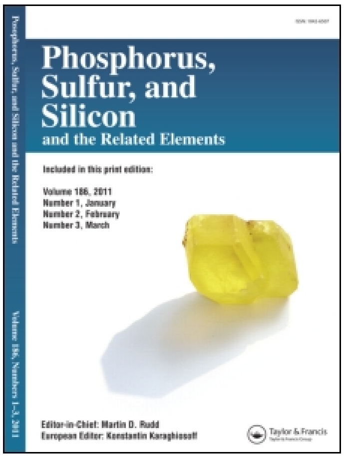

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A MODEL FOR CALCULATING CONFORMATIONAL ENERGIES IN PENTACOORDINATE PHOSPHORUS COMPOUNDS

Robert R. Holmes[a]
[a] Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Holmes, Robert R.(1995) 'A MODEL FOR CALCULATING CONFORMATIONAL ENERGIES IN PENTACOORDINATE PHOSPHORUS COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 98: 1, 151 — 182

To link to this Article: DOI: 10.1080/10426509508036947
URL: http://dx.doi.org/10.1080/10426509508036947

Phosphorus, Sulfur, and Silicon, 1995, Vol. 98, pp. 151–182
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A MODEL FOR CALCULATING CONFORMATIONAL ENERGIES IN PENTACOORDINATE PHOSPHORUS COMPOUNDS[1,2]

ROBERT R. HOLMES

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

(Received March 2, 1977)

A model is developed which allows the estimation of the relative stability of all trigonal bipyramidal (TP) and square pyramidal (SP) isomers of a given pentacoordinate phosphorus compound. It is based on the widely used pseudorotational hypothesis. The model makes use of activational energies governing fluxional behavior for simple acyclic derivatives of known structure and results of theoretical and spectroscopic studies defining TP-SP energy differences. Based on these criteria, apicophilicity scales are constructed for the TP and SP with the additional constraints that they have the same range and correlate linearly with each other as a function of ligand electronegativity. The resultant model which incorporates ring strain and steric terms has general applicability and should prove of considerable predictive value in quantifying pentacoordinate intermediates and transition states postulated in phosphorus reaction mechanisms. The model gives relative isomer energies in excellent agreement with those obtained from ab initio calculations and reproduces measured $\Delta G^{\ddagger}$ for intramolecular ligand exchange on cyclic and acyclic derivatives to within ±1.5 kcal/mol.

INTRODUCTION

In order to evaluate possible mechanistic alternatives in phosphorus reactions proceeding via postulated pentacoordinate intermediates,[3] it would be highly desirable to have the means of comparing the relative energies of the various isomers that may be involved. Not only is the structure of the intermediate or transition state of concern but also whether the entity postulated undergoes intramolecular reorientation during its lifetime.

It appears that sufficient information is at hand to construct a suitable model which would have predictive value in ascertaining the course of a chemical reaction in phosphorus chemistry. There are three principal sources of information. These are (1) structural and spectroscopic studies which establish the ground state configuration of isolatable pentacoordinate phosphorus compounds,[4,5] (2) theoretical studies[6–13] defining trigonal bipyramidal (TP)-square pyramidal (SP) energy differences for simple acyclic derivatives, and (3) temperature-dependent NMR

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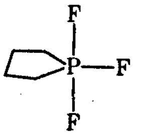
Note: With reference to *J. Am. Chem. Soc.*, **100**, 433 (1978), the following corrections to the article should be noted. Table IV: entry 9, TP C 16.4, SP B 16.0, SP F 17.0; entry 11, SP 9.1; entry 15, TP 14.5, SP 17.5; entry 16, TP 13.5; entry 18, SP 22.1; entry 25, SP 13.0; entry 26, SP 18.1; entry 27, SP 17.3; entries 34 and 35, SP 14.7; entry 41, TP 10.0; entry 43, SP 17.9. Table V, delete entry $R_2NC(CH_2)_2$. Table IX, successive entries under column labeled XI should read 44.8, 47.8, 50.8 and 56.8, and footnote c deleted. The next to the last sentence on p. 177 should read, "The SP XI is traversed on the way to the transition state X." Below isomers 52 and 35 of Figure 2, the number should be 26.6 and Formula f on p. 175 should have an R appended to the ring substituent.

studies[14-28] yielding energies of activation governing fluxional behavior of both acyclic and cyclic derivatives.

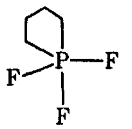
Structurally, the trigonal bipyramid is the most stable conformer for acyclic and monocyclic five-coordinate phosphorus compounds.[4,5] However, in derivatives[29-31] containing multiple small-membered rings coupled with the presence of electronegative ligands and ring unsaturation, the square or rectangular pyramid (RP) may become the most stable conformer. In all derivatives, two generalizations regarding positioning of ligands prevail, the "element effect," which states that the most electronegative groups prefer to locate at apical positions,[32] and the "ring strain" rule, which suggests that less strain results if four- and five-membered rings locate preferentially in apical-equatorial positions rather than in diequatorial positions of a trigonal bipyramid.[3a,20-24,27,32-35]

In comparing the TP with the SP, similar rules may be invoked for these two effects in the SP. The most electronegative ligands prefer basal positions and small-membered rings preferentially occupy dibasal positions. These "rules" are based on considerations[5] for an idealized SP having an apical-basal angle of 105°. This geometry is thought to represent the most stable conformer[7] and is the one postulated in a Berry pseudorotation for PF_5.[36]

With the dominant importance of these two effects in each of the two basic pentacoordinate structures, one has little difficulty in representing the lowest energy TP or lowest energy SP isomer, even for derivatives containing a variety of substituents. Difficulty arises when the two rules set up a competition for ligand sites. Thus, $(CH_2)_4PF_3$ is assigned the structure[32] I based on low-temperature NMR data

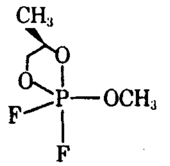


I

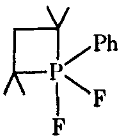


II

rather than II, whereas, when the electronegativity of the ligands does not differ as widely as C and F, as in III, the strain rule becomes dominant.[37] If one goes to a four-membered ring, however, e.g., IV, even with ligands differing widely in electronegativity, the fluorine atom appears to be displaced from its usual location at an apical site.[38] Although it is understandably more difficult to locate a four-membered ring in diequatorial positions of a TP, it would be advantageous to quantify substituent effects to resolve possible ambiguities.

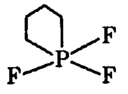


III

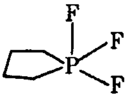


IV

Furthermore, one can argue that the NMR information which supported the structural conclusions in these examples also does not rule out the possibility of a SP representation. As an example, for $(CH_2)_4PF_3$, the SP isomers V and VI each



V



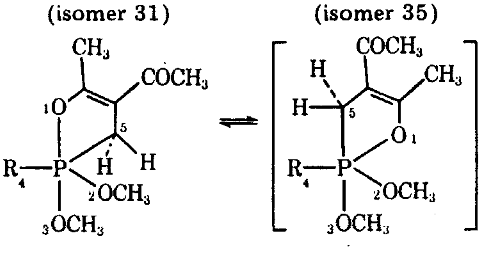
VI

have two fluorine atom environments consistent with the ^{19}F NMR data at −80°C, and presumably would have less ring strain than I since the angle distortion from the 90° "strain-free" ring angle at phosphorus to the phosphorus angles existing in the idealized TP is more than the corresponding angle distortions necessary to reach the idealized SP (90° C—P—C angle → 105° in V and essentially no change in forming VI). Hence, it appears necessary to sequence not only TP isomers in terms of relative energy but also both TP and SP isomers in one self-contained series.

We shall attempt the construction of a model of this sort, embodying the concepts outlined above. This will be done in terms of a numerical scale which will allocate a different value for each ligand, the value being a function of the position occupied in the TP or SP structure. In addition the presence of a ring strain term and a steric factor will be incorporated. In a more limited sense, π-bonding effects will be considered.

GENERAL CONSIDERATIONS

In order to see how a scale might be formulated in a qualitative manner, consider the following observations. Gorenstein[20] found that the free energy of activation for pseudorotation of the adduct of trimethyl phosphite and methyl vinyl ketone (VII) in methylene chloride-d_2 solution obtained from analysis of ^1H NMR spectra

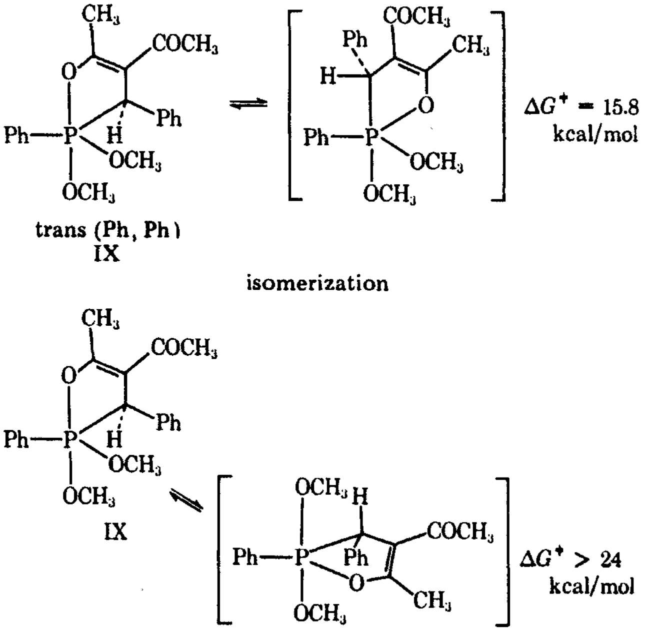


VII, R = OCH_3
VIII, R = Ph

run at 100 MHz is 9.6 ± 0.2 kcal/mol. He reported a[20] similar value, $\Delta G^{\ddagger} = 9.5$ (9.9) ± 1 kcal/mol, from line shape analysis of the adduct of dimethyl phenylphosphonite with methyleneacetylacetone (VIII) in methylene chloride-d_2 at 100 MHz. The pseudorotation, assuming the Berry mechanism, is conventionally reported to proceed via the least stable TP, shown in brackets. The similar values are not surprising since, in each case, a difference in apicophilicity between an oxygen and a carbon atom appears to be the major factor involved in reaching the transition state.

