A Conformational Analysis of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and Related Model Compounds

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Abstract: The energies for rotating around the P–O bond in H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and related model compounds have been studied by ab initio molecular orbital methods using minimal (STO-3G) and extended (4-31G) basis sets. This is the first case where the relative magnitude of V_2 ("anomeric" term) and V_3 ("bond staggering" term) have been calculated explicity for a molecule with more than one torsion angle. The results of these calculations have been analyzed in terms of empirical potential functions in order to elucidate the important physical effects playing a role in the barrier mechanism and to provide guidance for empirical potential function calculations on molecules involving phosphate groups. Finally, we report a number of molecules with unusually small "threefold" barriers.

In view of the important role of the phosphate group in the structure of nucleic acids and nucleotides[1] as well as energy transduction,[2] there has been much interest in its electronic structure,[3] hydration energy,[4] and metal complexing ability.[5] No one has, however, carried out a systematic conformational analysis of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} using quantum mechanical (ab initio molecular orbital) methods.

The dimethylphosphate anion has received (deserved) attention from quantum chemists; Newton[6] studied its conformational profile with ab initio methods using a STO-3G basis set. Pullman and co-workers[4] have studied the hydration of dimethyl phosphate and the role of d atomic orbitals on phosphorus; Marynick and Schaeffer[5] have examined metal-dimethyl phosphate interactions using an STO-3G basis set.

H_3PO_4 and $(CH_3)_3PO_4$ have been the subject of somewhat more accurate ab initio calculations by Lehn and Wipff,[7] these authors finding that the "anomeric" effect present in sugars and intermediates in amide hydrolysis was likely to be of importance in determining the properties of phosphate esters as well.

Probably the most definitive ab initio theoretical paper on rotational barriers in molecules was that by Radom et al.[8] These authors used a Fourier series in order to separate out various physical effects on the barrier mechanism when considering a single rotational degree of freedom in simple first row molecules. Later, Radom and Stiles[9] proposed a simple additivity scheme for substituent effects on barriers and pointed out where exceptions were likely to occur. We will make use of the findings of these authors in this study.

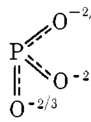
In this paper, we ask ourselves two general questions: First, what is the nature of the conformational profile for simultaneous rotation around more than one P–O bond and can such profiles be fit in a simple way by analytical potential functions? Second, how does the conformational profile change for rotating around the P–O bond as one changes the substituent around the phosphorus and what generalizations can one draw from this on the nature of rotational barriers in polar molecules?

Computational Details. These ab initio calculations were carried out with GAUSSIAN 70 (QCPE No. 236) using STO-3G[10] and 4-31G basis sets.[11]

Results and Discussion

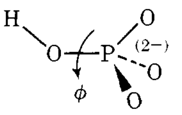
Internal Geometries of H_3PO_4 and $H_2PO_4^-$. Table I summarizes the results of P–O bond length and valence angle variations in H_3PO_4 and $H_2PO_4^-$. In each case the bond lengths were optimized using tetrahedral valence angles and then the angles were optimized. The qualitative features of the structures are in agreement with experiment (i.e., r(P=O) < r(P–O) and θ(O=P—O) > tetrahedral), but the bond lengths are predicted to be somewhat too long and the valence angles too large. The 4-31G basis set does a better job in reproducing the bond lengths in H_3PO_4, but it is clear that the agreement is still not as good as generally found for the many molecules with first row atoms studied by Lathan et al.[13] The role of the crystal in determining the experimental parameters and the use of one set of dihedral angles in carrying out the minimizations are further sources of possible disagreement between the calculations and experiment.

