1525, 1345, 1125 (br), 830 cm^{-1}. Anal. Calcd for $C_{17}H_{24}N_2O_{10}$: C, 49.04; H, 5.81; N, 6.73. Found: C, 49.22; H, 5.94; N, 6.69.

Registry No. 1, 87453-20-1; 2, 94978-62-8; 3, 87453-21-2; 4, 94978- 63-9; 5, 91-23-6; 6, 100-17-4; 7, 88548-59-8; 8, 88548-60-1; 9, 88-72-2; 10, 99-99-0; 11, 94978-64-0; 12, 94978-65-1; 13, 92670-57-0; 14, 94978-66-2; 15, 93824-65-8; 16, 588-04-5; 17, 94978-67-3; Li$^+$, 17341-24-1; Na$^+$, 17341-25-2; K$^+$, 24203-36-9; 3,3'-bis(bromomethyl)azo-benzene, 93824-64-7; 2-(hydroxymethyl)-15-crown-5, 75507-25-4; 2-(hydroxymethyl)-18-crown-6, 70069-04-4; 4,13-diaza-18-crown-6, 23978-55-4; 1-chloro-2-nitrobenzene, 88-73-3; 1-fluoro-2-nitrobenzene, 1493-27-2; aza-15-crown-5, 66943-05-3; 2-nitrobenzyl chloride, 612-23-7; 4-nitrobenzyl bromide, 100-11-8; 1,10-diaza-18-crown-6, 23978-55-4; poly(ethylene glycol) monomethyl ether, 9004-74-4; 3-nitrotoluene, 99-08-1; 1-chloro-2,4-dinitrobenzene, 97-00-7.

Ab Initio Structures of Phosphorus Acids and Esters. 1. Phosphinic, Phosphonic, and Phosphoric Acids[†]

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Abstract: The molecular structures of all stable conformations of phosphinic, phosphonic, and phosphoric acid have been computed by employing complete geometry optimization in a variety of basis sets. Phosphinic acid, the species with the fewest torsional degrees of freedom, was examined in detail to determine the origin of forces giving rise to its preferred conformation. These forces are due almost entirely to electrostatic effects such as dipole–dipole interactions, with stereoelectronic ("anomeric") and steric effects each being at most 12% as large. Bond lengths and angles generally agree with the limited prior theoretical and experimental values. In each acid one or more additional higher energy stable conformations are found in the STO basis set, but these usually do not appear when larger basis sets are employed. All three acids exhibit a minimum-energy conformation in which the acidic hydrogens are oriented toward the phosphoryl oxygen and a distance from it, typically 2.7–2.8 Å, which is nearly the same in each case. The conformations of all three acids may be described solely on the basis of dipole–dipole interactions plus relatively small internal hydrogen bonding and steric effects. In contrast to earlier studies little conformational evidence of "anomeric" effects is found in any of these compounds.

The oxyacids of phosphorus have long been the subject of theoretical study, due in large measure to the role played by the phosphates in biological systems. The most important single property of these compounds is their detailed molecular structure. Yet determining these structures has often proven elusive due to the absence of experimental data on isolated molecules and the computational difficulties encountered in comprehensive theoretical treatments. As an example of the latter, all previously reported computations on this class of compounds have employed a relatively small basis set (either minimal STO-3G or a larger basis lacking polarization functions) and have not determined the complete minimal-energy structure. Yet it is now generally recognized that polarization functions on phosphorus are essential in determining correct bond lengths and angles involving that element,[1] and it is probable that inaccuracies in structural parameters are reflected in inaccurate energies of the various conformations.

For these reasons we considered it essential to reexamine some of these systems using larger basis sets (such as 4-31G*) with complete geometry optimization at each step. The recent development of analytical-gradient optimization techniques has provided an extremely important tool for investigations of this type.[2] As will be shown below, complete geometrical optimization can lead to qualitatively different conclusions concerning molecular structure than are obtained by even quite careful partial optimizations.

As a first set of compounds for study, we have considered the three simplest tetracoordinate acids of phosphorus: phosphinic, phosphonic, and phosphoric (H_3PO_2, H_3PO_3, and H_3PO_4). These may be considered formally to be derived from the hypothetical phosphine oxide molecule, H_3PO, by replacement of one, two, or three hydrogens by hydroxyl groups.

These compounds have been the subject of some previous theoretical studies. The conformation of phosphinic acid has been computed in an STO-3G basis by Hayes et al.[3] These authors studied the conformation and partially optimized the geometry of phosphoric acid in STO-3G and 4-31G basis sets but without polarization functions. Recently, Emsley et al.[4] computed the energy of phosphonic acid in a 4-31G basis, optimizing the structure of the P–O–H linkage only. Somewhat earlier Lehn and Wipff[5] computed the energies and Mulliken populations of phosphoric acid in a split-valence basis with and without d functions on phosphorus at three preselected conformations but did not compute any structural parameters.