For a more highly substituted ring derivative, additional NMR exchange processes may be observed. For example, the addition product of dimethyl phenylphosphonite and benzylideneacetylacetone, IX, undergoes isomerization and, at higher temperature, epimerization.

The respective activational energies, $\Delta G^{\ddagger}$, are 15.8 and >24 kcal/mol,[20] presumably associated with the transition states.



trans (Ph, Ph)
IX

isomerization

IX

epimerization

Comparison of ground and transition states for the isomerization for IX with these states for the exchange process for VIII suggests that the near 6 kcal/mol difference in $\Delta G^{\ddagger}$ between the two processes is associated with a steric affect[20] due to the presence of the ring phenyl substituent in IX. For the epimerization of IX, the $\Delta G^{\ddagger}$ value appears to approximate the increase in strain energy associated with orienting the five-membered ring in diequatorial positions of a TP compared to the relatively strain-free apical-equatorial arrangement, since the ligand electronegativities are comparable in the ground and postulated transition states.

Proceeding in this manner, using $\Delta G^{\ddagger}$ data for other nonrigid phosphorus derivatives, our resultant model would be limited to the estimations of relative energies for TP isomers. In fact, for the processes associated with derivatives VII–IX above, the transition states may be better represented by SP rather than TP isomers.

The Berry mechanism,[36] which serves as a model for the postulated pseudorotations, involves the simultaneous bending of a pair of equatorial and a pair of apical bonds, causing the formation of an intermediate SP on the way to the interconverted trigonal bipyramid.

These interconversions have been summarized most conveniently in terms of topological representations[39] such as the one shown in Figure 1. The edges represent square pyramidal states under the Berry hypothesis. Equally well, topological maps represent the turnstile process[40] since this process is permutationally indistinguish-

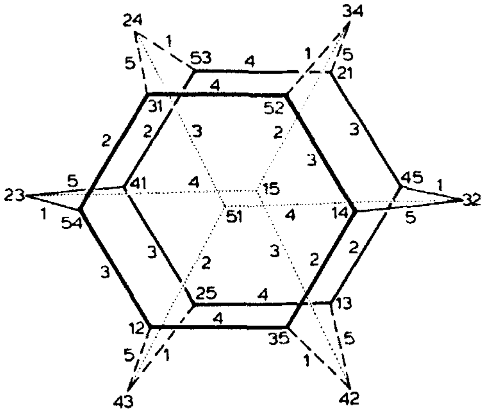


FIGURE 1 Topological diagram[39] for pseudorotations summarizing isomerization (heavy solid lines) and epimerization processes (light solid lines) for compound IX (see Figures 2 and 3). Higher energy epimerization are shown by dashed lines and forbidden isomerizations for IX are indicated by dotted lines. The numbers refer to the axial positions in the TP or apex position in the SP as shown in Figures 2 and 3. The placement of basal ligands in the SP is established by the pairs of numbers identifying the two connecting TPs. These will be trans pairs in the SP.

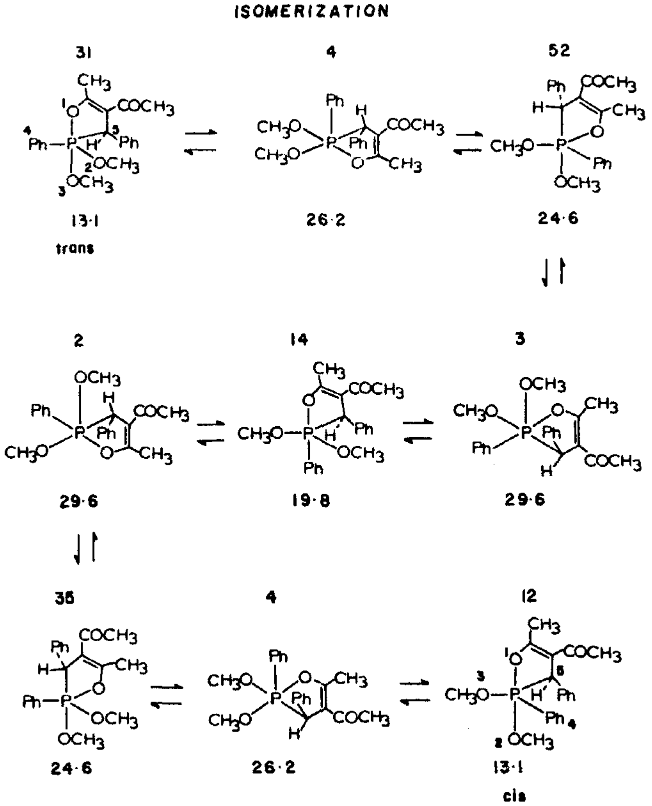


FIGURE 2 Intramolecular isomerization of the adduct of dimethylphenyl phosphonite and benzylideneacetylacetone IX via the low-energy pseudorotational pathway.[33] The numbers above each structure identify the isomer on the topological diagram shown in Figure 1. The numbers below each structure give the relative isomer energy in kcal/mol via the terms in Tables I, V, and VI.

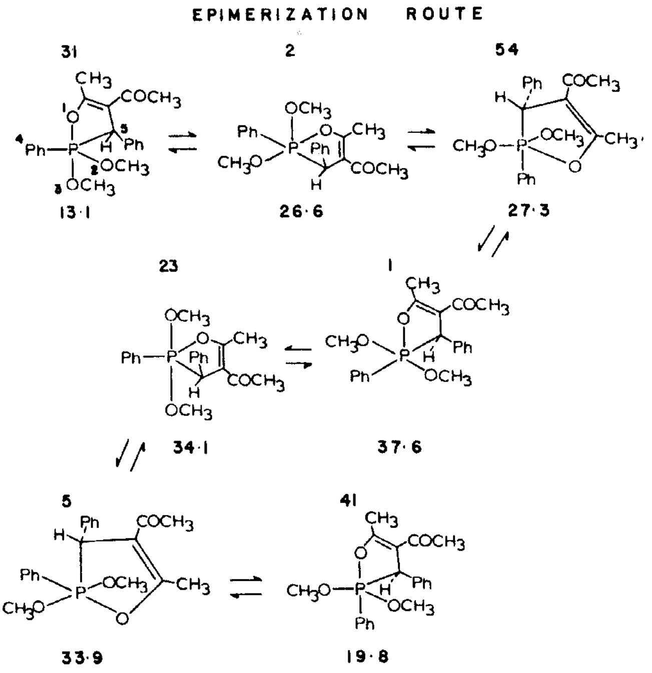


FIGURE 3 Part of the intramolecular epimerization route of the adduct of dimethyl phenylphosphonite and benzylideneacetylacetone IX via the low-energy pseudorotational pathway.[33] The numbers above each structure identify the isomer on the topological diagram shown in Figure 1. The numbers below each structure give the relative isomer energy in kcal/mol via the entries in Tables I, V, and VI.

able from the Berry process. If turnstile rotation is invoked, then the edges represent the transition state peculiar to that mechanism.[40] However, since most of the literature of interest here has been interpreted in terms of the Berry pseudorotational process, and both theoretical estimates[7–10,13,41] and solid-state structural distortions[5a] favor the Berry process, we will not consider the turnstile process further.

The relationship between a postulated SP and TP transition state may be seen more clearly by examination of the complete interconversions accompanying the isomerization (Figure 2) and epimerization (Figure 3) of the addition product of IX. With reference to the topological diagram[39] in Figure 1, the highest energy TP conformations that must be traversed for the isomerization process are the 35 and 52 isomers while the highest energy SPs are 2 and 3. For the epimerization of 31 to occur, a higher energy TP containing a diequatorial ring must be reached. This is the 23 isomer connecting the isomerization routes. The latter are shown by heavy solid lines in Figure 1. The high-energy SP isomer for this process is 1. As a result, if effective comparisons are to be made, it becomes necessary to devise complementary scales which will establish an order of isomer energies involving both trigonal bipyramidal and square pyramidal conformations. The best place to begin is with the simpler acyclic phosphoranes so that ring strain and steric factors do not unnecessarily complicate the problem.

