

Ab Initio Structures of Phosphorus Acids and Esters. 3. The P–O–P Bridged Compounds $H_4P_2O_{2n-1}$ for $n = 1$ to 4

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Abstract: The detailed molecular structures including the equilibrium conformations and energies of the four prototype phosphorus compounds exhibiting a P–O–P interconnection, $H_4P_2O_{2n-1}$ for $n = 1$ to 4, have been determined by ab initio quantum-chemical calculations. In addition the number and relative energies of the stable conformers, their dipole moments, and the changes in both energy and dipole as a function of torsional angle about the bridging O–P linkage were determined. For the three smaller compounds we compare the results obtained in two or more differing basis sets. The size, bending force constant, and barrier to linearity of the P–O–P angle for these $n = 1$ to 3 species is consistent with the large angles (up to 180°) seen in pyrophosphate salts. The angle is particularly large in $H_4P_2O_3$. The origins of conformational preference cannot be unambiguously determined, but appear to vary between species. Using ab initio computations, we have also determined the enthalpies and free energies of the important reactions $H_4P_2O_{2n-1} + H_2O \rightarrow 2H_3PO_n$ for $n = 1$ to 4. The results indicate that the energies of these hydrolysis reactions (involving scission of “high-energy phosphate bonds”) decrease slightly with increasing numbers of substituents, being positive or close to zero in the gas phase.

The P–O–P linkage plays a role of supreme importance in the chemistry of phosphorus compounds, somewhat analogous to the role of C–C bonds in the chemistry of carbon compounds (organic chemistry). Molecules incorporating this linkage are involved in a vast variety of chemical environments and applications, from inorganic to biological systems. However, because of its high susceptibility to hydrolysis, the P–O–P linkage is not found in nature except as produced by living organisms.

In the two preceding papers of this series, which deal with phosphorus acids and esters, we have reported systematic ab initio quantum-chemical studies of the (gas-phase) structures and energies of the simplest phosphorus oxyacids¹ (the phosphinic, phosphonic, and phosphoric acids H_3PO_2 , H_3PO_3 , and H_3PO_4) and their methyl esters.² These studies have not only permitted us to verify the accuracy of the computational methods by comparing our results with the experimental data in these cases, but also to compare structural trends among chemically related species. By combining the computed energy data on the acids and their esters, we were able to obtain meaningful values for the enthalpies of the esterification reactions of the acids. (This is, of course, the reverse of the hydrolysis of the esters, both reactions being simply a scrambling process involving exchange of substituents on oxygen, i.e., C for H between C–O–H and P–O–H.) Finally, by examining the molecular energy as a function of the torsional angles, we were able to demonstrate in all cases (except where there were several alkyl substituents, as in trimethyl phosphate) that the nature and relative energies of the equilibrium conformations were governed by the degree of the overall electrical inhomogeneity, reflected by the size of the molecular dipole moment.

In the present paper we extend this tenor of study to simple prototype species containing a P–O–P linkage. This is not only useful as an extension of the investigation reported in the preceding two papers, but serves as a good example of the problems encountered in the study of the structures and energetics of other third-period elements, particularly silicon and sulfur. In addition to the overall structural parameters of these species, we wish to focus here on three particular properties. The first deals with conformational preference, since it is of interest to determine whether these species assume equilibrium conformations dictated by electrostatic effects, as was the case in most of the previous molecules studied in this series. Secondly, P–O–P and Si–O–Si linkages are unusual since in some compounds these bond angles about the oxygen atom are not far from tetrahedral, while in others they are much larger, even being perfectly linear,³ and it is thus

important to investigate the equilibrium value and bending force for the POP angle in the subject series of gas-phase molecules and to see if there is a large variation of the equilibrium angle between them. Thirdly, since the P–O–P linkage has been assigned a central role in energy storage and transport in living cells, via the putative “high-energy phosphate bonds” as in ADP and ATP, and exhibits an unusually large and negative free energy of hydrolysis,^{4,5} we have paid particular attention to the series of hydrolysis reactions $H_4P_2O_{2n-1} + H_2O \rightarrow 2H_3PO_n$.

With respect to the hydrolysis of P–O–P linkages in vivo, there have, of course, been innumerable rationalizations of why this particular reaction might be unique. It is now generally agreed that “...there is nothing special about the bonds themselves. They are high-energy in the sense that much free energy is released when they are hydrolyzed...”.⁵ However, this free energy has been considered primarily due to an inherent difference in free energy between the products and reactants. In this connection there are two common explanations why the P–O–P linkage should be unstable in species such as diphosphates, both based on the intrinsic molecular structures (this despite the fact, noted above, that a strong tendency to hydrolyze is characteristic of the P–O–P linkage throughout phosphorus chemistry⁶). The first is that in dianionic forms, negative charges on either side of the linkage repel each other, thus creating a stress that weakens the bonds to the bridging oxygen. Since we deal herein only with neutral species, we cannot comment on this charge-repulsion theory directly. However, in the key experimental study⁷ in this field to date, it was shown that the free energy of hydrolysis is very nearly the same for charged as for uncharged species. A second widely held explanation is based on a speculative principle termed “opposing resonance”.⁸ This invokes the notion that in moieties such as the $>(P=O)-O-(P=O)<$ formulation⁹ of μ -oxo diphosphoryl it is impossible

(3) (a) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974. (b) For more detailed and recent data see: Nord, A. G.; Kierkegaard, P. *Chem. Scr.* **1980**, *15*, 27–39.

(4) Lehninger, A. L. *Biochemistry*; Worth: New York, 1975.

(5) Stryer, L. *Biochemistry*; Freeman: San Francisco, 1975.

(6) Van Wazer, J. R. *Phosphorus and Its Compounds*; Wiley: New York, 1958; Vol. I.

(7) George, P.; Wilonsky, R. J.; Trachtman, M.; Wu, C.; Dortwart, W.; Richman, L.; Richman, W.; Shurayh, F.; Lentz, B. *Biochim. Biophys. Acta* **1970**, *223*, 1–15.

(8) Kalckar, H. M. *Chem. Rev.* **1941**, *28*, 71–178.

(9) Formulations that include P=O representations of the phosphoryl group imply that the phosphorus atom requires d orbitals in the electronic description of its structure, thus exhibiting a deceit rather than an octet of electrons. Quantum-chemical studies show that d functions (if employed) serve only as “polarization functions” (to give more angular flexibility to the electronic descriptions) for phosphorus in its compounds (including those such as PF_5 in which the coordination number of the phosphorus is greater than 4), just as they do for carbon in its compounds. Therefore, the use of the P=O notation is not in accord with the present-day view of electronic structure, and rationalizations (including bond resonances) based on it are inappropriate.

(1) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965–1971.

(2) Van Wazer, J. R.; Ewig, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 4354–4360.

to draw resonance structures that involve the bridging and both phosphoryl oxygens simultaneously. After hydrolysis, however, each phosphorus is connected to two nonbridging oxygens and it is deemed possible to draw resonance structures for both simultaneously, increasing the stability of the products with respect to reactants. Any effect of this kind (regardless of its rational) should show up in a comparison of the hydrolysis energy of $\text{H}_4\text{P}_2\text{O}$ (no phosphoryls) with that of $\text{H}_4\text{P}_2\text{O}_3$ and higher members of this series.