Computational Details

All calculations reported here were carried out with the GAUSSIAN 80 program[6] and the analytical-gradient procedure for optimizing molecular structures that it contains. Each of the three title compounds was studied

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Table I. Computed Structural Parameters[a] of Phosphinic Acid

parameter/basis	STO-3G*	3-21G*	4-31G*	6-311G**
P=O	1.4422	1.4604	1.4551	1.4572
P—H_1	1.3837	1.3807	1.3867	1.3848
P—H_2	1.3870	1.3810	1.3860	1.3848
P—O	1.5942	1.5859	1.5824	1.5849
O—H	0.9883	0.9652	0.9488	0.9443
O—P—O	119.91	115.64	116.51	115.79
P—O—H	108.52	120.97	125.74	120.28
O=P—H_1	118.11	116.31	116.03	115.60
O=P—H_2	115.03	116.30	116.07	115.60
O—P—H_1	96.92	101.96	101.63	102.02
O—P—H_2	102.56	101.97	101.50	102.02
H—O—P=O[b]	45.18	0.06	−0.66	0.00

[a] Bond lengths in Å, bond angles in deg. H_1 precedes H_2 in clockwise rotation about the P—O bond viewing toward P. [b] Dihedral angle of the H—O—P plane with respect to the O—P=O plane. Angles are positive for clockwise rotation about the P—O axis viewing toward P.
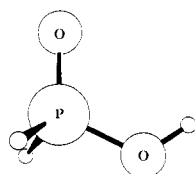
Figure 1. Structure of phosphinic acid computed in the 4-31G* basis.

in three basis sets: STO-3G,[7] 3-21G,[8] and 4-31G,[9] each with a fivefold set of d functions on the phosphorus atom. The exponent of the d function was 0.39 for the STO basis and 0.55 for the others.[10] We will refer to the resulting STO basis as STO-3G*. The notation 3-21G implies a 2,1 contracted pair of s functions on H, 3 s and 2,1 sp on oxygen, and similarly 3,3,2,1 on phosphorus. Other split-valence basis sets are defined in the same way. These will be refered to as 3-21G* and 4-31G* basis sets to indicate the presence of the d functions on phosphorus. Since the former type of basis set requires about 40% less computational effort than the latter, a comparison of their relative accuracies should be of importance to future calculations on larger systems. Optimization of molecular structures was in each case continued until successive changes in each bond length were less than 0.0001 Å, in each torsional angle less than 0.05° and in each of the other angles less than 0.02°.

For each basis we have computed the total energy of each compound at its optimized geometry both at the SCF level and, in order to estimate the importance of electron correlation in their relative energies, by employing the second-order Møller–Plesset perturbation correction (MP2).[12,13]

The Structure of Phosphinic Acid

The smallest compound of this series, H_3PO_2, was studied first in the three basis sets described above. The computed structural parameters are shown in the first three columns of data in Table I. The equilibrium structure obtained in the 4-31G* basis is also shown in Figure 1. All three give quite comparable results except the STO basis, which tends to give bond angles appreciably different from the other two basis sets, as shown by the last seven rows of data. Of particular interest is the H—O—P=O torsional angle. A value of zero corresponds to the acidic hydrogen eclipsing the phosphoryl oxygen. In the STO basis this angle is 45° so that the resulting molecular framework has C_s symmetry, while in the

larger basis sets it is nearly 0° resulting in a symmetry near C_s.

For every conformation exhibiting a nonzero torsional angle, there is of course another conformation in which this angle has the opposite sign. Throughout this paper we do not consider as separate conformations those which are symmetrically equivalent.

Since there are virtually no experimental data on the structure of phosphinic acid, it is especially useful to compare these computed values with those obtained from a more accurate calculation. Therefore we have recomputed these bond lengths and angles in a relatively large 6-311G** basis, which includes three contracted s and p functions in the valence region, d polarization functions on oxygen, and p functions on hydrogen.[11] This type of basis has not previously been published for phosphorus. We computed a 66-311G set by minimizing the restricted Hartree–Fock energy of the ^4S state of that atom. The results are shown in Table II. The corresponding energy of phosphorus is −340.5940 hartrees. Two fivefold sets of uncontracted d functions are added to the 66-311G basis and their exponents determined by minimizing the computed energy of phosphinic acid with respect to their orbital exponents. These are shown in the last two rows of Table II.

The complexity of the resulting 6-311G** basis makes it difficult to apply to larger molecules. But it is useful in accurately determining properties of phosphinic acid that may be shared with the higher acids and also as a test of the relative accuracies of smaller basis sets. The computed structural parameters are shown in the last column in Table I. In most cases, employing this much larger basis makes relatively little difference in the results. The only exception is the P-O-H angle, in which the 4-31G* and 6-311G** values differ by 5.5°. In general the 4-31G* basis gives slightly more accurate bond lengths, while the 3-21G* basis gives more accurate angles when compared against the 6-311G** values. The errors in the P-O-H angles shown in the first and third columns of data may reflect the lack of d functions on the oxygen atom, which the 3-21G* basis compensates for in some manner. Finally note that in the largest basis this molecule exhibits exact C_s symmetry. The total molecular energies obtained in the four basis sets are listed in Table III.

