

Hartree–Fock and Møller–Plesset (MP2) Treatment of Oxygen-Containing Phosphorus Compounds

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Ab initio calculations were carried out in order to obtain conformational, structural, and vibrational data for a set of small oxygen-containing phosphorus compounds. Many of these molecules are fundamentally important since they are analogous to macrostructures that play a central role in biological processes. It is anticipated that the chemical and physical properties of these phosphorus compounds will provide valuable insight into problems in structural biology. These calculations involved the use of the standard 6-31G** basis set at both the Hartree–Fock and Møller–Plesset levels of theory for the determination of rotational profiles, molecular geometries, and vibrational frequencies. Comparisons to experimental results are made when possible.

Introduction

In spite of extensive experimental studies of molecules containing phosphate moieties,¹ only sporadic data exist for small organophosphates. In addition, few *ab initio* studies, most of which involve low-level calculations with small basis sets, are available for these molecules.

With the overall goal of parametrization of an MM3 force field for biologically important phosphates, we have undertaken an *ab initio* study of small oxygen-containing phosphorus compounds. For example, complete and accurate parametrization of DNA is imperative before studying any details of activity or binding involving this molecule in the realm of MM3. Presently, many of the necessary DNA parameters are either absent or insufficient including all those involving phosphate groups. Before MM3 can accurately model the sugar phosphate backbone of DNA, the force field initially must be able to quantitatively reproduce conformational, structural, and vibrational data of small phosphorus compounds. This discussion will concentrate exclusively on *ab initio* work that could be useful for subsequent molecular mechanics parametrization of small oxygen-containing phosphorus compounds related to biologically important phosphate groups.

In general, structural and vibrational data to be modeled by molecular mechanics are obtained through experimental or *ab initio* results. In the case of phosphates, however, an overwhelming number of available experimental results come from room temperature X-ray diffraction with low resolution which, due to intermolecular interactions, are unsuitable for modeling the gas phase. Additionally, much of the necessary experimental data are unavailable or need to be supplemented. For these reasons, we have undertaken an extensive *ab initio* study of small oxygen-containing phosphorus compounds to obtain structures, vibrational frequencies, and rotational profiles. The compounds involved in this study

include phosphine oxide (1),² hypophosphorous acid (2), phosphorous acid (3),³ phosphoric acid (4a, 4b),⁴ dimethylphosphinic acid (5),⁵ dimethyl phosphonate (6),⁶ methyl dimethylphosphinate (7),⁷ trimethylphosphine oxide (8),⁸ trimethyl phosphite (9a, 9b),⁹ dimethylmethoxyphosphine (10),¹⁰ and trimethyl phosphate (11a, 11b).¹¹ These structures are shown in Table 1. For these compounds, reliable experimental structural and/or vibrational data are available and can be compared to the *ab initio* results in order to assess the effectiveness of these computational methods in reproducing such data.

For many of these compounds, *ab initio* studies have been previously reported. Ewig and Van Wazer,¹² for example, carried out *ab initio* calculations at the restricted Hartree–Fock (RHF) level of theory on hypophosphorous, phosphorus, and phosphoric acids. Others have carried out quantum chemical calculations on molecules of this type and found that the addition of a second set of 3d orbitals was necessary to reproduce accurate geometries at the RHF level.¹³ Basch et al.,¹⁴ has carried out calculations on similar compounds and found that the inclusion of electron correlation at the Møller–Plesset (MP) level of theory was more important than supplementation of the RHF basis functions.

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Table 1. *Ab Initio* and Experimental Bond Lengths^a and Bond Angles^b for Some Small Oxygen-Containing Phosphorus Compounds

Entry	Structure	Label ^c	RHF/STO-3G ^{*d}	RHF/3-21G ^{*e}	RHF/6-31G ^{**}	MP2/6-31G ^{**}	Experiment		
1		a	-----	-----	1.465	1.497	-----		
		b	-----	-----	1.396	1.403	-----		
		ab	-----	-----	116.9	117.6	-----		
		bc	-----	-----	101.1	100.3	-----		
2		a	1.442	1.460	1.457	1.488	-----		
		b	1.594	1.586	1.598	1.628	-----		
		c,d	1.387	1.381	1.388	1.393	-----		
		e	0.988	0.965	0.947	0.967	-----		
		ab	119.9	115.6	115.4	118.1	-----		
		ac	118.1	116.3	115.9	114.2	-----		
		ad	115.0	116.3	115.9	118.0	-----		
		bc	96.9	102.0	102.0	103.3	-----		
		bd	102.6	102.0	102.0	96.6	-----		
		be	108.5	121.0	113.1	111.9	-----		
		cd	-----	-----	103.5	103.7	-----		
		3		a	1.440	1.456	1.453	1.484	1.47
				b	1.594	1.578	1.586	1.624	1.54
c	1.594			1.578	1.586	1.613	1.54		
ab	116.8			114.1	114.3	113.8	113		
ac	116.8			114.1	114.3	118.5	116		
bc	105.2			106.1	105.3	102.9	102		
4a				a	1.439	1.451	1.450	1.481	1.502
		b,d	1.591	1.569	1.576	1.609	1.562		
		c	1.591	1.569	1.576	1.609	1.556		
		e	0.987	0.964	0.946	0.967	0.965		
		f	0.987	0.964	0.946	0.967	0.989		
		g	0.987	0.964	0.946	0.967	1.001		
		ab	117.4	115.5	115.5	116.5	113.3 (3)		
		ac	117.4	115.5	115.5	116.5	112.3 (3)		
		ad	117.4	115.5	115.5	116.5	113.2 (3)		
		bc	100.5	102.7	102.8	101.7	105.6 (2)		
		bd	100.5	102.7	102.8	101.7	104.9 (2)		
		cd	100.5	102.7	102.8	101.7	107.3 (3)		
		be	108.5	120.8	113.5	110.4	116.8		
cf	108.5	120.8	113.5	110.4	118.3				
dg	108.5	120.8	113.5	110.4	116.3				
4b		a	-----	-----	1.445	1.470	1.502		
		b	-----	-----	1.588	1.612	1.552		
		c	-----	-----	1.572	1.594	1.556		
		d	-----	-----	1.580	1.602	1.556		
		e	-----	-----	0.946	0.964	0.965		
		f	-----	-----	0.946	0.964	0.989		
		g	-----	-----	0.946	0.964	1.001		
		ab	-----	-----	113.7	114.7	113.3 (3)		
		ac	-----	-----	114.9	114.6	112.3 (3)		
		ad	-----	-----	117.3	118.2	113.2 (3)		
		bc	-----	-----	105.4	105.4	105.6 (2)		
		bd	-----	-----	102.3	101.6	104.9 (2)		
		cd	-----	-----	101.5	100.4	107.3 (3)		
be	-----	-----	112.5	111.4	116.8				
cf	-----	-----	115.8	115.2	118.3				
dg	-----	-----	114.4	113.3	116.3				
5		a	-----	-----	1.465	1.496	1.495 (4)		
		b	-----	-----	1.609	1.643	1.559 (4)		
		c	-----	-----	1.805	1.806	1.781 (6)		
		d	-----	-----	1.805	1.806	1.776 (6)		
		ab	-----	-----	112.9	114.0	112.7 (2)		
		ac	-----	-----	114.9	115.5	111.0 (2)		
		ad	-----	-----	114.9	115.5	112.1 (3)		
		bc	-----	-----	103.1	102.2	108.8 (2)		
		cd	-----	-----	106.6	105.9	107.3 (3)		
		be	-----	-----	103.1	102.2	104.6 (3)		