Conformational Analysis of HPO_4^{2-}. The conformational profile of HPO_4^{2-} is simple, involving only an O–H rotor rotating relative to a PO_3^{2-}

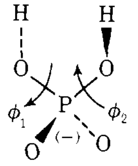


group (1). We used P-OH (r = 1.618 Å) and P-O$^{-2/3}$ (r = 1.771 Å) bond lengths extrapolated from the values found for H_3PO_4 and $H_2PO_4^-$.[14] With all internal angles tetrahedral, the energy for the ϕ = 0 (O–H eclipsed to a P$\overset{...}{-}$O bond) is −632.12526 au and the energy for ϕ = 60 (O–H staggered with respect to two P$\overset{...}{-}$O bonds) is 0.08 kcal/mol higher.

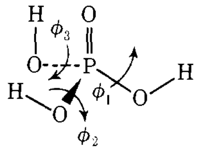
Conformational Analysis of $H_2PO_4^-$. Using our minimum energy bond lengths and tetrahedral bond angles, we calculated the conformational profile of $H_2PO_4^-$ as a function of ϕ_1 and ϕ_2 (Table II). We used the same conventions as Newton[6] did in his study of $(CH_3)_2PO_4^-$, i.e., ϕ_1 = (H(1)-O(1)-P-O(2)) and ϕ_2 = (H(2)-O(2)-P-O(1)) (**2**), with the angles defined by clockwise rotation of one HO bond relative to the other P–OH bond.[20]



(**1**)



(**2**)



(**3**)

The results are also presented in Figure 1; a cursory glance at this figure and that found in the paper by Newton[6] shows that the same physical effects appear to be operating in both $H_2PO_4^-$ and $(CH_3)_2PO_4^-$. Specifically, Newton pointed out that the "anomeric" effect, the tendency for lone pairs to be gauche relative to polar bonds, was an important factor in the $(CH_3)_2PO_4^-$ surface. Radom et al.,[8] in their study of single bond rotations, fit their ab initio calculated data to the Fourier

Table I. Results of P-O Bond Length and Valence Angle Variations in H_3PO_4 and $H_2PO_4^-$ [a]

	STO-3G	4-31G	Exptl[12]
	H_3PO_4 [b]		
r(P=O), Å	1.575	1.540	1.52
r(P-O), Å	1.657	1.642	1.57
θ(O—P=O), deg	116.6 (109.47)	(109.47)	112.0
E_T, au	−633.91344 (−633.89678)	−641.04660	
	$H_2PO_4^-$ [c]		
r(P—O$^-$), Å	1.607		1.508
r(P-O), Å	1.714		1.583
θ(O—P—O), deg	130.6		115.4
θ(HO-P-OH)	95.9		105.5
E_T, au	−633.14331		

[a] Values in parentheses are not energy optimized. [b] The dihedral angles $\phi(O{=}POH_1) = \phi(O{=}POH_2) = \phi(O{=}POH_3)$ were kept at 0 during the optimization of the internal coordinates. [c] $\phi(H_1OPO) = \phi(H_2OPO) = 60°$, near the dimethylphosphate anion minimum found by Newton.

Table II. STO-3G Conformational Energies of $H_2PO_4^-$ (energies in kcal/mol)

ϕ_1	ϕ_2	ΔE [a]	ΔE(calcd) [b]
0	0	6.61	6.13
60	0	3.30	3.37
120	0	2.12	2.43
180	0	4.53	4.66
240	0	2.12	2.44
300	0	3.30	3.39
60	60	0.36	0.36
120	60	0.02	−0.31
180	60	2.58	2.49
240	60	0.34	0.55
300	60	1.19	1.21
120	120	0	−0.40
180	120	2.70	2.67
240	120	0.29	0.45
180	180	5.47	5.46

Potential Terms in $H_2PO_4^-$ (eq 2) ($r^2 = 0.986$)[c]

Term	kcal/mol
V_1	−0.47
V_2	−3.31
V_3	0.14
V_1'	0.57

[a] Energies determined by ab initio techniques. [b] Energies calculated using eq 2. [c] Correlation coefficient of Fourier eq 2.