One additional energy minimum is found when the STO-3G* basis is employed. It is of C_s symmetry and lies 1.1 kcal/mol higher in energy than the other conformation. The resulting bond lengths and angles are shown in Table IV. No evidence of a second conformation is found with any of the three larger basis sets.

Origins of the Torsional Potential in Phosphinic Acid

The interactions that give rise to the torsional potential function, and hence to the energetic preference of one conformation over another, have been ascribed to three basic types:[14] steric, dipole–dipole, and stereoelectronic. The first is simply the repulsion of the electron distributions in distinct parts of the molecule, which generally keeps nuclei as far apart as possible. Dipole–dipole forces align the local dipole moments in various regions of the molecule in opposing directions so as to minimize the overall molecular dipole moment. The third, which is much less intuitively obvious, reflects the directional dependence of individual orbitals, particularly lone pairs. In compounds such as acids and esters it is usually termed the "anomeric effect".

The properties of the anomeric effect in the present compound would be rationalized as follows.[14] The acidic oxygen has four electrons in two orthogonal lone pair orbitals formed from oxygen 2p functions. The orbital of higher energy is perpendicular and antisymmetric with respect to the P-O-H plane, while the other lone-pair orbital, which is more tightly bound, lies in this plane and approximately bisects the P-O-H angle. In compounds such as phosphorus acids, in which there is an adjacent multiple bond to the phosphoryl oxygen, the latter lone-pair orbital is considered to be predominant in determining conformations. When the acidic hydrogen is adjacent to the phosphoryl oxygen, the in-plane lone

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Table II. 66-311G** Basis for Phosphorus

function	primitive	exponent	s coeff	p coeff	d coeff
1	1	5.2059E+03	9.08100E−03		
1	2	9.0386E+02	5.23310E−02		
1	3	2.4882E+02	1.75697E−01		
1	4	8.5511E+01	3.67502E−01		
1	5	3.3282E+01	4.06993E−01		
1	6	1.3704E+01	1.37076E−01		
2	1	2.6123E+02	−1.13720E−02	6.46200E−03	
2	2	5.8647E+01	−1.47689E−01	5.04890E−02	
2	3	1.8213E+01	−2.38178E−01	1.83183E−01	
2	4	6.8309E+00	7.61550E−02	4.15272E−01	
2	5	2.9398E+00	6.44711E−01	3.96279E−01	
2	6	1.1759E+00	4.37286E−01	1.42686E−01	
3	1	6.1601E+00	4.28512E−01	7.99800E−01	
3	2	3.0521E+00	1.02874E−01	2.20846E−01	
3	3	2.0753E+00	5.14925E−01	5.03500E−03	
4	1	4.3175E−01	1.00000E+00	1.00000E+00	
5	1	1.3463E−01	1.00000E+00	1.00000E+00	
6	1	8.0000E−01			1.00000E+00
7	1	3.0000E−01			1.00000E+00

Table III. Total Energies of Phosphinic Acid[a]

basis	method	energy
STO-3G*	SCF	−486.477572
3-21G*	SCF	−489.713712
4-31G*	SCF	−491.640684
4-31G*	MP2	−492.001618
6-311G**	SCF	−492.164805

[a] At the optimized molecular structure, in hartrees.

Table IV. Molecular Parameters[a] of the Higher Energy Conformation of Phosphinic Acid in the STO-3G* Basis

P=O	1.4400	P—O—H	109.29
P—H	1.3872	O=P—H	116.78
P—O	1.5920	O—P—H	102.44
O—H	0.9886	H—O—P=O[b]	180.00
O—P—O	116.03		

[a] Bond lengths in Å, bond angles in deg. [b] Dihedral angle of the H—O—P plane with respect to the O—P=O plane.

Table V. Summary of Conformational Effects in Phosphinic Acid

effect	predominant periodicity	sign	correction periodicity	sign
dipole	1	−	3	+
stereoelectronic	2	−	2	+
steric	3	+	1	+

Table VI. Fourier Coefficients of the Potential for Rotation about the H—O—P=O Axis in Phosphinic Acid

basis/coefficient[a]	V_1	V_2	V_3
STO-3G*	−1.213	−0.390	0.659
3-21G*	−3.102	0.167	0.139
4-31G*	−2.893	−0.102	0.120
6-311G**	−2.093	−0.269	0.155

[a] kcal/mol.

pair is aligned with the phosphoryl bond (hereinafter formally designated as P=O) and can mix with the P=O σ^* orbital. The result is a stabilization of this conformation and lengthening of the P=O bond.

There have been many instances in which the conformations of carbon compounds appear to be governed by interactions of the higher energy lone pair.[14] In the case of phosphinic acid this effect is expected to be less pronounced since (1) the more tightly bound lone-pair electrons are involved and (2) the P–O bond is considerably longer than typical C–O bonds.

