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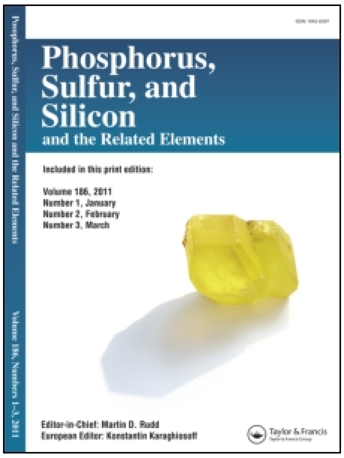

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COMPUTER SIMULATION OF PHOSPHORANE STRUCTURES

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COMPUTER SIMULATION OF PHOSPHORANE STRUCTURES[1]

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Parametrization of a molecular mechanics program to include terms specific for five-coordinate phosphorus compounds results in computer simulated structures of phosphoranes which compare favorably with structures obtained by x-ray diffraction. The principal new feature peculiar to five coordination is a term which measures the effect of electron pair repulsion modified by the ligand electronegativity for the two sets of bonds around phosphorus and takes into account the trigonal bipyramid and square pyramid as structural possibilities. The structures treated are HPF_4, $(CH_3)_nPF_{5-n}$ ($n = 0, 1, 2, 3$), the catechol derivative, $(C_6H_4O_2)_2PCH_3$, the dioxaphospholane $[(CF_3)_2CO]_2P[C(CH_3)_2CH_2C(CH_3)_2]C_6H_4Br$, the ephedrine derivative, $(OCHPhCH(CH_3)NCH_3)_2PH$, and $(PhO)_5P$. The good agreement between geometries obtained by computer simulation and x-ray diffraction suggests that application to phosphorus reaction mechanisms should result in a quantitative structuring of reaction intermediates and transition states.

Parametrization of molecular mechanics programs for use with organic compounds has been extensive.[3–9] Their application to conformational problems in general, gives very good results both in the reproduction of structural parameters and in the determination of relative configurational energies.[3–7] The principal terms that form a basis for these programs deal with bond stretching, bond bending, torsional motions, and nonbonded interactions.

$$E_{\mathrm{steric}} = \sum E_{\mathrm{str}} + \sum E_{\mathrm{bend}} + \sum E_{\mathrm{tors}} + \sum E_{nb} \qquad (1)$$

The stretch and bend terms are modified Hooke's law expressions. Minimization of these terms relative to a "strainless" set by successive alterations in atomic coordinates leads to a configuration of minimum steric energy.[6,7] This empirical approach can give insight into the relationship between energy, structure, and reactivity for systems that are too complex for most orbital calculations of the requisite sophistication.

When dealing with pentacoordinate phosphorus compounds, existing programs must be altered to differentiate between the two basic five-coordinate geometries, the trigonal bipyramid (TP) and the square pyramid (SP). Structures close to each type have been observed as well as a range of structures in between the two basic types.[10–12] Any program to be useful then must be sufficiently versatile to reflect the factors which favor one geometry over the other in order to reproduce known structures for five-coordinate phosphorus molecules.

We have made an initial effort in constructing an appropriate force field for small phosphorane molecules based on the extensive spectroscopic data that have

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been accumulated over the past decade.[10,13] The resulting parametrization was tested by calculating the reproducibility of the geometries of larger phosphoranes whose x-ray structures have been determined. As a basis of our treatment, we have extended the well developed program MMI of Allinger *et al.*[6,7] A detailed description follows.

FORCE FIELD MODIFICATIONS

Interactions between atoms bonded to a common atom (1,3 interactions) are not specifically included in eq 1 in Allinger's approach because these interactions are effectively already included in the bond length and bond angle "strainless" parameters.[5] However, for five-coordinate structures, there is a need to consider the effect of 1,3 interactions because an energy term is needed for ligand-ligand repulsion (1) to account for the stability difference of various geometries possible and (2) to account for structural effects due to the variation of ligand electronegativity.

For example, if no 1,3 interaction is included, the steric energy calculated for PF_5 is zero and the molecule assumes bond lengths and angles set by the particular set of "strainless" or equilibrium parameters chosen, whether these parameters correspond to the actual TP[14] or to a hypothetical SP[15] structure. However, a variety of ligand-ligand repulsion calculations and molecular orbital approaches estimate the TP to be more stable than the SP.[15–20] For PF_5, Strich and Veillard[15] using an ab initio treatment calculate that the TP is more stable than the SP by 4.8 kcal/mol. The latter value is close to estimates from spectroscopic data of 3.0–3.8 kcal/mol.[21,22] On the other hand, observance of a near SP conformation for some catechol derivatives[1b,23,24] suggests the importance of terms favoring the SP.[11]

The second inadequacy due to the neglect of 1,3 interactions is apparent in substituted PF_5 molecules. In CH_3PF_4, the axial and equatorial fluorine atoms are bent away from the methyl group,[25] $\angle F_{ax}PC = 91.8$ and $\angle F_{eq}PF_{eq} = 115.6°$, respectively. A similar effect, present in HPF_4[26] ($\angle F_{eq}PF_{eq} \approx 112°$), points to the operation of an electronegativity effect.

Consequently, an additional term was sought to include these effects peculiar to pentacoordinate phosphorus. Since the geometries of the methylfluorophosphoranes $(CH_3)_nPF_{5-n}$ ($n = 0 \rightarrow 3$) have been qualitatively correlated[27] with Gillespie's VSEPR theory,[17] this theory was adopted as a model for our approach. The manner in which bond electron pair repulsion (EPR) terms were introduced was via the nonbonded interaction term E_{nb} of eq 1 suitably modified to express bond electron pair repulsion effects for atoms bonded to phosphorus (1,3 bond EPR terms).

The unmodified nonbonded energy term that is used for all nonbonded interactions except 1,3 bond EPR terms is[28]

$$E_{nb(AB)} = \varepsilon[8.28 \times 10^5 \exp(-1/0.0736P) - 2.25P^6] \qquad (2)$$

where $P = (r_{VDW(A)} + r_{VDW(B)})/r_{AB}$, r_{VDW} is the van der Waals radius of the specific atom, and r_{AB} is the nonbonded distance between A and B for a given molecular configuration; $\varepsilon = (\varepsilon_A\varepsilon_B)^{1/2}$ where ε_A and ε_B are parameters specific to atoms A and B and are related to the hardness of the atoms. The constants in eq 2 were evaluated by Hill[28] and give the energy $E_{nb(AB)}$ in units of kilocalories per mole. van der Waals radii and ε values for some atoms of interest are given in Table I.