Table 1 (Continued)

Entry	Structure	Label ^c	RHF/STO-3G* ^d	RHF/3-21G* ^e	RHF/6-31G**	MP2/6-31G**	Experiment
6		a	1.439	-----	1.454	1.468	-----
		b	1.383	-----	1.379	1.389	-----
		c	1.585	-----	1.574	1.608	-----
		d	1.594	-----	1.586	1.623	-----
		e	1.440	-----	1.422	1.444	-----
		f	1.438	-----	1.421	1.443	-----
		ab	115.9	-----	115.7	116.0	-----
		ac	120.3	-----	117.6	119.3	-----
		ad	117.0	-----	114.1	114.6	-----
		bc	96.8	-----	99.9	98.1	-----
		bd	103.1	-----	105.0	105.5	-----
		cd	-----	-----	102.6	100.9	-----
		ce	116.9	-----	121.6	117.4	-----
		df	116.7	-----	121.7	117.9	-----
7		a	-----	-----	1.465	1.497	1.50
		b	-----	-----	1.602	1.639	1.56
		c	-----	-----	1.810	1.814	1.78
		d	-----	-----	1.803	1.804	1.78
		e	-----	-----	1.418	1.440	1.43
		ab	-----	-----	114.5	115.6	112.0
		ac	-----	-----	115.5	113.7	112.0
		ad	-----	-----	113.4	116.4	112.0
		bc	-----	-----	100.8	104.2	109.0
		cd	-----	-----	106.7	106.4	107.0
		be	-----	-----	121.4	116.9	118.0
8		a	-----	-----	1.474	1.506	1.476 (2)
		b	-----	-----	1.818	1.819	1.809 (2)
		ab	-----	-----	113.8	114.4	114.4 (7)
		bb	-----	-----	104.9	104.1	104.1 (8)
9a		a	-----	-----	1.618	1.652	1.620 (2)
		b	-----	-----	1.408	1.434	1.420 (8)
		aa	-----	-----	98.6	97.9	100.5 (6)
		ab	-----	-----	119.7	115.5	118.9 (10)
9b		a	-----	-----	1.622	1.656	-----
		b	-----	-----	1.604	1.636	-----
		c	-----	-----	1.636	1.673	-----
		d	-----	-----	1.408	1.433	-----
		e	-----	-----	1.417	1.444	-----
		f	-----	-----	1.408	1.434	-----
		ab	-----	-----	98.5	97.8	-----
		ac	-----	-----	96.8	95.3	-----
		ad	-----	-----	119.8	115.8	-----
		bc	-----	-----	102.7	103.4	-----
		be	-----	-----	123.8	119.7	-----
cf	-----	-----	119.3	115.3	-----		
10		a	-----	-----	1.654	1.688	-----
		b	-----	-----	1.404	1.429	-----
		c	-----	-----	1.838	1.835	-----
		d	-----	-----	1.843	1.845	-----
		ab	-----	-----	119.1	115.2	-----
		ac	-----	-----	97.9	96.0	-----
		cd	-----	-----	100.2	100.3	-----
11a		a	1.439	-----	1.453	1.485	1.477 (6)
		b	1.588	-----	1.572	1.608	1.580 (2)
		c	1.4384	-----	1.421	1.444	1.432 (5)
		ab	117.6	-----	115.4	116.4	-----
		bb	100.2	-----	102.9	101.8	105.0 (2.9)
bc	116.6	-----	121.0	116.6	118.3 (1.5)		

Table 1 (Continued)

Entry	Structure	Label ^f	RHF/STO-3G* ^d	RHF/3-21G** ^c	RHF/6-31G**	MP2/6-31G**	Experiment
11b		a	1.437	-----	1.447	1.479	-----
		b	1.589	-----	1.574	1.609	-----
		c	1.583	-----	1.569	1.604	-----
		d	1.598	-----	1.586	1.624	-----
		e	1.438	-----	1.421	1.444	-----
		f	1.438	-----	1.419	1.443	-----
		g	1.438	-----	1.421	1.444	-----
		ab	119.3	-----	117.2	118.8	-----
		ac	113.4	-----	114.0	113.9	-----
		ad	116.5	-----	114.1	114.8	-----
		bc	100.5	-----	102.3	101.2	-----
		bd	99.3	-----	101.7	100.1	-----
		be	116.6	-----	121.0	116.8	-----
		cd	105.5	-----	105.9	106.1	-----
cf	119.1	-----	123.6	119.1	-----		
dg	116.3	-----	120.6	116.3	-----		

^a RHF/6-31G** and MP2/6-31G** bond lengths are r_c values in angstroms. The experimental values vary in types from r_g to r_a and are given in angstroms. ^b All bond angles are given in degrees. ^c A single small case letter represents a bond between two atoms. Two small case letters represent a bond angle formed by the labeled bonds, i.e., a bond angle labeled "ab" would be formed by the adjacent bonds "a" and "b". ^d RHF/STO-3G* results are taken from ref 12a except for structures **6**, **11a**, and **11b** whose results are taken from ref 12b. ^e RHF/3-21G** results are taken from Ref 12a.

