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CONFORMATIONAL ANALYSIS—131

A MOLECULAR MECHANICS TREATMENT OF PHOSPHINES[1,†]

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Abstract—The molecular mechanics method (1973 force field) has been extended to include the general class of phosphaalkanes. Structural data on simple molecules were fit well, and equilibria between conformations can be calculated in general in agreement with experiment, in sofar as experimental data are known. Phosphacyclohexane and a few simple derivatives have been studied in some detail. It is concluded that the force field developed is adequate for the prediction of structures and energy differences, but it is not possible to calculate heats of formation, due to the lack of experimental data.

The molecular mechanics method for determining the structures and energies of molecules has now been rather extensively applied to hydrocarbons, and to molecules which are hydrocarbons substituted with a single functional group or heteroatom.[2-7] The more important functional groups found in organic molecules, which contain oxygen,[4] nitrogen,[5] sulfur[2,6] and silicon,[7] have been studied in some detail. In this paper we will discuss the extension of these calculations in a preliminary way to the remaining biologically important element, phosphorus. While it is desirable to further extend the work to functional groups which contain P–O bonds, this paper will be limited to the phosphaalkanes.

In the present work the MMI program was used (1973 force field).[2,8] The additional parameters needed to accommodate phosphorus were developed and are listed in Table 1. It was found in earlier work[4] that to reproduce some of the available data, it was desirable to explicitly treat the lone pairs present on ether-type oxygen and amine-type nitrogen. It was found unnecessary, however, to treat explicitly the lone pairs on sulfide-type sulfur,[6] possibly because the available experimental data are less numerous and less accurate for the second-row elements. Similarly, in this work, it was found that there was no advantage to treating explicitly the lone pair on phosphorus. The stretching and bending force constants were either taken from the literature, or if we were unable to find the necessary data, the constants from analogous compounds were used. The structural data were fit according to the experimental values from electron diffraction, in general. If electron diffraction data were unavailable, microwave data were substituted if possible. The torsional constants were then determined to fit the observed data.

The experimental and calculated structures for some simple phosphines are listed in Table 2. Conformational energies, rotational barriers and dipole moments calculated are compared with the experimental data in Table 3. In most cases there were no serious problems in fitting the available structural data to within experimental error.

Methylphosphine, di- and trimethylphosphines are all calculated to exist preferentially, in agreement with the experimental observations[9-12] and CNDO calculations,[13,14] in the staggered conformation. The rotational barriers in these compounds were intentionally calculated to be about 0.1 ckal/mole lower than the barriers derived from microwave spectra, for reasons previously discussed.[8]

According to conclusions drawn from the Raman and IR spectra,[15] ethylphosphine exists as a mixture of conformations, containing 45% *gauche* and 55% *trans* at 24°. These results were confirmed by microwave studies.[16] The enthalpy difference between the two conformers was determined as 0.57 ± 0.28 kcal/mole, favoring the *trans* (Fig. 1). The rotational barrier about the C–P bond was found to be 1.82 kcal/mole in the *gauche* conformation, and 2.97 kcal/mole in the *trans*. It was not found possible to reproduce these barriers very well using only a V_3 term. Consequently, a small V_1 term was added to improve the fit.

Somewhat surprising is the relatively large observed

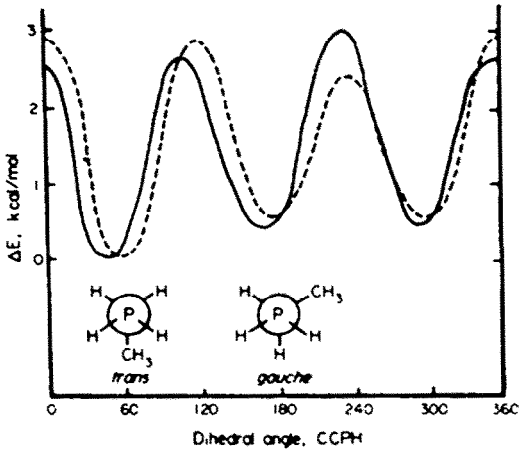

Fig. 1. Calculated (—) and observed (– – –) energy functions for ethylphosphine torsion

