental geometry of ammonia (NH bond length of 1.01 Å and HNH angle of 106.7 or 120° for a planar amino group).



the SP structures is 3.4 kcal/mol for a PX<sub>5</sub> compound, decreases to 1.4 kcal/mol for a PRX<sub>4</sub> system, and raises to about 6 kcal/mol for a PR<sub>2</sub>X<sub>3</sub> system (then the energy difference between the two isomeric TBP structures is 6.9 kcal/mol). Compared with our results, the model of Rauk, *et al.*, seems to predict energy differences which are relatively low, possibly as a result of the neglect of factors other than the inductive electronic effects.<sup>45</sup>

Hoffmann, *et al.*, have suggested that C<sub>s</sub> geometries could serve as transition states for site interchange mechanisms of PX<sub>3</sub>Y<sub>2</sub> compounds (with X more electronegative than Y) since the C<sub>s</sub> structure has three sites of high electron density.<sup>8</sup> For this reason we have computed and reported in Table VI the energy difference between the idealized C<sub>s</sub> and the TBP structures for PF<sub>3</sub>H<sub>2</sub>. In fact the C<sub>s</sub> structure appears highly unfavorable, the destabilization with respect to a SP structure being even larger in PF<sub>3</sub>H<sub>2</sub> than in PF<sub>5</sub>. The turnstile mechanism has indeed been considered as an alternate possibility for PY<sub>2</sub>F<sub>3</sub> molecules, the barrier for this mechanism being 10 kcal/mol in the CNDO approximation compared with 6 kcal/mol for the mechanism through the SP transition state.<sup>4</sup> The CNDO approximation seems to underestimate the barriers associated with the exchange mechanisms.

(45) One will notice that the energy differences from Rauk, *et al.*, parallel our results reported in Table VI when no d functions are included for the P atom (respectively 8.5, 7.5, and 10.2 kcal/mol for PF<sub>5</sub>, PF<sub>4</sub>H, and PF<sub>3</sub>H<sub>2</sub>). These authors do not mention whether their model calculations for the phosphoranes PR<sub>n</sub>X<sub>5-n</sub> included d functions or not. Anyway the results of Table VI point to the importance of d functions with respect to the calculation of such energy differences, since the trend of the variation may depend on these d functions (*cf.* in Table VI the increase from PF<sub>5</sub> to PF<sub>4</sub>H when d functions are included compared with the decrease in the absence of d functions). That the actual energies are sensitive to the presence of 3d functions has already been emphasized by Hoffmann, *et al.*, for the relative stabilities of isomeric structures<sup>8</sup>.

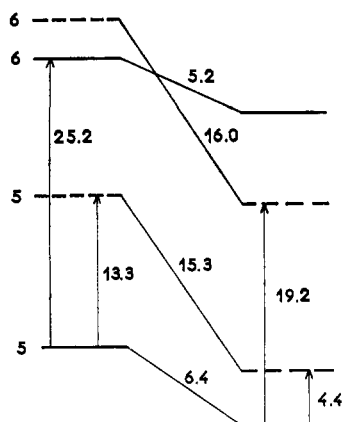


Figure 1. Barrier to rotation about the P-N bond for  $\text{PF}_4\text{NH}_2$ : left, no d functions on nitrogen; right, with d functions on nitrogen; (—) planar structure at nitrogen; (-----) pyramidal structure at nitrogen.