Methodology

Calculations on compounds **1–11** were carried out at the restricted HF and MP2 levels of theory with the standard 6-31G** basis set using the Gaussian 92¹⁵ software package on an IBM RS/6000 machine. As has been suggested by some,¹³ the addition of a set of 3d orbitals (a 6-31G(2D,P) basis set) may be necessary to accurately reproduce the experimental geometries and frequencies. Because 3d orbital exponents and coefficients for these functions were unavailable, we chose to utilize the 6-31G** basis set and improve the results by including electron correlation as suggested by Basch et al.¹⁴

The procedures followed in this study were quite standard for acquiring the information necessary for MM3 parametrization and are detailed below: **(1) Initial Geometry Selected.** Geometries usually were taken from any available experimental data. Otherwise, the molecule was created through some molecular graphics package and exported to Gaussian 92. **(2) Coordinate Driving Method Implemented To Characterize an Unknown Torsional Profile.** The reaction coordinate method employed a constrained rotation of the torsion in 15° angle increments from 0 to 180 or 360° as dictated by the symmetry of the torsion. At each step, the remaining degrees of freedom were optimized. **(3) Minima Located.** The local minima and global minimum were located by inspection of the calculated torsional profile, and unconstrained optimizations were carried out to obtain the fully minimized structures. **(4) Analytical Frequency Calculations.** To verify that these structures were minima, analytical frequency calculations were carried out to ensure that no imaginary frequencies existed. Additionally, MP2 frequencies, when practical, were calculated for subsequent use in force field parametrization.

It should be noted that the goal of our reaction coordinate method is not to locate transition states *per*

se and obtain rigorous energies for barriers of rotation but to simulate the MM3 coordinate driving algorithm and reproduce a reasonable torsional potential surface that could be modeled with this force field.

Lastly, it should be mentioned that, to account for anharmonicity, some type of electron correlation is necessary for calculation of frequencies that are compared to experiment or used to augment experimental vibrational spectra. Even with this type of correction, scaling factors are still necessary in order to account for other errors inherent in the calculation. Thus, for calculated frequencies of these molecules, a standard scaling factor (0.9) is used for correcting all frequencies throughout each spectrum. Although, the calculated frequencies are not discussed here in any detail, these spectra (along with comparisons to available experimental results) are available upon request from the authors. Also available upon request are the dipole moments of each of the optimized structures at the various levels of theory.

Results and Discussion

Phosphine Oxide (H₃PO). Since this molecule is the simplest of the oxygen-containing phosphorus compounds and has previously been calculated at the MP2 level of theory,¹⁶ we began our investigation with this system. Although experimental structure is lacking, this molecule is interesting since its IR spectrum has been determined experimentally.² Table 1 illustrates the final structures at each level of theory for this molecule. As expected, the calculated vibrational frequencies were all within 10% of experiment and in most cases much better.

Hypophosphorus Acid (H₃PO₂). Although this molecule has no available experimental data (either vibrational or structural), this was the simplest phosphinate that contained a dihedral of interest: the O=P—O—H torsion. Thus, following the procedures detailed earlier, we began rotational profile calculations of this dihedral. The resulting profiles are shown in Figure 1. The main concern with the RHF and MP2 potential energy curves is that the minima differ by a significant number of

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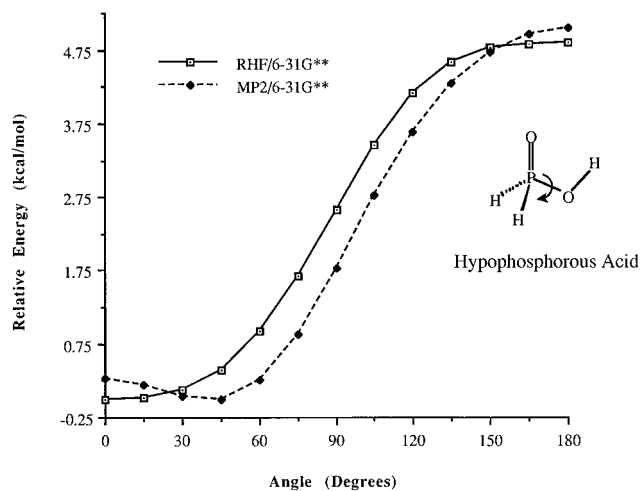


Figure 1. RHF/6-31G** and MP2/6-31G** rotational profiles for hypophosphorous acid.

torsional degrees. At the RHF level, the minimum occurs at 0° while the minimum at the MP2 level is approximately 45°. As can be seen, the energy difference between the 0 and 45° conformations at the MP2 level is negligible but is of little concern due to *ab initio* error in torsional profile calculations. Ewig and Van Wazer¹² observed this same 45° minimum with the STO-3G basis set. They attributed the minimum to steric interactions between the hydroxyl hydrogen and the phosphinic oxide due to a decrease in the P–O–H bond angle. At the MP2/6-31G** level, this steric interaction is not observed since the bond angle actually increases from the 0° (110.5°) to the 45° conformer (111.9°). Ewig and Van Wazer also reported a minimum near the 180° conformation which is not observed at the MP2 level. This implies that there is a definite steric interaction determined by the STO-3G basis set, but the MP2 minimum may be due to some electronic effect.

Once the minima at both the RHF and MP2 levels were located, full optimizations on these structures were initiated. The resulting bond lengths and angles are illustrated in Table 1. Unfortunately, no experimental data are available for comparison. Vibrational frequencies were then calculated on the resulting structures and are given elsewhere. Again, no comparisons could be made due to the lack of experimental data.