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Table 1. Parameters

van der Waals Parameters for the Hill equation		
Atom	r^*(Å)	ϵ(kcal/mole)
P	2.05	0.157

Bond stretching		
Bond	l_0(Å)	K (mdyn/Å)
H–P	1.437	3.33
$C_{sp}3$–P	1.848	2.91
$C_{sp}2$–P	1.828	2.91

Angle bending		
Angle	θ_0(deg)	K (mdyn Å/rad^2)
H–P–H	93.4	0.366
$C_{sp}3$–P–H	93.8	0.40
H–$C_{sp}3$–P	111.0	0.30
$C_{sp}3$–P–$C_{sp}3$	94.8	0.48
$C_{sp}3$–$C_{sp}3$–P	111.5	0.40
$C_{sp}2$–P–$C_{sp}2$	93.2	0.48
$C_{sp}2$–P–$C_{sp}3$	92.5	0.48
$C_{sp}2$–$C_{sp}2$–P	120.0	0.38
$C_{sp}2$–P	Out of plane	0.05

Torsional parameters			
Dihedral angle	Torsional constants (kcal/mole)		
	V_1	V_2	V_3
H–$C_{sp}3$–P–H	0.05	0.	0.29
H–$C_{sp}3$–P–$C_{sp}3$	0.05		0.37
H–$C_{sp}3$–$C_{sp}3$–P			1.0
$C_{sp}3$–$C_{sp}3$–P–H	−0.25		0.6
$C_{sp}3$–$C_{sp}3$–P–$C_{sp}3$	−0.05		0.8
$C_{sp}3$–$C_{sp}3$–$C_{sp}3$–P			1.1
$C_{sp}2$–$C_{sp}2$–$C_{sp}2$–P		16.25	
$C_{sp}2$–$C_{sp}2$–P–$C_{sp}2$			1.1
H–$C_{sp}2$–$C_{sp}2$–P		16.25	
H–$C_{sp}3$–P–$C_{sp}2$	0.05		0.37
$C_{sp}2$–$C_{sp}2$–P–$C_{sp}3$			1.0
$C_{sp}3$–$C_{sp}3$–P–$C_{sp}2$	−0.05		0.8
$C^*_{sp}2$–$C_{sp}3$–$C_{sp}3$–P			1.1

Dipoles	
Atom type	Bond moment (D)
H–P	0.41
$C_{sp}3$–P	0.90
$C_{sp}2$–P	1.09

*Indicates a carbonyl C-atom.

difference between the barriers to internal rotation of the Me groups, which are 3.74 and 3.14 kcal/mole in the *trans* and *gauche* conformations respectively. Our calculated values are more similar (Table 3).

After the parameterization was completed, two papers appeared which discussed isopropylphosphine[17] and *t*-butylphosphine.[18] These data were consequently not used in the parameterization, but will be discussed here.

Durig and Cox[17] have interpreted the IR and Raman spectra of isopropylphosphine as indicating that the *trans* conformation is favored over the *gauche* by about 0.26 kcal/mole, although because of experimental problems they do not seem to place much faith in the accuracy of this number. We calculate the *gauche* form as slightly more stable than the *trans* (Table 3). They assign a rotational barrier to the Me group of 4.3 kcal/mole, while our calculated value is 3.85 kcal/mole for both isomers.

Durig and Cox[18] report the barrier to internal rotation about the P–C bond of t-butylphosphine from the IR and Ramon spectra as 2.79 ± 0.01 kcal/mole, and our calculated value is 3.19 kcal/mole. They also report rotational barriers for the Me group of 4.22 and 3.81 kcal/mole in the solid and gas phases, while we calculate 4.31 kcal/mole.