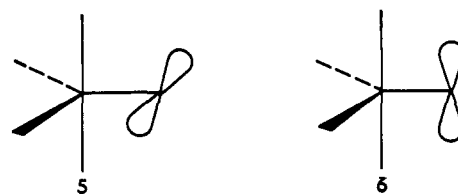
From Table VI, it is found that the energy difference between the TBP and SP structures are dramatically increased for  $\text{PH}_4\text{X}$  and  $\text{PF}_4\text{X}$  when X is a substituent bearing a single  $\pi$  system (X = SH or  $\text{NH}_2$ ). This energy difference amounts to 11.9 kcal/mol for  $\text{PH}_4\text{SH}$  and 16–18 kcal/mol for  $\text{PH}_4\text{NH}_2$  and  $\text{PF}_4\text{NH}_2$  compared with 7.9 kcal/mol for  $\text{PH}_4\text{F}$  or 4.8 kcal/mol for  $\text{PF}_5$ . According to Muetterties, *et al.*, "essentially all  $\text{XPF}_4$  molecules in which there is no extensive  $\pi$  bonding between X and P or those in which that  $\pi$  bonding is cylindrical undergo a very rapid intramolecular rearrangement, while the amino- and alkylthiotetrafluorophosphoranes show experimentally a slow exchange limit."<sup>46</sup> They suggest that "the difference in rearrangement rates for these two classes of  $\text{XPF}_4$  molecules is due to P-N multiple bonding, with the P-N bond rotation and a Berry rearrangement inextricably coupled." From the data of Whitesides and Mitchell,<sup>47</sup> they have estimated the rearrangement barrier in  $(\text{CH}_3)_2\text{NPF}_4$  to 9.5 kcal/mol (a value somewhat lower than our energy difference for  $\text{PF}_4\text{NH}_2$ ). Since they have estimated the P-N rotational barrier to 11.1 kcal/mol, they suggest that "the resistance to P-N bond rotation makes a major contribution to the Berry rearrangement barrier in  $\text{R}_2\text{NPF}_4$  molecules."<sup>46</sup>

The rotation barriers in  $\text{PR}_4\text{X}$  compounds, with X a substituent bearing a single  $\pi$  system, have been discussed previously by Hoffmann, *et al.*,<sup>8</sup> with the conclusion that an equatorial donor will prefer to have its donor orbital in the equatorial plane mostly as the result of donor-framework  $\pi$  bonding effects. From extended Hückel calculations, conformation 5 of  $\text{PF}_4\text{NH}_2$  with the nitrogen lone pair in the equatorial plane was found more stable than conformation 6 by 6 kcal/mol when d orbitals were not included and 17 kcal/mol with d orbitals.

We have computed the energy difference between the two conformations 5 and 6 in  $\text{PH}_4\text{SH}$ ,  $\text{PH}_4\text{NH}_2$ , and  $\text{PF}_4\text{NH}_2$ . For  $\text{PH}_4\text{SH}$  conformation 5 is found more stable by 10.5 kcal/mol with d functions on phosphorus and 9.9 kcal/mol without d functions.<sup>48</sup> This

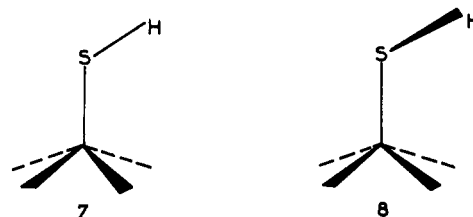
(46) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972).

(47) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).



substantiates the conclusion of Hoffmann, *et al.*, that the differential effect of d functions is a smaller effect than the interaction of donor and framework orbitals. Experimentally, the nmr spectra of S-substituted thio-tetrafluorophosphoranes show nonequivalence of the axial fluorines,<sup>49,50</sup> hence supporting conformation 5 as the most stable, and the rotation barrier in  $(\text{C}_6\text{H}_5)_3\text{P}-\text{SC}_2\text{H}_5$  has been estimated to 5.2 kcal/mol.<sup>51</sup>

We have also computed the energy difference between the two configurations 7 (staggered) and 8 (eclipsed) of the SP structure for  $\text{PH}_4\text{SH}$ . The eclipsed configuration 8 is found more stable by 0.2 kcal/mol, a difference which is hardly significant. However, this result supports the assumption of Muetterties, *et al.*, that the barrier to P-N rotation for the SP transition state in  $\text{R}_2\text{NPF}_4$  should be much lower than in the ground state because of the fourfold character of the barrier.<sup>46</sup>