Phosphoric Acid (H₃PO₄). In the case of this molecule, both experimental structure and vibrational frequencies were available. The structural determination was carried out with neutron diffraction but, unfortunately, at room temperature.^{4b} The available experimental IR data had been obtained in the liquid phase which makes them less suitable for comparison with calculated vibrational frequencies than gas-phase results.^{4c}

The rotational profile of phosphoric acid is an interesting one considering the conformational flexibility of the hydroxyl group. Additionally, the rotation of one hydroxyl group has a tremendous effect on the conformational preference of the remaining hydroxyl groups. To illustrate this point, two rotational profiles were calculated spanning the entire rotational space of one hydroxyl group (from –180 to 180°) starting with the experimental neutron diffraction structure. The first curve was calculated using only one of the hydroxyl groups as the reaction coordinate and allowing the other hydroxyl groups to optimize along their respective coordinates. The second rotational profile calculation used the same reac-

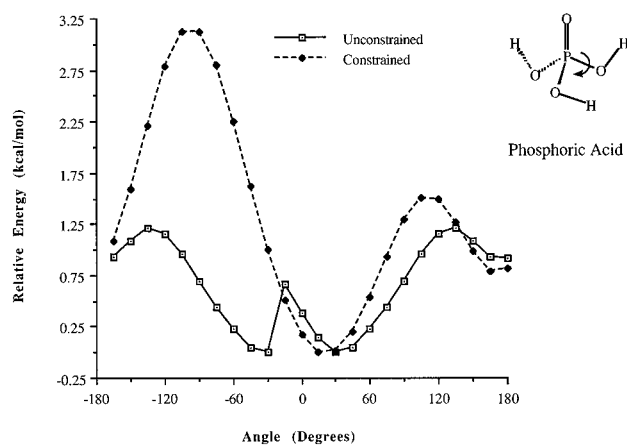


Figure 2. Constrained and unconstrained RHF/6-31G** rotational profiles for phosphoric acid.

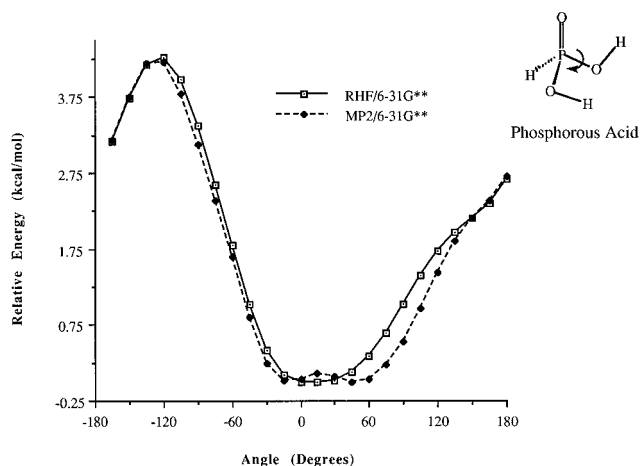


Figure 3. Constrained RHF/6-31G** and MP2/6-31G** rotational profiles for phosphoric acid.

tion coordinate but with the two remaining hydroxyl torsions fixed at the neutron diffraction torsional values. Both rotational profiles were calculated only at the RHF level of theory. The results of these calculations are shown in Figure 2. As seen in the figure, the first procedure resulted in a torsional profile that was discontinuous but was able to determine the locations of the energy minima. The second profile is continuous and also located the proper low-energy conformers. The second profile is important since a continuous curve will be necessary for the parametrization of the MM3 force field, while the first profile provides a better estimate of the barrier between the low-energy conformers. In the case of both curves, the absolute minimum at 30° and another local minimum at 180° were located and chosen for optimization followed by frequency calculations at both the RHF and MP2 levels. The results of the calculations on both conformers are shown in Table 1. In this case, only the P–O bonds were calculated to be much too long.

Phosphorous Acid (H₃PO₃). The structure of this molecule has been determined using X-ray diffraction but, unfortunately, at room temperature.³

In a manner similar to that of phosphoric acid, the rotational profiles of phosphorous acid were calculated at the RHF and MP2 levels with the 6-31G** basis set. The results are shown in Figure 3 and again demonstrate the phenomenon of a shifting minima as found in hypophosphorous acid. The minima at the RHF and MP2 levels correspond to the 15 and 45 degree conformers, respec-

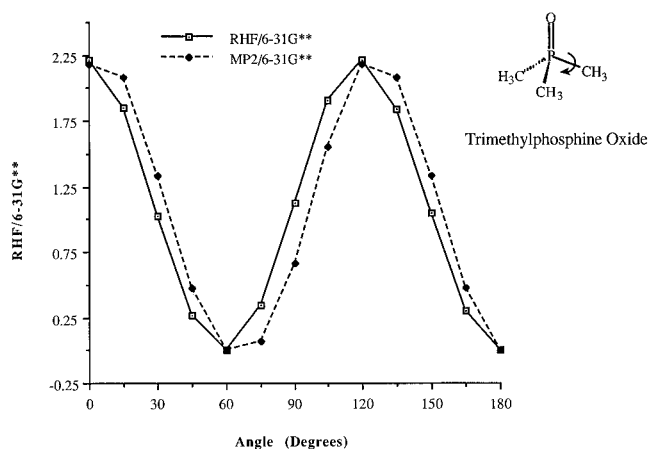


Figure 4. RHF/6-31G** and MP2/6-31G** rotational profiles for trimethylphosphine oxide.

tively. As before, the minima were optimized without constraints, and vibrational frequency calculations were carried out after convergence. The results are tabulated in Table 1. The resulting structures show a significant difference in the experimental and calculated bond lengths. In most cases, the *ab initio* bond length is much longer than those obtained by the X-ray diffraction study. This is quite unusual since the calculated bond lengths should be r_e bond lengths and thus shorter than the experimental ones. It has been suggested that the bond lengths are too long due to the lack of a sufficient number of 3d functions.¹³ This may be the case, but the forces within the crystal may also be responsible for many of these differences. Since no gas-phase structures are available for phosphorous acid, it is difficult to determine which has the greater influence on these differences.

Trimethylphosphine Oxide (H₃PC₃O). Initial calculations focused on trimethylphosphine oxide whose structure has been determined by electron diffraction.⁸ In this case, a gas-phase structure has been determined, thus little or no intermolecular forces should be present in this system.

In the case of trimethylphosphine oxide, the characterization of the methyl rotational potential energy curve (O=P-C-H) was possible. This profile was calculated at both the RHF and MP2 levels of theory in the method previously discussed and is shown in Figure 4. As hypothesized, the global minimum of this structure is in the *anti* conformation in which the O=P-C-H torsion is 180° (two *gauche* hydrogens and one *anti*). The estimated barrier height is similar to that of other methyl-substituted species adjacent to double bonds¹⁷ and is approximately 2.25 kcal/mol.