There are no experimental data available on dimethylethylphosphine, but the calculations indicate that the *gauche* conformer is favored over the *trans* by 1.0 kcal/mole, not unexpectedly. The *gauche*-to-*trans* and *gauche*-to-*gauche* barriers are calculated to be 3.6 and 3.2 kcal/mole, respectively.

The barrier to rotation about the C–P bond in tri-t-butylphosphine was determined experimentally by proton NMR to have an enthalpy of 9.0 ± 0.4 kcal/mole ($\Delta G\ddagger$ = 8.6 ± 0.1 kcal/mole[18]). Our calculated value is 8.3 kcal/mole. Worth mentioning is the bond length of the P–C bond, which is calculated to be 1.879 A, significantly longer than the other P–C bonds mentioned previously (1.853A), as well as the large C–P–C angle (113.5°). The t-Bu groups here, in contrast to the less crowded, almost perfectly staggered, triphenylphosphine, are considerably distorted, each being rotated from the ideal staggered geometry by 15.2°, in such a way as to maintain C_3 symmetry.

Table 2. Calculated and experimental molecular geometries

	Calc. (Å or deg)	Obs. (Å or deg.)	Method/Ref.
Phosphine			
P–H	1.437	1.437 ± 0.004	ED,10a
H–P–H	93.5	93.5	
Methylphosphine			
P–H	1.438	1.423 ± 0.007	ED,10b
P–C	1.857	1.858 ± 0.003	
H–P–H	94.5	93.4	MW,9a
H–P–C	95.9	96.5 (assumed)	
		(93.4)	
P–C–H	110.5	109.6 ± 1.0	
Dimethylphosphine			
P–H	1.439	1.445 ± 0.02	ED,8
P–C	1.853	1.853 ± 0.003	
H–P–C	97.0	96.5 (assumed)	
		(96.95)	MW,9b
P–C–H	110.4	109.8 ± 0.7	
C–P–C	98.0	99.2 ± 0.6	
Trimethylphosphine			
P–C	1.847	1.846 ± 0.003	ED,12
P–C–H	110.4	110.7 ± 0.5	
C–P–C	99.3	98.6 ± 0.3	
Ethylphosphine, gauche			
P–C	1.864	1.880 ± 0.002	MW,16
C–C–P	112.5	110.1 ± 0.2	
Ethylphosphine, trans			
P–C	1.861	1.876 ± 0.002	
C–C–P	115.2	115.2 ± 0.1	
Triphenylphosphine			
P–C	1.828	1.828 ± 0.048	X-ray,21
C–P–C	103.1	103.0 ± 0.2	
P–C–C	123.5	124.0 ± 0.38	
	117.5	116.08 ± 0.37	

Whitesides *et al.*[20] determined the energy difference between the *gauche* and *trans* conformers of 1-diphenylphosphinyl-3,3-dimethylbutane using NMR. These authors found the *trans* conformer to be more stable by 1.99 kcal/mole. Now in our calculations we had to consider three possible conformations for the *trans* form, depending upon the orientation of the diphenylphosphinyl group: two equivalent *trans-gauche* forms (1A, 1B) and one less stable (by 1.5 kcal/mole) (1C) *trans-trans* conformer. In the *gauche* series, the *gauche-gauche* conformer 1D has the lowest energy, while the second *gauche-gauche* and the *gauche-trans* forms are of considerably higher energy. Thus, we determined that the energy difference between the *trans* and *gauche* conformers was 2.6 kcal/mole, favoring the *trans* form by a somewhat larger margin than was found experimentally. The torsional angle between the t-Bu group and the phosphinyl substituent in the *gauche* conformation was calculated to be 82°, while Whitesides estimated 65°.

Triphenylphosphine was fit to the X-ray data of Daly.[21] This investigation showed that the benzene rings adopted a conformation in which the molecule possessed no symmetry. Starting from Daly's coordinates, we obtained a conformation in which the benzene rings were all similarly twisted into a propeller geometry with C_3 symmetry. The dihedral angles between the phenyl planes and the C_3 axis were 31.5°. Stopperka[22] suggested from vibrational spectra that the phenyl groups were oriented perpendicular to the base of the pyramid, while a recent force field calculation by Brack[23] show a large range of possible conformations having similar energies. In the absence of experimental data, we assumed the P–C_{sp^2} torsional constants were the same as in the P–C_{sp^3} case.