The modification of eq 2, which we found adequate to express 1,3 bond EPR terms is

$$E_{(1,3)\mathrm{AB}} = D\varepsilon[8.28 \times 10^5 \exp(-1/0.0736P^*) - 2.25P^{*6}] \quad (3)$$

The addition of a scaling factor D, to obtain a suitable balance between the energy of this 1,3 interaction term and the other energy terms in eq 1, and replacement of P with

$$P^*(\text{where } P^* = (r_{\mathrm{VDW(A)}} + r_{\mathrm{VDW(B)}})/r^*_{\mathrm{AB}} \quad (4)$$

and r^*_{AB} is the distance between atoms A and B calculated from modified bond lengths, d^*_{PA} and d^*_{PB}, between phosphorus and either atom A or B, provide the necessary adjustments to quantitatively reproduce the $(\mathrm{CH_3})_n\mathrm{PF}_{5-n}$ structures determined by electron diffraction.[14,25,29]

The variation in ligand electronegativity is introduced by a distance factor R_A (or R_B) in the relation $d^*_{\mathrm{PA}} = d_{\mathrm{PA}}R_\mathrm{A}$ (or $d^*_{\mathrm{PB}} = d_{\mathrm{PB}}R_\mathrm{B}$). The magnitude of R is inversely related to the electronegativity difference between phosphorus and atom A (or B). The R factors are the means of including the concept of bond EPR between atoms A and B. If the electronegativity difference ΔX_{PA} is large, the bonding electron pair can be considered to move away from phosphorus, thus decreasing the bond electron pair repulsion between the P—A and P—B bonds. When $\Delta X_{\mathrm{PA}} > \Delta X_{\mathrm{PA'}}$, the repulsion term $E_{(1,3)\mathrm{AB}} < E_{(1,3)\mathrm{A'B}}$ even when the actual bond lengths are equal.

A specific set of distance factors R' may be obtained by estimating the ionic character (I) of a bond, for example, from the expression,[30]

$$I = 1 - e^{-(1/4)(\Delta X_{\mathrm{PA}})^2} \quad (5)$$

and using the relation

$$R' = (Ir_\mathrm{A} + r_\mathrm{P})/(r_\mathrm{A} + r_\mathrm{P}) \quad (6)$$

where r_A and r_P are covalent radii[31] of atoms A and P. As the ionic character of the bond approaches 100%, $R' \rightarrow 1$. The resulting R' values for some atoms of

TABLE I

van der Waals Parameters for Nonbonded Interactions and for 1,3 Interactions

	ε, kcal/mol	r_{VDW}, Å
H	0.063	1.50[b]
C	0.041	1.75[b]
N	0.039	1.70[a]
O	0.046	1.65[a]
F	0.056	1.60[a]
P	0.150[c]	1.85[d]
Cl	0.214	1.95[a]

[a] Allinger's value as programmed in MMI.[6,7] [b] See ref 7. [c] ε_P extrapolated from Allinger's values[6,7] for atoms close to phosphorus in atomic weight. [d] For the value for $r_{\mathrm{VDW(P)}}$ see ref 16.

TABLE II
Distance Factors for 1,3 Interactions between Atom A and B in the System A—P—B

A (or B)	R'	R
H	0.786	0.550[a]
C	0.604	0.550
N	0.682	0.681
O	0.770	0.822
F	0.851	0.952

[a] Because of the unique properties of H as a ligand, a smaller factor was used to improve the simulation of the HPF_4 structure.

interest are listed in Table II. These served to initialize the calculations. However, as discussed below, these values were adjusted to the set R (also included in Table II).

In summary, we are considering 1,3 nonbonded interaction energy for the five electron pair bonds about phosphorus. For a bond P—A, the bonding electron pair has been moved a certain distance along that bond depending on the electronegativity difference of P and A. However, in the actual calculation of 1,3 interactions, we have maintained the form of eq 2 as nearly as possible. As a consequence, the van der Waals radius of atom A instead of an electron pair radius is used. This resulted in the introduction of a parameter D so that the 1,3 energy would not swamp the other energy terms.

"STRAINLESS" PARAMETERS

In order to carry out conformational minimizations, a set of "strainless" bond lengths and angles formed by the atoms attached to the phosphorus atom in both the TP and SP geometries are needed as well as accompanying force constants for bond stretching and angle bending. The approach we used was to assume an average bond length and force constant for each pair of atoms based on known bond lengths and force constants for related phosphorus compounds.[13] These values are listed as average values in columns 2 and 7, respectively, of Table III. The "strainless" bond lengths and force constants for each of the four possible positions, Tp (ax, eq) and SP (ap, bas), result from the relations for the Tp

$$l_0(\mathrm{av}) = [3l_0(\mathrm{eq}) + 2l_0(\mathrm{ax})]/5 \tag{7}$$

and

$$k_s(\mathrm{av}) = [3k_s(\mathrm{eq}) + 2k_s(\mathrm{ap})]/5 \tag{8}$$

and the relations for the SP

$$l_0(\mathrm{av}) = [4l_0(\mathrm{bas}) + l_0(\mathrm{ap})]/5 \tag{9}$$

and

$$k_s(\mathrm{av}) = [4k_s(\mathrm{bas}) + k_s(\mathrm{ap})]/5 \tag{10}$$

when combined with the ratios discussed in footnotes a and b of Table III.

TABLE III

"Strainless" Bond Lengths and Bond Stretching Force Constants

	l_0, Å					k_s, mdyn/Å				
		TP[a]		SP[b]			TP		SP	
Bond	Av	Ax	Eq	Ap	Bas	Av	Ax	Eq	Ap	Bas
P-H	1.456	1.480	1.440	1.421	1.465	6.00	4.91	6.73	7.64	5.59
P-C	1.760	1.789	1.740	1.717	1.770	3.00	2.46	3.36	3.80	2.80
P-N	1.650	1.677	1.632	1.610	1.660	3.50	2.86	3.92	4.46	3.26
P-O	1.625	1.652	1.607	1.589	1.639	4.00	3.27	4.48	5.09	3.72
P-F	1.551	1.577[c]	1.534[c]	1.514[d]	1.561[d]	5.45	4.46[e]	6.11[e]	6.94	5.08
P-Cl	2.053	2.087	2.030	2.003	2.065	2.90	2.37	3.25	3.69	2.70

[a] The ratio $l_0(ax)/l_0(eq)$ obtained from electron diffraction values for bond lengths in PF_5,[14] when combined with eq 7 and 8, was used in calculating all other strainless TP bond lengths. [b] The ratio $l_0(bas)/l_0(ap)$ obtained from calculated bond lengths in $PF_5(SP)$,[15] when combined with eq 9 and 10, was used for determining all other "strainless" SP bond lengths. [c] From an electron diffraction study of PF_5.[14] [d] From an ab initio study[15] of PF_5 (SP). [e] From a valence force field for PF_5.[32,33]

This method applied to all l_0 and k_s parameters except that for P—F bonds. Here, the parameters for the TP were obtained for the equatorial and axial bonds from the known structure[14] and force field[32,33] for PF_5. The average values were then determined from eq 7 and 8 and used with the ratio given in footnotes *a* and *b* of Table III and eq 9 and 10 to obtain the parameters for the SP form. Table III lists the resulting values of the "strainless" parameters, l_0 and k_s, for some bonds that will concern us.

