

Ab Initio Structures of Phosphorus Acids and Esters. 2. Methyl Phosphinate, Dimethyl Phosphonate, and Trimethyl Phosphate

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Abstract: The detailed molecular structure of methyl phosphinate, the simplest ester of the tetracoordinate phosphorus oxyacids, has been determined by ab initio quantum-chemical calculations. The optimized structure, dipole moment, number and relative energies of stable conformers and the change in energy as a function of the torsional angle about the esteric P-O bond were studied in three basis sets of varying complexity. ΔH°_{298} of formation from phosphinic acid and methanol was also computed. The optimized structures, dipole moments, and relative energies of the stable conformers of dimethyl phosphonate and trimethyl phosphate were obtained in a modified STO basis set and the energies in a larger basis. ΔE of the esterification reaction to form these species from phosphonic and phosphoric acids were also computed. The structural results are compared with the limited experimental data for the latter two species. In both cases stable conformers of comparable energy are found, in agreement with experiment.

In recent years considerable interest has developed concerning the detailed structures of organophosphorus compounds. Much of this attention has been focused on the phosphorus esters, due primarily to the importance of the P-O-C linkage in predicating the structures of biological species such as the phospholipids and nucleotides. However, there has been a lack of systematic and quantitative studies, whether experimental or theoretical, on representative compounds of this class for the purpose of elucidating the factors contributing to their molecular structures, conformations, and other molecular properties.

In the preceding paper in this series¹ we described a systematic theoretical study of the structures, conformations, and relative energies of the simplest oxyacids of phosphorus: the gaseous phosphinic, phosphonic, and phosphoric acids. That work showed that (a) ab initio methods give quite reliable results for molecules of this type, (b) the differing chemical species are structurally quite similar, and (c) each species tends to assume a conformation in which the acidic hydrogen is adjacent to the phosphoryl oxygen due to electrostatic (dipolar) effects.

In this paper we have calculated several properties of the esters of phosphorus oxyacids that have been the subject of speculation and dispute for nearly 30 years (vide infra), but which have never received even a cursory theoretical explication. The specific species studied here are the fully methylated esters of the oxyacids described in our previous work: methyl phosphinate, dimethyl phosphonate, and trimethyl phosphate. The first of these, which is the simplest phosphoryl species containing a phosphorus ester linkage (P-O-C), was studied in particular detail. The properties derived include (a) the complete molecular structure in three basis sets of varying complexity, (b) the number of stable conformers in each basis set, along with their structures and relative energies, (c) the dipole moment as a function of basis for each conformer, since this property reflects electrostatic contributions to the torsional potential and has been frequently employed to correlate experimental data, (d) Fourier coefficients of the torsional energy about the P-O-C linkage to delineate the origin of forces that determine the conformation, and (e) ΔH°_{298} for the simplest phosphorus esterification reaction—formation of this ester from phosphonic acid and methanol—including both vibrational corrections and electron correlation at the second-order Møller-Plesset (MP2) level. For each of the remaining two esters we have computed ΔE for their formation from methanol and phosphonic or phosphoric acid, the number of the stable conformers, and for each of these conformers derived its structure, relative energy, and dipole moment employing the same approach as for the

phosphinate ester. The results for these species, particularly for trimethyl phosphate, were found to shed considerable light on the maze of conflicting experimental data that has been reported for their molecular structures and related properties.

Computational Details

We have employed the ab initio quantum-theoretical approach in this study since (a) the accuracy obtained at various levels of sophistication in treating compounds of this type is now well established by our previous work and that of others and (b) a comparison of the results garnered at individual computational steps or levels of approximation may be intercompared to provide an internal check on their accuracy.

All calculations were carried out with the GAUSSIAN 80 and GAUSSIAN 82 programs² and the default analytical-gradient procedure for optimizing molecular structures that they contain. The first of the title compounds, methyl phosphinate ($\text{H}_2\text{PO}(\text{OCH}_3)$), was studied in three basis sets: STO-3G,³ 3-21G,⁴ and 4-31G,⁵ each with a fivefold set of d functions on the phosphorus atom. The exponent of the d function was 0.39 for the STO basis⁶ and 0.55 for the others.⁷ Following common practice, we will refer to the thus augmented STO basis as STO-3G*. Similarly, the notation 3-21G* will be employed to describe the following: a 2,1 contracted pair of s functions on H; 3 s and 2,1 sp on oxygen and carbon; and 3 s plus 3 sp for the phosphorus core with 2,1 sp and 1 d for its valence. The other split-valence basis sets are defined in the same way. These will be referred to as 3-21G* and 4-31G* basis sets to indicate the presence of the d functions on only the phosphorus. All structural parameters were allowed to vary independently, the only exception being the three CH bonds and the three OCH bond angles of each methyl group, for which

(2) GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A., Quantum Chemistry Program Exchange, Indiana University: Bloomington, IN. We thank Dr. John H. Yates, University of Pittsburgh, for a DEC version of this program. GAUSSIAN 82: Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Frisch, M. J.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon University: Pittsburgh, PA.