It has been proposed[15] that in molecules possessing some symmetry, the relative importance of each of the three types of interactions may be distinguished by resolving the torsional potential into a Fourier expansion and identifying each effect with a single term in the expansion. In the case of phosphinic acid, dipole–dipole interactions would be onefold since the interaction energy would change sign as one dipole is rotated through 180°. The stereoelectronic effect, based on the overlapping of p orbitals, would be twofold. The steric effect would be threefold, since the O–H group is adjacent to an approximately tetrahedral hindering group. Phosphinic acid has been treated this way by Hayes et al.[3]

Of course this is a highly idealized analysis. It assumes that there are only two bond dipoles to be considered, that only one of the two lone-pair orbitals affects the conformation, and that P=O and P—H bonds have the same steric repulsion. However, the periodicity and anticipated sign of the most important correction to each of the three effects can be deduced by similar reasoning. Thus if the P=O bond has a greater steric repulsion

than P—H it will make a positive onefold contribution to the potential. Dipole–dipole interaction between the P–H and O–H bond dipoles should be repulsive and of roughly threefold symmetry. If the other lone-pair orbital contributes to the torsional potential, since it is at a 90° angle to the predominant orbital its effect will again be twofold but of the opposite sign. The analysis of the torsional potential in terms of these six effects involving three periodicities is summarized in Table V.

The total energy of phosphinic acid was computed in each of the four basis sets, keeping all structural parameters constant except the torsional angle, which was varied by 30° increments. The resulting function was then fit to an expansion of the form

$$V(\theta) = V_0 + V_1 \cos(\theta) + V_2 \cos(2\theta) + V_3 \cos(3\theta)$$

the torsion angle θ being set to 0° when the O—H and P=O bonds are adjacent. This expansion fit the computed energies very well except for those found with the STO-3G* basis, since this one has its angle of lowest energy shifted by 45° from the others and also possesses a second local minimum in the energy—both factors lending a more complex shape to the energy curve. The coefficients V_1, V_2, and V_3 computed in each basis set are listed in Table VI.

From Table VI it is clear that V_1, the predominantly dipole-dipole interaction term, is consistently the largest one, stabilizing $\theta = 0°$ with respect to all other torsional angles. Dipole moment data discussed below (see Tables XIII and XIV) also support this conclusion. As might be expected on the basis of the anomeric effect, V_2 is generally negative and hence stabilizing this same conformation, but it is much smaller than the dipole term and even changes sign on going from the 3-21G* to 4-31G* basis. Steric forces, represented by V_3, are positive and hence repulsive in each case. They are large only in the STO basis. This is most likely due to the relatively small value of the P–O–H angle found in this basis, which brings the H into closer contact with the rest

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Table VII. Computed Structural Parameters[a] of Phosphonic Acid

parameter/basis	STO-3G*	3-21G*	4-31G*
P=O	1.4403	1.4558	1.4515
P—H	1.3812	1.3632	1.3701
P—O	1.5936	1.5777	1.5725
O—H	0.9870	0.9651	0.9488
O=P—O	116.75	114.10	114.76
O—P—O	105.19	106.09	105.28
P—O—H	108.64	120.80	125.74
O=P—H	119.09	119.41	118.31
O—P—H	97.93	100.58	100.84
H—O—P=O[b]	±25.16	±19.94	±15.46

[a] Bond lengths in Å, bond angles in deg. [b] Dihedral angle of the H—O—P plane with respect to the O—P=O plane.

Table VIII. Total Energies of Phosphonic Acid[a]

basis	method	energy
STO-3G*	SCF	−560.059195
3-21G*	SCF	−564.226852
4-31G*	SCF	−566.453606
4-31G*	MP2	−566.703889

[a] At the optimized molecular structure, in hartrees.
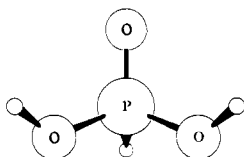
Figure 2. Structure of phosphonic acid computed in the 4-31G* basis.

of the molecule. In comparing the coefficients in the smaller basis sets with those obtained with the 6-311G**, which should be the most accurate, it can be seen that the STO-3G* results are the most dissimilar but are nonetheless qualitatively correct and give the proper relative ordering of the three terms. The 3-21G* and 4-31G* basis sets give very similar results, but those obtained with the 4-31G* basis are appreciably more accurate.

The relatively large steric component in the STO-3G* potential shows why the minimum-energy torsional angle is different from 0° in this case. Steric forces push the H to one side, partially overcoming the dipolar terms which tend to make this angle zero. Similarly, it explains the presence of the local minimum in the energy at $\theta = 180°$ since positive odd-fold terms tend to stabilize this angle.

Finally, from Table V we note that only the dipole interactions can give rise to a large negative V_1 term as we have computed. Anomeric effects due to participation of both lone-pair orbitals may cancel in the V_2 term, and the fact that V_2 changes sign in Table V suggests that this may be happening to some extent. The first correction to V_1 is positive and due to steric effects. This shows why V_1 in the STO-3G* basis is relatively more positive than that found in the other basis sets since in the smaller basis steric effects are large.