MODEL CONSTRUCTION

Both experimentally and theoretically, the most studied pentacoordinate molecule in PF_5 whose ligands are presumed to exchange rapidly on the NMR time scale even down to $-200°C$.[42,43] Various estimates[9-12] put the energy difference between the SP and TP around 4 kcal/mol. A recent two-dimensional potential function applied to spectroscopic data has led to an estimate[13] near 3 kcal/mol while an ab initio calculation gave 4.8 kcal/mol.[7] Furthermore, interpretation of the spectroscopic data indicates that indeed the Berry process is operating in PF_5.[13] For both $PClF_4$ and PCl_2F_3, temperature-dependent NMR studies gave exchange barriers of 4.2[14] and 7.2 kcal/mol,[16] respectively. For H_2PF_3[17] and $(CH_3)_2PF_3$,[19] similar studies gave values of 10.2 and 17.8 kcal/mol, respectively, for ligand exchange in these fluxional molecules.

Although it is probable that the exchange barrier cited for $PClF_4$ represents an energy difference between the ground state TP and transition state SP, since one ligand acts as a pivot in the favored Berry process,[44] the exchange barriers for PCl_2F_3, $(CH_3)_2PF_3$, and H_2PF_3 are more ill defined. Under the Berry pseudorotational hypothesis, one or two pseudorotations are needed to account for the exchange (Figure 4), depending on which process represents the lower energy path.

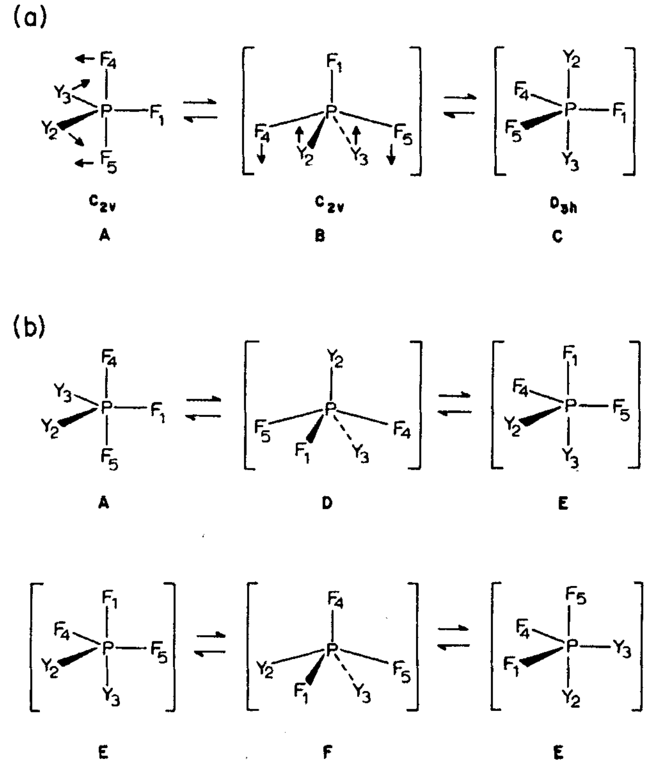


FIGURE 4 Pseudorotational processes for intramolecular exchange in Y_2PF_3 derivatives: (a) simple Berry process; (b) successive Berry processes. Bracketed isomers represent transition states or intermediates.

Rauk *et al.*[6] performed nonempirical molecular orbital calculations on a model system applicable here, PH_2X_3 (where X is approximately 0.8 unit more electronegative than the proton on the Pauling scale). According to their results, process (b) is favored for PH_2X_3 and the SP isomer of the type F in Figure 4 would represent the barrier configuration, since it is estimated to have the highest energy of the isomers in process (b). Steric factors could alter the preferred exchange route. However, the derivatives PH_2F_3, PCl_2F_3, and $(CH_3)_2PF_3$ are minimal in that respect.

Proceeding on this basis then, we are in a position to construct an isomer sequencing scale which will be internally calibrated to reproduce the activational exchange energies $\Delta G^\ddagger$ for this well-characterized series of acyclic phosphoranes. A numerical value of an element effect, which varies with the position occupied in the TP and SP, will be established for each ligand. This is accomplished by equating the $\Delta G^\ddagger$ value for an exchanging member to the difference in the sum of terms representing the positions occupied in the SP transition state l_i(SP), and the TP ground state, l_i(TP).

An additional term must be included to reflect the inherent instability of the acyclic SP relative to the TP. We will refer to this term as Δ. The $\Delta G^\ddagger$ value that we adopt for PF_5 places the SP 4 kcal/mol above the TP. However, the phosphorus and fluorine atoms differ in electronegativity by about 2 units. To remove the electronegativity factor which is to be incorporated in the scale itself, $\Delta G^\ddagger$ for the hypothetical PY_5 molecule must be obtained where the electronegativities of P and Y are the same. Accordingly, we have

$$\sum l_i(\mathrm{SP}) - \sum l_i(\mathrm{TP}) + \Delta = \Delta G^\ddagger \quad (1)$$

where l_i is the value of the element effect appropriate to the position occupied. For PF_5,

$$l(\mathrm{F_{ap}}) + 4l(\mathrm{F_{bas}}) - 2l(\mathrm{F_{ax}}) - 3l(\mathrm{F_{eq}}) + \Delta = \Delta G^\ddagger(\mathrm{PF_5}) \quad (2)$$

where ap and bas are the two types of positions in the SP and ax and eq are the two types in the TP. Similarly for $(CH_3)_2PF_3$

$$l(\mathrm{F_{ap}}) + 2l(\mathrm{F_{bas}}) + 2l(\mathrm{C_{bas}}) - 2l(\mathrm{F_{ax}}) - l(\mathrm{F_{eq}}) - 2l(\mathrm{C_{eq}}) + \Delta = \Delta G^\ddagger((\mathrm{CH_3})_2\mathrm{PF_3}) \quad (3)$$

Since the l_i values are relative, we choose zero values for l_C for carbon ligands (assigned an electronegativity of 2 representing one extreme of the scale) which occupies an equatorial TP or the complementary apical SP position. Correspondingly, at the other end of the scale, the element effect for fluorine (electronegativity of 4) is assigned a zero reference value when it is present in an axial TP or complementary basal SP site. This reduces 2 to

$$l(\mathrm{F_{ap}}) - 3l(\mathrm{F_{eq}}) + \Delta = \Delta G^\ddagger(\mathrm{PF_5}) \quad (4)$$

and simplifies Equation 3 to

$$2l(\mathrm{C_{bas}}) + l(\mathrm{F_{ap}}) - l(\mathrm{F_{eq}}) + \Delta = \Delta G^\ddagger((\mathrm{CH_3})_2\mathrm{PF_3}) \quad (5)$$

Subtraction of Equation 5 from Equation 4 gives

$$l(\mathrm{F_{eq}}) + l(\mathrm{C_{bas}}) = 6.9 \quad (6)$$

TABLE I

Relative Values of the Element Effect (l_i) for Use in Estimating Isomer Energies (kcal/mol)[a]

		TP		$\mathcal{A}^b$	$-\mathcal{A}$	SP		$-\mathcal{A}^b$	$\mathcal{A}$
	χ^c	eq	ax	ax–eq	(ref C = 0)	ap	bas	bas–ap	(ref C = 0)
C	2	0.0	7.0	7.0	0.0	0.0	4.0	4.0	0.0
H	2.5	1.3	4.7	3.4	3.6	2.3	2.2	−0.1	4.1
Ph	2.7	1.7	3.9	2.2	4.8	3.0	1.7	−1.3	5.3
N, Cl	3.0	2.2	2.8	0.8	6.2	3.8	1.2	−2.6	6.6
O	3.5	2.8	1.3	−1.3	8.3	5.1	0.4	−4.7	8.7
F	4.0	3.0	0.0	−3.0	10.0	6.0	0.0	−6.0	10.0

[a] To the sum of these element values for a SP, 7.0 kcal/mol must be added to obtain the energy of an acyclic SP relative to a TP isomer. If steric and/or ring strain effects are present, these terms must be included. Ring strain values are summarized in Table VI and steric effects are listed in Tables V and VII. [b] Relative values for apicophilicity $\mathcal{A}$ in a TP (ax–eq) or SP (ap–bas). The smaller or more negative values of $\mathcal{A}$ indicate a greater stabilization for a particular element in an apical position of either a TP or SP. [c] Electronegativity scale.

Considerations such as the pseudorotation process discussed for the phosphoranes VII and VIII suggest an apicophilicity difference of the order of 10 kcal between ligands having extremes in electronegativity values. Accordingly, we adopt this range as a convenient one to use for the element scales for both the TP and SP.

It remains to apportion this range in apicophilicities to the equatorial and axial sites of the ground state TP as a function of the ligand electronegativity. Fortunately, the well-studied series, $(CH_3)_nPF_{5-n}$ (n = 0–3), whose structures have been fully characterized by electron diffraction,[45] allows insight into how the apportionment might be approximated. It is noted that the apical P—F and equatorial P—C bond distances increase nearly linearly with progressive methyl substitution and the percent increase for the axial bond is about twice that for the equatorial changes. The P—F equatorial bond changes are even a more slowly varying function. The greater variation in the axial bonds of the TP are consistent with electron pair repulsion arguments,[46] while other workers[47] have shown that axial P—F force constants successively decrease in a linear fashion in accord with the bond distance increase in this series. Consequently, we assign a variation in the element effect to the axial position of the TP about double that for the equatorial site over the range of the electronegativity scale. In other words, with $l(C_{eq}) = 0$, the element effect, $l(F_{eq})$, is assigned a value of 3. This leaves a value of 7 for $l(C_{ax})$.