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

(4) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 939-947. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* 1982, 104, 2797-2803.

(5) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* 1971, 54, 724-728. (b) Hehre, W. J.; Lathan, W. A. *J. Chem. Phys.* 1972, 56, 5255-5257.

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

(7) 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.

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

Table I. Computed Structural Parameters^a of Methyl Phosphinate, H₂PO⁰(OCH₃)

	basis					
	STO-3G*		3-21G*		4-31G*	
	conf 1	conf 2	conf 1	conf 2	conf 1	conf 2
P=O ⁰	1.4430	1.4405	1.4631	1.4561	1.4579	1.4504
P—O	1.5886	1.5887	1.5773	1.5785	1.5717	1.5710
P—H	1.3866	1.3873	1.3824	1.3898	1.3881	1.3941
O—C	1.4376	1.4369	1.4605	1.4497	1.4464	1.4351
C—H	1.0936	1.0937	1.0781	1.0801	1.0746	1.0763
∠O ⁰ PO	119.40	115.89	115.36	115.49	115.99	115.91
∠O ⁰ PH	116.66	116.79	115.97	115.96	115.62	115.55
∠OPH	100.31	102.45	102.56	103.08	102.52	103.18
∠HPH	100.22	100.00	102.42	101.22	102.56	101.51
∠POC	118.53	117.50	126.18	125.97	129.34	131.81
∠OCH	110.09	110.36	108.51	109.28	108.43	109.03
tor. ∠COPO ⁰ ^b	0.00	180.00	0.00	180.00	0.00	180.00
tor. ∠HCOP ^b	0.00, ±120.21	±60.19, 180.00	0.00, ±120.21	±60.13, 180.00	0.00, ±120.22	±60.22, 180.00

^aBond lengths in Å, angles in deg. ^bTorsional angles ABCD between planes defined by ABC and BCD; values positive for clockwise rotation about BC viewed toward C.

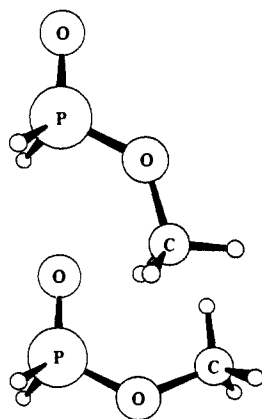


Figure 1. Stable conformers 1 (lower) and 2 (higher) of methyl phosphinate computed in the 4-31G* basis and reproduced to scale.

each set of three was constrained to be equal. Optimization of molecular structures was continued in each case 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 0.01°. In the case of methyl phosphinate, the electron-correlation correction to the energy was computed at the second order of Møller–Plesset perturbation theory (MP2),⁸ including all valence orbital excitations. Vibrational corrections to the energy and enthalpy thus computed were derived from the frequencies obtained by diagonalizing the analytically computed force-constant matrix.

Methyl Phosphinate

Computed Structure. The simplest compound of this series is methyl phosphinate, H₂P=O(OCH₃). (Hereinafter we employ the purely formal notation P=O to denote the phosphoryl bond. The electronic structure of this bond is of course very different than this simple notation implies, and it was carefully studied⁹ some time ago.) All geometrical parameters were independently optimized in each of the three basis sets described above. In each case two conformers were found, characterized primarily by a difference in the torsional angle of the methyl group about the P—O bond of 180° and of the methyl group about its axis of approximately 60°. The conformer of lowest energy corresponds to a torsional angle about the P—O axis of 0°, with the methyl eclipsing the phosphoryl oxygen. In the higher energy conformer this angle is 180°, so that the methyl group is opposed to the

Table II. Computed Total Energies^a of Methyl Phosphinate

basis	energy
STO-3G*	-525.055 78
3-21G*	-528.526 19
4-31G*	-530.604 90
4-31G* ^b	-531.040 71
4-31G* ^c	-530.599 13

^aIn hartrees; at the SCF approximation unless otherwise noted. ^bWith electron correlation at the MP2 level. ^cEmploying the structure optimized in the STO-3G* basis.

Table III. Computed Dipole Moments^a and Relative Energies^b of Methyl Phosphinate Conformers

basis	conf	rel energy	μ
STO-3G*	1	0.00	1.77
STO-3G*	2	-1.05	3.87
3-21G*	1	0.00	2.65
3-21G*	2	4.20	5.84
4-31G*	1	0.00	3.01
4-31G*	2	4.84	6.29
4-31G* ^c	1	0.00	2.33
4-31G* ^c	2	3.79	6.15

^aDebye units. ^bkcal/mol. ^cEmploying the structure optimized in the STO-3G* basis.

phosphoryl oxygen. The structures computed in each of the three basis sets and for both of the conformers are shown¹⁰ in Table I. The structures found in the 4-31G* basis are depicted in Figure 1. There is generally good agreement between the structures computed in the three basis sets, with the primary exception being the angle POC about the bridging oxygen.¹ Also differences between conformers are consistently reproduced; for example, the decrease in the length of the phosphoryl bond between conformations 1 and 2 is 0.0025 Å in the STO-3G* basis, 0.0070 in the 3-21G* basis, and 0.0075 in the 4-31G* basis.