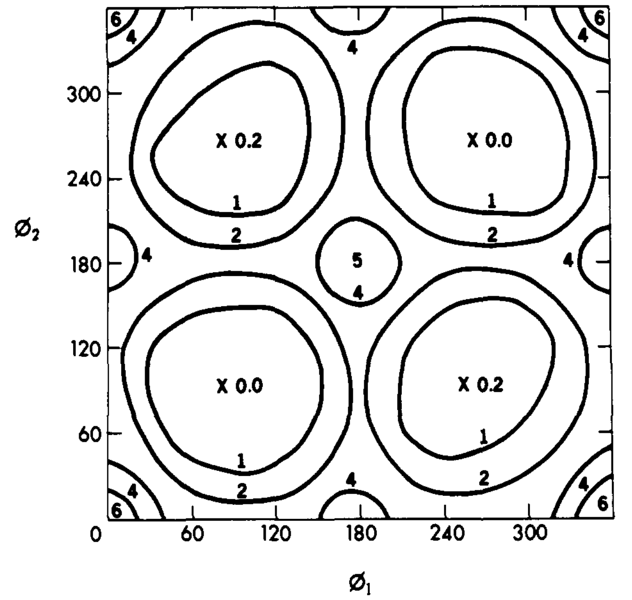


Figure 1. Energy of $H_2PO_4^-$ as a function of HOPO (ϕ_1) and H_2OPO (ϕ_2) angles. In each case one is rotating the OH bond clockwise relative to the PO bond.

Table III. STO-3G Conformational Energies of $(CH_3)_2PO_4^-$ (energies in kcal/mol)

ϕ_1	ϕ_2	ΔE [a]	ΔE(calcd) [b]
120	0	4.5	4.5
180	0	5.5	5.5
240	0	4.5	4.5
60	60	1.0	1.1
120	60	1.8	1.6
180	60	3.3	3.4
240	60	2.7	2.9
120	120	3.0	2.8
180	120	4.8	5.1
240	120	3.8	4.1
180	180	7.2	6.9
75	75	0	0.2
270	90	2.5	2.0
30	120	3.2	3.2
220	180	6.0	6.1

Potential Terms in $(CH_3)_2PO_4^-$ (eq 2) ($r^2 = 0.986$)[c]

Term	kcal/mol
V_1	0.38
V_2	−2.58
V_3	−0.64
V_1'	0.87

[a] Estimated from Newton's[6] Figure 2. [b] Calculated using potential function (eq 2). [c] Correlation coefficient.

series shown in the equation

$$V(\phi) = (V_1/2)(1 - \cos\phi) + (V_2/2)(1 - \cos 2\phi) + (V_3/2)(1 - \cos 3\phi) + V_1'\sin\phi + V_2'\sin 2\phi \quad (1)$$

We have taken our $H_2PO_4^-$ surface and carried out a linear regression analysis on the ϕ_1, ϕ_2 surface to fit the energies to the equation

$$V(\phi_1,\phi_2) = \sum_{i=1}^{2} [(V_1/2)(1 - \cos\phi_i) + (V_2/2)(1 - \cos 2\phi_i) + (V_3/2)(1 - \cos 3\phi_i)] + V_1'\cos(\phi_1 - \phi_2) \quad (2)$$

Our reasoning in choosing the particular functions of ϕ_i was as follows: (1) we wished to use the same type of cosine terms as Radom et al.[8] and see how well we could fit the conformational map; (2) one might expect dipole-dipole repulsions between the O-H groups, which could be approximated by the V_1' cosine term.[15] The results of this analysis are presented in Table II and they show that the V_2 term, which is the Fourier component which reflects "anomeric" effects, is by far the most important in representing the data; the V_3 term which is often used in empirical potential function studies of nucleotides is the smallest and is not significant in a statistical sense. We also subjected Newton's data on $(CH_3)_2PO_4^-$ to the same analysis and the results are presented in Table III. It is not clear how significant the somewhat larger V_3 term (−0.62 kcal/mol) is here, since we estimated the values in Table III from the ϕ_1, ϕ_2 map in Newton's paper,[6] and our errors in these estimations are probably ±0.3 kcal/mol. However, it is clear that the V_2 term is again the largest term and the V_3 component much less