The three Fourier coefficients V_1, V_2, and V_3 for phosphinic acid were also computed by Hayes et al.[3] in an STO-3G basis. They obtained, in the present notation, −1.85, −1.40, and −0.14 kcal/mol, respectively. Although they found, as do we, that V_1 is the largest term and negative, they also found a large V_2 and a negative V_3. Probably these large differences are due to the limitations of their basis set and their assumed values of the P=O and P—O bond lengths (1.575 and 1.657 Å, respectively).

The Structure of Phosphonic Acid

We have computed all of the structural parameters of phosphonic acid in the same way as for phosphinic acid, employing STO-3G*, 3-21G*, and 4-31G* basis sets. The results are summarized in Table VII, and the equilibrium structure obtained in the largest basis is shown in Figure 2. The optimized energies are listed in Table VIII. All the parameters except the torsional angles are essentially the same as were found in the preceding compound, with slight differences that might be expected in re-

**Table IX.** Computed Structural Parameters[a] of Phosphoric Acid

parameter/basis	STO-3G*	3-21G*	4-31G*
P=O	1.4389	1.4513	1.4494
P—O	1.5911	1.5689	1.5617
O—H	0.9869	0.9641	0.9478
O=P—O	117.41	115.47	115.58
O—P—O	100.49	102.86	102.73
P—O—H	108.46	120.84	125.31
H—O—P=O[b]	41.01	43.49	42.02

[a] Bond lengths in Å, bond angles in deg. [b] Dihedral angle of the H—O—P plane with respect to the O—P=O plane.

Table X. Total Energies of Phosphoric Acid[a]

basis	method	energy
STO-3G*	SCF	−634.299257
3-21G*	SCF	−638.734523
4-31G*	SCF	−641.259887
4-31G*	MP2	−641.852232

[a] At the optimized molecular structure, in hartrees.
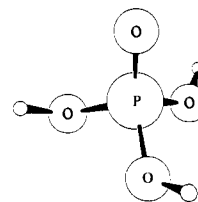
Figure 3. Structure of phosphoric acid computed in the 4-31G* basis.

placing an H by a more electronegative OH group. Thus all bond lengths involving phosphorus become shorter, and the O—P—O and O—P—H angles are compressed slightly. However, the O=P—H angle increases. The P-O-H angle is virtually unchanged. Note that in comparing the two molecules, the direction of change in any parameter in a given basis set is independent of which basis set is used.

Both OH groups have a large deviation from the O—P=O plane. In the lowest energy conformation, the resulting rotations were found to be in opposing directions, so that the molecule retains C_s symmetry. In contrast to phosphinic acid, the rotation angles are more nearly the same in the three basis sets. The STO basis again gives the greatest deviation from planarity, since it undoubtedly places artificially large steric forces on the OH group due to the small computed P-O-H angle.

Analogously to phosphinic acid, two additional local minima in the energy hypersurface are found when employing the STO basis. These have one acidic H adjacent to the phosphoryl oxygen and one opposed, or both acidic H atoms opposed. The torsional angles of these two conformations are 35.2° and −178.7° for one and ±171.7° for the other. They lie higher in energy than the lowest conformation by 0.13 and 3.50 kcal, respectively. The energy surface was systematically searched for local minima with the two larger basis sets. No clearly defined high-energy minima could be found. However, analysis of the energies calculated with the 4-31G* basis indicated the presence of two relatively flat regions in the energy surface which may contain very shallow minima. These occur at torsional angles of roughly 6.8° and −137.3° for one conformation and ±164.8° for the other, with relative energies of 0.4 and 9.4 kcal, respectively.

Interpretation of the torsional potential function is more difficult for molecules more complex than phosphinic acid, due to the presence of more internal degrees of freedom and the lower symmetry of the torsional potential function. Attempts to analyze the potential in terms of Fourier series generally have required many additional terms in the expansion, the physical significance of each term becoming quite unclear.[16] However, the general features of the conformations are again consistent with stabilization by dipole–dipole interactions. We discuss this in a subsequent section below.

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Ab Initio Structures of Phosphorus Acids and Esters

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Table XI. Molecular Parameters[a] of the First Higher Energy Conformation of Phosphoric Acid in the 4-31G* Basis

P=O	1.4445	O—P—O	102.97, 103.29
P—O	1.5711, 1.5545	P—O—H	124.66, 127.33
O—H	0.9481, 0.9479	H—O—P=O[b]	±7.39, 180.00
O=P—O	115.13, 115.59		

[a] Bond lengths in Å, bond angles in deg. Where two values are given, the first refers to the O—H bond nearer the phosphoryl oxygen. [b] Dihedral angle of the H—O—P plane with respect to the O—P=O plane.

Table XII. Nonbonded P=O···H Distances (Å)

molecule	basis	distance
H_3PO_2	STO-3G*	2.773
	3-21G*	2.758
	4-31G*	2.837
	6-311G**	2.740
H_3PO_3	STO-3G*	2.625
	3-21G*	2.737
	4-31G*	2.802
H_3PO_4	STO-3G*	2.700
	3-21G*	2.837
	4-31G*	2.879

The Structure of Phosphoric Acid

All of the structural parameters of phosphoric acid were optimized in the same way as for the preceding two compounds employing the STO-3G*, 3-21G*, and 4-31G* basis sets. The optimized parameters are listed in Table IX and the corresponding molecular energies in Table X. The equilibrium structure of lowest energy obtained in the largest basis is shown in Figure 3. Again replacing the H atom in phosphonic acid by an OH decreases all the bond lengths slightly in each basis set. However, in this case the O–P–O angle is increased. The P–O–H angle is again essentially unchanged.