Once the profile to methyl rotation was established, the global minima was located and calculated at both levels of theory. These fully optimized structures of the global minimum are illustrated in Table 1. As seen, both RHF and MP2 levels of theory employing the 6-31G** basis set are able to reproduce the P-C bond lengths, averaging approximately 1.82 Å for both methods. The shortening of the bond lengths in trimethylphosphine oxide when compared to those of other phosphines can be easily attributed to the electronegative influence of the oxygen in this structure. This phenomenon also can be observed through a series of trimethylphosphine oxide derivatives: the substitution of oxygen-containing groups

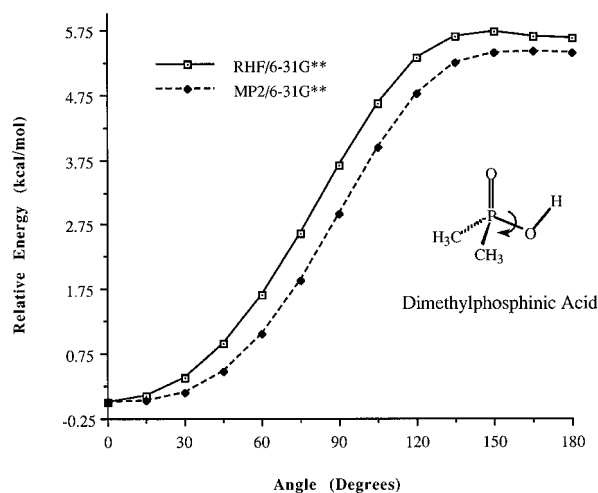


Figure 5. RHF/6-31G** and MP2/6-31G** rotational profiles for dimethylphosphinic acid.

(hydroxyl or methoxy) to trimethylphosphine oxide causes further reduction in the P-C bond lengths.

Dimethylphosphinic Acid (H₇PC₂O₂). The available experimental data for this compound consists exclusively of a room temperature X-ray diffraction study.⁵ In this particular compound, a more effective comparison of the calculated and experimental results is possible since the crystal-packing forces, specifically hydrogen bonding, may be reduced due to the methyl substituents.

Since the methyl conformational preference had been previously established with trimethylphosphine oxide, the rotational profile of interest in this molecule was the O=P-O-H coordinate. The results of the RHF and MP2 calculations of this potential energy curve are shown in Figure 5. Essentially, the profile contains only one minimum at the *eclipsed* conformer but appears to have a second extremely shallow minimum at the *anti* conformation. The estimated barrier between these two conformations is approximately 5.75 kcal/mol and higher than that of hypophosphorous acid (approximately 4.80 kcal/mol). This energy increase can be attributed to the steric repulsion of hydroxyl and methyl groups of dimethylphosphinic acid. Little or no steric repulsion due to the hydroxyl-hydrogen interaction is present in hypophosphorous acid. Additionally, unlike the case of hypophosphorous acid, both levels of theory calculate the dimethylphosphinic acid global minimum to be the *eclipsed* conformation and not a *gauche* conformation. Once again, this result could be due to the steric repulsion of the hydroxyl and methyl substituents.

Once the global minimum was located, comparisons between the calculated structure and the experimental X-ray diffraction data were made. The results of these calculations and the experimental diffraction study are shown in Table 1. The calculated geometry is in good agreement with the experimental data. The largest deviation appears to be in the P-O bond length which is calculated much too long. Once again, this bond contains a site for possible hydrogen bonding within the crystal, and this hydrogen bonding could result in errors in the experimental bond lengths. The bond angles are calculated well with most angles being somewhat smaller than the experimental ones. Once again, the P-C bond length shortening upon oxygen substitution is observed. In this case, the P-C bond lengths are much shorter than the 1.85 Å found in phosphines, averaging 1.78–1.81 Å.

(17) (a) Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 868. (b) Souter, C. E.; Wood, J. L. *J. Chem. Phys.* **1970**, *52*, 674.

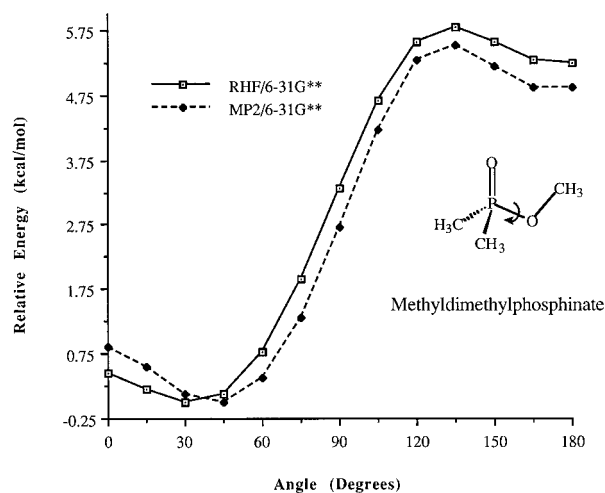


Figure 6. RHF/6-31G** and MP2/6-31G** rotational profiles for methyl dimethylphosphinate.

Again, this shortening is the results of the substitution of two oxygen-containing groups on the phosphine skeleton.

Methyl Dimethylphosphinate ($H_9PC_3O_2$). For this particular molecule, the gas-phase IR spectrum has been determined, and on the basis of these data, an experimental estimate of the structure of this molecule has been made.⁷ Unfortunately, though, an accurate structural determination of this molecule has not been carried out, but the estimate is, at least, a very crude gas-phase structure.

With this molecule, the rotational profile of interest involved the $O=P-O-CH_3$ torsion angle. The remaining dihedrals had been investigated in other systems. The results of the RHF and MP2 reaction coordinate methods from 0 to 180° (2-fold symmetry) are shown in Figure 6. Interestingly, the estimated height of this rotational barrier is quite similar to that calculated in the dimethylphosphinic acid case, being approximately 5.75 kcal/mol. This result implies that these heights may be due to methyl–oxygen interactions rather than a methyl–hydrogen (dimethylphosphinic acid) or methyl–methyl (methyl dimethylphosphinate) interactions. Energetically, whether it is sterics or electronic effects, the oxygen may dominate the interaction with the methyls since the estimated barriers in both cases are nearly identical. The global minimum, however, has shifted somewhat in the case of methyl dimethylphosphinate, occurring at a slightly *gauche* conformation (approximately 45°). This phenomenon could be simply the result of a steric interaction of the methoxy group and the phosphinate oxygen, or perhaps the interaction of the bond moments of the $P=O$ and $O-CH_3$ groups. Additionally, the substitution of a hydroxyl group with a methoxy group has caused the second minimum at the *anti* conformation to become more pronounced, which may be due to a charge–charge interaction between the positively charged phosphorus and the negatively charged methyl group in the *anti* conformation. In the case of dimethylphosphinic acid, the interaction was a repulsive one with the positively charged phosphorus moiety interacting with the positively charged hydrogen of the hydroxyl group.