Corresponding bending parameters, "strainless" angles and angle force constants, are summarized in Table IV for the TP and SP. The TP angles taken are those for a regular TP. For the SP, the angles are those calculated by Zemann for a minimum energy structure.[16a] The angle bending force constants are estimates from spectroscopic data on PF_5 and related PX_5 derivatives.[13,32] These constants have been determined to be low along the Berry[34] intramolecular exchange coordinate relative to 90° axial–equatorial angle bending. The latter is a manifestation of the structural nonrigidity common for pentacoordinate phosphorus molecules,[10] and allows easy excursion between the TP and SP form.[12] Since other energy terms are more restrictive, the variation in angle bending constants along the Berry coordinate are rather insensitive to the type of atom bonded to phosphorus. Hence, "average" values are used as indicated in Table IV. By analogy, a similar set of bending constants is used for the SP.

The parameters in Tables III and IV are applied without further adjustment to simple and more complex phosphoranes to be described except where noted; e.g. refer to footnotes for PF_5 comparisons in Table V.

In order to focus on an energy comparison for isomeric forms of a molecule, the steric energy for PF_5 was calculated for the TP structure determined by electron diffraction[14] and a model SP form resulting from ab initio calculations of Strich and Veillard.[15] To accomplish this particular structural reproduction, two types of calculations were carried out. In calculation A, k_s values were set as in Table III and l_0 values were decreased sufficiently to give the desired bond lengths in the minimum energy structure. In calculation B, l_0 values were set as in Table III and k_s values were increased to 100 mdyn/Å in order to prevent bonds from stretching. For each calculation, the TP results as the more stable structure.

TABLE IV

"Strainless" Bond Angles and Angle Bending Force Constants at Phosphorus for the TP and SP

	α_0, deg	k_b, mdyn-Å/rad^2
TP		
ax-P-ax	180	0.2
ax-P-eq	90	1.5
eq-P-eq	120	0.2
SP		
ap-P-bas	104.1	0.2
bas-P-bas (cis)	86.6	1.5
bas-P-bas (trans)	152	0.2

TABLE V

Steric Energy for Calculated TP and SP Structures of PF_5

TP	A[a]	B[b]	SP	A[a]	B[b]
	Bond length, Å			Bond length, Å	
$P-F_{ax}$	1.576	1.577	$P-F_{ap}$	1.514	1.514
$P-F_{eq}$	1.534	1.534	$P-F_{bas}$	1.563	1.561
	Angle, deg			Angle, deg	
$F_{ax}PF_{ax}$	180	180	$F_{ap}PF_{bas}$	103.1	101.3[c]
$F_{ax}PF_{eq}$	90	90	cis $F_{bas}PF_{bas}$	87.0	87.8
$F_{eq}PF_{eq}$	120	120	trans $F_{bas}PF_{bas}$	153.7	157.3
	Energy, kcal/mol			Energy, kcal/mol	
Bond stretch	0.66	0.00		0.76	0.00
Bond bend	0.0	0.00		0.08	0.56
Bond EPR (1,3 VDW)	9.01	8.97		9.20	9.17
Total	9.67	8.97		10.04	9.73

[a] The l_0 values for calculation A are for the TP: $P-F_{ax} = 1.550$, $P-F_{eq} = 1.520$ Å; for the SP: $P-F_{ap} = 1.505$, $P-F_{bas} = 1.540$ Å. The k_s, α_0, and k_b values are as in Tables III and IV. $D = 0.6$. [b] The l_0 values for calculation B are set equal to the electron diffraction values[14] for the TP and to the MO values[15] for the SP. The stretching force constants, k_s, were set at 100 mdyn/Å for all bonds. The α_0 and k_b values are as in Table IV. $D = 0.6$. [c] It is interesting that the SP angle, $F_{ap}-P-F_{bas}$, from calculation B agreed with that, 101.34°, from the MO calculation.[15]

TABLE VI

Comparison of Observed and Computer Simulated Structures For Simple Phosphoranes[a]

	CH_3PF_4			$(CH_3)_2PF_3$	
	Calcd	Exptl[25]		Calcd	Exptl[25]
	Bond Lengths, Å				
$P\text{-}F_{ax}$	1.61	1.612	$P\text{-}F_{ax}$	1.62	1.643
$P\text{-}F_{eq}$	1.55	1.543	$P\text{-}F_{eq}$	1.55	1.553
$P\text{-}C_{eq}$	1.79	1.780	$P\text{-}C_{eq}$	1.80	1.798
	Bond Angles, deg				
$F_{ax}PF_{ax}$	176.4	176.4	$F_{ax}PF_{ax}$	175.5	177.8
$F_{ax}PF_{eq}$	89.1		$F_{ax}PC_{eq}$	91.0	
$F_{ax}PC$	91.7	91.8	$F_{ax}PF_{eq}$	87.7	88.9
$F_{eq}PF_{eq}$	117.9	115.6	$C_{eq}PC_{eq}$	126.6	124.0
$F_{eq}PC_{eq}$	121.1	122.2	$C_{eq}PF_{eq}$	116.7	118.0
D	0.20			0.175	
	Energy, kcal/mol				
Bond stretch	1.27			2.95	
Bond bend	0.42			1.14	
Stretch-bend	0.00			0.0	
1,4 VDW	1.13			1.90	
Bond EPR (1,3 VDW)	13.07			21.79	
Other VDW	0.00			−0.23	
Total	15.89			27.55	
δ	0.012			0.032	

	$(CH_3)_3PF_2$[29]			HPF_4[26]	
	Calcd	Exptl		Calcd	Exptl
	Bond Lengths, Å				
$P-F_{ax}$	1.63	1.685	$P-F_{ax}$	1.60	1.594
$P-C_{eq}$	1.81	1.813	$P-F_{eq}$	1.54	1.55
			$P-H_{eq}$	1.45	1.36[b]
	Bond Angles, deg				
$F_{ax}PF_{ax}$	180	180	$F_{ax}PF_{ax}$	178.6	
$F_{ax}PC_{eq}$	90	90	$F_{ax}PF_{eq}$	89.6	
$C_{eq}PC_{eq}$	120	120	$F_{ax}PH_{eq}$	90.7	~90
			$F_{eq}PF_{eq}$	118.5	112
			$F_{eq}PH_{eq}$	120.8	124
D	0.15			0.10	
	Energy, kcal/mol				
Bond stretch	5.53			0.35	
Bond bend	0.48			0.07	
Stretch-bend	0.0			0.0	
1,4 VDW	3.04			0.0	
Bond EPR (1,3 VDW)	32.61			7.26	
Other VDW	−0.72			0.0	
Total	40.94			7.68	
δ	0.029			0.004[c]	

[a] Values of l_0, α_0, k_s, and k_b are those listed in Tables III and IV. [b] This P-H bond length is an assumed value.[26] [c] Due to a high degree of uncertainty in the experimental values for bond angles, only the first term for the deviation function, δ, was used.