Having now defined the necessary parameters for the force field, we examined some 6-membered rings containing phosphorus. The parent phosphorinane (phosphacyclohexane) and several of its 1-alkyl deriva-

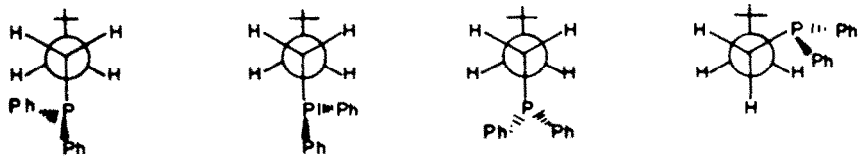


Table 3. Barriers to internal Rotation and Dipole Moments

	Barrier			Dipol Moment		
	Calc.	Obs.	Method/Ref.	Calc.	Obs.	Ref.
Phosphine				0.68	0.58	33
Methylphosphine	1.84	1.96	MW,9	0.98	1.10 ± 0.01	9a
Dimethyl-phosphine	2.20	2.22	MW,10	1.18	1.23	33
Trimethyl-phosphine	2.53	2.6	MW,11	1.28	1.19	33
Ethyl-phosphine						
trans-gauche	0.40[a]	0.57[a] ± 0.28	MW,16	0.98	1.22 ± 0.07	16
					1.17 ± 0.02	34
trans-gauche	2.58	2.97	IR,RA,15			
gauche-gauche	2.58	1.82	IR,RA,15			
trans	3.57[b]	3.74[b] ± 0.05	IR,RA,15			
gauche	3.61[b]	3.14[b] ± 0.05	IR,RA,15			
Isopropyl-phosphine						
gauche-trans	0.34[c]	−0.26[i]	IR,RA,17	0.37		
gauche-gauche	2.85	—				
gauche-trans	3.31	—				
trans/gauche	3.85[b]	4.3[b]				
t-butylphosphine	3.19	2.79 ± 0.01	IR,RA,18	0.37		
	4.31[b]	4.22[g]				
		3.81[h]				
Dimethylethyl-phosphine						
gauche-trans	1.05[c]	—		1.27 (g)		
				1.19 (t)		
gauche-trans	3.56	—				
gauche-gauche	3.17	—				
Tri-tert-butyl-phosphine	8.31	9.0[d] ± 0.4	NMR,19	0.70		
		8.6[e] ± 0.1				
1-diphenylphos-phinyl-2-tert-butyl-ethane						
trans-gauche	2.6[e]	1.99[e] ± 0.2	NMR,20	1.50 (t)		
Triphenyl-phosphine				1.40	1.40[f] ± 0.03	34

[a]Energy-diff. t–g; trans favored. [b]Methyl-Barrier. [c]Energy-diff. g–t; gauche favored. [d]ΔH‡. [e]ΔG‡. [f]Dipole Moment in benzene. [g]solid state. [h]gaseous state. [i]Energy-diff. t–g; *trans* favored but assignment and accuracy said to be uncertain.

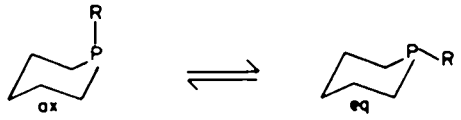
tives were studied, and the results are summarized in Table 4, together with our calculated results. The parent phosphorinane has been studied by proton NMR,[24] which has shown that the hydrogen on phosphorus is at least 90% in the axial position. Our calculated energy difference is 1.2 kcal/mole favoring the axial proton.