The total energies of conformation 1 in each of the three basis sets are shown in the first three rows of data in Table II. Also shown here are the MP2 approximation to the energy in the 4-31G* basis and, for later reference, the SCF energy in the 4-31G* basis computed at the STO-3G* structure.

In Table III the relative energies and dipole moments of methyl phosphinate are reported for calculations in various basis sets. Note that the STO-3G* basis gives conformation 2 as being lower in energy, while the two split-valence basis sets give conformation 1 as the lower.

Origin of the Torsional Potential. In our previous work¹ on the oxyacids of phosphorus we noted that the relative energies of the

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(9) Marsmann, H.; Groenweghe, L. C. D.; Schaad, L. J.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6107–6112. See also: Absar, I.; Van Wazer, J. R. *J. Phys. Chem.* **1971**, *75*, 1360–1365. Absar, I.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 6294–6297.

(10) In this and subsequent tables of structural data we report a sufficient level of precision to permit intercomparison of the various species and conformers. This of course has no necessary connection to their accuracy, as reflected in particular by Table IX.

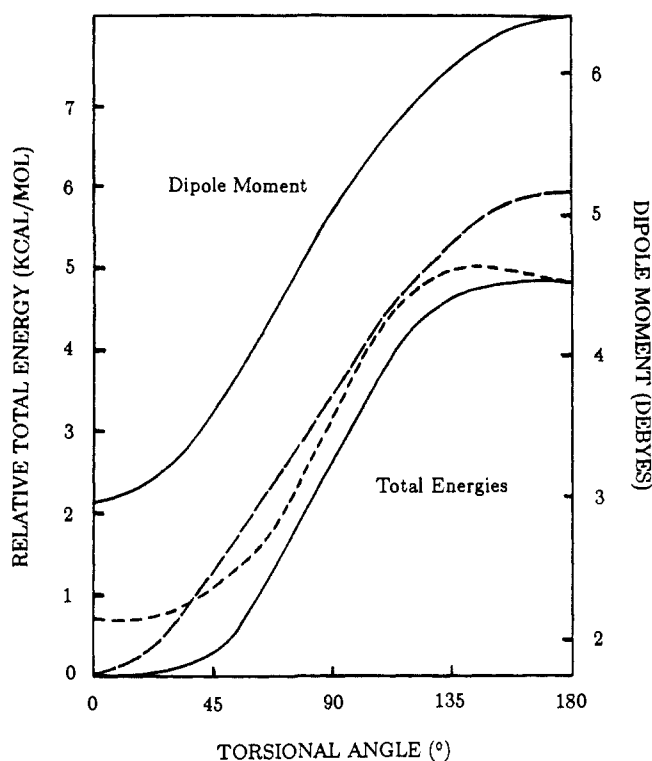


Figure 2. Bottom curves: the energy of methyl phosphinate as a function of torsional angle, with structure optimized for conformation 1 (---), conformation 2 (-.-), and optimized throughout (—). Top curve: Corresponding total dipole moments for completely optimized structures.

stable conformations tend to parallel their total dipole moments, with structures of lower energy tending to exhibit smaller dipoles as would be expected from an alignment of bond dipoles that minimizes the distances between charges of opposite sign. This is seen from Table III to be the case for methyl phosphinate as well for results obtained in the two split-valence basis sets, but not in the smaller STO-3G* basis. As is often the case, the latter overestimates steric repulsion, causing the conformation with the methyl group adjacent to the phosphoryl to be too high in energy.

In the last two rows of Table III are listed for later comparison the relative energies and dipole moments computed in the 4-31G* basis at the geometry optimized in the STO-3G* basis. These results are appreciably closer to the 4-31G* values at the 4-31G* structure than to the STO-3G* results at the STO-3G* structure.

In order to delineate the forces that give rise to conformational preference, we have computed the energy of torsion about the OP-OC ester linkage in the 4-31G* basis for the complete range of torsional angles (0° to 180°). As a check on the method, this was done in three ways, two of which may be termed "adiabatic" processes and one "isothermal". The two adiabatic procedures consisted of employing (a) the minimal-energy (conformation 1) structure for all structural parameters except the OP-OC torsional angle and (b) similarly using the geometrical parameters of conformation 2. The isothermal approach consisted of reoptimizing all of the structural parameters, except the OP-OC torsional angle, for a series of values of that torsional angle. The resulting energy curves are shown in the lower part of Figure 2. By employing the structure obtained in conformation 2 throughout, the barrier from conformation 1 → 2 is 4.3 kcal/mol, and the 2 → 1 barrier is 0.2 kcal/mol. For the conformation 1 structure, the 1 → 2 barrier is 5.9 but the 2 → 1 barrier equals zero, so that only a single stable form is found. By employing fully optimized structural parameters throughout, the 1 → 2 barrier is 4.9 while the 2 → 1 barrier is only 0.02. So in this basis there is effectively only one conformation, conformation 1, with the additional stationary point approximating an energy maximum.