Of the five species to be described here only one, $\text{H}_4\text{P}_2\text{O}_7$, to our knowledge has been the subject of previous quantum-chemical investigation. A particularly ambitious study by Hayes, Kenyon, and Kollman¹⁰ computed the total energy and the energy of hydrolysis of this and 35 similar "high-energy molecules". Unfortunately, technical limitations in the way this study was carried out limit its definitiveness and precluded the calculation of very accurate hydrolytic energies by those authors. Recently a more sophisticated study of the P–O–P bond angle and hydrolysis energy for $\text{H}_4\text{P}_2\text{O}_7$ and some related species has been reported by O'Keeffe, Domenges, and Gibbs.¹¹ Although as we will show below these authors apparently misassigned the equilibrium conformation of this species, resulting in an incorrect value for the reaction energy, their general conclusions as well as those of Hayes et al. are in agreement with ours and complement our results both for this species and to some extent for the additional ones we describe herein.

There is apparently no experimental structural data for any of the molecules studied here and, except for the largest one, virtually no quantitative data of any kind. Nonetheless, we found no indication that any of them are unstable in the sense of having imaginary vibrational frequencies. Therefore, in addition to being of interest for theoretical comparisons of computed structures and properties, all of them may well be isolated and characterized experimentally at some time in the future.

In the rest of this paper we first summarize the computational techniques employed in this study. Then, for each species we list the computed structural parameters and energy for each stable conformer. In describing the structural parameters we focus on the P–O–P bond angle, not only in terms of its magnitude but also its bending force constant and barrier to linearity. For each of the first three species we also report the variation in the energy and dipole moment with the torsional angles. For each of the four species we also present the computed enthalpy for hydrolysis of the P–O–P linkage. In the final section we summarize how our computed values of hydrolysis enthalpies and free energies compare with current experimental and previous computed results.

Computational Details

As in the earlier studies of this series, we have employed *ab initio* procedures throughout because the accuracy obtained for similar phosphorus compounds, particularly with respect to the basis sets we employ, has been by now quite well established by our work and that of others. Also comparison of the results obtained with a number of differing basis sets, such as between relatively large basis sets and the smaller ones that are the necessary choice in studying larger molecules, gives a measure of the reliability of each computed property.

All calculations were carried out with the GAUSSIAN 80¹² and GAUSSIAN 82¹³ programs. Three basis sets were employed. The first is an STO-3G* basis, consisting of the standard STO-3G set¹⁴ for each element but augmented by a d primitive function (with exponent 0.39) only on the phosphorus.¹⁵ The second basis consisted of the 4-31G set¹⁶ for each

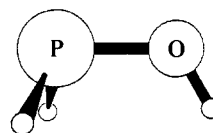


Figure 1. The structure of hydroxyphosphine, H_3POH , viewed perpendicular to the POP plane, as computed in the largest basis set (III) and reproduced to scale.

Table I. Computed Structural Parameters^a of Hydroxyphosphine, H_2POH

	basis		
	I	II	III
P–O	1.6177	1.6364	1.6389
P–H	1.3870	1.4156	1.4099
O–H	0.9877	0.9480	0.9423
$\angle\text{HOP}$	111.29	124.67	120.56
$\angle\text{HPO}$	99.83	100.56	101.14
$\angle\text{HPH}$	91.28	92.09	93.3

^a Bond lengths in Å, angles in degrees. The conformation is depicted in Figure 1.

element again augmented by a d primitive function (with exponent 0.55) on the phosphorus.¹⁷ The final basis was described in our earlier paper¹ and consists of the standard 311G contraction for hydrogen and 6-311G for oxygen combined with a 66-311G contraction¹ for phosphorus. In this basis the polarization functions consist of a set of p functions on the hydrogens, d functions on the oxygens, and two sets of molecularly optimized d functions on the phosphorus. Since there is no clear and widely accepted nomenclature for basis sets of this type, we will refer to them simply as sets I, II, and III, respectively.

In this work, the default procedure ("Bernie" optimization¹⁸) embodied in the program was found to be quite inefficient for the species studied. For example, in optimizing the structure of $\text{H}_4\text{P}_2\text{O}_7$, typically 100 optimization cycles were required to converge to an acceptable degree of accuracy for each set of torsional angles examined. The procedure proposed by Murtaugh and Sargent,¹⁹ which the program contains as an option, converged in significantly fewer cycles.

For each species we first used basis I to search for all possible stable (or metastable) conformations. This search was carried out by employing a series of different postulated molecular geometries as starting guesses for the optimization. We have found for reasonably flexible molecules that only by such a time-consuming sequence of optimizations from various carefully considered starting geometries is it possible to arrive at a final equilibrium structure that has a good probability of exhibiting the lowest possible energy. For all except the largest compound ($\text{H}_4\text{P}_2\text{O}_7$), the structure was similarly refined and checked in one or more larger basis sets. For the molecules studied in this work, our STO-3G representation (basis set I) gave a reliable indication of the number, torsional angles, and relative energies of the conformers—more precisely, in fact, than was anticipated based on our previous work. In carrying out the optimization of the molecular structures, all geometric parameters were varied simultaneously without imposing any constraints. Convergence was assumed to be reached when bond lengths varied by less than 0.0001 Å, torsional angles by less than 0.05°, and other angles by less than 0.01° between cycles. These criteria were also found to be sufficient to guarantee existence of a true minimum in the energy hypersurface (as demonstrated by force-constant calculations or repeated single-point computations corresponding to small structural changes).

Finally, electron-correlation corrections to the total energy were computed at the second order of the Møller–Plesset perturbation theory²⁰ (MP2), employing both core and valence excitations. For the monophosphorus species and $\text{H}_4\text{P}_2\text{O}$, vibrational frequencies and the resulting thermodynamic quantities that depend on nuclear motions (reported in Tables III and V) were obtained from the force-constant matrix com-

(10) Hayes, D. M.; Kenyon, G. L.; Kollman, P. A. *J. Am. Chem. Soc.* **1975**, *97*, 4762–4763; **1978**, *100*, 4331–4340.

(11) O'Keeffe, M.; Domenges, B.; Gibbs, G. V. *J. Phys. Chem.* **1985**, *89*, 2304–2309.

(12) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, Quantum Chemistry Program Exchange: Indiana University, Bloomington, IN. We thank Dr. John H. Yates for a DEC version of this program.

(13) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University: Pittsburgh, PA.

(14) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769–2773.

(15) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142–5151.

(16) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.

(17) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.

(18) Schlegel, H. B. *Theor. Chim. Acta* **1986**, *66*, 330–340.

(19) Murtaugh, B. A.; Sargent, R. W. *Comput. J.* **1970**, *13*, 185–194.

(20) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622. For a review of applications see: Pople, J. A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 806–811.