Table IV. Conformational Energies of H_3PO_4 STO-3G Basis, Optimized P-O and P=O Bond Lengths; θ = tetrahedral (energies in kcal/mol)

ϕ_1	ϕ_2	ϕ_3	ΔE^a	$\Delta E(\text{calcd})^b$
0	0	0	1.44	1.35
60	60	60	4.47	4.52
120	120	120	5.45	5.96
180	180	180	6.18	6.29
60	0	0	2.63	2.34
120	0	0	1.64	1.45
180	0	0	0^c	0.27
60	300	0	5.46	6.04
120	240	0	7.19	6.46
300	60	0	4.75	5.23
240	120	0	3.59	4.00
60	60	0	3.64	3.39
120	120	0	3.01	2.99
120	120	180	6.33	6.00
180	180	0	1.68	1.92
60	300	180	5.43	4.69

Potential Terms in H_3PO_4 (eq 3) ($r^2 = 0.96$)[d]

Term	kcal/mol
V_1	1.42
V_2	2.81
V_3	0.23
V_1'	2.35
V_1''	−0.14
V_1'''	−0.96

[a] Energy determined by ab initio calculations. [b] Energy calculated from eq 3. [c] Total energy = −633.896804 au. [d] Correlation coefficient of eq 3.

significant. These are important results and emphasize that a V_2 rather than a V_3 term should be used in classical potential function studies of molecules with an $R_2PO_4^-$ linkage. This is the first direct application of the Fourier analysis[8] to a two rotor problem and this method appears to be very well suited to treat such a case.

Conformational Analysis of H_3PO_4. We have also carried out a conformational analysis of H_3PO_4 (**3**). The majority of the calculations used the optimized values for r(P=O) and r(P-O) with tetrahedral valence angles; we also carried out a few calculations with energy optimized θ(O=P—O), as well as a few with experimental values of r(P=O) and r(P-O) and tetrahedral bond angles. The results are summarized in Table IV. The lowest energy conformation was found to be $\phi_1 = 0$, $\phi_2 = 0$, $\phi_3 = 180$ (ϕ= H—O—P=O) and appears to be a compromise between anomeric and dipolar effects. One expects the O=P-OH group to favor $\phi = 0$ for both electrostatic and resonance $^-$O—(P=O)$^+$H reasons. In analogy with $(CH_3O)_2PO_2^-$, we expect H-O-P-OH anomeric effects to favor α(H-O-P-O) = 60° and so the minimum energy geometry may well be a compromise between these different factors. We thus subjected our largest collection of ϕ_1, ϕ_2, and ϕ_3 points to the linear regression analysis using a potential function

$$
\begin{aligned}
V = \sum_{i=1}^{3} [(V_1/2)(1 - \cos \phi_i) + (V_2/2)(1 - \cos 2\phi_i) \\
+ (V_3/2)(1 - \cos 3\phi_i) + (V_1'/2)(1 - \sin \phi_i)] \\
+ V_1''[\cos (\phi_1 + 120) \cos (\phi_2 + 240) \\
+ \cos (\phi_2 + 240) \cos (\phi_3 + 120) \\
+ \cos (\phi_3 + 120) \cos (\phi_1 + 240)] \\
+ V_1'''[\sin (\phi_1 + 120) \sin (\phi_2 + 240) \\
+ \sin (\phi_2 + 240) \sin (\phi_3 + 120) \\
+ \sin (\phi_3 + 120) \sin (\phi_1 + 240)] \quad (3)
\end{aligned}
$$

Table V. Comparison of Different H_3PO_4 Calculations (energies in kcal/mol)

ϕ_1, ϕ_2, ϕ_3	STO-3G[a]	STO-3G[b]	4-31G[c]	Lehn and Wipff[d]
60, 60, 300	7.39	8.60	8.72	6.1 (6.2)
60, 60, 60	4.47	5.15	1.82	0
180, 180, 180	6.18	8.16	25.81	21.9 (24.2)
0, 0, 180	0	0	0	

[a] Values from Table IV. [b] Used geometry of Lehn and Wipff.[7] [c] Used geometry of Lehn and Wipff;[7] total energy of 0, 0, 180 conformation is −641.03988 au. [d] Values in parentheses used sp basis, others spd; total energy of 60, 60, 60 is −640.8819 (spd) and −640.6555 au (sp).