DETERMINATION OF R AND D FACTORS

In order to calibrate the magnitude of the bond EPR term, $E_{(1,3)AB}$, which will reproduce phosphorane structures, variation in the D term in eq 3 and the associated R factor was explored to give a "best" fit for the series, $(CH_3)_nPF_{5-n}(n = 1 \rightarrow 3)$, and HPF_4. The resulting D values meeting this condition for each member of the "test" series are tabulated in Table VI along with the agreement achieved between observed and calculated structural parameters. The R value set chosen is listed in the last column of Table II. The values of the D and R factors, the "strainless" parameters, l_0 and α_0, and accompanying force constants, k_s and k_b, given in Tables III and IV now form the fully calibrated expression of the bond EPR term, $E_{(1,3)AB}$, and are used in conformational minimization for more complex phosphoranes.

In establishing the chosen R set, initially the R' set (Table II), calculated directly from partial ionic bond character as described above, was used. However, the range of values in the R' set was too small to cause large enough F—P—F angle changes encountered on substitution of equatorial fluorine atoms by methyl groups. Therefore the range of the R' scale was increased. This was accomplished by doubling the ratio, $E_{(1,3)CF}/E_{(1,3)FF}$, calculated from eq 3 for the R set relative to the same ratio for the R' set. Intermediate atom values between these two extremes in electronegativities for C and F were similarly proportioned. Because of the uniqueness of the hydrogen atom, e.g., causes a greater repulsion effect than a methyl group (cf. the structures of HPF_4 and CH_3PF_4 in Table VI), its R value was varied independently to achieve a "best" fit for HPF_4. The resulting value was 0.55, but even this smaller value did not compress the F_{eq}—P—F_{eq} angle to the reported value[26] of 112°. However, its use proved satisfactory in the more complex P—H compounds, $(OCH_2CH_2NH)_2PH$ and $(OCHPhCH(CH_3)NCH_3)_2PH$, discussed later, primarily because many other energy terms are present in these derivatives and the competition among the increased number of structural determining features relegates any one term to a lesser role.

To arrive at the scaling factors, associated with eq 3 (D values as listed in Table VI), the variation that this factor has on the minimum energy configuration was examined for each of the molecules. An example of this variation is shown in Table VII for CH_3PF_4. Variation of the value of D alters the magnitude but not the direction of bond stretching and bending. As to be expected, the bonds stretch further from their l_0 values as D increases. In order to arrive at a "best" fit between the calculated minimum energy configuration and the observed structure,[25] the value was successively incremented by 0.025 unit over the range of D = 0 to D = 4.75. The results are shown in Figure 1, where the fractional contribution of 1,3 interaction (EPR) energy to the total energy for the minimized structure is plotted as a function of the value of D.

The structural deviation, $\delta = \Delta(\mathrm{bl}) + \Delta(\mathrm{ang})$, which measures the sum of the average bond length (bl) deviation (Å),

$$\Delta(\mathrm{bl}) = \sum_{i=1}^{5} |(l_i(\mathrm{expt}) - l_i(\mathrm{calcd}))/5|$$

TABLE VII

Effect of Varying the Scaling Factor (D) on Simulated Structures for CH_3PF_4

	Scaling factor, D[a]				
	0.0	0.10	0.20	0.30	0.40
	Bond Lengths, Å				
$P\text{-}F_{ax}$	1.579	1.595	1.608	1.619	1.630
$P\text{-}F_{eq}$	1.534	1.540	1.545	1.550	1.555
P-C	1.766	1.777	1.788	1.797	1.806
	Bond Angles, deg				
$F_{ax}PF_{ax}$	178.4	177.3	176.4	175.7	175.1
$F_{ax}PF_{eq}$	89.6	89.3	89.1	88.9	88.7
$F_{ax}PC$	90.6	91.2	91.7	92.0	92.3
$F_{eq}PF_{eq}$	120.0	118.8	117.9	117.1	116.7
$F_{eq}PC$	120.0	120.6	121.1	121.4	121.7
	Energies, kcal/mol				
Total strain energy[b]	2.01	9.19	15.89	22.18	28.14
Total 1,3 interaction[c]	0.0	6.99	13.07	18.48	23.35
Largest 1,3 interaction[d]	0.0	2.03	3.72	5.18	6.47
δ	0.045	0.024	0.012[e]	0.018	0.028

[a] As defined in eq 3. [b] From the sum of terms in eq 1 and 3. [c] From eq 3 summed over all bonds to phosphorus. [d] Largest single term in eq 3. [e] A best fit with observed[25] parameters for CH_3PF_4 was obtained with $D = 0.20$.

and the average bond angle (α) derivation expressed in radians,

$$\Delta(\text{ang}) = \sum_{i=1}^{10} |(\alpha_i(\text{expt}) - \alpha_i(\text{calcd}))/10|$$

was used as a criterion for choosing the "best" fit and, hence, the D value associated with a given structure. The change in δ with D is also shown in Figure 1. A minimum in δ is obtained at a D value of 0.20 for CH_3PF_4. For the other "test" derivatives, a minimum in structural deviation δ occurred at D values between 0.10 and 0.20.

The graph in Figure 1 represents a typical type of curve obtained for minimum energy structures except that the contribution of the 1,3 (EPR) term to the total energy summation decreases as the molecule under consideration increases in complexity and, hence, in the total number of energy interactions that are present. For example, a minimum in δ is obtained at $D = 0.075$ for the catechol derivative, $(C_6H_4O_2)_2PCH_3$, while D for the spiro compound, $(OCH_2CH_2NH)_2PH$, for a "best" structural fit is 0.10.

In Figure 2, the variation in the energy ratio, 1,3 (EPR)/total E, with the D value selected to give a minimum in δ is plotted for the phosphoranes treated in this paper. For each derivative, an energy minimum was obtained at each D value as it was incremented over a range, similar to the procedure used for CH_3PF_4. A graph of the type displayed in Figure 1 was obtained which showed a relatively flat section after a certain D value was reached. Accordingly, Figure 2 may be used with some confidence when a phosphorane of unknown conformation is being investigated, particularly since Figure 2 indicates that the D term varies predictably with molecular complexity.