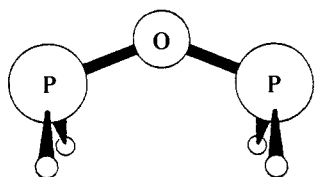


Figure 2. The structure of μ -oxo-diphosphine, $\text{H}_2\text{P-O-PH}_2$, viewed perpendicular to the POP plane, as computed in the largest basis set (III) and reproduced to scale.

Table II. Computed Structural Parameters^a of μ -Oxo-diphosphine, $\text{H}_2\text{P-O-PH}_2$

	basis		
	I	II	III
P-O	1.6167	1.6350	1.6347
P-H	1.3875	1.4163	1.4114
\angle POP	128.78	139.76	137.84
\angle HPO	99.26	99.10	99.80
\angle HPH	91.24	92.00	93.07

^a Bond lengths in Å, angles in degrees. The conformation is shown in Figure 2.

puted analytically by the GAUSSIAN 82 program. For $\text{H}_4\text{P}_2\text{O}_3$ and $\text{H}_4\text{P}_2\text{O}_5$ bending force constants about the P-O-P linkage were found by making 2° displacements in this angle to each side of the equilibrium value. For each species this bending force constant was taken to be the second derivative of the total energy with respect to the P-O-P angle, with all other internal coordinates held constant.

μ -Oxo-diphosphine

Computed Structures. Since one of our objectives was to study the energies of the hydrolysis reactions $\text{H}_4\text{P}_2\text{O}_{2n-1} + \text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_n$, in order to include the $n = 1$ compound, $\text{H}_4\text{P}_2\text{O}$, it was first necessary to treat the as-yet unknown hydroxyphosphine molecule, H_2POH . Its computed molecular structure is depicted in Figure 1. The optimized structural parameters in basis sets I, II, and III are listed in Table I. Only one stable conformer, exhibiting C_s symmetry, was found in each basis. With the exception of the HOP angle, all three basis sets (particularly II and III) give values of the bond lengths and angles that are in reasonable agreement with each other.

The structure of μ -oxo-diphosphine, $\text{H}_2\text{P-O-PH}_2$, was optimized in the same fashion. Its molecular structure is shown in Figure 2 and the structural parameters are given in Table II. Again only one stable conformer, with C_{2v} symmetry, was found. The four parameters that are in common with H_2POH are very nearly the same as for that molecule when computed in the same basis set, and comparison of Figures 1 and 2 shows that the two molecules also possess closely related equilibrium conformations.

In our previous studies we found that the conformations of the monophosphorus oxyacids and their methyl esters appear to reflect a dominant role played by interaction of the electrical-charge concentrations within the molecule, leading to the minimal-energy conformation corresponding to the minimal dipole moment. This would not be expected to be the case for the μ -oxo-diphosphine because there are no strongly polar groups, such as phosphoryl oxygens. Figure 3 shows the variation of the relative energy (solid line) and the molecular dipole moment (dashed line) with variation in the torsional angle about the P-O bond. In computing these curves, and all analogous ones below, we employed basis set II since we have found in the past that it provides a physically meaningful estimate of dipole moments and relative energies. All bond lengths and angles were constrained to their values in the equilibrium conformation as one PH_2 group was rotated in increments of 30° . Clearly dipole-moment effects have no role here, since the minimum energy corresponds to a dipole maximum, as shown in Figure 3. There is a broad energy barrier 2.7 kcal/mol in height, while the dipole moment decreases from 1.9 to 1.1 D as the torsional angle is rotated through 180° .

The energy barrier that determines the preferred conformation in both H_2POH and H_2POPH_2 seems to be dominated by the diffuse nature of the lone pair of electrons on the phosphorus

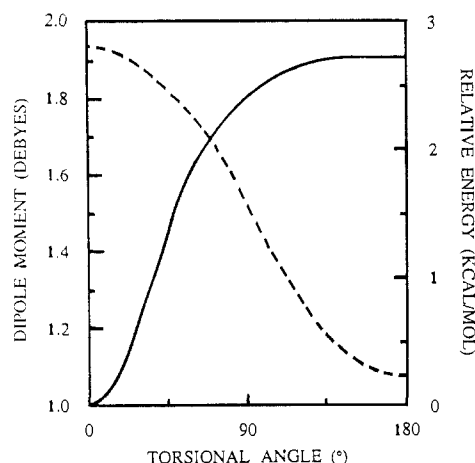


Figure 3. The total energy (solid line) and dipole moment (dashed line) of μ -oxo-diphosphine as functions of the torsional angle about the O-P bond, computed in the largest basis set (III) and corresponding to the rotation of one $-\text{PH}_2$ from its position in the stable conformation.

Table III. Computed Electronic and Thermal Energies^a

approximation	energy
H_2POH	
SCF basis I	-412.56637
SCF basis II	-416.84742
MP2 basis II	-417.08090
SCF basis III	-417.25879
E_{nm}	23.05
ST_{298}	17.57
H_2O	
SCF basis I	-74.96590
SCF basis II	-75.90864
MP2 basis II	-76.03714
SCF basis III	-76.03240
E_{nm}	15.80
ST_{298}	13.40
$\text{H}_4\text{P}_2\text{O}$	
SCF basis I	-750.17119
SCF basis II	-757.79102
MP2 basis II	-758.13085
SCF basis III	-758.48367
E_{nm}	29.96
ST_{298}	20.75

^a At the geometrically optimized structures, in hartrees/molecule, except the nuclear motion correction E_{nm} and entropy term ST_{298} in kcal/mol.

atoms.²¹ Repulsion of substituents by the lone pair is apparently responsible, for example, for the high barrier to inversion in PH_3 relative to NH_3 and for the stable conformation of the P_2H_4 molecule. The preferred equilibrium conformations of both H_2POH and H_2POPH_2 simply allow all substituents and groups to be as far as possible from the phosphorus lone pairs, concurrently producing a maximum in the dipole moment.

Table III lists the total SCF energies corresponding to the optimized geometries in each of the three basis sets. For later reference we report in this table (1) the energy including the second-order Møller-Plesset approximation to the electron-correlation energy, MP2, (2) the nuclear-motion correction, E_{nm} , which is the sum of the translation, rotation, and vibration energies at 298 K, and (3) the entropy effect, ST for $T = 298$ K, due to the entropies of all the nuclear motions, with all quantities computed in basis set II.

Since the P-O-P angle is of particular interest, we compare in Table IV the size, the bending force constant, and the barrier

(21) Van Wazer, J. R.; Absar, I. *Electron Densities in Molecules and Molecular Orbitals*; Academic Press: New York, 1975. For diagrammatic comparisons of phosphorus and nitrogen lone pairs, see pp 47, 50, and 52, and also pp 91-98 for the lone pairs in a diphosphine molecule being twisted.