We included terms analogous to our potential function (eq 2) with the exception of V_1', which was included to take into account the fact that the ϕ_i optimum for H-O interacting with the P=O via the above mentioned mechanism was not the same ϕ as that for optimum H-O-P-O anomeric interaction. We also broke up the cos ($\phi_1 - \phi_2$) term into its components.[15]

In this case, unlike $H_2PO_4^-$, the Fourier potential function does not give as satisfactory a fit to the ab initio calculated energies. The V_2 term is the most important, followed by the V_1 and V_1' terms.

Lehn and Wipff[7] recently noted the importance of the anomeric effect in H_3PO_4 and $(CH_3)_3PO_4^-$ in their ab initio calculations for these molecules with $\phi_1 = 60$, $\phi_2 = 60$, $\phi_3 = 60$; $\phi_1 = 300$, $\phi_2 = 60$, $\phi_3 = 60$, and $\phi_1 = \phi_2 = \phi_3 = 180°$ using a basis set significantly lower in energy than the STO-3G. We thus repeated our calculations (using the Lehn and Wipff internal geometry) at the STO-3G and 4-31G level for the above three combinations of dihedral angles as well as for $\phi_1 = \phi_2 = 0$, $\phi_3 = 180$. The results, presented in Table V, show that the H-O-P-O anomeric effect is important, as stressed by Lehn and Wipff, but that the H—O—P=O interactions also play a role in the conformation of H_3PO_4 and make the $\phi_1 = \phi_2 = 0$, $\phi_3 = 180$ geometry lower in energy than those considered by Lehn and Wipff.

Very recently, Gorenstein et al.[16] carried out CNDO/2 calculations on the dimethylphosphate anion and trimethyl phosphate; they pointed out a significant dependence of COPO dihedral angles on the OPO internal angles. For example, for the dimethylphosphate anion, those molecules with smaller OPO angles prefer the g,t ($\phi_1 = 60$, $\phi_2 = 180$) over g,g ($\phi_1 = 60$, $\phi_2 = 60$) conformations; those with larger OPO angles prefer g,g. These very important findings are supported by x-ray evidence and can be interpreted in terms of a compromise between anomeric effects, which favor g,g, and steric effects, which favor g,t or t,t; the latter become more important the smaller the OPO angle. Empirical potential functions[1] for conformational analysis usually contain torsional nonbonded (dispersion plus exchange repulsion) and electrostatic terms. Our calculations have stressed the importance of using a V_2 torsional term; the nonbonded and electrostatic terms will be of crucial importance as well in reproducing the observed tendency of highly charged phosphate groups to be in more extended conformations and the tendency for phosphate groups with small OPO angles to be in g,t rather than g,g forms.

Model Calculations on H_3P^+-OH F_3P-OH, F_3COH, and FH_2P^+OH. In order to gain further understanding of the nature of the rotational barriers of these compounds, we decided to carry out some calculations on simpler model compounds in which we replaced the doubly bonded oxygen and all but one of the OH groups by -H and -F.[17] We first examined H_3P^+-OH and F_3P^+OH (Table VI). The hydrogen compound is calculated to have a barrier (0.81 kcal/mol) of the magnitude of that of the methanol, but no barrier *at all* is found for

Table VI. Conformational Energies for $^+PF_3OH$, $^+PH_3OH$, $^+PH_2FOH$, $^+PHF_2OH$, and CF_3OH (kcal/mol)