Consequently, after the data, comparable to that used to obtain Figure 1 is computed, an estimate of the fractional contribution, 1,3 (EPR)/total E, may be made. Using this estimate and comparing the molecular complexity of the phos-

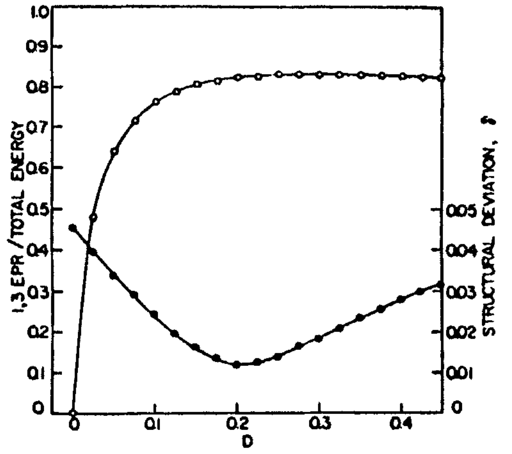


FIGURE 1 The variation in the fractional contribution of the 1,3 term to the total interaction energy (left scale) as a function of D for CH_3PF_4 (unfilled circles). The variation of the structural deviation, δ (right scale), with D for CH_3PF_4 (filled circles).

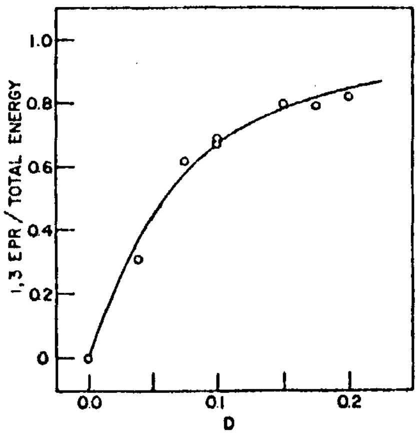


FIGURE 2 The variation in the fractional contribution of the 1,3 term to the total energy as a function of *D* for phosphoranes of varying molecular complexity.

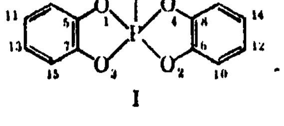
phorane of interest with those used to construct Figure 2, a reasonable choice of *D* value may be made.

Although the tables to follow in this paper list only the main structural parameters for computer simulated structures, the coordinates for all atom positions were obtained in each case. The accompanying energy terms listed refer to the total interactions for the entire molecule.

ENERGY OF THE TP VS. THE SP

The steric energies in Table V calculated for the simulated TP and SP structures of PF_5 show that the TP is the more stable conformation. This is a direct consequence of the introduction of bond EPR via the modified 1,3 interaction expression (eq 3). In view of the approximate method of choosing the magnitude of this energy term compared to the other contributing terms (expression 1), as described above, no great significance can be attached to the actual value of the energy difference. However, the direction of the energy difference is important and must allow the prediction of the relative stability of the TP and SP for more complex phosphoranes if this approach is to be useful. As pointed out, other ligand constraints encountered with more complex molecules may provide terms which are more important in determining structure than the bond EPR term, but the inclusion of the latter should lead to a conformation which more accurately reproduces observed data.

A case in point are some catechol derivatives of five-coordinate phosphorus, which have x-ray structures[12,23,24] near a square or rectangular pyramid. We have



I

TABLE VIII

Comparison of the Structure of $(C_6H_4O_2)_2PCH_3$ by Conformational Minimization and X-Ray Diffraction[a]

	Bond distances, Å					
	Calcd,[b] D					k_s,[d]
	0.025	0.075	0.20	X-ray[c]	l_0	mdyn/Å
O(1)-C(5)	1.366	1.365	1.362	1.363	1.369	4.89
P-O(1)	1.663	1.676	1.706	1.674		
O(3)-C(7)	1.369	1.368	1.366	1.381	1.369	4.89
P-O(3)	1.616	1.625	1.640	1.654		
C(5)-C(7)	1.328	1.328	1.328	1.327	1.330	9.60
C(5)-C(9)	1.382	1.382	1.381	1.381	1.380	6.00
C(7)-C(15)	1.382	1.382	1.381	1.380	1.38	6.00
C(9)-C(11)	1.387	1.387	1.387	1.394	1.38	6.00
C(11)-C(13)	1.336	1.336	1.336	1.332	1.330	9.60
C(13)-C(15)	1.387	1.387	1.385	1.401	1.380	6.00
P-C(17)	1.753	1.768	1.797	1.777		

	Bond angles, deg					k_b[d]
	Calcd, D					mdyn
	0.025	0.075	0.20	X-ray	α_0[d]	Å/rad²
PO(1)C(5)	110.4	110.6	110.6	111.7	111.5	0.97
PO(3)C(7)	111.5	111.8	112.2	111.5	111.5	0.97
O(1)C(5)C(7)	112.3	112.3	112.4	112.0	113.0	0.66
O(1)C(5)C(9)	126.4	126.3	126.2	125.6	123.5	0.66
C(7)C(5)C(9)	121.4	121.4	121.4	122.4	123.5	0.66
O(3)C(7)C(5)	112.9	113.0	113.4	112.1	113.0	0.66
O(3)C(7)C(15)	126.0	125.9	125.5	124.2	123.5	0.66
C(5)C(7)C(15)	121.1	121.1	121.2	123.7	123.5	0.66
C(5)C(9)C(11)	117.8	117.7	117.7	114.3	120.0	0.66
C(9)C(11)C(13)	120.9	120.9	121.0	123.6	123.5	0.66
C(11)C(13)C(15)	120.9	121.0	121.0	121.3	123.5	0.66
C(7)C(15)C(13)	117.9	117.8	117.8	114.6	120.0	0.66
O(1)PO(2)	152.0	157.9	165.0	156.9		
O(1)PO(3)	93.0	92.3	91.1	90.2		
O(1)PO(4)	79.0	81.0	83.2	82.8		

O(1)PC(17)	104.0	101.1	97.5	102.1
O(3)PO(4)	146.5	144.2	135.6	148.1
O(3)PC(17)	106.8	107.9	112.2	105.6

	Energy, kcal/mol		
	0.025	0.075	0.20
Bond stretch	0.33	0.84	3.02
Bond bend	1.63	1.60	1.55
1,4 VDW	3.70	3.78	3.88
1,3 VDW	3.70	10.31	23.99
Other VDW	−2.12	−2.10	−2.07
Torsional	0.02	0.05	0.27
Total	7.25	14.48	30.64
δ	0.070	0.048	0.102

[a] All bending force constants, k_b, around phosphorus were set equal to 0; C_2 symmetry along the P-C(17) axis was assumed; C(17) and P were constrained to move only along the C(17)-P bond axis; torsional constants were set at 10.0 to keep the benzo-fused five- and six-membered rings planar. [b] Calculations based on TP parameters, l_0 and k_s, for P-O and P-C bonds in Tables III and IV. [c] X-ray diffraction values for molecule I of ref 23a. [d] "Strainless" parameters and force constants for bonds other than P-O bonds.

chosen the first such derivative to be reported as rectangular pyramidal, $(C_6H_4O_2)_2$-PCH_3[23a] (I), to test our conformational minimization scheme.