The global minimum of this potential energy surface was then optimized, and the resulting structural features are illustrated in Table 1. Again, one observes the shortening of the $P-C$ bond lengths upon substitution of hydroxyl or methoxy groups.

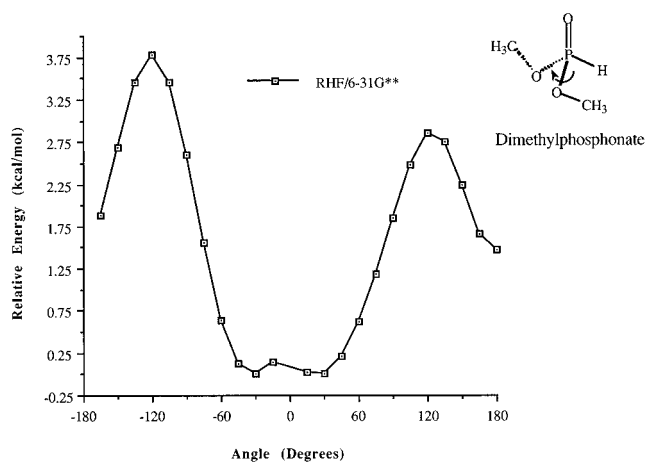


Figure 7. Constrained RHF/6-31G** rotational profile for dimethyl phosphonate.

Dimethyl Phosphonate ($H_7PC_2O_3$). For this particular compound, only the liquid IR spectrum has been reported.⁶ Due to its obvious conformational flexibility, this molecule would present a significant problem in an experimental structural study. Besides the disadvantage of being in the liquid phase, the IR spectrum may also contain a mixture of various conformers and, thus, differ somewhat from any spectrum calculated for any one structure. An attempt to assign the calculated frequencies of the global minimum has been made, though, in order to resolve the true low-energy conformation of this molecule.

As in the case of methyl dimethylphosphinate, the reaction coordinate of interest was the $O=P-O-CH_3$ torsion angle. In this case, however, the primary problem with the characterization of this rotational profile involved the flexibility of this structure: the conformation of one methoxy group strongly dictates the conformational preference of the other methoxy group. This coupling phenomenon was verified through an initial torsional profile calculation and is similar to those of phosphoric and phosphorous acid. Importantly, an initial structure from neutron diffraction or electron diffraction was not available, so it was assumed that the minimum energy conformation of this molecule would contain a methoxy group *eclipsed* to the phosphate moiety. The initial structure with the eclipsed methoxy group was fully optimized to a local minimum. Once this minimum was discovered, one methoxy group was fixed at its optimal value, while the other group was rotated from -180 to 180° to scan the entire potential energy surface. Due to the computational intensity of this calculation and the size of the molecule, this procedure was only carried out at the RHF level of theory. The result of this torsional profile calculation is shown in Figure 7. Like phosphoric acid, this procedure produced a continuous energy profile which could be examined for minima. As predicted, the global energy minimum was the conformation in which both methoxy groups were *gauche* to the $P=O$ bond, which is consistent with other global minima of other structures. A second minimum was located approximately 1.75 kcal/mol higher in energy and is the conformation with one *gauche* and one *anti* methoxy group.

The global minimum having both *gauche* methoxy groups was chosen for full optimization at both the RHF and MP2 levels of theory. The structural data obtained from this calculation are shown in Table 1. The most interesting structural feature obtained from this calcula-

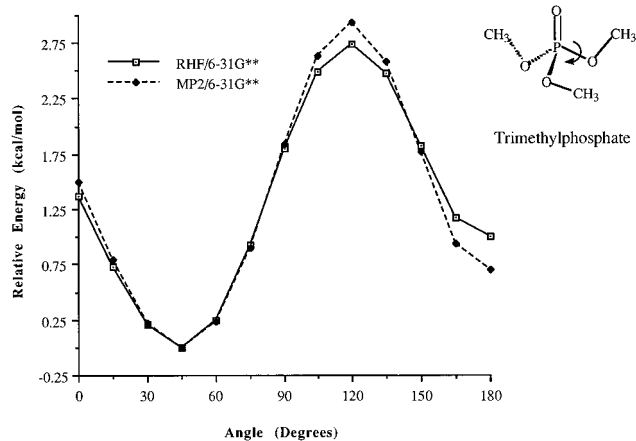


Figure 8. RHF/6-31G** and MP2/6-31G** rotational profiles for trimethyl phosphite.

tion is the observed decrease in the P–H bond lengths on substitution of a second methoxy group. If one compares the P–H bond lengths calculated in hypophosphorus acid (approximately 1.392 Å) to that calculated in dimethyl phosphonate (approximately 1.386 Å), one observes a slight shortening due to the electronegativity effect of the additional methoxy group. Upon comparing the O–CH₃ and P–O bond lengths of methyl dimethylphosphinate (1.440 and 1.639 Å, respectively) with those of dimethyl phosphonate (about 1.420 and 1.593 Å, respectively), a substantial decrease in the measured bond lengths is discovered. Once again, this phenomenon is possibly the result of the addition of another electronegative methoxy group inducing a bond shortening in the P–O and O–CH₃ bonds. Unusually, the RHF results show an opposite effect: the P–O and O–CH₃ bond lengths have actually increased from 1.602 to 1.623 Å and 1.440 to 1.443 Å, respectively. This result is quite interesting considering the effect of the methoxy group at the MP2 level and may simply be due to the inadequacy of RHF theory to account for the electronegativity effect of the additional methoxy group.