Having fixed the value of the element effect of the axial fluorine atom in a TP, the value of $l(C_{bas})$ in a SP is obtained from Equation 6 as 3.9. With this value

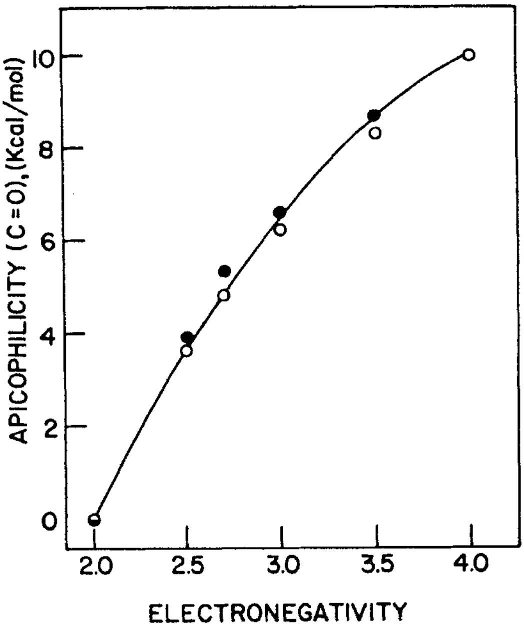


FIGURE 5 Apicophilicity values (from Table I) relative to the carbon atom set equal to zero (half-filled circle) for the trigonal bipyramid (open circles) and square pyramid (filled circles) as a function of electronegativity.

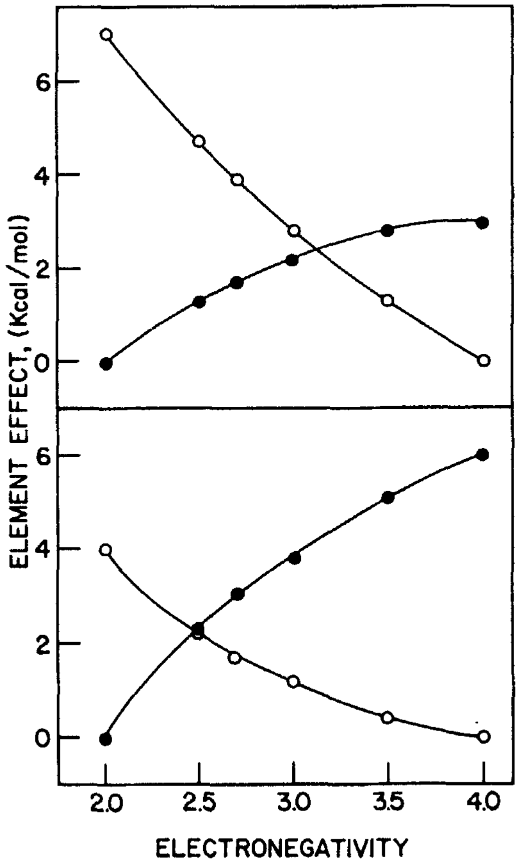


FIGURE 6 Element effect (from Table I) as a function of electronegativity (upper) for axial (open circles) and equatorial (filled circles) positions of a trigonal bipyramid and (lower) for basal (open circles) and apical (filled circles) positions of a square pyramid.

rounded to 4, and noting that we are using the same range of apicophilicity values for the SP and the TP (namely, 10), the element effect for an apical fluorine atom in the SP results as $l(F_{ap}) = 6$. From expression 4 or 5 then, Δ of 7 is obtained.

A smooth variation in the values of the element effects as a function of electronegativity is expected. Under the constraints already defined, a linear variation was at first used, but later modified slightly to get a best fit with the $\Delta G^{\ddagger}$ values for the acyclic derivatives employed to calibrate the apicophilicity scales. Making the range in apicophilicities for the SP different from that for the TP did not improve the fit. The resultant values of the element effects are summarized in Table I and a plot of the apicophilicites for the TP ($-A$, column 6) and SP (A, column 10) vs. χ is shown in Figure 5.

The variation in the values of the element effect with χ for each position of the TP (upper) and SP (lower) is presented in Figure 6. The agreement between $\Delta G^{\ddagger}$ calculated from Table I and those determined from NMR studies is seen in Table II to be within ±0.9 kcal/mol.

TABLE II

Comparison of Observed and Calculated Values of $\Delta G^{\ddagger}$ for Intramolecular Ligand Exchange (kcal/mol)

$\Delta G^{\ddagger}$	PF_5	$PClF_4$	PCl_2F_3	PH_2F_3	$P(CH_3)_2F_3$
Calcd.	4.0	2.5	8.0	11.8	18.0
Obs.	4.0[a]	4.2	7.2	10.2	17.8
Ref[b]	7, 9-13	14	16	17	19

[a] As discussed in the text, this is an average value calculated from spectroscopic data and theoretical estimates. It refers to a SP which has an apical basal angle in the range of 101-105°. [b] References for observed $\Delta G^{\ddagger}$ values.

COMPARISON WITH NONEMPIRICAL CALCULATIONS

A major achievement of the use of this scale (Table I) is the close correspondence of relative isomer energies for the series PH_nF_{5-n} with those reported by Rauk *et al.*[6] based on nonempirical MO methods. This agreement is shown in Table III where not only is the order of isomer energies the same with one exception, the second and third isomer for PH_4X, but the values average to within ±0.5 kcal/mol with each other over the entire series.

The series, PH_nX_{5-n}, is for an X atom of about 0.8 electronegativity unit greater than that for the proton[6]; whereas we obtain the best agreement between values for the fluoro series, PH_nF_{5-n}, with a somewhat higher electronegativity difference, about 1.5 units based on our assignment of electronegativities. Other series with a reduced ligand electronegativity difference give relatively lower values but a similar order of isomer energies as that shown in Table III.

This lowering in values for comparable ligand electronegativity differences to that of Rauk *et al.*,[6] i.e., ~0.8, is somewhat expected since our series was internally calibrated with respect to $\Delta G^{\ddagger}$ values from NMR behavior of pseudorotating phosphoranes. Since these molecules are deforming intramolecularly through SP transition states along the Berry coordinate, and it has been shown from x-ray diffraction data that it is unrealistic to expect that an idealized transition state will be reached,[5a] our element effect values (Table I) then underestimate idealized SP isomer energies compared to that resulting from the MO calculations[6] which deal with idealized states. Further, X in the series PH_nX_{5-n} is a proton with a nuclear charge increased to 1.1 to bring about the X difference of ~0.8 unit.[6] In this regard, it should not behave precisely like any real atom.

The excellent agreement in isomer energies between the molecular orbital method[6] and that based on $\Delta G^{\ddagger}$ data for fluxional behavior provides confirmation that the transitional states are those involved in the Berry exchange mechanism. Single-crystal x-ray analysis[2b,5a,29-31,48-52] on a wide variety of cyclic phosphoranes also establishes that the Berry coordinate is the appropriate one correlating[5a] observed structural distortions between TP and SP geometries.

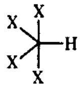
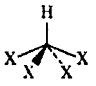
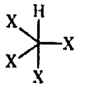
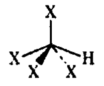
STERIC AND RING STRAIN TERMS

Having established a firm basis to deal with the element effect in "sterically free" acyclic phosphoranes, the next step is to ascertain energy terms for ring and steric

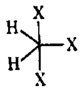
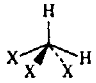
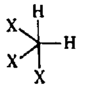
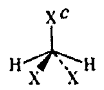
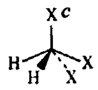
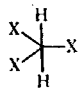
TABLE III

Isomer Energies Relative to Ground State Trigonal Bipyramids of PH_nX_{5-n} and PH_nF_{5-n} Molecules (kcal/mol)

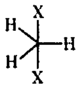
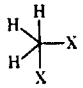
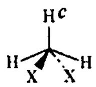
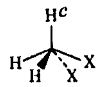
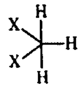
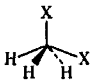
PHX_4[a] (PHF_4[b])

			
	1.4 (2.0)	6.5 (6.4)	7.0 (7.9)

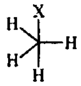
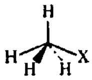
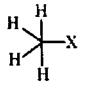
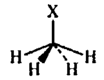
PH_2X_3 (PH_2F_3)

					
	5.5 (5.9)	6.9 (6.4)	~11[d] (11.8)	11.7 (11.8)	13.0 (12.8)

PH_3X_2 (PH_3F_2)

					
	7.0 (6.4)	~8.5 (9.8)	9.5 (9.8)	~13.5[e] (12.8)	15.7 (15.7)

PH_4X (PH_4F)

			
	6.5 (7.3)	6.9 (6.4)	13.3 (13.2)

[a] Values not in parentheses are from ref 6. It was not stated in ref 6 whether d orbitals were included or not. [b] Values in parentheses are obtained from Table I for members of the PH_nF_{5-n} series. [c] The order of isomer stabilities predicted from the EHMO method of Hoffman et al.[8] agrees with the ordering in this table except for the interchange of these square pyramidal pairs. However, trigonal bipyramid and square pyramid orders were compared as independent sets and no values were given. [d] Approximate value estimated from Figure 5 of ref 6. [e] Approximate value estimated from Figure 4 of ref 6.

strains. As discussed above for derivatives VIII and IX, values for ring and steric strain terms as a function of site occupancy in a TP may be qualitatively deduced when $\Delta G^‡$ data for a series of related phosphorane derivatives are available, in which these effects are systematically incorporated. Now, however, instead of entertaining only the possibility of a TP transition state, SP transition states appearing along the pseudorotational coordinate are likely candidates. For the acyclic derivatives used in developing the values for the element effect (Table I), we have shown that the SP transition state is the favored one. However, as other factors enter in more structured cyclic derivatives, with or without bulky groups, TP transition states may compete with SP transition states, especially for ligand exchange behavior requiring multiple pseudorotations.