Table IV. Computed Properties of the Bond Angle Containing a Bridging Oxygen in Related Species

	basis II	basis III
$\angle\text{HOH}$ in H_2O		
angle magnitude ^a	111.23	107.53
bending force constant ^b	0.1777	0.1918
barrier to linearity ^c	26.087	34.219
$\angle\text{HOP}$ in $\text{H}_2\text{P}(\text{OH})$		
angle magnitude	124.67	120.56
bending force constant	0.1180	0.1145
barrier to linearity	11.136	13.317
$\angle\text{POP}$ in $\text{H}_2\text{P}(\text{O})\text{PH}_2$		
angle magnitude	139.76	137.84
bending force constant	0.0890	0.1026
barrier to linearity	4.411	5.553

^aIn degrees. ^bIn hartrees/rad² (note that 1 hartree/rad² = 0.800 kJ/deg² = 0.191 kcal/deg²). ^cIn kcal/mol.

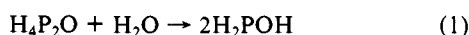
Table V. Computed Enthalpies^a for the Hydrolysis of $\text{H}_4\text{P}_2\text{O}$ and $\text{H}_4\text{P}_2\text{O}_3$

approximation	enthalpy
$\text{H}_4\text{P}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}$	
SCF basis I	3.07
SCF basis II	3.36
MP2 basis II	4.22
SCF basis III	-0.61
$\text{H}_4\text{P}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_2$	
SCF basis I	0.37
SCF basis II	-1.08
MP2 basis II	2.25

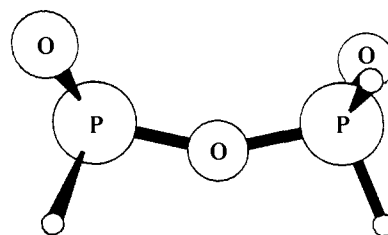
^aIn kcal/mol reactants.

to linearity of the apical angle about oxygen in $\text{H}_2\text{POP}(\text{H})_2$ (the P–O–P linkage), as well as in H_2O (H–O–H linkage) and H_2POH (P–O–H linkage) computed in basis sets II and III. It is instructive to compare the results of these two basis sets in light of the finding by O’Keeffe et al.,¹¹ in which a basis set including d functions on the bridging oxygen, such as III, gave a significantly different value for the size of the P–O–P angle. This is seen not to be the case here since the results computed in the two basis sets for the force constant and barrier height as well as for the value of the angle itself are quite similar. On going from the H–O–H to the P–O–H and P–O–P linkages, there is a regular increase in the magnitude of this angle, with an accompanying regular decrease in the force constant and the barrier to linearity. We conclude that at least in these simple prototype compounds there is nothing unique about the P–O–P linkage per se, its properties simply reflecting the simultaneous linkage to the oxygen of two third-period atoms.

Enthalpy of the Hydrolysis Reaction. From the data in Table III we may derive the energy, enthalpy, and free energy of the prototype hydrolysis reaction



Not surprisingly, since this consists of scrambling of substituents on oxygen or in other words is an “isodesmic” reaction²² (i.e., the number of formal linkages of each type is conserved), the reaction energy is small. Employing basis II, the zero-point energy change in the reaction is only 1.1 kcal/mol, the change in the energies of all nuclear motion (translation, rotation, and vibration) at 298 K is 0.3, and the change in $T\Delta S_{298}$ is 1.0. The reaction enthalpies ΔH°_{298} at the SCF level in each of the three basis sets, as well as the MP2 enthalpy computed in basis II (at the SCF structure in this basis), are listed in the upper portion of Table V. In obtaining these enthalpies, the same nuclear-motion correction of 0.3 kcal/mol was applied to the reaction energy in each basis set. This value should also serve as an estimate of this correction for the hydrolysis reactions described below and therefore will

**Figure 4.** The structure of phosphinic anhydride viewed perpendicular to the POP plane, as computed in basis set II and reproduced to scale. Note that the hydrogen on the left side of this structure is obscured by an oxygen.**Table VI.** Computed Structural Parameters^a of Phosphinic Anhydride, $\text{H}_2(\text{O}^1)\text{P}-\text{O}^0-\text{P}(\text{O}^2)\text{H}_2$

	basis I	basis II
P–O ⁰	1.5987	1.5912
P–H ¹	1.3843	1.3841
P–H ²	1.3843	1.3830
P–H ³	1.3843	1.3841
P–H ⁴	1.3843	1.3830
P–O ¹	1.4404	1.4500
P–O ²	1.4404	1.4500
$\angle\text{PO}^0\text{P}$	125.84	154.64
$\angle\text{H}^1\text{PO}^0$	101.17	101.71
$\angle\text{H}^2\text{PO}^0$	97.48	99.89
$\angle\text{H}^3\text{PO}^0$	101.17	101.71
$\angle\text{H}^4\text{PO}^0$	97.48	99.89
$\angle\text{H}^1\text{PH}^2$	101.58	104.09
$\angle\text{H}^3\text{PH}^4$	101.58	104.09
$\angle\text{O}^1\text{PO}^0$	118.94	116.01
$\angle\text{O}^2\text{PO}^0$	118.94	116.01
$\angle\text{H}^1\text{PO}^1$	116.79	116.22
$\angle\text{H}^2\text{PO}^1$	117.50	116.53
$\angle\text{H}^3\text{PO}^2$	116.70	116.22
$\angle\text{H}^4\text{PO}^2$	117.50	116.53
tor $\angle\text{PO}^0\text{PO}^1$	52.93	54.74
tor $\angle\text{PO}^0\text{PO}^2$	52.93	54.74

^aBond lengths in Å, angles in degrees. O⁰ is the bridging oxygen atom, while O² and O³ are the phosphoryl oxygens. O¹, O², and the other atoms are numbered clockwise from upper right in Figure 4.

Table VII. Computed Total Energies at the Optimized Structures (Hartrees)

	approximation	energy
$\text{H}_2(\text{O})\text{POH}$	SCF basis I	-486.477 57
	SCF basis II	-491.640 69
	MP2 basis II	-492.001 62
$\text{H}_2(\text{O})\text{POP}(\text{O})\text{H}_2$	SCF basis I	-897.989 29
	SCF basis II	-907.370 47
	MP2 basis II	-907.969 15

be employed in calculating their enthalpies.

Phosphinic Anhydride

Computed Structure. The structure of the $\text{H}_4\text{P}_2\text{O}_{2n-1}$ compound with $n = 2$, phosphinic anhydride, was optimized in basis sets I and II. In both basis sets only one stable conformation, exhibiting C_2 symmetry, was found. This is depicted in Figure 4.

The computed structural parameters are listed in Table VI. With the exception of the P–O–P angle and the torsional angles, the two sets of values are quite similar. Overall, basis I gives surprisingly good results compared to basis II. However, it grossly underestimates the P–O–P angle.

The total energies corresponding to these optimized structures are listed in Table VII. For future reference we also include here the energies of phosphinic acid in the same two basis sets, and the MP2 values as computed in basis II.

Since phosphinic anhydride, $\text{H}_2(\text{O})\text{POP}(\text{O})\text{H}_2$, contains two phosphoryl moieties, it might be anticipated that electrostatic effects such as dipole–dipole interactions might dominate the torsional potential and govern conformational preference. Unfortunately the modified Fourier analysis previously employed^{1,2}

(22) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* 1970, 92, 4796–4801.