Trimethyl Phosphate (H₉PC₃O₄). This structure is important due to its conformational flexibility and its important role in the conformations of DNA. Additionally, this molecule is one of the few compounds in the molecular data set that has both experimental structural and vibrational data.¹¹ The structural data were derived from an electron diffraction experiment, but unfortunately, the conformational preference of the molecule (*C*₃ versus *C*₁) could not be deduced from the experimental data.^{11a} The liquid-phase IR spectrum of this molecule is also known; again, a mixture of conformations most likely exists due to its flexibility and may cause a difficulty in the assignment of one particular conformer to the spectrum.^{11b}

The rotational profile of interest was the O=P–O–CH₃ reaction coordinate. In this situation, the conformations are known: a *C*₃ conformer in which all of the methoxy groups are *gauche* to the P=O bond and a *C*₁ conformer in which two of the three methoxy groups are *gauche* and the remaining group is *anti* to the phosphate moiety. Since these conformations are known, a standard reaction coordinate method as discussed in the Methodology was followed to map out a reaction pathway from the *C*₃ to the *C*₁ conformer. The RHF and MP2 calculated profiles are illustrated in Figure 8. As in the case of most phosphates, the conformational preference for *gauche* methoxy groups (the *C*₃ conformation) is observed favor-

ing an interaction with the P=O bond. As compared with methyl dimethylphosphinate, the estimated barrier to rotation is lower, being approximately 3.0 kcal/mol, while in the case of methyl dimethylphosphinate it is approximately 5.75 kcal/mol. Additionally, the energy difference in the conformers has changed dramatically. In the case of methyl dimethylphosphinate, the energy difference between the *gauche* and *anti* conformers was approximately 4.8 kcal/mol, while for trimethyl phosphate the difference has been reduced to about 1.0 kcal/mol upon substitution of two additional methoxy groups. This lowering in energy may be the result of an electrostatic attraction between the methyl of the *anti* methoxy group (a positively charged methyl) with the remaining methoxy groups (negatively charged groups as a whole) in the *C*₁ conformer. The phosphorus atom could also be more negatively charged in the case of trimethyl phosphate, and thus, an attraction between the methyl of the *anti* methoxy group could be possible.

Once the *C*₃ conformer was fully optimized at both the RHF and MP2 levels of theory, a comparison was made with the available electron diffraction data under the assumption that the *C*₃ conformer was exclusive in the gas phase. The comparison is illustrated in Table 1. A comparison of the electron diffraction data and the RHF and MP2 results for the *C*₁ conformer was made in an attempt to deduce the conformation of this molecule in the gas phase. This comparison is also shown in Table 1. If the calculated *C*₃ and *C*₁ structures are compared with the electron diffraction data, no significant differences in the bond lengths or angles can be found that would establish the true conformation of this molecule in the gas phase. The difference in bond angles and lengths are only slight for the two conformations and, in most cases, are within the experimental error. Once again, since the approximate barrier to interconversion of these two conformers is small, the gas phase may be a mixture of the two conformations, and the resulting structure may simply be an average over the two structures. The reported structure for the diffraction study was also derived under the assumption that the dominant conformer was the *C*₃ conformer. This assumption could also effect the reported experimental structure if a mixture exists in the gas phase.

Dimethylmethoxyphosphine (H₉PC₃O). For this particular molecule, the only available data are an experimental IR spectrum in the gas phase.¹⁰ Although the data reports stretching and bending frequencies, the lower torsional modes were not identified and assigned in the vibrational spectrum.

A reaction coordinate method was undertaken for this molecule and, due to the absence of the P=O bond, one of the C–P–O–CH₃ torsions was chosen. Additionally, because of the symmetry of this molecule, the entire torsional space had to be examined (from –180 to 180°). For computational ease, the torsional energy profile was determined only at the RHF approximation. The minima, though, were optimized at both the RHF and MP2 levels. The results of this reaction coordinate method are illustrated in Figure 9. As seen in the figure, the global minimum energy conformation is the –120° conformer which corresponds to methoxy group eclipsing the phosphorus lone pair. This conformer is also calculated to be the energy minimum for methyl dimethylphosphinate, an analogous structure containing the P=O bond. A second minimum for dimethylmethoxyphosphine is also found at the 60° conformer, corresponding to the *anti* conformation in methyl dimethylphosphinate. Thus, the

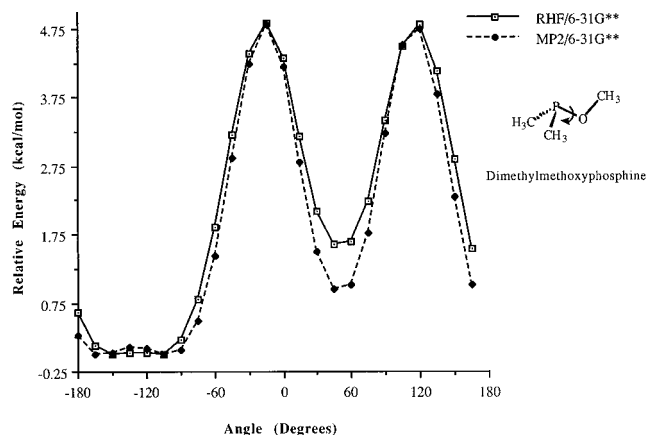


Figure 9. RHF/6-31G** and MP2/6-31G** rotational profiles for dimethylmethoxyphosphine.

presence or absence of the P=O bond in these molecules does not affect the conformational preference and verifies our hypothesis that the maxima and minima are simply a result of steric interactions between the methyl groups and the methoxy group. A significant energy lowering of the *anti* dimethylmethoxyphosphine has occurred, though, and may be the result of an electrostatic attraction of the methoxy group and the phosphorus. In the absence of the oxygen, the phosphorus is more negatively charged and somewhat more attractive to the positively charged methoxy group. This electrostatic interaction may cause the lowering of this *anti* conformation as compared to the energy differences found in methyl dimethylphosphinate.

The global energy minimum was fully optimized, and the geometry obtained is shown in Table 1. As evidenced in Table 1, the phosphate moiety has a significant affect on the P–C bond lengths. When the P=O group is present, the electronegativity effect of this group causes the P–C bond lengths to decrease dramatically from approximately 1.84 Å in dimethylmethoxyphosphine to 1.81 Å in methyl dimethylphosphinate, a decrease of nearly 0.03 Å. Thus, as hypothesized initially, the electron-withdrawing phosphate group affects the geometry, particularly the P–C bond lengths, drastically.