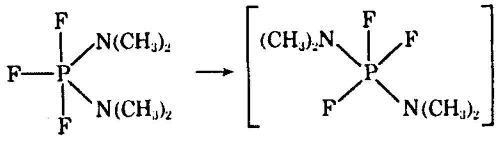
In one sense, the procedure for establishing a steric or ring strain contribution is simplified, since the wide assortment of phosphoranes, whose NMR exchange behavior has been adequately characterized, provides several examples (in many cases) where the same steric or ring strain interaction is present.

Hence, the procedure is to first sum up the element effect terms (Table I) for each isomer potentially representative of a ground or transition state in a system undergoing intramolecular exchange. Next, an estimate is made of steric or ring strain terms for both the ground state isomer (usually a TP) and a transition state in a series undergoing systematic substitutions. Finally, readjustments are made in a last recycling stage. However, none of the values in Table I are altered in this procedure.

The usefulness of the approach depends then on the ability of a simple set of terms to reproduce observed $\Delta G^\ddagger$ data. This is shown in Table IV where calculated values of $\Delta G^\ddagger$ for exchange phenomena are compared with $\Delta G^\ddagger$ values determined from NMR measurements (observed).[14-28] Steric and ring strain terms used in conjunction with element effects are summarized in Tables V and VI, respectively. A set of steric interactions between the biphenylene substituent and the R group for derivatives 43–52 of Table IV are listed separately in Table VII. The use of these tables results in an average deviation of ±1.5 kcal/mol between measured and calculated $\Delta G^\ddagger$ values for the phosphoranes listed in Table IV. Only those elements appear in Table I for which a sufficient number of $\Delta G^\ddagger$ values have been determined to allow cross-checking. After construction of these tables, $\Delta G^\ddagger$ values for epimerization of a variety of oxaza spirocyclics were noted.[56] Application of the model here gave $\Delta G^\ddagger$ values within the 1.5 kcal/mol limit.

ILLUSTRATIVE CALCULATIONS

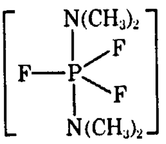
As an example of the calculation of a $\Delta G^\ddagger$ value from Tables I and V–VII, consider the exchange process for entry 8 in Table IV which is predicted by the model to go by way of the SP transition state of type B in Figure 4. The difference gives $\Delta G^\ddagger$ = 20 kcal/mol (obsd, 19.6 kcal/mol[19]) for activation by path (a) of Figure 4.



type B (via path (a))

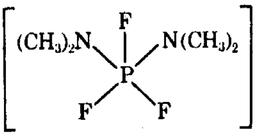
Σl_i	7.4	Table I	Σl_i	8.4	Table I
			Δ	7.0	Table I (footnote *a*)
			$N(CH_3)_2$ π loss	12.0	Table V (footnote *d*)
				27.4	

The other possible transition states, type C and F of Figure 4, are respectively lower in isomer energy by the same path (a) (type C) or higher in energy by a different path (path (b) of Figure 4 for F).



type C (via path (a))

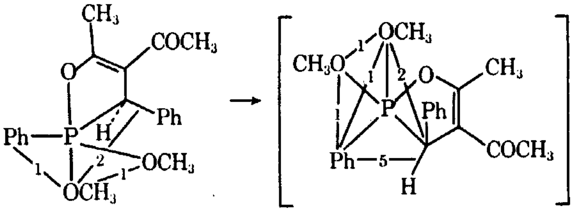
		Table
Σl_i	14.6	I
$N(CH_3)_2$ π loss	12.0	V (footnote *d*)
	26.6	



type F (via path (b))

		Table
Σl_i	8.4	I
$N(CH_3)_2$ π loss	12.0	V (footnote *d*)
Δ	7.0	I (footnote *a*)
$(CH_3)_2NPN(CH_3)_2$ steric	6.5	V
	33.9	

A somewhat more complex example is illustrated by entry 16 of Table IV which is predicted by the model to isomerize (Figure 2) by way of the SP transition state.



IX

(individual steric terms are indicated)

Σl_i	7.1	Table I
Ring strain	2.0	Table VI
Steric	4.0	Table V
	13.1	

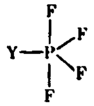
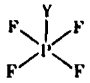
Σl_i	11.6	Table I
Ring strain	1.0	Table VI
Steric	10.0	Table V
Δ	7.0	Table I (footnote *a*)
	29.6	

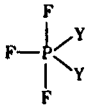
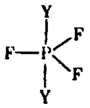
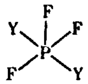
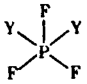
The difference gives $\Delta G^{\ddagger} = 16.5$ kcal/mol (obsd, 15.8 kcal/mol[20]). Other isomers along the isomerization route (Figure 2) are of lower energy. A similar calculation for the epimerization process, encountered at higher temperatures for this phosphorane (Figure 3), suggests that the SP is likewise favored over the TP for the transitional state representation (see entry 19 of Table IV).

Thus, for both these exchange processes, possible TP transition states, isomers 52 or 35 of Figure 2 for the isomerization and isomer 23 of Figure 3 for the

TABLE IV

Calculated and Observed $\Delta G^{\ddagger}$ (kcal/mol) for Intramolecular Ligand Exchange for Phosphoranes

No.[a]	Ground state	Transition state	$\Delta G^{\ddagger}$, kcal/mol		Ref
			SP	Obsd	
					
	Y				
1	F		4.0	4.0[b]	7,9–13
2	Cl		2.5	4.2[b]	14
3	$N(CH_3)_2$		8.6	8.8	14
4	$N(i\text{-}Pr)_2$		8.6	7.5	15

		Transition states				
						
		C	B	F		
		(via path (a) of Figure 4)		(via path (b) of Figure 4)		
		$\Delta G^{\ddagger}$, kcal/mol				
	Y	TP C[c]	SP B[c]	SP F[c]	Obsd	Ref
5	Cl	7.2	*8.0*	*8.0*	7.2[b]	16
6	H	12.8	11.8	*11.8*	10.2[b]	17
7	NH_2	19.2	*20.0*	*20.0*	*d*	18
8	$N(CH_3)_2$	19.2	*20.0*	26.5	19.6	19
9	Ph	*14.4*	*14.4*	16.0	18.7	19
10	CH_3	20.0	18.0	*18.0*	17.8[b]	19

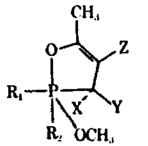
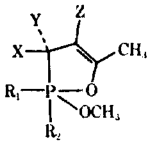
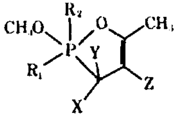
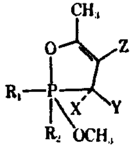
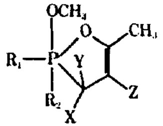
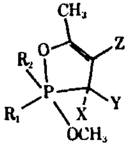
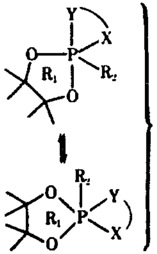
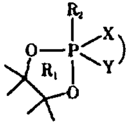
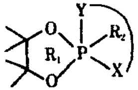
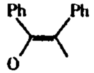
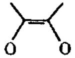
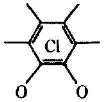
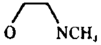
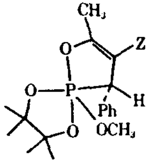
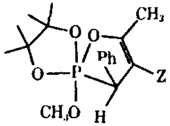
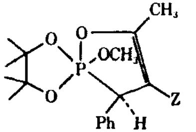
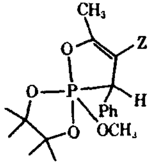
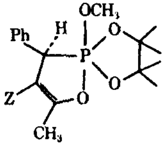
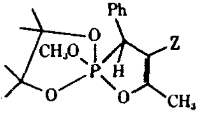
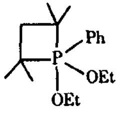
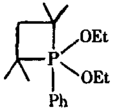
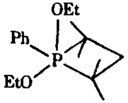
	Ground state[e]				Transition states					Ref
	 Z = COCH$_3$									20
							$\Delta G^{\ddagger}$, kcal/mol			
	R$_1$	R$_2$	X	Y			TP	SP	Obsd	
11	OCH$_3$	OCH$_3$	H	H			8.5	8.6	9.7	
12	OCH$_3$	OCH$_3$	CH$_3$	CH$_3$			12.5	13.1	14.5	
13	OCH$_3$	OCH$_3$	H	Ph			10.5	11.0	12	
14	Ph	OCH$_3$	H	H			8.5	11.5	9.7	
15	Ph	OCH$_3$	CH$_3$	CH$_3$			10.1	17.1	17.2	
16	Ph	OCH$_3$	H	Ph			11.5	16.5	15.8	
17	OCH$_3$	OPh	H	Ph			10.5	11.0	12.5	
	 Z = COCH$_3$									20
18	OCH$_3$	OPh	H	Ph			21.0	23.1	21.8	
19	Ph	OCH$_3$	H	Ph			21.0	24.5	>24	
										21
	R$_1$	R$_2$	Y⁀X							
20	CH$_3$	Ph					8.2	6.7	8.9	
21	CH$_3$	OPh					16.0	16.1	14.1	