The conformation of lowest energy was found to exhibit C_3 symmetry, i.e., all of the O–H groups bent away from the phosphoryl oxygen by the same angle and in the same direction. The values of the torsional angle found with the three basis sets are remarkably similar, probably reflecting the constraints imposed on this angle by the crowding of neighboring OH groups.

In the STO basis three higher energy conformations were found with torsional angles of ±23.3°, 180.0°; 0.0°, ±166.8°; and all angles 180°. These are higher in energy by 0.8, 3.0, and 9.4 kcal, respectively.

Examination of the energy surface in the larger basis sets revealed only one additional stable conformation. This is a shallow minimum found in the 4-31G* basis with torsional angles of ±7.4° and 180.0° corresponding to C_s symmetry. However, it lies only 0.2 kcal higher in energy than the lowest energy conformation. The molecular parameters of this conformation of phosphoric acid are shown in Table XI. All bond lengths and angles except the torsional angles are very similar to those of the minimum-energy conformation, the primary difference being an increase in one P–O–H angle.

Comparison of Phosphinic, Phosphonic, and Phosphoric Acids

The most pronounced difference between computed structures of the three compounds in various basis sets is the torsional angle of the acidic hydrogen about the P–O bond. Thus in phosphinic acid it is computed to be 45.18° in the STO basis but near 0° in the three larger basis sets. In the 4-31G* basis, the largest we have employed for all three species, it varies from about 0° in phosphinic acid to 15.5° in phosphonic acid and 42° in phosphoric acid. The origin of this variation is suggested by comparing the nonbonded distance between that hydrogen and the phosphoryl oxygen, since the conformation causes these to be adjacent in each case. These distances are listed in Table XII. They are remarkably constant both among molecular species and basis sets. For example, in comparing the first two entries, the distance differs by only 0.015 Å although the torsional angles of this hydrogen

Table XIII. Computed Dipole Moments

molecule	basis	dipole moment[a]
H_3PO_2	STO-3G*	2.046
	3-21G*	2.404
	4-31G*	2.765
	6-311G**	2.783
H_3PO_3	STO-3G*	1.598
	3-21G*	2.049
	4-31G*	1.897
H_3PO_4	STO-3G*	0.124
	3-21G*	0.593
	4-31G*	0.793

[a] Debye units.

Table XIV. Relative Energies and Dipole Moments of All Minimum-Energy Conformations in the STO-3G* Basis

molecule	H—O—P=O dihedral angle,[a] deg	rel energy, kcal/mol	dipole moment, D
H_3PO_2	45.2	0.0	2.046
	180.0	1.11	3.770
H_3PO_3	±16.3	0.0	0.752
	+35.2, −178.7	0.13	2.940
	±171.7	3.50	4.946
H_3PO_4	41.0, 41.0, 41.0	0.0	0.124
	±23.3, 180.0	0.83	2.525
	0.0, ±166.8	3.00	3.835
	180.0, 180.0, 180.0	9.36	6.047

[a] Dihedral angle of the H—O—P plane with respect to the O—P=O plane.

differ by over 45° between the two basis sets. The molecule appears to resist allowing this distance to be any shorter, even though the P–O–H angle here is smaller than that found in the other basis sets. The lowest energy deformation that will keep the O···H distance constant is a change in the torsional angle. Similarly, in comparing the three acids it is clear that, since adding successive OH groups decreases all bond lengths to phosphorus, which tends to shorten the O···H distance as well, the larger acids must have larger torsional angles to relieve the O···H repulsion. In cases where more than one stable conformation of the same molecule is found, this nonbonded distance (when present) again assumes virtually the same value.

In describing the structure of phosphinic acid, we showed that the forces leading to the energetically preferred conformation are almost entirely due to cancellation of internal dipoles, so as to reduce the overall molecular dipole moment. Due to their lower symmetry with respect to rotation of the OH group, a similar analysis is not as useful for the other two acids. However, their conformational preferences strongly suggest that similar forces are at work in these species as well. In Table XIII we summarize the total dipole moments computed for each molecule in each basis set. Phosphinic acid has the largest dipole moment, and it is greatest in the larger basis sets. The 4-31G* basis gives a dipole moment quite close to that computed in the much larger 6-311G** basis. The dipole moments of the other two acids are consistently smaller, due to cancellation between the P=O dipole and that formed by the OH bonds plus the oxygen lone-pair electrons. The two smaller basis sets predict dipole moments that are always too small, that computed in the STO-3G* basis being smaller by a factor of six from the 4-31G* value in phosphoric acid. In the latter basis there is a consistent decrease on going from the smaller to the larger acid molecule, reflecting the summation of bond dipoles which are relatively constant between molecules.