ϕ (XPOH)	ΔE $^+PF_3OH$	 $^+PH_3OH$	 $^+PH_2$-FOH[a]	 $^+PF_2$-HOH[b]	 CF_3OH
	Relative Conformational Energies				
0	0 (0)[c]	0	0	0	0
60	0 (0)[c]	−0.81	−0.65	−0.29	−0.23 (−0.52)[c]
120	0	0.0	0.90	−1.20	0
180	0	−0.81	1.52	−2.56	−0.23 (−0.52)[c]
240	0	0	0.90	−1.20	0
300	0	−0.81	−0.65	−0.29	−0.23 (−0.52)
	Potential Function Terms (eq 1 $V_1' = V_2' = 0$ by symmetry)				
V_1			2.05	−2.31	
V_2			−0.85	0.71	
V_3	0 (0.0)[c]	0.81	−0.53	−0.25	0.23 (0.52)[c]

[a] X = F. [b] X = H. [c] Values in parentheses found with 4-31G basis; others used STO-3G.

Table VII. STO-3G Conformational Energies and Potential Functions for $H_2P(=O)OH$ and $HFP(=O)OH$ (energies in kcal/mol)

ϕ(O=POH)	ΔE H_2PO_2H	 F_2PO_2H	 $HFPO_2H$[a]
0	0	0	0
60	2.75	2.40	1.61
120	4.87	2.76	3.45
180	3.42	1.30	2.44
240	4.87	2.76	4.40
300	2.75	2.40	3.71
	Potential Function Terms (eq 1)		
V_1	3.69	1.11	2.96
V_2	2.80	2.57	2.27
V_3	0.27	0.19	0.52
V_1'			−1.06
V_2'			−0.51

[a] At ϕ = 120, O-H eclipses P-F.

the cationic species F_3P^+–OH at *both* the STO-3G and 4-31G levels. This is not so surprising, since this molecule is isoelectronic to HPO_4^{2-}, which has a calculated barrier of 0.08 kcal/mol, with the minimum energy found with the O-H eclipsing the P$\overset{\text{--}}{-}$O bond.

Radom and Stiles[9] have already discussed the effect of successive geminal substitutions on the magnitude of rotational barriers. They pointed out that as one successively fluorinates ethane, the barrier goes up for CH_2FCH_3 relative to CH_3-CH_3 then begins to decrease for CF_2HCH_3 and CF_3CH_3 relative to CFH_2CH_3. In view of this, we expected a similar decrease in barrier height for CF_3OH relative to CH_3OH and $^+PF_3OH$ relative to $^+PH_3OH$. We thus studied the barrier in CF_3OH, because we expected it to have an analogous conformational profile to $^+PF_3OH$. Indeed it does, with a barrier of 0.23 (STO-3G) and 0.52 kcal/mol (4-31G) (CH_3OH has a 4-31G calculated barrier[8] of ~1.12 kcal/mol). It appears that the hyperconjugative effect used to rationalize the smaller barrier in CF_2HCH_3 and CF_3CH_3 relative to CH_2FCH_3 is playing a role in causing the small barriers in $^+PF_3OH$ and CF_3OH.[18] However, the calculations[9] and experiments find CF_3CH_3 to have a larger barrier than CH_3CH_3, whereas $^+PF_3OH$ and CF_3OH have significantly smaller barriers than the corresponding trihydrosubstituted compounds. Thus, it is likely that electrostatic attraction P-$F^{\delta-}\cdots{}^{\delta+}H$-O is also playing an important role in reducing the barrier heights in the trifluoro compounds; such effects would be much smaller in the substituted ethanes. This is supported by the fact that at both the STO-3G and 4-31G levels the fluorines in CF_3OH and $^+PF_3OH$ have a partial negative charge and the hydrogen a partial positive charge.

We also studied $^+PF_2HOH$ and $^+PH_2FOH$. Fourier component analysis of this surface shows that the V_1 term is dominant; this term which represents dipolar (electrostatic) effects favors ϕ values where the H-O bond is eclipsed to the fluorine ($^+PH_2FOH$) or bisects the two F substituents ($^+PF_2HOH$). The fact that the minimum energy conformation in $^+PF_2HOH$ has ϕ(FPOH) $\neq$ 0 (the minimum calculated with the Fourier series (eq 1) is at ϕ = 55) is due to the V_2 and V_3 terms, which favor ϕ = 90 and 60, respectively.