TABLE IV (*Continued*)

No.	R_1	R_2	Y⌒X	$\Delta G^{\ddagger}$, kcal/mol TP	SP	Obsd	Ref
22	CH_3	OCH_3		21.0	14.7	21.2	
23f	CH_3	OPh		21.0	14.7	20.5	
24	CF_3	OPh		22.3	14.0	21.8	
25f	CF_3	OPh		17.3	14.0	17.4	
26	CF_3	$OCH(CF_3)_2$		20.0	20.3	21.0	
27	CF_3	OPh		17.4	19.5	20.4	
		Transition states					
28				21.0	21.1	17.6	21
29				18.0	22.1	>23	21
30				3.7	8.4	11	22

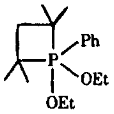
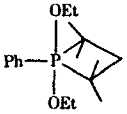
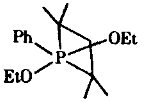
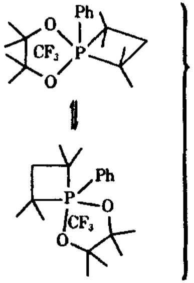
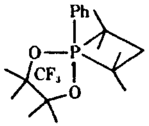
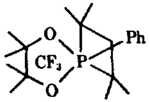
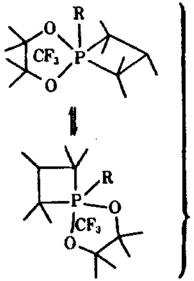
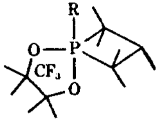
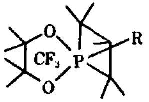
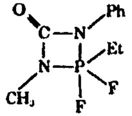
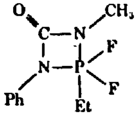
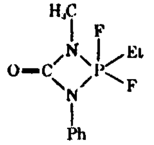
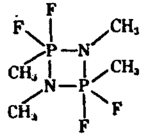
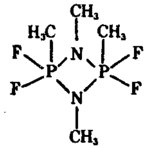
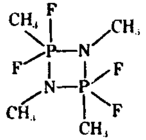
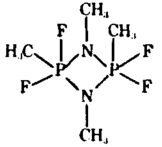
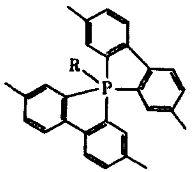
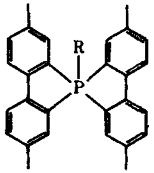
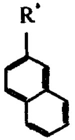
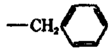
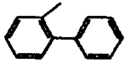
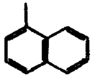
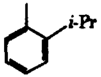
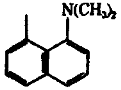
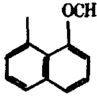
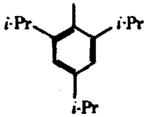
31				9.5	16.7	15	23
32				14.2	11.7	20.1	23
							24
	$R^{g,h}$						
33	OPh			9.5	6.8	~9	
34	$N(CH_2)_4$			17.6	17.2	16.2	
35	$N(CH_3)_2$			17.6	17.2	16.2	
36	Ph(cis)			14.2	11.7	19.6	
37	Ph			14.2	11.7	>22	
38	$HC{=}C(CH_3)_2$			20.3	14.0	19.1	
39	*i*-Pr			20.3	14.0	17.8	
40	CH_3			20.3	14.0	16.9	

TABLE IV (*Continued*)

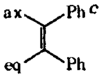
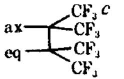
No.	$R^{g,h}$	Transition state		TP	SP	Obsd	Ref
41				3.0	12.4	11.6	25
42	 			10.0	15.4	~13.3	25
							
43					12.6	<11.9	26
44	$-CH_3$				12.6	12.5	26
45	$-C_2H_5$				12.6	13.6	26

46		12.6	12.0	26
47		15.9	15.7	26
48		16.9	17.1	26
49		17.9	17.8	27
50		21.9	>21	28
51		21.9	>23	28
52		25.9[i]	26.0	27

[a] Italicized number entries signify that the ground state SP structure is equal to or lower in energy than the TP. [b] $\Delta G^{\ddagger}$ values used in constructing Table I. [c] The favored transition state is italicized. [d] Although $\Delta G^{\ddagger}$ for ligand exchange has not been measured, $\Delta G^{\ddagger}$ for uncorrelated rotation of the amino groups was determined to be 12.3 kcal/mol.[18] This value should set a lower limit to the exchange energy. [e] For these and the following entries in this table only one isomer of each configuration is shown for simplicity, e.g., cis and trans x and y to R_1 unless stated otherwise. Refer to the respective references for additional detail. [f] Related derivatives containing R_2 = SPh show similar values to R_2 = OPh, implying a similar apicophilicity.[21b] However, this may reflect steric relief in the transition state by the SPh ligand. Further, the ground state of the analogous substance,[2b] $R_1 = CH_3$, $R_2 = NMe_2$, and Y-X = Ph(O)C=C(O)Ph is considerably displaced toward the rectangular pyramid.[5a] Additional $\Delta G^{\ddagger}$ values for other thio derivatives are needed before an element effect, steric terms, and a π bonding contribution may be ascertained. [g] The x-ray structure of a related substance (ref 29) shows a SP conformation. In agreement, the calculation shows an equal or greater stability for the SP relative to the TP ground state for derivatives 33 and 38–40. [h] All derivatives are located trans to 3-CH_3 except OPh which is reported as a mixture of cis and trans and Ph(cis) as shown. [i] The SP transition state formulated here for the triisopropyl derivative differs from that postulated in ref 27. See text for a discussion of this apparently unique example.

TABLE V

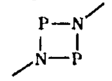
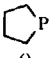
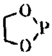
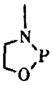
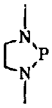
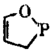
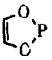
Relative Values of Steric Factors for Use in Estimating Isomer Energies[a]

Steric interaction[b] (R = CH_3, C_2H_5)	Steric factor, kcal/mol	Steric interaction[b]	Steric factor, kcal/mol
R_2NPNR_2	6.5	$CH_3\overset{\vert}{N}PCH_3$	2.0
$R_2NPC(CH_3)_2$		$PhOP\overset{\vert}{C}HPh$	
PhPPh	6.0	$ROP\overset{\vert}{C}HPh$	
$PhP\overset{\vert}{C}(CH_3)_2$		$CH_3\overset{\vert}{N}PCl$	
$PhP\overset{\vert}{C}HPh$	5.0	FPPh	
$PhNPC_2H_5$		ROPPh	1.0
$(CH_3)_2NP\overset{\vert}{C}(CH_3)_2$	4.0	ROPOR	
RPPh		ROPOPh	
$ORP\overset{\vert}{C}(CH_3)_2$		$CH_3\overset{\vert}{N}POCH(CF_3)_2$	
$CH_3\overset{\vert}{N}PPh$			3.0
$PhOP\overset{\vert}{C}(CH_3)_2$	3.0		2.0
$CH_3\overset{\vert}{N}PC_2H_5$		NR_2, NH_2[d]	6.0
$CH_3\overset{\vert}{N}POPh$		$R\overset{\vert}{N}P$[e]	4.0

[a] For application to axial–equatorial orientations in the TP and both apical–basal and basal–basal cis ligand orientations in the SP. All interactions for a particular isomer should be summed up to obtain the steric destabilization. The only exception that arises is when two identical steric interactions are present which involve a single apical substituent and this substituent (not a member of a ring) has no other steric interactions. In this case, a value is taken for these two interactions which equals 1.5 times that for a single interaction. See entry 32 of Table IV, which represents this type of exception.
[b] The P–C– and P–N– bonds are part of ring systems. [c] These represent steric terms between substituents of the ring which are applied only when these rings are oriented in axial–equatorial positions of a TP. [d] This is not a steric term but represents a loss in π bonding and is applied in an additive sense when these groups are in locations other than the equatorial site of a TP. [e] This is the same type of term as in (*d*) but refers to an NR group as part of a four- or five-membered ring. It is applied in the same manner as the term in (*d*). If the ring is oriented diequatorially, it might be expected that this term should also be applied since the equatorial nitrogen atom is not properly oriented for effective π bonding, at least according to extended Hückel calculations.[8] However, the resultant loss in π bonding must not be as great as that encountered when a nitrogen atom is located in other than an equatorial site of a TP. See footnote *c* to Table VI. X-ray structures of phosphoranes containing Me_2N groups in equatorial sites show these groups in planes rotated 20-30° from the axial direction.[2b] Presumably changes in π bonding effects for oxygen as a function of TP or SP site occupancy are even less important than those for nitrogen.