In the STO-3G* basis, one or more higher energy conformations were found for each molecule. These completely geometrically optimized conformations and their relative energies and dipole moments are listed in Table XIV, which illustrates the effect of changing torsional angles on the total dipole. In every case the conformation of lowest energy has the smallest dipole moment. The increases in dipoles of higher conformations roughly parallel

Table XV. Enthalpies of Scrambling[a]

method	$\Delta H°$
computed, SCF, STO-3G* basis	−0.1
computed, SCF, 3-21G* basis	3.4
computed, SCF, 4-31G* basis	4.2
computed, MP2, 4-31G* basis	4.7
experiment, crystal	10.8
experiment, "aqueous"	8.1

[a] For the reaction $2OPH(OH)_2 \rightleftharpoons OPH_2(OH) + OP(OH)_3$ in kcal/mol of product.

their increases in energy. We conclude that dipole–dipole interactions are likely to be as important in the conformational stability of phosphonic acid and phosphoric acid as they were shown to be in the case of phosphinic acid.

Finally, since we have determined the total energies of these three species at their equilibrium structures, we can compute the enthalpy of the scrambling reaction

$$2OPH(OH)_2 \rightleftharpoons OPH_2(OH) + OP(OH)_3$$

The results obtained in the three basis sets are summarized in Table XV along with the experimental reaction enthalpy[17] in the solid and liquid phases. Our computed results pertain of course only to the gas phase. The STO-3G* basis is seen to give the smallest and apparently the least accurate results, larger basis sets giving larger enthalpies. The two split-valence basis sets are in reasonable agreement, and the effect of adding correlation energy by using the second-order Møller–Plesset perturbation correction is small in comparison to any of the other differences between the $\Delta H°$ values shown in this table. The small effect of incorporating electron correlation is to be expected for the scrambling of H and OH on a phosphoryl moiety—a process which lies within the class of isodesmic reactions.[18] The accuracy of the experimental enthalpies is not known, but based on the fact that the "aqueous" value is 2.7 kcal/mol lower than the crystal, it is likely that the experimental gas-phase value would be considerably lower still.

Discussion

To our knowledge the only previously reported computation of the structure of any of these acids was that of Hayes et al.[3] They optimized only the P=O and P—O bond lengths of phosphoric acid, obtaining P=O bond lengths of 1.575 and 1.540 Å in STO-3G and 4-31G basis sets, respectively. For the P—O bond lengths they reported values of 1.657 and 1.642 Å in the same two basis sets. Errors of this magnitude, about +0.1 Å in each case, are evidently the result of not including d functions on phosphorus.[1]

Our computed structures of phosphonic acid and phosphoric acid may be compared with those obtained by X-ray diffraction studies of their crystals. Phosphoric acid crystals contain considerable hydrogen bonding to the phosphoryl oxygen and exhibit P=O and P—O bond lengths of 1.52 and 1.57–1.58 Å, respectively.[19] The P—O bond length is considerably longer in the crystal than the gas-phase value that we obtain, 1.45 Å. This is due to the weakening of this bond by hydrogen bonding in the crystal, causing the P=O bond to become more like a P—O single bond. However, phosphonic acid exhibits a different crystal structure, with a considerably different arrangement of hydrogen bonds.[20] Accordingly it has a P=O bond length of only 1.485 Å and P—O bond lengths of 1.544 and 1.552 Å, in substantial agreement with the values we obtained. So although the different acids may exhibit markedly different structures as crystalline solids, we have shown that in the gas phase they are quite similar.

The equilibrium conformation of phosphoric acid described by Lehn and Wipff[5] is of C_3 symmetry, as we also find. Hayes et al. found a conformation for phosphinic acid in which the acid hydrogen is adjacent to the phosphoryl oxygen, in agreement with our results. However, they determined the equilibrium structure of phosphoric acid to consist of two hydrogens adjacent to the phosphoryl oxygen and one opposed with an overall symmetry of C_s, analogous to our first higher energy conformation. Comparing Tables IX and XI it may be seen that the choice of conformation has a relatively small effect on other structural parameters.

In attempting to identify the origin of the conformational preferences of these molecules, Lehn and Wipff assumed that since the OH groups are rotated away from the P=O bond, this is evidence of stereoelectronic effects. However, their argument was based on a questionable description of the spatial arrangement of the oxygen lone-pair orbitals.[14] Also, as we have shown, each computed structure displays the same P=O···H distance regardless of the values of other structural parameters. It is not reasonable to assume that any property of the P—O or P=O bonds alone would have precisely this effect.

For phosphinic acid Hayes et al. found, as we do, that the potential is predominantly due to dipole–dipole interactions, but they assumed that phosphoric acid is controlled by anomeric effects. They expanded the potential for phosphoric acid in a six-term Fourier expansion but, since in this type of treatment individual terms tend to lose their simple intuitive significance, it was not possible to reach a quantitative assay of the importance of the anomeric effects in this molecule.