Curves (similar to those in the lower part of Figure 2) corresponding to the adiabatic cases (a) and (b) of the preceding paragraph were obtained for the STO-3G* and 3-21G* basis sets

and exhibited considerably larger differences between the results for the geometries of conformations 1 and 2 than are shown in this figure. For the STO energy calculations, the 1 → 2 barrier was 3 kcal/mol and the 2 → 1 was 2.3 kcal/mol for the conformation 1 geometry; but the barrier was 3.5 and 0.2, respectively, for conformation 2, which exhibited its energy minimum at 50° instead of 0°. For the 3-21G* basis, the 1 → 2 barrier was 5.3 and the 2 → 1 barrier was zero for the conformation 1 geometry; but the barrier was 3.2 and 0.2 for conformation 2, for which there was an additional energy minimum (0.2 kcal deep) at 75°.

The isothermal torsional process is particularly interesting, not only because internal rotation in a solution must occur primarily by this mechanism but also because it shows what molecular deformations are required for a smooth transition from one conformer to another. As would be expected, the methyl group must twist considerably in order to avoid a close encounter with one of the phosphorus-bonded hydrogens. Therefore the PO-CH torsion angle computed in the 4-31G* basis increases to a value about 50° larger when the OP-OC torsion angle reaches about 60° and then drops by about 30° (at OP-OC = ca. 120°) before rising by about 40° to give the final value of 60° corresponding to configuration 2. The POC angle varies in concert with the PO-CH torsion angle, first becoming smaller and then larger before backing down to a value (corresponding to configuration 2) about 30° larger than its starting value. The observed concerted deformations include both a change in bond length and OPH bond angle for each of the two hydrogens directly bonded to the phosphorus. As the distance between one of these hydrogens and the closest methyl hydrogen begins to decrease, this P-H distance begins to shrink, dropping to a low (at OP-OC = ca. 60°) about 0.05 Å smaller than that of configuration 1 before gradually lengthening to the larger value of configuration 2. The other P-H distance gradually increases to a maximum value (at OP-OC = ca. 135°) nearly 0.09 Å above that of configuration 1 and then shortens somewhat to the value of configuration 2. The only appreciably varying geometrical feature of the structure that is not directly associable with the avoidance of close encounter is the P=O bond distance, which shortens gradually upon going from conformation 1 to 2—with the P=O distance varying sinusoidally through one cycle as the OP-OC torsional angle is increased from 0° to 360°.

The barrier to internal rotation of the methyl group was determined employing the optimized structures for both conformations 1 and 2 by a rigid rotation of the methyl group through 60°. In conformation 1 it is 0.5 kcal/mol and in conformation 2 it is 0.8 kcal/mol. From this it is clear that internal hydrogen bonding between the methyl hydrogen and the phosphoryl oxygen plays no role in the stability of conformation 1.

The dipole moments computed with the three types of structures (conformation 1, conformation 2, and optimized throughout) as a function of the torsional angle are very similar and on the scale of Figure 2 would be nearly indistinguishable. The dipole moment for the fully optimized model only is shown in the upper portion of Figure 2.

To interpret quantitatively the curves of the lower part of Figure 2, we have employed the procedure based on a Fourier expansion of the energy as proposed by Radom et al.¹¹ We have previously described its implementation^{1,12,13} for compounds of this type. In this analysis the energy V as a function of the OP-OC torsional angle, τ , is expanded in a modified Fourier series of the form

$$V(\tau) = V_0 + V_1 \cos(\tau + \alpha_1) + V_2 \cos 2(\tau + \alpha_2) + V_3 \cos 3(\tau + \alpha_3) \quad (1)$$

Here V_1 is the dipolar term and has the symmetry of the electrostatic interaction of a monopole with a dipole or between

(11) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371-2381.

(12) Ewig, C. S.; Van Wazer, J. R. *J. Mol. Struct. (THEOCHEM.)* **1985**, *122*, 179-187.

(13) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.*, in press.

Table IV. Fourier Coefficients of the Methyl Phosphinate Torsional Potential^a

term	using the geometry of		
	conf 1	conf 2	optimized
V_0	-376.32	-376.58	-377.08
V_1	-2.92	-2.46	-2.75
V_2	-0.24	-0.22	-0.11
V_3	-0.05	0.39	0.32

^a kcal/mol.**Table V.** Computed^a Electronic, Zero-Point, and Thermal Energies for Structures Optimized in the 4-31G* Basis Set

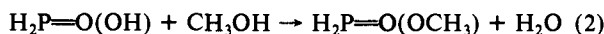
species	SCF ^b	MP2 ^b	E_{zp} ^c	E_{corr} ^d	TS ₂₉₈ ^e
H ₂ O	-75.908 64	-76.037 14	14.0	15.8	13.4
CH ₃ OH	-114.870 82	-115.088 51	34.3	36.4	17.0
H ₂ (P=O)(OH)	-491.640 69	-492.004 05	25.0	27.6	19.8
H ₂ (P=O)(OCH ₃)	-530.604 90	-531.058 51	44.8	48.2	23.4