The preference of the proton on phosphorus for the axial position in this force field is traced to the following effects. First, there is a substantial contribution of torsional energy favoring the axial conformation. The C–C–PC–H interaction for the equatorial proton has an energy of + 0.16 kcal/mole, mainly from the positive V_3 term (the dihedral angle is 158.5°). On the other hand, the axial proton receives a contribution of −0.15 kcal/mole, mainly from the V_1 term (dihedral angle 48.4°). Since there are two of these interactions, the difference in energy contributed by them to the axial-equatorial equilibrium amounts to 0.6 kcal/mole.

The "*gauche* hydrogen" interaction[2] contributes something here, too. For the equatorial hydrogen, the repulsion with each equatorial proton amounts to +0.15 kcal/mole, whereas if the proton is axial, this difference is −0.05 kcal/mole. Thus, there is a contribution of 0.4 kcal/mole from this interaction to the equilibrium. The remainder of the interactions are difficult to sort out. Whether or not the physical model here is correct in this detail is not known, but the preferential axial position of the proton is correctly calculated.

Featherman and Quin[25] determined the equilibrium constants for a series of 1-substituted phosphorinanes by low temperature phosphorus NMR. All of the substituents display a preference for the equatorial position (Table 4), but considerably less so than in the cyclohexane analogs. There are significant entropy effects measured, however, and extrapolation of the experimental data to room temperature shows that the axial conformers predominate in the cases of Me, Et and Ph substituents. The authors concluded that the interactions

Table 4. Calculated and observed thermodynamic data for the equilibrium axial-equatorial in phosphorinanes



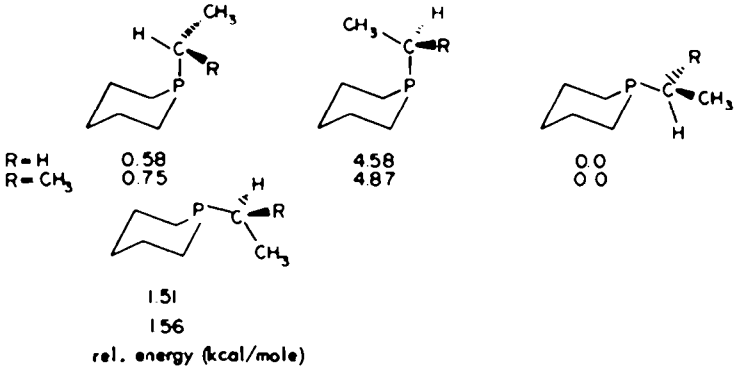
R	calc. ΔG (kcal/mole)	ΔH (kcal/mole)	exp.[25] ΔG (kcal/mole) 163°K	ΔG (kcal/mole) 300°K
H	+1.6		c. 90% axial[24]	
CH_3	−0.48	−0.68 ± 0.05	−0.12 ± 0.06	+0.35 ± 0.07
C_2H_5	−0.52	−0.71 ± 0.12	−0.18 ± 0.13	+0.6 ± 0.12
i-propyl	−0.58	—	ca. −0.5	—
phenyl	+0.2	−0.58 ± 0.07	−0.16 ± 0.08	+0.19 ± 0.10

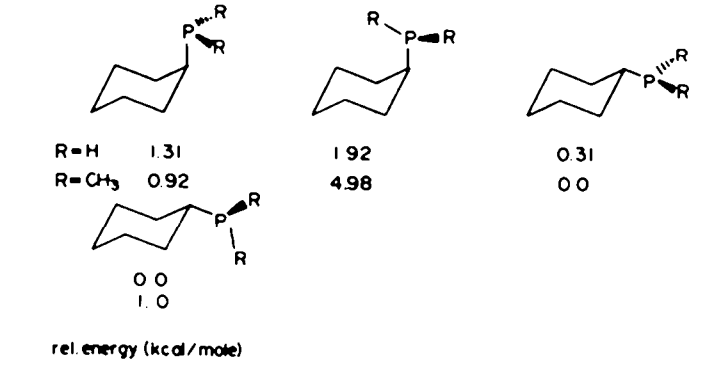
between the synaxial hydrogens and the substituents are repulsive. Our calculated values for Me and Et substituents agree well with the observed NMR values, and there is a calculated repulsion between these axial substituents and the synaxial hydrogens.