Each of the systems we have studied, employing each of the various basis sets, exhibits a preferred equilibrium conformation that may be explained entirely on the grounds of dipole–dipole interactions plus steric repulsion by the phosphoryl oxygen. There is no conformational property that suggests the presence of stereoelectronic effects except the relatively small V_2 terms in the Fourier expansion of the torsional potential of phosphinic acid. However, it was found in the calculations leading to Tables IV and XI, as well as every other optimized structure, that higher energy conformations invariably have shorter P=O bond lengths than are found in the conformation of lowest energy. For example, in the STO-3G* basis, the P=O bond length in phosphoric acid decreases with remarkable regularity with increasingly higher energy conformations from 1.439 to 1.437, 1.435, and 1.433 Å. This is exactly the direction of change predicted by the anomeric effect resulting from the mixing of oxygen lone pairs into the P=O σ^* orbital when a hydrogen is adjacent to the P=O bond. However, the changes are considerably smaller than analogous values in carbon acids, which may be a few hundredths of an angstrom. Also it should be noted that most of the other structural parameters show similar trends. For example, the P—O length increases consistently from 1.591 to 1.597 Å, and the O=P—O angle decreases from 117.4° to 113.7° on going from the lowest to the highest energy conformation. This suggests that although stereoelectronic effects are present, they are relatively small and more complicated than has thus far been considered by proponents of the anomeric effect.

The data shown in Table XII are also clearly consistent with the formation of internal P=O···H—O—P hydrogen bonds. These are predominantly electrostatic and very similar in nature to dipole–dipole interactions, so that it is difficult to distinguish between the two effects. The O···H distances shown in Table XII are comparable to those found experimentally for intermolecular P=O···H—O bonds, which are in the range 2.48–2.84 Å.[21] However, if internal hydrogen bonds were to exist, they would be broken as the torsional dihedral angle goes from 0° to 90° and 180°. A torsional potential that is the same at 90° as at 180° would be proportional to $2 \cos(\theta) + \cos(2\theta)$. Since V_2 is small in phosphinic acid, we conclude that internal hydrogen bond formation is probably not significant in this compound. In this paper we have attributed the bulk of the conformational forces

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to dipole–dipole interactions, primarily on the basis of the Fourier coefficients and the data shown in Tables XIII and XIV. Further computations, particularly on the esters of the title compounds, are clearly required to resolve the relative importance of dipole–dipole and hydrogen bond interactions with more certainty.

Torsional and Steric Control of Stereoselectivity in Isodicyclopentadiene Cycloadditions

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Abstract: An MM2 model to calculate the relative energies of stereoisomeric transition states of Diels–Alder reactions of isodicyclopentadiene and substituted derivatives has been developed. The model is based upon ab initio and constrained-synchronous MNDO transition-state calculations on unsubstituted systems. Trends in observed stereoselectivities as a function of diene and dienophile substituents are reproduced. The success of this model supports the hypothesis that torsional factors influence the stereoselectivities of the reactions of the parent system, while this torsional preference for attack on the bottom face of isodicyclopentadiene can be overridden by steric effects involving substituents on either the dienophile or the isodicyclopentadiene.

Isodicyclopentadiene (**1a**) undergoes Diels–Alder cycloadditions with a variety of dienophiles from the *bottom* face.[1–5] This stereoselectivity contrasts with that observed for additions and cycloadditions to norbornene, which occur from the *top* (exo) face.[6–10] What property of the norbornene skeleton causes attack on the *bottom* of an exocyclic double bond of **1a** and on the *top* of the endocyclic double bond of norbornene? In this paper, we develop a consistent hypothesis to explain these phenomena and the variations in stereoselectivity which are observed upon substitution of isodicyclopentadiene or upon alterations of the dienophile. Our explanation is based upon torsional and steric effects and permits predictions of stereoselectivities for as yet unstudied cases. A computational model is also developed to provide semi-quantitative predictions of stereoisomer ratios in reactions of substituted species.
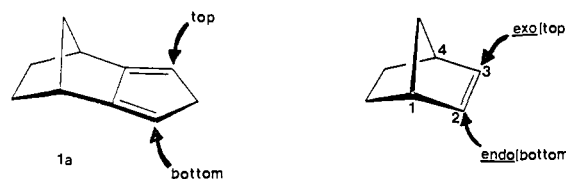
There is general accord that the stereoselectivities of the reactions of norbornene are a result of the asymmetric arrangement of the allylic CH and CC bonds. This asymmetric arrangement is enforced by the rigid norbornene skeleton. However, the specific mechanism by which this asymmetric arrangement directs attack is controversial. Brown proposed that the exo attack by a variety of reagents is a result of steric effects,[6] since the enthano bridge is larger than the methanol bridge. In partial accord with this proposal, reactions of norbornadiene are less selective than those of norbornene, but additions and cycloadditions still occur preferentially from an exo face of a double bond.[10] Schleyer proposed that torsional strain between the C_1H and C_2H bonds, and between the C_3H and C_4H bonds, is relieved upon exo attack but increases upon endo attack.[11] Tee et al. noted that less nuclear motion is involved in the formation of the exo product, so that exo attack is in accord with the principle of least nuclear motion.[12] Fukui

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