If either the TP or SP set of α_0 values (Table IV) is chosen for the calculation, the resulting minimum energy structure is constrained to assume a geometry near the "idealized" TP or SP. To eliminate this constraint, the angle bending force constants, k_b, were set to zero for all angles at phosphorus. The TP parameters, l_0 and k_s, for P—O and P—C bonds (Tables III and IV) were used in the calculation. The value of D was chosen at 0.075, in accord with the criteria discussed above. Other conditions are mentioned in footnote *a* of Table VIII.

Conformational minimization under these constraints leads to the calculated bond lengths and angles listed in Table VIII for I (column 3). Calculations also were performed to show the effect of varying the bond EPR term ($D = 0.025$, column 2, and $D = 0.20$, column 4).

Agreement with the x-ray structure[23a] (cf. columns 3 and 5) is quite good at this stage of the parametrization. In particular, it is encouraging that a structural minimum is reached at angles near the SP, as found for structure I, even though the initializing parameters, l_0 and k_s, for a TP were used. The calculated O—P—O trans basal angles are 157.9 and 144.2°, which compares with 156.9 and 148.1°, respectively, as reported from the x-ray diffraction study.[23a]

As we have demonstrated elsewhere,[12] the x-ray structures of cyclic phosphoranes fall along the Berry coordinate. As indicated here, the principal reason is associated with low force constants for angle bending at phosphorus. The latter is a manifestation of nonrigidity for five-coordinate phosphorus and a consequence of two sets of bond properties, which leads to close energy structures, the TP and SP.[10] Thus, in contrast to other coordination numbers which have more bond rigidity, added flexibility is available to five-coordinate phosphorus in allowing easy angular "slippage" along the Berry coordinate. As a result, ligands, which undergo repulsion effects from a single basic conformation, minimize their interactions with each other by relative motions that accompany ready movement between the TP and SP. The particular point reached along the TP–SP path will then depend on the ligand construction and associated constraints.[12]

The effect on conformational energy of moving along the Berry[34] coordinate may be seen by performing another series of calculations for I in which the force constants for angle bending (k_b) at phosphorus are allowed to assume their usual values (Table IV) and the set of "strainless" parameters, l_0 and α_0, as well as the bond stretching force constants, k_s, for bonds to phosphorus were varied incrementally from the TP to the SP. The effect of this variation is to force the molecule to assume first a TP geometry, then to move along the Berry coordinate toward the SP geometry. It was established that the same value of D is applicable over the entire Berry coordinate. This was done by performing conformational energy minimizations as D was varied in 0.025 steps from 0 to 0.3 for both 100% TP and 100% SP. These results give graphs similar to that in Figure 1 for CH_3PF_4. In each case, the "best fit" (minimum value of δ) occurred at $D = 0.10$.

The minimum energy structures corresponding to points uniformly displaced along the Berry coordinate are shown in Figure 3. The SP is seen to be the more stable structure. Accompanying data are listed in Table IX for some of the minimized bond parameters at phosphorus. The principal term causing the energy

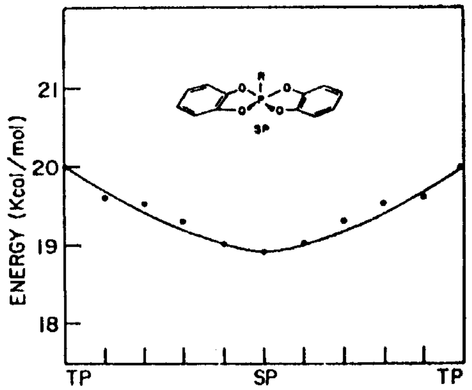


FIGURE 3 Relative energy calculated via molecular mechanics for structures of $(C_6H_4O_2)_2PCH_3$ (I) along the Berry coordinate.

variation over the series is the 1,4 ver der Waals expression. It provides almost 1 kcal in stabilizing the SP over the TP. The point which agrees closest with the experimental structure[23a] has about 85% SP character. This is in surprisingly excellent agreement with the value of 82% SP character estimated along the Berry coordinate from the sum of the dihedral angles[12] associated with the polyhedral faces for I. The parameters for this best structure are listed in Table X.

If the C(5)-C(7) and C(6)-C(8) distances are increased, the TP structure is favored. This is in accord with calculations by Kepert,[16b] which show that the relative TP-SP stability is a function of the size of the ligand bite. Increasing this distance is what occurs on going from unsaturated ring systems, as in I, to saturated rings, like that in the spirophosphorane. These structures have been reported[35] to be TP. We have commented[11] on the reasons for this structural change upon detailed examination of the resulting alteration in ring strain and changes in P—O and C—O bonding requirements.

A HIGHLY STRAINED PHOSPHOLANE

For more strained cyclic phosphoranes, such as the near "square" pyramidal dioxaphospholane[35] (II), the influence of a bond EPR term should be even less important than that in catechol derivatives.[23,24] In addition to the increased number of steric terms for the phospholane (II) compared to a simple acyclic phosphorane, the presence of a four-membered ring causes a large increase in bending energy.

We carried out some early calculations based on slightly different sets of initializing parameters for the SP and TP than those in Tables III and IV. However, the results should not be substantially altered. The angles at phosphorus obtained from this computation are listed in Table XI. The comparison of the energy obtained for the two geometries, constrained near the SP and TP by the choice of initial conditions, shows the SP to be more stable. Correspondingly, the angles at phosphorus based on the SP parameters compare well with x-ray diffraction values.[35]

TABLE IX

Conformational Minimization of $(C_6H_4O_2)_2PCH_3$ at Different Points Along the Berry Coordinate[a]

	% SP ($D = 0.10$)					
	100	80	60	40	20	0
	Bond Distances, Å					
P-O(1) = P-O(2)	1.671	1.676	1.681	1.685	1.688	1.693
P-O(3) = P-O(4)	1.671	1.662	1.653	1.634	1.634	1.626
P-C(17)	1.749	1.755	1.761	1.769	1.776	1.784
	Bond Angles, deg					
O(1)PO(2)	152.5	158.9	165.3	170.2	174.0	177.1
O(3)PO(4)	152.5	146.6	141.1	135.0	128.2	123.5
O(1)PC(17) = O(2)PC(17)	103.7	100.6	97.3	94.9	93.0	91.4
O(3)PC(17) = O(4)PC(17)	103.7	106.7	109.5	112.5	115.9	118.2
O(1)PO(4) = O(2)PO(3)	84.5	84.8	85.6	86.4	87.1	88.1
	Energy, kcal/mol					
Bond stretch	1.68	1.68	1.67	1.67	1.66	1.71
Bond bend	2.81	2.79	2.63	2.47	2.33	2.33
VDW, 1,4	3.84	3.90	4.10	4.32	4.55	4.77
VDW, 1,3	12.61	12.68	12.81	12.88	12.92	12.96
VDW, other	−2.04	−2.05	−2.07	−2.07	−2.07	−2.07
Torsional	0.00	0.01	0.16	0.26	0.22	0.34
Total	18.90	19.01	19.30	19.53	19.61	20.04

[a] The "strainless" parameters and force constants for bonds at phosphorus are from Tables III and IV for the SP and TP. These initializing parameters were divided up incrementally for intermediate points as mentioned in the text. The "strainless" parameters and force constants for bonds other than P-O and P-C bonds are the same as in Table VIII (cf. footnote *d*).