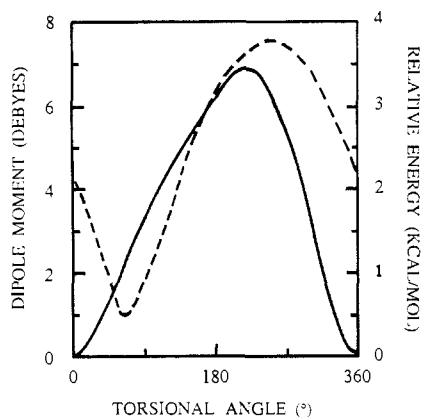


Figure 5. The total energy (solid line) and dipole moment (dashed line) of phosphinic anhydride as functions of the torsional angle about the O-P bond, computed in basis II and corresponding to the rotation of one -P(O)H₂ group from its position in the stable conformation.

Table VIII. Computed^a Properties of the Bond Angles about the Bridging Oxygen in Phosphinic Acid and Phosphinic Anhydride

	\angle HOP in H ₂ (O)POH	\angle POP in H ₂ (O)POP(O)H ₂
angle magnitude ^a	116.51	154.64
bending force constant ^b	0.0871	0.0249
barrier to linearity ^c	6.911	0.710

^a In degrees. ^b In hartrees/rad² (note that 1 hartree/rad² = 0.800 kJ/deg² = 0.191 kcal/deg²). ^c In kcal/mol.

in our studies of the monophosphorus oxyacids and their esters cannot be applied here because the overall molecule cannot be treated in a tetrahedral framework. In particular, the elongated shape of the molecule renders ineffective the dipole-moment analysis that was used in the prior work,^{1,2} so that we are left with no quantitative tools to probe the role of the electrostatic effects. However, inspection of the stable form of phosphinic anhydride does show that (1) the substituents on one phosphorus are eclipsed with respect to those on the other, with the phosphoryl oxygen on each phosphorus being moderately close (3.77 Å) to the opposing hydrogen on the other phosphorus due to the bend (ca. 155°) in the P-O-P linkage; and (2) the two phosphoryl oxygens (the negative ends of P-O dipoles) are aimed away from each other and from the small dipole resulting from the bending of the P-O-P linkage. This arrangement implies a significant contribution from P-O dipole-dipole interactions augmented by electrostatic attraction between each phosphoryl oxygen and the adjacent hydrogen on the other phosphorus. In Figure 5 we show the relative energy and molecular dipole moment as functions of the torsional angle for rotation of one H₂P(O) group about its axis to the bridging oxygen, while the other such group retains the orientation to the P-O-P plane found for the stable conformation. Although the dipole moment varies with the torsional angle in about the same way that the energy does, there is a phase shift of about +60° (instead of the shift of 180° in the H₂POPH₂ molecule). Not surprisingly, the minimum dipole corresponds to the phosphoryls being in opposition and the maximum dipole to their being at closest approach. The barrier to internal rotation is 3.4 kcal/mol, less than 1 kcal/mol higher than in μ -oxo-diphosphine.

It may be seen from Table VI that the P-O-P bond angle is computed in basis II to be quite large, 154.6°. This is about 15° larger than in μ -oxo-diphosphine, and nearly 20° larger than is predicted by basis I. (In fact, basis I gives this angle as being slightly smaller in H₄P₂O₃ than in H₄P₂O.) In Table VIII we present a comparison of the P-O-P angle in phosphinic anhydride with the P-O-H angle in phosphinic acid,¹ with all values computed in basis II. The P-O-P bond angle is seen to be extremely large not only with respect to the P-O-P in H₄P₂O but also compared to the P-O-H bridging angle in H₃PO₂, with concomitant decreases in the bending force constant and barrier to linearity. In the H₄P₂O₃, only 0.7 kcal/mol is required to linearize

Table IX. Computed Structural Parameters^a of Diphosphonic Acid, (HO)H(O¹)PO⁰P(O¹)H(OH)

	basis I	basis II
P-(OH)	1.5845	1.5585
P-H	1.3798	1.3674
O-H	0.9887	0.9534
P-O ¹	1.4398	1.4509
P-O ⁰	1.6056	1.6033
\angle PO ⁰ P	118.94	127.93
\angle HOP	109.11	126.08
\angle HP(OH)	98.11	101.60
\angle HPO ⁰	99.01	102.80
\angle HP(O ¹)	118.53	118.70
\angle (HO)PO ¹	119.26	117.66
\angle (HO)PO ⁰	104.36	104.21
\angle O ⁰ PO ¹	114.39	109.97
tor \angle O ¹ PO ⁰ P	-46.88	-48.83
tor \angle HOPO ¹	46.36	57.11

^a Bond lengths in Å, angles in degrees. O⁰ is the bridging oxygen. O¹ is the phosphoryl oxygen.

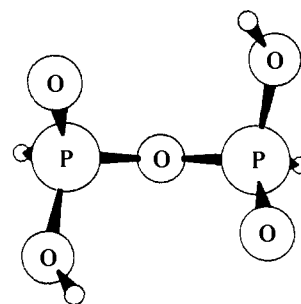
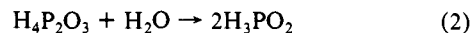


Figure 6. The structure of the most stable conformer of diphosphonic acid viewed from a point in the POP plane, as computed in basis set II and reproduced to scale.

the P-O-P angle. In other words, this molecule should exhibit a flexible but essentially linear bond angle about the bridging oxygen in the gas phase at room temperature.

Enthalpy of Hydrolysis. The SCF computed enthalpies in basis sets I and II of the reaction



as well as the enthalpies in the MP2 approximation in basis II are listed in the lower portion of Table V. These values are all seen to be significantly smaller than the analogous enthalpies for reaction 1. However, as in the previous case, electron correlation at this level makes the reaction enthalpy more positive.

Diphosphonic Acid

The structure of the H₄P₂O_{2n-1} compound with $n = 3$, diphosphonic acid, was optimized first in basis set I. In this case three stable conformations were found, each of them with two substituents on each phosphorus atom eclipsed to those on the other phosphorus. However, one conformation exhibiting C₂ symmetry, which we will term conformer 1, was found to be significantly more stable than the other two. It was therefore optimized further in basis II. The optimized geometric parameters are listed in Table IX. The structural parameters are again similar to those obtained for the two previous P-O-P bridged compounds, with the exception of the P-O-P angle. Both basis sets give this angle as being significantly smaller than in the two preceding cases.