Calculation of the rotation barrier about the P-N bond in the aminophosphoranes  $\text{PH}_4\text{NH}_2$  and  $\text{PF}_4\text{NH}_2$  has been carried out with either a planar amino group or a pyramidal one. From a first set of calculations with only s and p functions on the N atom, conformation 5 with a planar amino group was found the most stable for  $\text{PF}_4\text{NH}_2$  and the barrier to rotation about the P-N bond with the amino group kept planar amounts to 25 kcal/mol (*cf.* Figure 1),<sup>52</sup> a value somewhat higher than the experimental estimate of 11.1 kcal/mol in  $\text{PF}_3(\text{NH}_2)_2$ <sup>46</sup> (the computed rotation barrier with the amino group kept pyramidal is lower, 15 kcal/mol). The lack of d functions on the N atom certainly tends to favor the planar nitrogen conformation<sup>34</sup> so we performed another set of calculations by including d functions on the N atom.<sup>53</sup> From Figure 1 it is found that although the d functions on nitrogen stabilize much more in the pyramidal conformation, the most stable conformation still corresponds to a planar amino group (however, the energy difference between these two conformations is only 4.4 kcal/mol). It may be that the addition of more d functions would predict the pyramidal structure to be the most stable; however, our result is similar to the one obtained for the mole-

(48) Since our calculations on  $\text{PH}_4\text{SH}$  were only intended as model calculations for thiofluorophosphoranes, we assume that the thio group occupies an equatorial or apical position in  $\text{PH}_4\text{SH}$ .

(49) S. C. Peake and R. Schmutzler, *Chem. Commun.*, 1662 (1968).

(50) S. C. Peake and R. Schmutzler, *J. Chem. Soc. A*, 1049 (1970).

(51) M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *Zh. Strukt. Khim.*, **10**, 1113 (1969).

(52) The results for  $\text{PH}_4\text{NH}_2$  parallel the ones for  $\text{PF}_4\text{NH}_2$  and will not be reported in detail.

(53) The exponent of the d functions on the N atom was taken as 0.75.



cules  $R_2NPX_2$  ( $R = H$  and  $Me$ ,  $X = H$  and  $F$ ) where it was found both theoretically and experimentally that the nitrogen atom adopts a planar structure.<sup>54-57</sup> However, if the planar structure is the most stable for conformation 5, the pyramidal one is the most stable for conformation 6. Then the rotation process around the P-N bond appears coupled to the inversion process at the N atom. The computed value for the rotation barrier from conformation 5 (with a planar nitrogen) to conformation 6 (with a pyramidal nitrogen) is now 19.2 kcal/mol, still much higher than the experimental estimate of 11.1 kcal/mol in  $PF_3(NH_2)_2$ . We consider these numbers as indicative; for instance, we have not attempted to optimize the pyramidal angle at nitrogen in conformation 6 (furthermore the pyramidal angle at nitrogen was treated as a single variable, namely  $\angle HNH = \angle HNP$ ).

## Conclusion

Through *ab initio* calculations with a medium-size basis set, we have investigated the electronic structure of  $PF_5$  together with the energetics and stereochemistry of polytopal rearrangements for a number of model phosphoranes. We have shown that the description of the bonding given previously for  $PH_5$ ,<sup>7,8</sup> may be extended to  $PF_5$  and that, although d functions on the phosphorus atom may be omitted for a qualitative description of the bonding, they do play a significant role in the bonding as shown by the population analysis. The difference between the axial and equatorial P-F bond lengths is well accounted for by our calculation.

The computed barrier to the Berry's pseudorotation, represented by the energy difference of 4.8 kcal/mol between the TBP and SP structures for  $PF_5$ , is in good agreement with "experimental estimates." A higher value of 8.5 kcal/mol is obtained in the absence of d functions. The influence of d functions on the barrier is traced to their effective participation in the bonding. The mechanism of turnstile rotation seems to be ruled out as an alternative to Berry's pseudorotation since the corresponding  $C_s$  structure is found less stable than the TBP structure by 18 kcal/mol.