TABLE X

Bond Parameters for the "Best" Simulated Structure for $(C_6H_4O_2)_2PCH_3$[a]

Bond Lengths, Å[b]			Bond Angles, deg[b]		
O(1)-C(5)	1.362	PO(1)C(5)	113.3	C(9)C(11)C(13)	121.0
P-O(1)	1.675	PO(3)C(7)	113.6	C(11)C(13)C(15)	121.0
O(3)-C(7)	1.362	O(1)C(5)C(7)	111.9	C(7)C(15)C(13)	117.6
P-O(3)	1.664	O(1)C(5)C(9)	126.6	O(1)PO(2)	157.4
C(5)-C(7)	1.323	C(7)C(5)C(9)	121.4	O(1)PO(3)	89.1
C(5)-C(9)	1.381	O(3)C(7)C(5)	112.0	O(1)PO(4)	84.7
C(7)-C(15)	1.381	O(3)C(7)C(15)	126.5	O(1)PC(17)	101.3
C(9)-C(11)	1.387	C(5)C(7)C(15)	121.4	O(3)PO(4)	148.1
C(11)-C(13)	1.336	C(5)C(9)C(11)	117.6	O(3)PC(17)	106.0
C(13)-C(15)	1.387				
P-C(17)	1.753				
		Energies, kcal/mol			
Bond stretch	1.68	VDW, 1,4	3.88	VDW, other	−2.04
Bond bend	2.80	VDW, 1,3	12.66	Torsional	0.01
				Total	18.99

[a] The initializing parameters are the same as discussed in footnote *a* to Table IX and accompanying text. $D = 0.10$. [b] The x-ray values[23a] are listed in Table VIII in the same order for comparison.

TABLE XI

Calculated and X-Ray Diffraction Bond Angles at Phosphorus for II

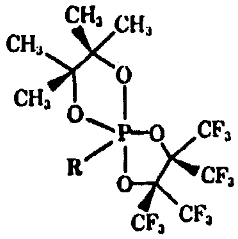
	Exptl[a]	SP calcd	TP calcd
	Angle, deg		
O(2)PC(1)	100.0	102.2	89.5
O(1)PC(1)	101.6	101.8	118.0
C(7)PC(1)	105.6	107.7	95.0
C(9)PC(1)	110.7	109.2	123.0
O(2)PO(1)	85.0	88.4	89.4
O(1)PC(7)	92.7	90.9	93.3
C(7)PC(9)	78.1	75.3	77.2
O(2)PC(9)	90.3	89.7	95.8
O(2)PC(7)	154.2	149.6	172.9
O(1)PC(9)	147.7	148.6	118.8
	Energy, kcal/mol		
Bond stretch		3.74	3.69
Bond bend		18.10	21.53
Stretch-bend		−0.17	−0.08
VDW, 1,4		8.01	9.35
VDW, other		1.11	−0.15
Torsion		1.02	2.17
Torsion-bend		−0.22	−0.70
Total		31.34	35.82

[a] For molecule Ia of ref 35.

STRUCTURE SIMULATION OF THE EPHEDRINE DERIVATIVE $(OCHPhCH(CH_3)NCH_3)_2PH$(IV)

Recently, we reported the x-ray structure of the ethanolamine derivative $(OCH_2CH_2NH)_2PH$ (III),[36] a near TP conformation. Computer simulation according to the procedure described here reproduced most structural features including the direction of ring puckering.[36] In order to account for the unusually large $N_{eq}PN_{eq}$ angle, 130.8; the effect of an intermolecular hydrogen bond, N—H···O (3.04 Å), present in the unit cell,[36b] was included in the calculation. The related (—)-ephedrine derivative IV, whose x-ray structure has been reported,[37] shows ring puckering at the flap atom C(2) in a direction opposite to that in III.

The conformational minimization scheme applied to IV gave the results shown in Table XII. Calculated parameters are also included for III. The initial atom



R = SPh, p-OC_6H_4Br

TABLE XII

The structure of $(OCH_2CH_2NH)_2PH$ (III) and $(OCHPhCH(CH_3)NCH_3)_2PH$ (IV) by Conformational Minimization[a] and X-Ray Diffraction for IV

Bond Lengths, Å

	Calcd[b] III	Calcd IV	Exptl[c] IV		Calcd[b] III	Calcd IV	Exptl[c] IV	l_0	k_s, mdyn/Å
P-O(1)	1.71	1.69	1.700	O(1)-C(2)	1.44	1.44	1.434	1.44	3.58
P-N(1)	1.68	1.68	1.690	N(1)-C(1)	1.45	1.47	1.500	1.47	5.00
P-H(1)	1.46	1.46		C(1)-C(2)	1.51	1.54	1.545	1.54[e]	4.40

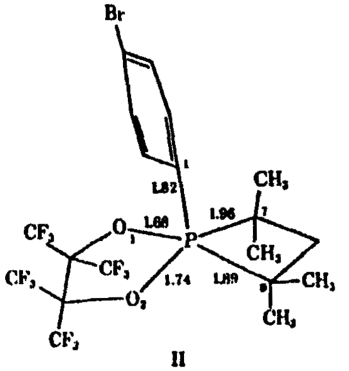
Bond Angles, deg

	Calcd III	Calcd IV	Exptl IV		Calcd III	Calcd IV	Exptl IV	α_0	k_b, mdyn-Å/rad²
O(1)PO(1)′	179.3	176.9	176.6	PO(1)C(2)	112.0	112.5	111.9	111.5	5.0[f]
N(1)PN(1)′	125.2	129.6[d]	123.3	PN(1)C(1)	116.7	117.8	115.4	120	0.7
O(1)PN(1)	90.3	90.8	89.2	O(1)C(2)C(1)	107.1	108.8	103.2	109.5	0.3
O(1)PN(1)′	89.4	90.5	92.4	N(1)C(1)C(2)	104.4	101.7	100.3	109.5	0.3
N(1)PH(1)	117.4	115.2		C(1)N(1)H(2)	119.7				
O(1)PH(1)	90.3	88.5		PN(1)H(2)	123.6				