The optimized structure of the most stable conformer of diphosphonic acid is depicted in Figure 6. (For this optically active species we have, for simplicity, characterized only the optical isomer presented.) This figure shows that in the gas phase diphosphonic acid appears to form two coexisting internal hydrogen bonds. The computed distance between the hydrogen of each hydroxy group and its opposing phosphoryl oxygen is 2.78 Å, which is within the experimentally determined range of PO...HO intermolecular hydrogen bonds (2.48 to 2.84 Å).^{3a}

The two stable structures of higher energy, conformers 2 and 3, correspond to the two additional ways in which substituents

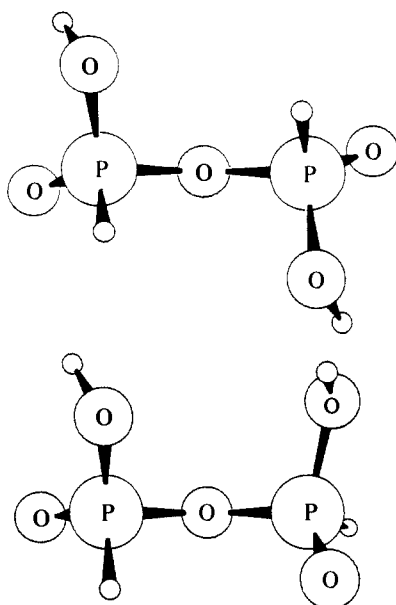


Figure 7. The structures of the metastable conformers, 2 (lower) and 3 (higher), of diphosphonic acid viewed from a point in the POP plane, as computed in basis set I and reproduced to scale.

Table X. Computed Total SCF Energies (hartrees)

	approximation	energy
H(O)P(OH) ₂	basis I	-560.388 33
	basis II	-566.453 61
(HO)H(O)POP(O)H(OH)	conf 1, basis I	-1045.815 58
	conf 1, basis II	-1056.999 49
	conf 1, basis II ^a	-1056.979 23
	conf 2, basis I	-1045.812 17
	conf 2, basis II ^a	-1056.975 62
	conf 3, basis I	-1045.810 36
	conf 3, basis II ^a	-1056.971 66

^aStructure optimized in basis I.

on the two phosphorus atoms can be adjacent. The structures computed in basis I are depicted in Figure 7. The structural parameters were found to be quite similar to those of conformer 1 except for the torsional angles and the P-O-P angle. In basis I the computed value of this angle increases from 118.94° to 127.41° and 130.02° on going from conformer 1 to 3. Comparing the structure of each (HO)H(O)P- moiety with that of phosphonic acid shown in Figure 2 of ref 1, particularly the POH torsional angles, demonstrates that diphosphonic acid closely resembles a pair of conjoined phosphonic acid molecules.

The energies computed in basis sets I and II for both phosphonic acid and the three conformers of diphosphonic acid are listed in Table X. Basis II energies for conformers 2 and 3 were computed at the basis I optimized structures. These two conformers are computed to have energies higher than conformer 1 by 2.14 and 3.28 kcal/mol in basis I, and 2.27 and 4.75 in basis II.

Figure 8 shows the changes in relative energy and dipole moment computed for conformer 1 in basis II as one (HO)H(O)P- moiety is rotated about its axis to the bridging oxygen. Again, although there is an obvious similarity between the two curves, the minimum in the energy does not correspond to a minimum in the dipole moment. Note also that simultaneously minimizing all structural parameters lowers considerably the energy of the local energy minimum near 225°, which corresponds to conformers 2 and 3, and would likely decrease the barrier height by even more. The dipole moments are also lower than this graph indicates, being 2.3 and 4.8 D respectively for conformers 2 and 3 in basis II.

In Table XI we compare the magnitudes of the bond angle, bending force constant, and barrier to linearity computed in basis II for phosphonic and diphosphonic acids. This table shows that, although ∠POH in (HO)H(O)P(OH) is about the size of ∠POP (and also ∠POH, see Table IX), in (OH)H(O)POP(O)H(OH),

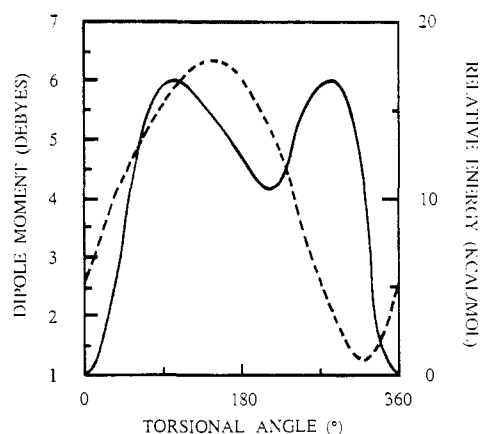


Figure 8. The total energy (solid line) and dipole moment (dashed line) of diphosphonic acid as functions of the torsional angle about the O-P bond, computed in basis II and corresponding to the rotation of one -P(O)H(OH) group from its position in the stable conformation.

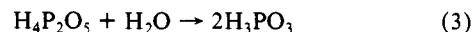
Table XI. Computed^a Properties of the Bond Angles about the Bridging Oxygen in Phosphonic and Diphosphonic Acids

	∠HOP in H(O)P(OH) ₂	∠POP in (HO)H(O)POP(O)H(OH)
angle magnitude ^a	125.74	127.93
bending force constant ^b	0.1822	0.0958
barrier to linearity ^c	6.868	2.958

^aIn degrees. ^bIn hartrees/rad² (note that 1 hartree/rad² = 0.800 kJ/deg² = 0.191 kcal/deg²). ^cIn kcal/mol.

the bending force constant and barrier to linearity are about twice as large for the P-O-P than the P-O-H angle. Also, the P-O-P angle in diphosphonic acid is computed to be considerably smaller than in phosphonic anhydride (see Table VIII), while the bending force constant and barrier to linearity of this angle are larger. This may be at least partly attributable to the internal hydrogen bonds in diphosphonic acid, which would tend to draw the two (HO)H(O)P- moieties together, thus decreasing the P-O-P angle.

Enthalpy of Hydrolysis. The enthalpy of the reaction



computed at the SCF level for the most stable conformer of H₄P₂O₅ is +3.36 kcal/mol in basis I and +0.91 in basis II. It is thus about 3 and 2 kcal/mol, respectively, higher than the analogous enthalpies for reaction 2. However, as shown above this is essentially the same amount as that by which conformer 1 is more stable than conformers 2 and 3. This strongly indicates that this unusually positive enthalpy for reaction 3 involving the most stable form of H₄P₂O₅ is due to the internal hydrogen bonding that is unique to this conformer.