Model Calculations on $H_2P(=O)OH$, $F_2P(=O)OH$, and $HFP(=O)OH$. We carried out calculations on other single O-H rotor models in which interaction with both the P=O bond and P-F (P-H) bonds are possible. The results of these studies (including the derived Fourier components) are presented in Table VII. The results show clearly the tendency for the O-H to eclipse the P=O bond. The V_2 term favors ϕ = 0 and 180 (these allow hyperconjugation with both P=O and P-F bonds). However, the V_1 term is significantly different between $H_2P(=O)OH$ and $F_2P(=O)OH$. This is easily understood on the basis of bond dipoles, the P-F bonds being of comparable polarity to the P=O and thus ϕ = 180 is almost as favorable as ϕ = 0; in the P-H compound, dipole-dipole interactions favor O-H eclipsed with the P=O group. In the $HFP(=O)OH$ compound, the conformation ϕ = 60 is significantly favored over that with ϕ = 300, probably because the latter puts a lone pair trans to the polar P-F bond. As noted by Lehn and Wipff,[7] this is a very unfavorable interaction.

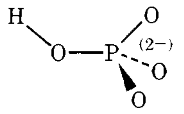
Summary and Conclusions

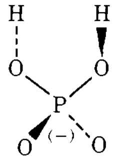
We have carried out ab initio calculations on the conformational profiles of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and related model compounds. For $H_2PO_4^-$ and the related $(CH_3)_2PO_4^-$, our direct fit to analytic potential functions shows the importance of the V_2 Fourier component and the smallness of the V_3 term, which gives quantitative support to Newton's statement[6] that "anomeric" effects are important in $(CH_3)_2PO_4^-$. H_3PO_4 is a more complex case and simple potentials do not fit the conformational profile well. For this molecule, we found that the ϕ = 0, 0, 180 conformation was lower in energy than the 60, 60, 60 conformation expected on the basis of qualitative consideration of the anomeric effect. As we noted above, however, it appears that the P=O bond in H_3PO_4 is far more important in influencing the conformation than the O$\overset{\text{--}}{-}\bar{P}\overset{\text{--}}{-}$O group was in the case of $R_2PO_4^-$.

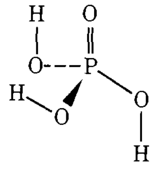
Calculations on the conformation of model compounds of the form $RR'P(=O)OH$ and $RR'R''P^+OH$ (R, R′, R″ = H or F) indicate that anomeric (V_2) interactions with both P-F and P=O bonds are important and these, together with V_1 (dipolar) effects, play the dominant role in determining the conformation. The contributions of resonance forms of the type P=F^+ as well as dipolar effects in H_2FP^+OH makes it less costly to eclipse the ^+P-F bond (0.65 kcal/mol) than the ^+P-H (1.55 kcal/mol). In the case of $^+PF_3OH$ and CF_3OH we find an extremely small barrier; these results are consistent with the importance of geminal interactions[9] in both of these compounds, since the calculated barrier of CF_3OH is about one-half of that of CH_3OH. In fact, at both the minimal and extended basis set level, the barrier to rotation in $^+PF_3OH$ is predicted to be <0.01 kcal/mol.

We should emphasize here the limitations of these calculations—most of the conformational calculations have been carried out with a minimal basis set without extensive variation of internal geometrical parameters (bond lengths and valence angles). However, comparisons with our 4-31G calculations and those by others[4,7] including "d" functions on phosphorus indicate that the qualitative features of the potentials are likely to be correctly represented at the minimal basis level.