TABLE VI

Relative Values of Ring Strain for Use in Estimating Isomer Energies (kcal/mol)

	TP		SP	
Ring structure	ax, eq	eq, eq[a]	bas, bas	ap, bas
	8	24	2	16
	2		1	
	2	15	1	9
	2	18[c]	1	14
	2	21[c]	1	14
	2	24[c]	1	14
	2	15	1	9
	2	21	1	13
	2	23	1	15

[a] Values for rings spanning apical-basal sites of a SP are approximately 0.6 times the values for strain estimates for rings positioned in diequatorial sites of a TP. [b] Present in the bisbiphenylene derivatives, 43-52 of Table IV. [c] The variation in the strain energy for the oxaza rings in the TP reflects a 3 kcal/mol loss in π bonding for this orientation of a nitrogen atom.

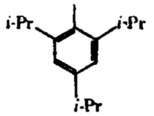
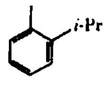
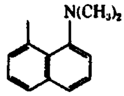
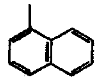
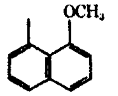
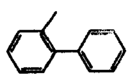
epimerization, discussed earlier under "general considerations," appear less favored as pseudorotational barriers, although isomer 23 is only 3.5 kcal/mol lower in energy then the SP transition state cited for the epimerization. The TP isomer (14 of Figure 2) along the isomerization route would appear at a trough in the potential energy surface, approximately 10 kcal/mol below the SP transition state (isomers 3 or 2), according to the model calculations. This figure is sufficiently outside the average uncertainty of the present model to suggest possible stabilization and detection as an intermediate by experimental methods.

MODEL PREDICTIONS

In this section, the utility of the numerical scales associated with the model will be explored. In this way, the degree of confidence which should be attached to the development presented here will become apparent. This is done by considering recent x-ray structures and exchange phenomena for cyclic phosphoranes. For the

TABLE VII

Relative Values of Steric Effects for Substituents in Bisbiphenylene Derivatives[a–c]

R	Steric factor, kcal/mol	R	Steric factor, kcal/mol
	10		6
	8		5.5
	8		5

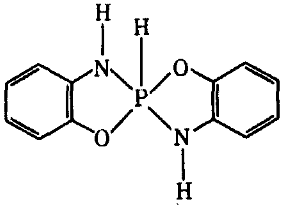
[a] For application when the R group relative to a site occupied by the bisbiphenylene group is in an axial–equatorial orientation in the TP and apical-basal or cis basal-basal orientations in the SP. [b] In addition, a steric effect between the two bisbiphenylene groups is applied when the SP transition state (shown for derivatives 43–52 in Table IV) is encountered. The value of this steric term is 4 kcal/mol. [c] The element effect to be applied for the P–C bonds formed by the biphenylene ligands is that for the phenyl group (Table I). Also a steric term (Table V) between the unique ligand and the phenyl groups applies.

latter, barrier energies have not been determined but have interesting features associated with them.

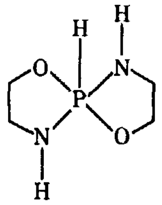
Correlation with X-Ray Data

We have recently completed the single-crystal x-ray analyses[2b,31a–d,48,49] of the cyclic phosphoranes (a–f). The availability of these structures (a–f), coupled with the appearance of those of the more constrained derivatives (g–i),[50–52] serves as an interesting test by comparing possible ground state isomer energies obtained from terms in Tables I, V, and VI. Other phosphoranes of the type (e) have been studied by x-ray diffraction. Inclusion of the derivatives[30] (e) with R = CH_3 and F extends the range of substituent electronegativities and provides an opportunity for comparison of this systematic variation with the model estimations.

The relative energies of the two isomers predicted to be the most stable by the model calculation, a TP with the rings spanning eq-ax sites and a SP with the ring system occupying basal positions (whenever possible), are summarized in Table VIII for the phosphorane structures (a–i). We have shown[5a,49] that distortions observed in these x-ray structures are along the Berry exchange coordinate between the idealized TP and SP. Quantitative evaluation of the degree of displacement along this coordinate was ascertained[5a] by considering the dihedral angles calculated from polyhedral surfaces, defined by the x-ray coordinates of the five atoms attached to phosphorus, and comparing these angles with a similar set for the idealized structures. The resulting percent displacement from the TP is listed in Table VIII for the cyclic phosphoranes of interest here.



a



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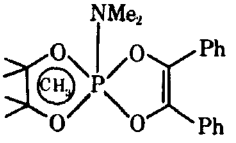
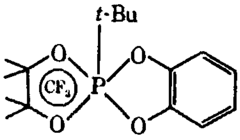
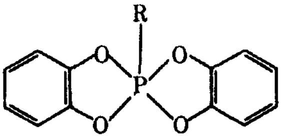


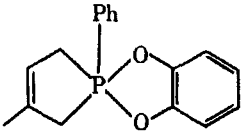
c



d

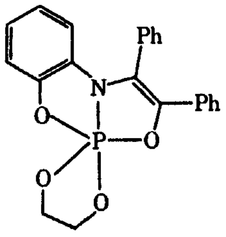


e R = Cl, Ph

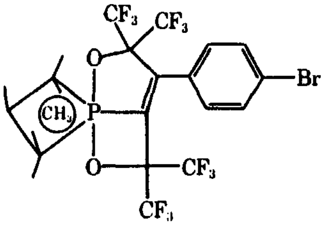


f

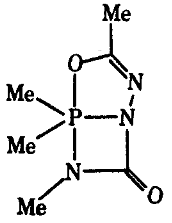
It is seen that in general the prediction of the ground state isomer representation correlates well with that observed from x-ray data. The trends in the relative ground state isomer stabilities from the model, Δ(SP-TP), and that calculated[5a] from x-ray data, percent displacement TP→SP, are directly comparable, except for derivatives (g) and (h). Because of the special ring requirements in the latter two phosphoranes, they would be expected to form a SP ground state isomer in which one of the rings must be positioned in apical-basal rather than cis-basal sites. Thus, Δ(SP-TP) is on a different scale from that of the others.



ref 50
g



ref 51
h



ref 52
i

TABLE VIII

Comparison of X-Ray Structures of Cyclic Phosphoranes with Predicted Ground State Isomer Energies

Structure	Ground state isomer energies,[a] (kcal/mol)		Δ(SP–TP)	% displacement[b] TP → SP	Ref[c]
	TP	SP			
a	12.3	22.5	10.2	~23[d]	48a
b	12.3	22.5	10.2	25	48a, c
i	14.3	19.8	5.5	(31)[d]	52
c	17.4	20.4	3.0	31	2b
d	11.6	10.6	1.0	37	48b
e (R = F)	15.2	16.6	1.4	65	30
e (R = Cl	14.4	14.4	0.0	72	31c
e (R = Ph)	13.9	13.6	−0.3	72	31a
e (R = CH_3)	12.2	10.6	−1.6	82	30
f (R = CH_3)	22.5	20.8	−1.7	~93[d]	31b
f (R = H)				81	31d
g	25.5	34.5	9.0	35	50
h	(32.6)	34.8	(2.2)		51

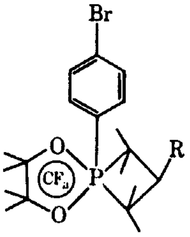
[a] From Tables I, V, and VI. [b] From dihedral angles[5a] of intersecting triangular faces formed by the positions of the five atoms attached to phosphorus using atom coordinates from x-ray data in each case. [c] Reference of x-ray studies used in determining the structural distortion (% displacement TP → SP). [d] These represent estimates and are probably within ±5%. For structure (a), the proton of the P–H bond did not refine and hence its position is somewhat uncertain. For f (R = CH_3), a disorder problem introduced some uncertainty in the positions of the five-membered carbon containing ring. For (i), the geometrical constraints associated with a four-membered ring make comparison with the idealized SP less appropriate than that for the other derivatives with only five-membered rings.

It is not expected that agreement will be quantitative, for calculation of the relative energies of possible ground state isomers is a much more severe test of the model than dealing with the greater energy differences encountered between ground and excited state configurations upon which the model was constructed. The latter energy difference, $\Delta G^{\ddagger}$, may range up to four times that of ground state isomer differences. Hence, the fact that the fluoro derivative (e) is predicted to have a TP ground state representation, but stabilized by only 1 kcal/mol, whereas that calculated[5a] from x-ray data[30] shows its structure to be slightly past the crossover point between idealized TP and SP representations (65%), is within limitations of the model.