^aAll data correspond to the 4-31G* basis set. ^bIn hartrees/molecule. ^cThe zero-point energy correction in kcal/mol computed in the SCF approximation. ^dThe energy correction in kcal/mol for all nuclear motion, calculated in the SCF approximation at 298 K. ^eSimilarly computed, in kcal/mol.

two dipoles. V_2 is the quadrupolar term and has the symmetry of the interaction of a monopole with a quadrupole or between two quadrupoles. Terms in the energy that reflect stereoelectronic effects such as hyperconjugation or "anomeric effects"¹⁴ are usually postulated to be represented by such twofold contributions to the energy. For torsion about bonds to a tetrahedrally coordinated atom V_3 is a measure of steric repulsion. Since steric effects necessarily have their maxima at angles corresponding to the minimal distances between nuclei, the corresponding phase, α_3 , is known in advance and may be set to zero in eq 1.

The results for the three types of computed geometries as shown in Figure 2 are listed in Table IV. Here we have set $\tau = 0^\circ$ when the methyl is adjacent to the phosphoryl, so that with respect to this arrangement negative terms are attractive and positive ones are repulsive. As can be seen from the figure the V_1 term, which is of the form of a dipolar electrostatic interaction, is by far the largest. The relative magnitudes of other terms are in qualitative agreement, with the primary difference being the V_3 term, which imposition of the conformation 1 structure causes to become slightly attractive. The completely reoptimized results, shown in the last column of Table IV, demonstrate that the V_2 or stereoelectronic term is the smallest of the three, with V_1 being 25 times larger.

Enthalpy of the Esterification Reaction. Finally, from the computed total molecular energy we may derive the energy of the simple prototype esterification reaction



The electronic reaction energy (i.e., the energy uncorrected for nuclear motion) computed in the SCF and MP2 approximations, as well as the energy correction due to zero-point and thermal motions at 298.15 K, and the product of this temperature with the entropy for each of the species appearing in eq 2 are listed in Table V.

From the first two columns of data appearing in this table, $\Delta E = -1.3$ kcal/mol at the SCF level and -1.9 kcal/mol including electron correlation at the MP2 level. As seen from Table V, both the energy corrections and TS terms precisely cancel in this reaction at 298 K, although the difference in zero-point energies is -0.5 kcal/mol. Thus at the MP2 level the quantities ΔE°_0 , ΔH°_0 , and ΔG°_0 are all computed to be -2.4 kcal/mol, while ΔE°_{298} , ΔH°_{298} , and ΔG°_{298} are all -1.9 within 0.1 kcal/mol for

(14) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983. A conclusion quite similar to ours regarding the weakness of this effect in phosphorus compounds has recently been reached, based on a much different type of evidence: Schleyer, P. v. R.; Eluvathingal, D. J.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393-6394.

Table VI. Computed Total Energies^a in the 4-31G* Basis but Employing the Structure Found in the STO-3G* Basis

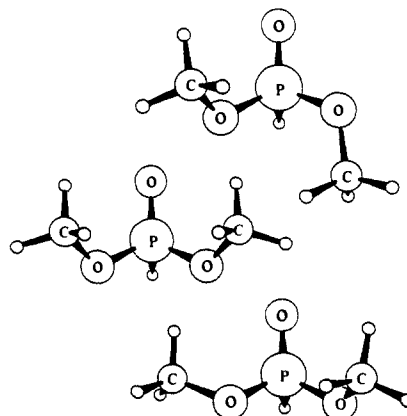
species	energy	species	energy
H ₂ O	-75.903 33	P=O(OH) ₃	-641.240 88
CH ₃ OH	-114.866 49	H ₂ P=O(OCH ₃)	-530.599 13
H ₂ P=O(OH)	-491.632 86	HP=O(OCH ₃) ₂	-644.370 61
HP=O(OH) ₂	-566.439 94	P=O(OCH ₃) ₃	-758.145 03

^aIn hartrees/molecule at the SCF approximation, not corrected for nuclear motion.

Table VII. Structural Parameters^a of All Stable Conformations of Dimethyl Phosphonate, H^δP=O^δ(O^δC^δH₃)(O^δC^δH₃), Computed in the STO-3G* Basis