Trimethyl Phosphite (H₂PC₃O₃). For this particular structure, both vapor-phase IR^{9a} and electron diffraction^{9b} results are available. The room temperature electron diffraction results report a structure that has C₃ symmetry similar to that of trimethyl phosphate, but the authors state that the true conformation of this molecule could not be determined and the gas phase may contain a mixture of the two conformations. On the basis of his interpretation of the IR data, Nyquist suggested that the conformation of this compound may be less than C₃ symmetry.^{9a}

In order to support Nyquist's findings, a rotational profile calculation was carried out over the entire conformational space of this molecule. The reaction coordinate for this molecule was chosen to be the O–P–O–CH₃ torsion. As in the case of phosphoric acid, the conformational flexibility of trimethyl phosphite required the constraining of the other methoxy torsions. These remaining torsions were constrained to 179.6 and –80.4° on the basis of a previously optimized RHF structure. The results of this calculation at the RHF level are illustrated in the torsional profile in Figure 10. Due to the constraining of portions of the molecule, a good estimate of the barrier of rotation could not be deter-

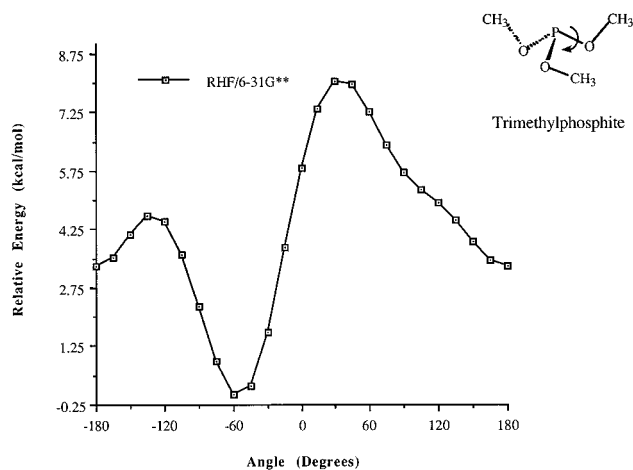


Figure 10. Constrained RHF/6-31G** rotational profile for trimethyl phosphite.

mined, but an energy difference between conformers (verified by unconstrained optimizations) could be calculated. In rotational profile shown in Figure 10, the –60° conformer corresponds to the C₁ structure and the 180° conformer corresponds to the C₃ conformer. As can be seen, the C₁ structure is the preferred conformer for this molecule, being 3.54 kcal/mol lower in energy at the RHF level and 4.22 kcal/mol lower at the MP2 level of theory. Thus, when these calculations are compared to those obtained for trimethyl phosphate, a preference is found for the eclipsing of the methoxy group in the presence of the P=O bond. The stabilization of the *gauche* conformer is most probably due to a hyperconjugative effect of the P=O bond on the methoxy group. The stabilization due to the presence of the P=O is quite significant, approximately 5.0 kcal/mol, and causes a drastic shift in the minimum energy conformer. Additionally, these results also verify the observation of Nyquist in his IR studies: the global minimum energy conformation appears to be less than C₃ symmetry, being, in fact, C₁.

Once these two conformers were located, the geometries were subjected to unconstrained optimizations at both the RHF and MP2 levels of theory. The results of these calculations for the C₃ conformer are shown in Table 1 with the available electron diffraction data. The C₁ results are also illustrated in Table 1. Since the electron diffraction data assumed a C₃ structure, only a comparison with the calculated C₃ structure was made. As can be seen in these figures, good agreement is found between the RHF-calculated C₃ structure and the experimental structure. It is noteworthy that MP2 results differ from the experimental values and, in most cases, the P–O bonds are much too long by approximately 0.032 Å. This difference may simply be the result of errors in the method of calculation or due to the assumption of C₃ symmetry by the experimentalists. Additionally, the influence of the P=O bond can also be observed when one compares the structures of trimethyl phosphate to trimethyl phosphite. A significant decrease in the P–O bond lengths (by approximately 0.046 Å at the RHF level and approximately 0.044 Å at the MP2 level of theory) is found on the addition of the P=O bond. This shortening may be due to the electronegativity effect of the P=O bond. Interestingly, the O–CH₃ bonds increases on addition of the P=O bond (approximately 0.010 Å at all levels) and may be due to the hyperconjugation of the methoxy groups with the P=O bond.

Conclusions

In this study, *ab initio* calculations at both the RHF and MP2 levels of theory utilizing the 6-31G** basis set have been carried out on a few small oxygen-containing phosphorus compounds. Rotational profiles for many of the torsions within these molecules have been determined in a reaction coordinate method. Full optimizations were also carried out to obtain minimum energy structures that were later subjected to vibrational frequency calculations for verification of these minima. These data in conjunction with the available experimental data will be used in the formulation of an MM3 force field for these particular molecules.

Energetically, little difference is observed between the torsional profiles calculated at the RHF and MP2 levels for the title compounds. Consistency appears to have been reached at the RHF level of theory with the 6-31G** basis set. The only significant differences in potential energy curves calculated at these two levels exist in hypophosphorus acid and phosphorus acid. In these cases, the two levels differ only in their predictions of the stability of the eclipsed conformations of these molecules. In both of these molecules, the difference between the RHF and MP2 barriers at the eclipsed conformers is small (less than 0.1 kcal/mol), but a significant change in geometry occurs at the MP2 level

stabilizing the *gauche* conformer over the *eclipsed* conformer. With these two exceptions and those molecules that are conformationally flexible, other torsional profiles are well behaved at both levels of theory.

The structural results are in some agreement with the available gas-phase data and illustrate predicted trends in the geometries. Although many of the gas-phase data are in good agreement, the molecules whose structures have been determined by X-ray or neutron diffraction differ from the calculated results. These differences are possibly due to the packing forces (hydrogen bonding, etc.) within the crystal. On the basis of on these calculations, the influence of the P=O bond on the remaining portion of the molecule can be predicted. It has been observed that the P=O is quite electronegative, causing adjacent bonds to become somewhat shorter. Hyperconjugation of methoxy groups to the P=O bond has also been predicted on the basis of these energetic and structural results.

Supporting Information Available: Experimental and calculated vibrational frequencies for compounds studied in this paper (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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