The implications of these results can be summarized in a simple fashion; a V_3 ethane-like conformational profile, where the conformation is dominated by the tendency to stagger lone pairs and bond pairs, is not correct for the phosphate linkage. HPO_4^- is slightly more stable with OH and PO bonds (**4**) eclipsed; $H_2PO_4^-$ prefers conformations where the oxygen lone pairs on the O–H groups can delocalize onto the other P–OH (**5**) bond and H_3PO_4 prefers conformations which allow both H–O → P–OH delocalization and H–O → P=O delocalization (**6**). The calculations of Newton on $(CH_3)_2PO_4^-$ and Lehn and Wipff on $(CH_3)_3PO_4$ seem to indicate that these effects are also present in alkyl phosphates. Empirical potential functions to model the phosphate conformational profile should use a functional form similar to the one described here for the conformational dependence; the necessity of including steric and electrostatic terms as well in such a potential is clear from the experimental data, as well as the need to relax the rigid geometry requirement.[16]


(**4**)


(**5**)


(**6**)

The empirical potential form incorporated in the consistent force field method implemented by Warshel and Lewitt[19] includes terms to take into account torsional, nonbonded, and electrostatic energies as well as a term which incorporates coupling between internal and torsional motions (this latter effect is the one discussed by Gorenstein et al.[16]) We are currently attempting to combine the torsional terms derived here with appropriate nonbonding, electrostatic, and coupling terms in order to derive a potential function consistent with these ab initio potentials and experimental data.[16]

Our finding of zero rotational barrier in $^+PF_3OH$ is of great relevance to an understanding of barrier mechanisms. The tendency of X–H bonds to eclipse double bonds (as in acetaldehyde) and stagger with respect to single bonds (as in methanol) appears to be perfectly balanced in this case; the P–F bond in this molecule has just the right amount of double bond character to make staggered and eclipsed conformations of the O–H bond relative to the P–F equally favorable. We cannot, however, rigorously separate this conjugative effect from $P\text{–}F^{\delta-}\cdots{}^{\delta+}H\text{–}O$ attractions, since this effect appears to be important here also.

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References and Notes

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(14) The P–O bond length was linearly extrapolated from the bond lengths in H_3PO_4 (1.657 Å) and H_2PO_4 (1.714). The $P\overset{\cdots}{-}O^{-2/3}$ bond length was extrapolated using the P=O length in H_3PO_4 (1.575) and the $P\overset{\cdots}{-}O^{-1/2}$ from H_2PO_4 (1.607), assuming the difference between $r(P\overset{\cdots}{-}O^{-2/3})$ and $r(P\text{—}O^{-1/2})$ was one-third of that of $r(P{=}O)$ and $r(P\overset{\cdots}{-}O^{-1/2})$.

(15) The equation for the interaction between two point dipoles is a complicated function of θ_1, θ_2, and $\Phi_1 - \Phi_2$, where θ_1 and θ_2 are the angles the dipoles make with the line connecting them and $\Phi_1 - \Phi_2$ is the relative dihedral angle of the dipoles; unfortunately, θ_1, θ_2, and $\Phi_1 - \Phi_2$ all change as one varies ϕ_1 and ϕ_2, so our cosine term (V_1') is a crude approximation to this term.

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(17) All angles tetrahedral, $r(P\text{–}F) = 1.54$, $r(P\text{–}H) = 1.40$, $r(P\text{–}O) = 1.65$, $r(O\text{–}H) = 0.99$, $r(C\text{–}F) = 1.38$, $r(P{=}O) = 1.575$ Å.

(18) A referee noted that this comparison is somewhat misleading since the hyperconjugative effect in CF_3CH_3 is largest ($C{=}F^+\cdots C\text{–}H$ interaction) at $\phi = 0$ (F and H eclipsed), whereas in CF_3OH, the main conjugative effect involves the oxygen lone pair interacting with a C–F bond, which corresponds to an FCOH dihedral angle of 90°.

(19) A. Warshel and M. Lewitt, Quantum Chemistry Program Exchange, Program No. 247.

(20) The arrows in Newton's figure are somewhat confusing on this point, but this is the same convention he used in constructing his Figure 2.