parameter	conf 1	conf 2	conf 3
P=O ^δ	1.4391	1.4377	1.4402
P-O ^δ 1	1.5936	1.5923	1.5904
P-O ^δ 2	1.5847	1.5892	1.5904
P-H ^δ	1.3833	1.3833	1.3807
O ^δ 1-C ^δ 1	1.4380	1.4398	1.4376
O ^δ 2-C ^δ 2	1.4399	1.4375	1.4376
C ^δ 1-H	1.0936	1.0936	1.0936
C ^δ 2-H	1.0935	1.0935	1.0936
∠O ^δ PO ^δ 1	117.03	118.80	117.34
∠O ^δ PO ^δ 2	120.30	113.20	117.34
∠O ^δ PH ^δ	115.93	117.72	118.77
∠O ^δ 1PH ^δ	103.14	96.32	97.10
∠O ^δ 2PH ^δ	96.82	102.85	97.10
∠PO ^δ C ^δ 1	116.73	116.48	117.78
∠PO ^δ C ^δ 2	116.88	118.09	117.78
∠O ^δ 1C ^δ H	110.22	110.20	110.20
∠O ^δ 2C ^δ H	110.12	110.31	110.20
tor. ∠C ^δ O ^δ 1PO ^δ b	-39.22	43.09	32.50
tor. ∠C ^δ O ^δ 2PO ^δ b	-52.90	176.55	-32.50
tor. ∠HC ^δ O ^δ 1P ^δ b	45.3, 165.4, -74.9	-50.1, 70.1, -170.2	-36.3, 84.1, -156.4
tor. ∠HC ^δ O ^δ 2P ^δ b	54.4, 174.3, -66.0	58.3, 178.4, -61.9	36.3, -84.1, 156.4

^aBond lengths in Å, angles in deg. ^bTorsional angles ABCD between planes defined by ABC and BCD; values positive for clockwise rotation about BC viewed toward C.

**Figure 3.** Stable conformers 1 (lowest), 2 (highest), and 3 (intermediate) of dimethyl phosphonate computed in the STO-3G* basis and reproduced to scale.

the esterification reaction of eq 2.

When dealing with larger species it is useful to determine structures in a smaller basis than employed for the final energy calculations. In Table VI are listed the SCF energies (not corrected for nuclear motion) obtained in the 4-31G* basis, but employing the structures optimized in the STO-3G basis for H₂O and CH₃OH, and in the STO-3G* basis for H₂P=O(OH) and H₂P=O(OCH₃). These give a ΔE for reaction 2 of -2.0 kcal/mol.

Dimethyl Phosphonate

Computing the energy-minimum structures of dimethyl phosphonate, HP=O(OCH₃)₂, in the STO-3G* basis resulted in three stable conformations. The geometric parameters of these

Table VIII. Dipole Moments^a and Relative Energies^b Computed with STO-3G* Optimized Structures

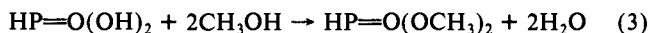
basis	conformer	rel energy	μ
Dimethyl Phosphonate Conformers			
STO-3G*	1	0.00	1.71
STO-3G*	2	0.08	3.25
STO-3G*	3	0.98	2.06
4-31G*	1	0.00	2.31
4-31G*	2	1.09	4.82
4-31G*	3	0.35	2.85
Trimethyl Phosphate Conformers			
STO-3G*	1	0.00	2.81
STO-3G*	2	0.22	0.35
4-31G*	1	0.00	4.14
4-31G*	2	1.00	0.15

^a Debye units. ^b kcal/mol.

three forms, conformations 1 through 3 in order of increasing energy, are listed in Table VII. With the exception of the torsional angles, they are quite similar to the analogous values for methyl phosphinate shown in Table I. Conformations 1 and 3 correspond to an arrangement with both methyl groups (and one hydrogen atom in each methyl) roughly adjacent to the phosphoryl oxygen, the methyl groups rotated slightly away from it in the same direction in the former and in opposite directions in the latter. Conformation 2 has one methyl adjacent to the phosphoryl and one opposed. These three forms are depicted in Figure 3.

The relative energies of the three conformations and their dipole moments are presented in the upper part of Table VIII. Included in this listing are the same quantities computed with the STO-3G* structure but in the 4-31G* basis. As was seen in the case of methyl phosphinate, the larger basis predicts a different ordering by relative energy from the smaller one; the 4-31G* basis yields a set of relative energies that correlates well with their dipole moments, whereas the STO-3G* basis again appears to overestimate steric repulsion by the phosphoryl oxygen, thus stabilizing conformation 2 relative to conformations 1 and 3. Therefore the same factors that govern the structure of methyl phosphinate apparently apply to dimethyl phosphonate as well. By the same token it is likely that reoptimizing the energy in the larger basis at points on the energy surface between conformations would significantly alter the heights and positions of the energy barriers.