Energy, kcal/mol

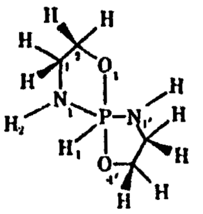
	III	IV		III	IV
Stretch	4.44	2.84	Other VDW	−1.33	−3.50
Bend	2.78	4.34	Torsional	0.18	0.18
1,4 VDW	3.21	5.49	Total	29.79	26.02
1,3 VDW	20.49	16.68	*D*	0.10	0.075

[a] The initializing parameters follow the standard values (Tables III and IV) for the TP set for the bonds at phosphorus. Others are indicated in the last two columns. During the energy minimization, the phenyl ring for IV was free to move and rotate as a unit, but the phenyl bond distances and angles and the ring planarity were held constant. A C_2 axis was assumed. A large torsional constant was used to maintain planarity of the D(1)PN(1)C(1) portion of each of the rings in III and IV. [b] In ref 36a a slightly different set of calculated values was given. The different set resulted from slight alterations in our computational procedure. [c] From the x-ray study reported in ref 37. The values included here represent average values for bond lengths and angles, since there is a near C_2 symmetry axis and the calculation here is not sufficient to discriminate among small variations. [d] This relatively large $N_{eq}PN_{eq}$ angle calculated for IV closed to 123.4° when the ring methyl was positioned on the side opposite the phenyl group. Also if the torsional constant for the OPNC portion of the rings in IV is reduced to allow ring puckering to approximate that in the actual structure (~3° for this dihedral angle), the NPN angle decreases from 29.6° to 127.1°. The other bond parameters are not appreciably altered. [e] l_0 = 1.51 for III and 1.54 Å for IV. [f] A large force constant was used for the PO(1)C(2) angle for IV in order to hold it from unduly opening. The same value was used for III.

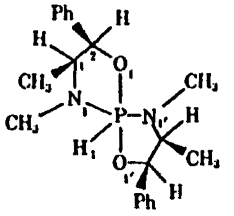


II

coordinates used in the computation for both dioxadiazaspirophosphoranes, III and IV, positioned the five-membered rings in planes and, in addition for IV, placed the methyl and phenyl substituents on the same side of the ring as the hydrogen atom bonded to phosphorus to agree with the conformation of the (—)-ephedrine ligand.



III



IV

A conformational minimum was obtained, which resulted in ring puckering with the flap atom, C(2) in III, toward the equatorial P—H bond, and in IV, away from the equatorial P—H bond, in agreement with that observed by the respective

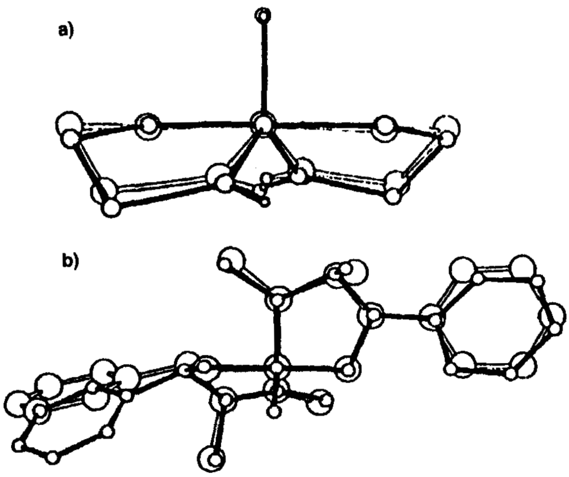


FIGURE 4 ORTEP plots of the computer structures compared to the x-ray structures for (a) $(OCH_2CH_2NH)_2PH$(III) and (b) $(OCHPhCH(CH_3)NCH_3)_2PH$ (IV). Calculated structures are shown with solid bonds overlaying the x-ray structures.

x-ray studies.[36,37] We did not investigate the cause of this alteration in puckering, but suspect it to be associated with lower non-bonded repulsions for the phenyls oriented away from the P—H bond compared to that obtained if the phenyl groups are brought closer to the P—H bond by the opposite puckering. ORTEP plots (Johnson's program) of the simulated structures of III and IV are superimposed on their x-ray structures in Figure 4.

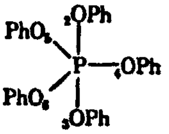
STRUCTURAL COMPARISON IN $(C_6H_5O)_5P$

As a final example, the x-ray parameters[38] for the phenyl groups of the pentaphenoxyphosphorane $(C_6H_5O_5)_5P$ were used as starting coordinates in a conformational minimization. The angles at phosphorus for the best minimum energy structure ($D = 0.04$) are given in Table XIII and are compared with x-ray values.[38]

It is noted that the three calculated equatorial angles, which differ from the 120° values expected for a D_{3h} structure, compare favorably with the corresponding x-ray values. This suggests that the canting of the phenyl rings, which tends to minimize nonbonded interactions between them, achieves a better conformational minimum by inducing these angle changes. Further, the agreement obtained indicates that intermolecular effects are relatively unimportant in determining the structure of the pentaphenoxy derivative.

TABLE XIII

Comparison of Computed and X-Ray Diffraction Angles at Phosphorus in $(C_6H_5O)_5P$[a]



	Calcd	Exptl[b]
	Bond Angles, deg	
O(2)PO(3)	179.2	176.6
O(2)PO(4)	89.5	88.9
O(2)PO(5)	90.0	91.4
O(2)PO(6)	90.4	87.9
O(3)PO(4)	90.0	88.2
O(3)PO(5)	90.8	91.6
O(3)PO(6)	89.4	92.1
O(4)PO(5)	118.3	118.3
O(4)PO(6)	123.1	125.5
O(5)PO(6)	118.6	116.2
	Energy, kcal/mol	
Stretch	1.16	
Bend	1.54	
1,4 VDW	15.16	
1,3 VDW	2.98	
Other VDW	−11.15	
Torsional	0.03	
Total	9.72	

[a] Standard parameters were taken from Tables III and IV for the TP set. $D = 0.040$. [b] X-ray data from ref 38.

DISCUSSION

We have shown that there is a strong correlation between ligand construction and the position of a cyclic phosphorane structure along the Berry coordinate.[12] The agreement indicated between this correlation and the results from the molecular mechanics method here suggests that conformational minimization will find useful application in quantitative assessment of pentacoordinate intermediates postulated in a wide variety of phosphorus reaction mechanisms.[39] Taking due cognizance of reaction requirements, such as the nature of the entering and leaving groups and their specific reaction coordinates (i.e., normally apical attack and departure in a TP intermediate), it should be possible to determine the minimum energy transition state with a greater degree of certainty than heretofore allowed.

These considerations need not be limited to simple derivatives. Currently, we are applying the above approach to the action of ribonuclease on dinucleoside phosphates.

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