Diphosphoric Acid

The final H₄P₂O_{2n-1} species, with *n* = 4, is diphosphoric ("pyrophosphoric") acid for which we have computed the equilibrium structure in basis set I only. We were able to identify two distinct stable conformations for diphosphoric acid, (HO)₂(O)POP(O)(OH)₂, conformations which differ by 2.3 kcal in energy as computed in basis I. The one of lower energy (-1193.631 40 hartrees) is asymmetric and has the staggered structure shown in the lower portion of Figure 9. The other conformation (with an energy of -1193.627 79 hartrees) exhibits an eclipsed structure of C₂ symmetry, as shown in the upper portion of this figure. Their dipole moments are computed to be 1.3 and 2.4 D, respectively. The computed structural parameters are listed in Table XII. In the conformation of lower energy, which we will term conformation 1, the P-O-P angle is approximately the same as in the preceding species, H₄P₂O₅. However, in the higher energy form, conformation 2, it is more than 8° larger. These two forms are analogous to the eclipsed and staggered forms which are often present simultaneously in crystals

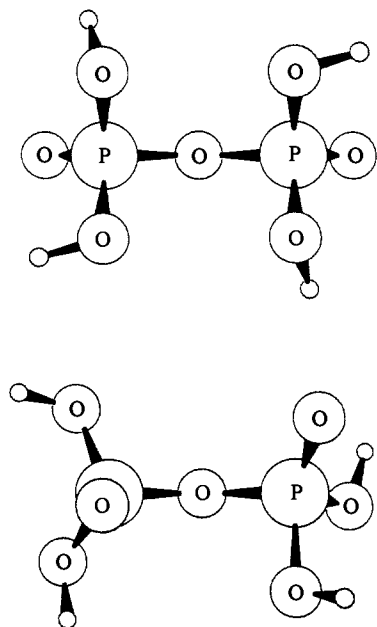


Figure 9. Stable conformers 1 (lower) and 2 (higher) of diphosphoric acid viewed from a point in the POP plane, as computed in basis I and reproduced to scale.

of diphosphates.^{3a} Comparison of both structures (particularly the lower one) shown in Figure 9 with the equilibrium structure of phosphoric acid shown in Figure 3 of ref 1 demonstrates that the orientation of the hydrogens in each form of diphosphoric acid is essentially the same as in the phosphoric acid. Thus diphosphoric acid closely resembles a pair of conjoined phosphoric acid molecules.

Enthalpy of Hydrolysis. For the hydrolysis of diphosphoric acid,



we have computed in basis I that the enthalpy is -0.42 kcal/mol, a value which is somewhat more negative than was found in the same basis for the hydrolyses described in eq 1 through 3 above.

Discussion

The four simple prototype compounds exemplifying the P-O-P linkage we have studied have several structural features in common. The stable form of all of them exhibits an equilibrium conformation in which the substituents on one phosphorus are eclipsed to those on the other. All are characterized by a large P-O-P angle in which both the bending force constant and barrier to linearity are small. The extreme case is $\text{H}_4\text{P}_2\text{O}_3$, which we find to be essentially linear in the gas phase at 298 K. O'Keeffe, Domenges, and Gibbs¹¹ have pointed out that in $\text{H}_4\text{P}_2\text{O}_7$ an STO-3G* basis similar to our basis I greatly underestimates the value of this angle relative to experiment. This is in fact the case for all the P-O-P bridged compounds we have studied as well, as is apparent from Tables II, VI, and IX. These authors found that adding d functions to the bridging oxygen increased the angle, and concluded that polarization functions on that atom were particularly important. However, as we have seen, particularly in Tables II and VI, simple Slater basis sets are inherently inaccurate for this property, and any increase in the size of the basis will greatly improve the result. For example, in Table II basis II, which has no d functions on any oxygen, gives nearly the same result as basis III, which places d functions on all oxygens.

Although in the case of $\text{H}_4\text{P}_2\text{O}$ the conformation appears to be dominated by the phosphorus lone-pair electrons, in $\text{H}_4\text{P}_2\text{O}_3$ and $\text{H}_4\text{P}_2\text{O}_5$ the torsional energy function is more complex. Although it roughly parallels the dipole-moment function in these two cases, other effects (particularly involving interaction between the substituents on one phosphorus and those on the other) are significant. The barrier to internal rotation about the P-O linkage is appreciable in all cases and increases with the size of the molecule. In $\text{H}_4\text{P}_2\text{O}_5$ it is computed to be approximately 17

Table XII. Computed^a Structural Parameters^b of Diphosphoric Acid, $(\text{HO})_2(\text{O}^1)\text{PO}^0\text{P}(\text{O}^2)(\text{OH})_2$

	conf 1	conf 2
P-O ⁰	1.5946	1.5886
P-(OH) ^a	1.5904	1.5898
P-(OH) ^b	1.5878	1.5898
P-(OH) ^c	1.5915	1.5989
P-(OH) ^d	1.5866	1.5898
P-O ¹	1.4370	1.4368
P-O ²	1.4375	1.4368
$\angle\text{PO}^0\text{P}$	126.272	134.782
$\angle\text{O}^1\text{PO}^0$	117.59	113.75
$\angle\text{O}^2\text{PO}^0$	117.21	113.75
$\angle\text{O}^a\text{PO}^0$	100.30	102.29
$\angle\text{O}^b\text{PO}^0$	99.06	102.29
$\angle\text{O}^c\text{PO}^0$	102.05	102.29
$\angle\text{O}^d\text{PO}^0$	97.62	102.29
$\angle\text{O}^a\text{PO}^1$	116.70	117.99
$\angle\text{O}^b\text{PO}^1$	118.88	117.41
$\angle\text{O}^c\text{PO}^2$	116.55	117.41
$\angle\text{O}^d\text{PO}^2$	119.46	117.99
$\angle\text{O}^a\text{PO}^b$	100.94	100.71
$\angle\text{O}^c\text{PO}^d$	100.59	100.71
$\angle\text{HO}^a\text{P}$	108.43	108.24
$\angle\text{HO}^b\text{P}$	108.70	108.24
$\angle\text{HO}^c\text{P}$	108.45	108.24
$\angle\text{HO}^d\text{P}$	108.51	108.24
tor $\angle\text{O}^1\text{PO}^0\text{P}$	60.23	180.58
tor $\angle\text{O}^2\text{PO}^0\text{P}$	7.49	180.58
tor $\angle\text{O}^a\text{PO}^0\text{P}$	-172.16	52.22
tor $\angle\text{O}^b\text{PO}^0\text{P}$	-69.20	-51.79
tor $\angle\text{O}^c\text{PO}^0\text{P}$	136.08	-51.79
tor $\angle\text{O}^d\text{PO}^0\text{P}$	-121.32	52.22
tor $\angle\text{HO}^a\text{PO}^1$	34.10	36.95
tor $\angle\text{HO}^b\text{PO}^1$	31.49	36.95
tor $\angle\text{HO}^c\text{PO}^2$	36.30	36.95
tor $\angle\text{HO}^d\text{PO}^2$	44.78	36.95

^aIn basis I. ^bBond lengths in Å, angles in degrees. O⁰ is the bridging oxygen, while O¹ and O² are the phosphoryl oxygens. The OH groups (specifically their oxygen atoms) are lettered clockwise from the upper right in Figure 9.

kcal/mol (without reoptimizing the structure).

The free energy of hydrolysis of phosphatic P-O-P linkages has been accurately measured⁷ for a variety of systems. For molecules of interest in biochemistry it is generally found to be in the range of -2 to -15 kcal/mol,^{4,5} and depends strongly on such factors as pH and the concentration of counterions.⁴ As with the molecular geometry, to our knowledge the only one of the species described here whose energy of hydrolysis has been either computed previously or measured experimentally is $\text{H}_4\text{P}_2\text{O}_7$. The energy of hydrolysis (for the isolated molecules in the gas phase at 0 K) for adenosine diphosphate (ADP) and triphosphate (ATP) were computed by Pullman and Pullman²³ employing semi-empirical techniques. They obtained -7.0 and -7.6 kcal/mol, respectively, which are almost exactly the experimental values under nominal conditions in solution. Similarly Boyd and Lipscomb²⁴ computed the energy of this reaction using the extended Hückel method and also arrived at exactly the contemporary experimental value for the reaction in solution. Unfortunately it was subsequently proved by George et al.⁷ that the free energy of this type of reaction in aqueous solution is due almost entirely to differential heats of solution of the various species involved in the reaction, and *not* to the relative energies of the isolated molecules in vacuo.