The total energies computed in the 4-31G* basis at the STO-3G* structure, not corrected for nuclear motion, for both dimethyl phosphonate and trimethyl phosphate are listed in Table VI. From these data we obtain a value of $\Delta E = -2.7$ kcal/mol for the reaction



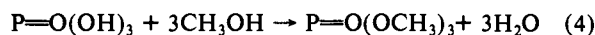
Trimethyl Phosphate

The structure of trimethyl phosphate, $\text{P}=\text{O}(\text{OCH}_3)_3$, was computed in the STO-3G* basis. A search of all possible values and permutations of the torsional angles yielded only two stable conformations. The geometric parameters of these two forms, conformations 1 and 2 in order of increasing energy, are listed in Table IX. These are also shown in Figure 4. To our knowledge trimethyl phosphate is the only one of the three species described in this paper for which there is quantitative experimental structural data. This is the electron-diffraction study reported by Oberhammer.¹⁵ His results, which are based on an analysis that presupposed C_3 symmetry, are listed in the last column of Table IX. Note that we find the lower energy form to be completely asymmetric, while only the higher energy form exhibits C_3 symmetry. The agreement of these experimental values with our computed parameters for conformation 1 (averaging over groups of bond lengths and angles which analysis of the experiment assumed to be equal) is quite good and is generally within the estimated experimental error limits. The agreement of the experiment with the parameters of conformation 2 is noticeably

poorer. The primary difference among the three sets of parameters is the set of torsional angles. Conformation 1 corresponds to two methyl groups adjacent to the phosphoryl and one opposed, conformation 2 corresponds to all three adjacent, while the reported experimental structure has all three opposed.

In Table VIII the relative energies are presented for the two conformers of trimethyl phosphate for the structures given in Table IX as computed in both the STO-3G* and 4-31G* basis sets. Also listed are their dipole moments. In this case both basis sets predict the same ordering by energy of the two forms; and, unlike the two other esters described in this study, the form of lower energy has the higher dipole moment. This higher value would be expected to result from the lesser cancellation between the $\text{P}=\text{O}$ and the three $\text{P}-\text{O}$ bond moments in this completely asymmetric conformer.

From the energies of trimethyl phosphate and other pertinent molecules given in Table VI, ΔE is found to be -9.2 kcal/mol for the reaction



Discussion

Molecular Structures. The results presented in this paper are consistent with a description of the esteric $\text{P}-\text{O}-\text{C}$ linkage in which the overall molecular structure is governed by a rotation about the $\text{OP}-\text{OC}$ bond to minimize the electrical inhomogeneity of the species. This is equivalent to minimizing the total dipole moment. An exception to this principle occurs for trimethyl phosphate, in which steric interaction among the three methyl groups shifts the conformer with the smaller dipole to a slightly higher energy.

To our knowledge the only prior quantum-theoretical calculations on any of the three esters described herein was a study of methyl phosphinate by Gordon et al.¹⁶ They optimized its structure in an STO-2G* basis and reported that conformation 2 (methyl group opposed to the phosphoryl) is the stable form. This is in accord with our finding here that the STO-3G* basis gives a spurious stability to this type of conformer due to a marked overestimation of steric repulsion. However, the use of larger basis sets, whether employing an STO-optimized structure or a more accurately computed one, gives the correct result.

There is a paucity of reliable experimental results for both methyl phosphinate and dimethyl phosphonate. On the basis of infrared and dipole-moment data a *cis* ($\tau = 0^\circ$) structure has been attributed to methyl dimethylphosphinate¹⁷ in agreement with our finding for methyl phosphinate, although for phosphinates with more bulky substituents *gauche* ($\tau = 60^\circ$) forms have been reported.¹⁸ Similar studies of dimethyl methylphosphonate have shown the presence of two stable conformers,¹⁹ and dipole moment data indicate that they are a mixture of structures similar to the ones we have computed.

Trimethyl phosphate has been extensively studied by a number of experimental techniques and interpretational schemes, based on its infrared spectrum,²⁰⁻²² dipole moments and Kerr constants,^{23,24} electron diffraction,¹⁵ and NMR in liquid crystals.²⁵ These have all given differing and in many cases diametrically

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Table IX. Structural Parameters^a of Trimethyl Phosphate, H⁰P=O⁰(O¹C¹H₃)(O²C²H₃)(O³C³H₃), Computed in the STO-3G* Basis

parameter	computed conf 1	computed conf 2	exptl (elec. diff.) ^b
P=O ⁰	1.4370	1.4389	1.477 ± 0.006
P—O ¹	1.5891	1.5888	1.580 ± 0.002
P—O ²	1.5979	1.5888	1.580 ± 0.002
P—O ³	1.5831	1.5888	1.580 ± 0.002
O ¹ —C ¹	1.4383	1.4384	1.432 ± 0.005
O ² —C ²	1.4382	1.4384	1.432 ± 0.005
O ³ —C ³	1.4379	1.4384	1.432 ± 0.005
C ¹ —H	1.0936	1.0935	1.103 ± 0.012
C ² —H	1.0936	1.0935	1.103 ± 0.012
C ³ —H	1.0934	1.0935	1.103 ± 0.012
∠O ⁰ PO ¹	119.34	117.62	
∠O ⁰ PO ²	116.53	117.62	
∠O ⁰ PO ³	113.40	117.62	
∠O ¹ PO ²	99.25	100.24	105.0 ± 2.9
∠O ¹ PO ³	100.54	100.24	105.0 ± 2.9
∠O ² PO ³	105.45	100.24	105.0 ± 2.9
∠PO ¹ C ¹	116.57	116.55	118.3 ± 1.5
∠PO ² C ²	116.32	116.55	118.3 ± 1.5
∠PO ³ C ³	119.14	116.55	118.3 ± 1.5
∠O ¹ C ¹ H	110.14	110.15	110.3 ± 1.9
∠O ² C ² H	110.24	110.15	110.3 ± 1.9
∠O ³ C ³ H	110.10	110.15	110.3 ± 1.9
tor. ∠C ¹ O ¹ PO ⁰ ^c	52.08	46.16	150.6 ± 6.5
tor. ∠C ² O ² PO ⁰ ^c	39.29	46.16	150.6 ± 6.5
tor. ∠C ³ O ³ PO ⁰ ^c	179.08	46.16	150.6 ± 6.5
tor. ∠HC ¹ O ¹ P ^c	65.21, -55.16, -175.07	70.97, -49.34, -169.38	
tor. ∠HC ² O ² P ^c	72.67, -47.46, -167.67	70.97, -49.34, -169.38	
tor. ∠HC ³ O ³ P ^c	54.20, -65.95, -185.87	70.97, -49.34, -169.38	