The computed energy differences between the TBP

(54) I. G. Csizmadia, A. H. Cowley, M. W. Taylor, L. M. Tel, and S. Wolfe, *J. Chem. Soc., Chem. Commun.*, 1147 (1972).

(55) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, **93**, 6772 (1971).

(56) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(57) It has been found that either the nitrogen inversion barriers are small or the nitrogen sites are planar in those compounds where  $d_{\pi}-p_{\pi}$  interaction might be important. However, Lehn has pointed out that the computed inversion barrier in silylamine is small independently of the introduction of d functions on silicon, so that other factors like inductive electron release by the silicon atom may also account for these low barriers.<sup>34</sup> This is substantiated by our results for  $PF_3NH_2$ . The planar conformation at nitrogen is found the most stable independently of the presence of d functions on phosphorus, and the energy difference between the planar and pyramidal conformations at nitrogen is 4.4 kcal/mol with d functions on phosphorus and 4.1 kcal/mol without d functions.

and SP structures together with the energy differences between the TBP isomeric structures account for the following characteristics of the intramolecular exchange in the substituted fluorophosphoranes  $PR_nF_{5-n}$ : for  $PF_4H$  the computed barrier to Berry's pseudorotation is 9 kcal/mol, in agreement with the experimentally rapid intramolecular exchange for  $RPF_4$  species; the computed energy difference between the TBP and SP structures for  $PF_3H_2$  raises to 13 kcal/mol with an energy difference between the two isomeric TBP structures of 14.6 kcal/mol, so that both energy differences account for the slow intramolecular exchange in  $R_2PF_3$  species; for  $PH_4F$ , the energy difference between the TBP and SP structures is only 7.9 kcal/mol, so that it is the energy difference of 15.8 kcal/mol between the two isomeric TBP structures which accounts for the absence of intramolecular exchange in  $PR_4F$  systems.

The slow exchange limit shown experimentally by the amino- and alkylthiotetrafluorophosphoranes, in contrast to other  $XPF_4$  molecules, is well accounted for by the high barriers to Berry's pseudorotation computed for  $PH_4SH$ ,  $PH_3NH_2$ , and  $PF_4NH_2$ . Finally, the aminophosphorane molecule  $PF_4NH_2$  is predicted to have a planar nitrogen in its most stable conformation (5) and a pyramidal nitrogen in the less stable conformation (6), so that the rotation process around the P-N bond appears coupled to the inversion process at the N atom.

There are several limitations in the above treatment. The use of a limited basis set certainly affects the computed energy differences. Apart from  $PF_5$ , only idealized models were considered for the ground state and the transition state, and it has been emphasized that, if the actual geometry in the molecule departs significantly from the idealized one, it is unrealistic to consider any of the idealized mechanisms.<sup>8</sup> With this respect, geometry optimization will change the reported energy values.<sup>58</sup> Furthermore we have limited ourselves to a few points on each energy surface, when an intricate process like the exchange mechanism in aminophosphoranes would require the computation of a complete potential surface. Still, our limited results seem to account for a number of experimental facts.

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(58) One of the referees called our attention to the fact that in molecules of the type  $PX_3Y_2$  with X the electronegative ligands, the established equilibrium parameters<sup>8</sup> rather correspond to a distortion away from  $C_s$ , with a significant difference in bond distances for the so-called axial and equatorial ligands. Such a distortion away from the  $C_s$  may lead to a relative stabilization of the turnstile mechanism with respect to the values reported in Table VI for an idealized  $C_s$  structure. Another referee pointed out that the "square pyramid" structure is no longer square for most species other than  $PF_5$ ; hence one should search for extrema on the potential surfaces. However, this is presently beyond the scope of this work.