To calculate these conformational energies in the case of ethyl and isopropyl phosphoranane, the various conformations possible for the substituent must be taken into account. These conformations, together with their calculated relative energies are shown in the figure. As expected, the more stable axial conformations are those in which there is one hydrogen of the substituent back over the ring. The participation of the higher energy conformers in the equilibrium does not affect things very much.

Phenylphosphorinane was calculated to be 0.2 kcal/mole more stable in the axial conformation, in contrast to experiment. The perpendicular orientation of the phenyl ring is favored over the parallel arrangement in both conformations. While the energy difference is small with the equatorial conformers (0.1 kcal/mole), it is large between the axial conformations (4.3 kcal/mole) as was found also with the hydrocarbons.

The energy differences between the conformations of cyclohexylphosphine and its dimethyl derivative were next calculated. In general, the *trans* conformers were found to be more stable than the *gauche*. Only in the case of the equatorial cyclohexylphosphine was the *gauche* conformation more favored, due to favorable van der Waals' interactions. The calculated conformational free energies of these compounds are 1.5 and 1.1 kcal/mol for the parent and the dimethyl derivatives (favoring the equatorial) respectively, compared with the experimental values (1.6 ± 0.2 and 1.5 ± 0.2) derived from phosphorus-NMR measurements.[26] The calculated results are good for cyclohexylphosphine, while the value calculated for the dimethyl phosphinyl group is a bit low, but reasonable.



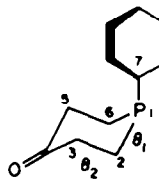


Experimental structural data on the cyclohexylphosphines and on the phosphacyclohexanes discussed above is lacking, but there are crystal structures available for 1-phenyl-4-phosphorinanone[27] and for the *cis* and *trans* isomers of 1-methyl-4-t-butyl-4-phosphorinanol.[25,28] The structural data, compared with our calculated values, are listed in Tables 5 and 6. It is seen experimentally that the ring in 1-methyl-4-t-butyl-4-phosphoranol is less puckered when the Me group is axial than when it is equatorial. Our calculations reproduce this effect well, with the P–C–C angle opening by about 5° upon going from the equatorial to the axial Me. Another trend which is correctly reproduced, although not quantitatively very well, is the lengthening of the ring-carbon quaternary-carbon bond (observed 1.583, calculated 1.563A), as compared to a normal alkane C–C bond (1.535A). An analogous phenomenon has been observed previously in other substituted cyclohexane rings.[28]

1-Phenyl-4-phosphorinanone exists in the crystal according to X-ray data[27] with the phenyl substituent in the axial position, oriented so that the phenyl is perpendicular to the phosphorinane ring. Our calculations (Table 5) confirm this orientation: the perpendicular conformation is more stable than the parallel by 4.1 kcal/mole. In the latter conformation, the *ortho*-hydrogen over the ring interacts severely with the synaxial hydrogens. This is also found with phenylcyclohexane.[30] On the other hand, in phenylcyclohexane, the phenyl is more stable in the equatorial position, because of the unfavorable interaction of the *ortho*-hydrogens on the phenyl with the equatorial hydrogens on the saturated ring in the 2- and 6-positions. Here the calculated differences in energy between the most favorable conformers in the axial and equatorial positions is small (0.4) kcal/mole. However, we do calculate the phenyl to be preferentially equatorial, rather than axial as found in the crystal.

Finally, the transition state for the ring inversion of 1-methyl-phosphacyclohexane was calculated. The experimental value is known to be 8.7 kcal/mole,[25] which is a little less than is found in cyclohexanes (10–11 kcal/mole[31]). The main reason for this lower value in the phosphacyclohexane ring appears to be the smaller torsional energies required for rotations about the C–P bonds. Our calculated value is 9.8 kcal/mole, as determined by beginning with a dihedral angle C–P–C–C– in the chair form, and driving it through the planar configuration, and on to a boat form. As with cyclohexane, the high point on the barrier occurs after the planar conformation is passed[32] (by about 20° in this case).