George, et al. also measured accurately ΔH°_{298} and ΔG°_{298} for the hydrolysis of $\text{H}_4\text{P}_2\text{O}_7$ (1 molal aqueous solution, 298 K, extrapolated to $I = 0$) obtaining -7.6 and -9.5 kcal/mol, respectively. (Note that this corresponds to the entropy of products being more than that of the reactants by an amount approximately twice our computed value for the gas-phase reaction.) They concluded that

(23) Pullman, B.; Pullman, A. *Quantum Biochemistry*; Interscience: New York, 1963.

(24) Boyd, D. B.; Lipscomb, W. N. *J. Theor. Biol.* **1969**, *25*, 403-420.

"for the hydrolysis of pyrophosphoric acid a tentative estimate of the solvation energy of $\text{H}_4\text{P}_2\text{O}_7$ suggests that the gas-phase reaction may be nearly thermoneutral, the favorable value of $\Delta H^\circ = -7.6$ kcal/mol...arising largely from the greater solvation energy of the products".

In the study of diphosphoric acid by Hayes, Kenyon, and Kollman,¹⁰ STO-3G, STO-3G*, and 4-31G basis sets were employed, but only very limited optimization of the requisite molecule structures were made. O'Keeffe et al.¹¹ computed both the structure and hydrolysis energy in an STO-3G* basis (our I) and a 6-31G basis with d functions on only the phosphorus atoms, analogous to our basis II. They point out that Hayes et al. made a number of relatively poor choices for their geometric parameters in $\text{H}_4\text{P}_2\text{O}_7$, particularly their value of the P-O-P angle based on a partial optimization in the STO-3G basis (117°), which would make the reactants too high in energy. O'Keeffe et al. employing their 6-31G basis obtain a reaction energy of -5.5 kcal/mol for the gas-phase reaction. In comparing their results employing basis I to ours, note that we find a different equilibrium conformation. Their structure has the phosphoryl groups staggered to two POH groups on the other phosphorus, while ours has the phosphoryl staggered to a POH and the other phosphoryl. Our energy for the lowest energy conformation is approximately 4.5 kcal/mol lower than the one reported by O'Keeffe et al. in this basis. This apparently accounts for most of their large negative reaction enthalpy. Further, adding the nuclear-motion correction of 0.3 kcal/mol (not included in the results reported by O'Keeffe et al.) to their corrected energy difference gives ΔH°_{298} equal to -0.7 kcal/mol.

Equilibrium conformations such as those employed by Hayes et al. may also be a source of error in computed reaction energies. Of all the phosphorus compounds we have studied in this series of papers that were also treated by Hayes et al., our computed conformation is different from their assumed conformation in every case. As shown, in particular, by Figure 8, energy differences of several kcal/mol can easily arise even between stable conformers. The energy is, of course, even more strongly dependent on the other structural parameters such as bond lengths. It must be emphasized that attempting to compute physically meaningful reaction enthalpy based on guessed or approximated molecular structures makes no sense at all. Further, as noted by the authors in ref 10, the limited geometry optimization carried out there can lead to substantial absolute errors in reaction enthalpies. The computed reaction enthalpy can be, at best, only as accurate as the degree of concomitant structural optimization.

Comparing the reaction enthalpies among the four $\text{H}_4\text{P}_2\text{O}_{2n-1}$ species studied here allows us to test the hypothesis that adding substituents, particularly oxygens, causes a more negative free-energy difference. In basis I we find enthalpies of $+3.07$, $+0.37$, $+3.36$, and -0.42 as n goes from 1 to 4. This suggests that adding oxygens does in fact decrease the reaction enthalpy except in the case $n = 3$ ($\text{H}_4\text{P}_2\text{O}_5$) which, as shown above, receives additional stabilization because of internal hydrogen bonding of 2 to 4

kcal/mol that is not available to the other species. Similarly in basis II the SCF enthalpies are $+3.36$, -1.08 , and $+0.91$ as n goes from 1 to 3. So we conclude that the addition of oxygens to the phosphorus *slightly* decreases the reaction enthalpy in accord with (but not because of⁹) the principle of "opposing resonance".

In our study² of methyl esters of phosphorus oxyacids, we found the enthalpy of hydrolysis in the gas phase to be in the range of roughly $+1$ to $+3$ kcal/mol of P-O-C linkages. (This type of linkage is often termed a "low-energy phosphate bond".⁴) Experimental values in solution are typically in the range -2 to -4 and the effect of the solvent has been estimated²⁵ to be about -7 kcal/mol per P-O-C linkage. A similar situation appears to be present here. For example, our best estimate for $\text{H}_4\text{P}_2\text{O}_5$, combining the results in basis III with the basis II vibrational and MP2 corrections is $+0.25$. The reaction enthalpies reported above for the hydrolysis of the $\text{H}_4\text{P}_2\text{O}_{2n-1}$ series indicate that for $n = 4$, use of larger basis sets and correlation-energy corrections will probably have roughly opposing effects. (However, as is clear from Table V, differences in the *absolute* reaction enthalpies of 5 kcal/mol are possible depending on the choice of basis set and whether or not correlation effects are included.) We thus tentatively conclude from intercomparison of these four species that, as suggested by George et al.,⁷ the hydrolysis of P-O-P linkages would be an essentially thermoneutral process in the gas phase. This is qualitatively also the conclusion reached by Hayes et al. Recently, as more accurate theoretical reaction enthalpies and free energies have been computed, it has become increasingly clear that the energetics of reactions in aqueous media are much less strongly dependent on the relative energies of the isolated reactants and products than on their relative energies of interaction with the solvent water, especially when charged or polar species are involved.^{26,27} Hydrolysis of P-O-P linkages appears to be another example of this principle.

Our overall conclusion is that the systematic study of chemically related species, such as the phosphorus acids, esters, and diacids, is a useful theoretical procedure for elucidating basic trends in molecule structures and energies, even when some or all of the species involved have not yet been characterized experimentally.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grants AFOSR-82-0100 and AFOSR-86-0146. The computations were carried out on the set of combined DEC-10 central processors at the Vanderbilt University Computer Center and on a VAX 11/750 in our laboratory. The VAX computer and requisite programs were acquired and installed by us under Grant AFOSR-85-0072.

(25) Wolfenden, R.; Williams, R. *J. Am. Chem. Soc.* **1983**, *105*, 1028-1031.

(26) Dewar, M. J. S.; Storch, D. M. *J. Chem. Soc. Chem. Commun.* **1985**, 94-96.

(27) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 4774-4783.