It is noted that the ground state isomer trend toward increasing SP stabilization with a decrease in substituent electronegativity for the "catechol" derivatives (e) parallels that obtained from the x-ray data. In terms of the model calculation, this is related to the relatively greater stabilization of an equatorial ligand (TP) compared to that of an apical ligand (SP) for the two competing ground state structures as electronegativity decreases. Of course, since the ranges in element effects (Table I) for the various positions in the TP and SP are in some measure referenced to electron pair repulsion arguments,[46,53] the increasing SP character with decreasing substituent electronegativity in (e) is a function of the increased P—R axial bond pair-equatorial bond pair repulsions in the TP (idealized angle of 90°) compared with the apical-basal bond pair repulsions in the SP (idealized angle of 105°). The importance of a steric term is also indicated in this series in enhancing the formation of the SP,[31c] particularly since the hydrido derivative is a TP.[31d]

Similarly, one can examine the makeup of the contributing terms in other cases in Table VIII to rationalize the observed structural distortions. In (g), for example, the appearance of an axial ring nitrogen atom in a structure approximating a TP rather than at an equatorial location of a TP (as possible in derivative (h)) is associated with the large ring strain for the diequatorial five-membered ring placement that would be required. This would result in a relative isomer energy of 38 kcal/mol, even higher than that for the SP (34.5 kcal/mol, Table VIII).

The ground state geometry suggested by the model calculations for the ligand exchange behavior of the series of dioxaphospholanes, entries 32–40 of Table IV, is a SP for all derivatives, except entries 34 and 35, which contain an $N(CH_2)_4$ or $N(CH_3)_2$ group in the fifth position. In agreement, the x-ray structure[29] of the *p*-bromophenyl derivative (j) approximates a SP, estimated[5a] to be 84% along the distortion coordinate from the TP to the SP.



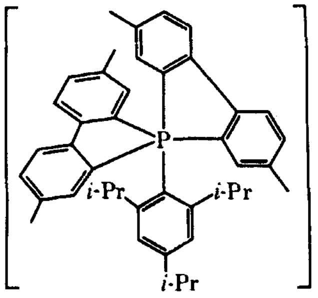
R = H, CH_3 .

j

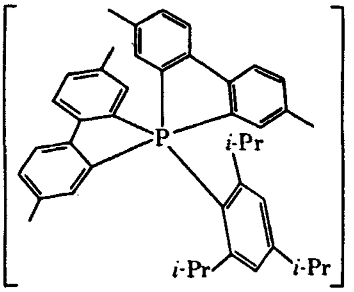
Correlation with NMR Exchange Behavior

A study of the fluxional behavior of the bisbiphenylene derivative containing the bulky triisopropyl substituent, entry 52 of Table IV, poses a unique situation. It represents the first example of a RPY_4 derivative for which the simple Berry process (with R as the pivotal ligand) is unsupported.[27] Whitesides *et al.*[27] propose the exchange intermediate X consistent with their NMR data. The model calculation is in accord with this result. The simple Berry process is favored until the steric factor for the substituent R (Table VII) exceeds 7 kcal/mol; then the isomeric state X becomes lower in energy.

For the triisopropyl derivative, X is estimated to be stabilized by 3 kcal/mol relative to the Berry state shown in Table IV. This difference appears just outside the limits of the model, ±2 kcal/mol. These results are consistent with a pseudorotation which uses one of the ring carbon atoms as a pivotal ligand. The SP transition state is then XI on the way to X. The relative energy of these isomers, as the steric factor of R changes, is given in Table IX.



X

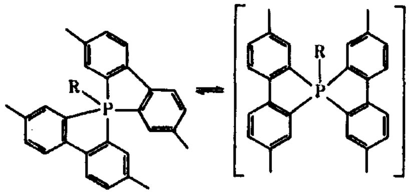


XI

TABLE IX

Relative Isomer Energies for Bis(4,4′-dimethyl-2,2′-biphenylene)-organyl-(R)-phosphoranes as a Function of the Steric Factor of R[a]

Simple Berry process

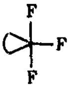


A B

R steric factor, kcal/mol	Isomer energy, kcal/mol[b]			
	A	B	X	XI
6	28.9	*46.8*	47.9	48.8
7	30.9	*50.8*	50.9	51.8
8	32.9	*54.8*	53.9	*54.8*
10	36.9	62.8	59.9	*60.8*[c]

[a] See entries 43–52 of Table IV. [b] The isomer energy italicized refers to the isomer representing the transition state. Thus, until a steric factor for R of 8 kcal/mol is reached, the simple Berry process prevails, whereas at higher steric values, the pseudorotation from the ground state A via the transition state XI to the intermediate X is indicated as the exchange process. [c] Accepting this mechanism for the triisopropyl derivative means that we should increase the steric factor for this group by 2–3 kcal/mol to obtain better agreement with $\Delta G^{\ddagger}$ observed.

TABLE X
Relative Isomer Energies for Cyclic $(CH_2)_4PF_3$ and $(CH_2)_5PF_3$ (kcal/mol)

Compd	a	b	c	d
$(CH_2)_4PF_3$	18	15	20	22
$(CH_2)_5PF_3$	3	13	11	21
				

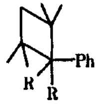
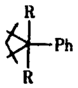
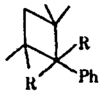
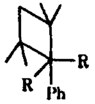
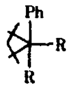
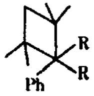
No known monocyclic phosphorane exists with a large distortion from the TP geometry.[5] The cyclic fluorophosphorane $(CH_2)_4PF_3$ mentioned in the introduction represents a limiting case in that the ligand electronegativities are most divergent and, as a consequence, sets up the possibility of the existence of a SP ground state. Even for this case the isomer sequence obtained from the model (Tables I and VI) shows that the preferred ground state is the TP isomer (b) with (a) only 3 kcal/mol higher. These isomer energies are listed in Table X. Ligand exchange by a simple Berry mechanism through SP isomer (d) suggests a $\Delta G^\ddagger$ value of 7 kcal/mol. In contrast, the much lower ring strain in the related six-membered cyclic phosphorane, $(CH_2)_5PF_3$, shows the same isomer distribution as $(CH_3)_2PF_3$ and, accordingly, should proceed by the same exchange mechanism, i.e., via path (b) of Figure 4. The activational energy indicated, 18 kcal/mol (the energy of transition state (d) minus that for ground state (a)), is over twice that indicated for exchange in $(CH_2)_4PF_3$. Although neither of these $\Delta G^\ddagger$ values has been measured, these results agree with the much higher exchange rate observed[32] for $(CH_2)_4PF_3$ compared to $(CH_2)_5PF_3$.

Extremely interesting observations were reported by Denney and co-workers[38] on the cyclic fluorophosphorane IV containing a four-membered ring. The low-temperature NMR spectra revealed[38] the presence of two isomers in the approximate ratio of 2.3:1. Rapid exchange occurred at ambient temperatures.

In Table XI tabulation of the relative isomer energies obtained by application of the model shows that isomer (c) is more stable than (e). This is in contrast to that usually reported and, in particular, reverses the order of these isomers relative to that postulated[22] in the closely related phosphorane having ethoxy groups in place of the fluorine atoms (cf. $\Delta G^\ddagger$ data for entries 30 and 31 of Table IV). The reversal, in terms of the numerical scales developed here, is due somewhat to the greater electronegativity of fluorine compared to oxygen but also due to a lower steric factor with fluorine atoms in place of ethoxy groups. Thus, the conclusions for compound IV stating[38] that the major isomer involves the (a–b) pair undergoing rapid exchange at −100°C and a minor component, identified as isomer (c), containing the ring in a diequatorial orientation, are consistent with the results in Table XI. There is a substantial barrier between the (a–b) pair and isomer (c). In order to go from isomer (a) to (c), pseudorotation through the high-energy form (d) is required (cf. Figure 3).

TABLE XI

Relative Isomer Energies for the Cyclic Fluorophosphorane IV and the Ethoxy Analogue (kcal/mol)[a]

R	a	⇄	b	c	⇄	d	e	⇄	f	g	⇄	h
F	27.7		36.0	29.7		38.7	35.9		34.7	44.9		42.7
OEt	36.8		43.8	46.3		53.5	40.5		45.2	54.0		55.5
												

[a] Each of the four TP–SP pairs shown is related by a BR process.

CONCLUSION

Although the tabulations given in this paper for element effects, ring strains, and steric terms are a first approximation and subject to some modification as further details become available regarding specific interactions in new examples, they appear sufficiently refined at present to warrant their use in correlating exchange phenomena and giving additional insight into the structural relationships among pentacoordinate isomers of phosphorus.

The correlation of the model calculations with distortions observed in x-ray structures of cyclic phosphoranes (Table VIII and accompanying discussion) suggests the manner by which idealized representations of TP and SP ground and transition states, advanced for ligand exchange phenomena, should be modified. This structural refinement should prove of assistance in considering the relative merits of possible pentacoordinate transition states invoked in phosphorus reaction mechanisms.[54,55]

ACKNOWLEDGEMENT

Grateful appreciation is expressed to the National Science Foundation (Grant MPS 74-11496) and the National Institutes of Health (Grant GM 21466) for generous financial support.

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