Table 6. Calculated and observed molecular geometry of 1-phenylphosphorinanone



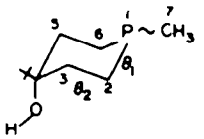
length (Å)/ Angle (deg)	Calc.	⊥ (phenyl perpendic.) Obs. (X-Ray)[27]
$P-C_2$	1.850	1.837 ± 0.005
$P-C_7$	1.835	1.837 ± 0.005
C_7-P-C_4	95.8	98.2 ± 0.2
C_6-P-C_7	102.6	101.8 ± 0.2
C_7-P-C_7	102.9	103.0 ± 0.2
$P-C_7-C_3$	115.2	117.0 ± 0.2
$P-C_4-C_5$	115.1	115.9 ± 0.2
θ_1	51.2	47.6
θ_2	59.0	56.3
	re. Energy	
Phenyl-ax ⊥	0.4	
Phenyl-ax ∥	4.55	
Phenyl-eq ⊥	0.0	
Phenyl-eq ∥	0.0	

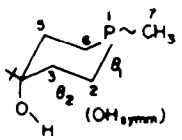
CONCLUSIONS

Relatively little structural and thermodynamic information is available on phosphalkanes. A reasonably good parameter set was devised, however, to extend calculations for the alkanes to include the phosphaalkanes. Some predictions have been made regarding this class of compounds, and many more predictions are easily possible using this molecular mechanics technique.

It is possible to calculate energy differences between conformations with reasonable accuracy. It is not possible to calculate heats of formation at this time, because too few experimental data on this class of compounds have previously been recorded in the literature.

Table 5. Calculated and observed molecular geometries of *trans* and *cis* 1-methyl-4-tert-butyl-4-phosphorinanol





Angle (deg)	CH_3-axial Calc.	OH_{sym}	Obs. (X-Ray)[28]	CH_3-equatorial Calc.	OH_{sym}	Obs. (X-Ray)[25]
C_7-P-C_4	97.4	98.1	97.7	94.1	94.7	98.0
C_7-P-C_7	104.0	103.6	101.9	100.9	101.3	102.8
C_6-P-C_7	103.1	102.8	101.9	101.2	101.6	102.8
$P-C_7-C_3$	115.9	115.5	116.0	109.7	109.9	110.6
$P-C_4-C_5$	116.9	116.6	116.0	111.3	111.5	110.6
θ_1	44.8	44.9	46.0	60.9	60.2	57.0
θ_2	59.9	59.4	58.8	68.0	66.6	62.0
rel. Energy	0.9	1.4		0.0	1.3	

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[32]The geometry of the transition state for the inversion of cyclohexane has been widely discussed in the literature. (For reviews, see Ref. 31; J. E. Anderson, *Topics Current Chem.* **45**, 139 (1974); K. B. Wiberg and R. H. Boyd, *J. Am. Chem. Soc.* **94**, 8426 (1972)). The four atoms in-a-plane vs five atoms in-a-plane transition state was considered and the general consensus is that the former is of lower energy. Using the "driver" technique, we find that with both of our current force fields (1973, MM1 and 1977, MM2) as one drives the dihedral angle from the chair to the four atoms in a plane conformation, the energy does indeed rise as described by Wiberg and Boyd. However, if one continues to drive the angle further, the energy continues to increase, reaching a maximum value at about 13° past the four atoms in a plane arrangement. The energy here is about 1.6 kcal/mole greater than in the four atoms in-a-plane arrangement. While the dihedral angle which has gone from 0° to 13° has improved significantly, the other dihedral angles in the ring have, in general, worsened, sufficiently to increase the energy as indicated. We also find that the transition state to ring inversion can undergo a large pseudorotational motion with very little energy change, as pointed out earlier by H. M. Pickett and H. L. Strauss, *J. Am. Chem. Soc.* **92**, 7281 (1970).
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