^aBond lengths in Å, angles in deg. ^bFrom ref 15. ^cTorsional angles ABCD between planes defined by ABC and BCD; values positive for clockwise rotation about BC viewed toward C.

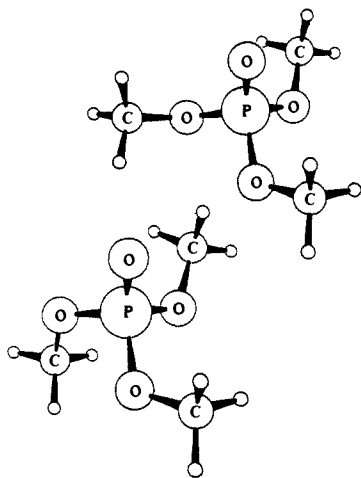


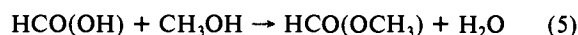
Figure 4. Stable conformers 1 (lower) and 2 (higher) of trimethyl phosphate computed in the STO-3G* basis and reproduced to scale.

opposing results. It is now clear that, although the electron-diffraction findings of Oberhammer¹⁵ may include accurate values for some structural features, the conformation he reports as being the lowest in energy (with all three methyl groups in nearly maximal proximity, $\tau = 151^\circ$) is unlikely to be correct. Not only is this unreasonable on steric grounds but it also would correspond to a dipole moment roughly twice the experimental value.²³ Oberhammer's result may partially be due to his considering only structures of at least C_3 symmetry. Similarly a recent NMR study²⁵ concluded that there are two conformations, both implicitly assumed to have C_3 symmetry, in which all three torsional angles, τ , about the P—O bond are reported as gauche (near 60°) in the one of lower energy and 155° in the higher one. It should be emphasized that, as demonstrated by our present findings, there

is no reason to assume that phosphate structures exhibit any overall symmetry. Analyses based on infrared spectra, dipole moments, and Kerr constants have generally considered the possibility of asymmetric structures, but these analyses have been restricted by a lack of data relative to the number of features (number, relative energies, and torsional angles of the conformers) to be derived. Also these studies have often omitted from consideration all species in which alkyl groups are situated close to the phosphoryl oxygen, an arrangement which we compute to be the favored one. Indeed, either this or the assumption of high molecular symmetry appears to be an unwarranted implicit or explicit interpretational bias in the majority of the experimental studies to date.

Thermodynamics of Esterification Reactions. The entropy change in reaction 2, the formation of methyl phosphinate and water from phosphinic acid and methanol, was computed to be less than 0.3 eu as shown by Table V. This is consistent with the finding by Guthrie²⁶ that in the analogous hydrolysis reaction for triethyl phosphate in aqueous solution it is "2.32 ± 3.55" eu per P—O—C linkage.

We have previously computed,¹³ employing the 4-31G basis, ΔH°_{298} for the gas-phase reaction



to be -3.7 kcal/mol at the SCF level and -3.0 kcal/mol with MP2, in good agreement with the experimental value of -3.1 kcal/mol. The experimental result in aqueous solution is 0.3 kcal/mol. ΔH°_{298} for esterification reactions to form phosphates in the gas phase are apparently not known experimentally. In aqueous solutions they are almost invariably positive, generally in the range from 2 to 4 kcal/mol per P—O—C linkage.^{26,27} However, our computed enthalpy differences for the gas phase are all negative, ranging from -1.3 kcal/mol in methyl phosphinate to -3.1 kcal/mol per P—O—C linkage in trimethyl phosphate.

All of these observations lend considerable support to the premise advanced by Wolfenden and Williams²⁸ concerning the free energies of the reactions that form such phosphorus esters in aqueous solution. They point out that there is a long-recognized ambiguity in the thermochemical data concerning the assignment of the observed positive free energies as being inherent in the reacting species as opposed to reflecting their interactions with the solvent water. They found that the interaction with water causes a positive shift in the free energy for the formation of phosphates that is appreciably greater than that for carboxylic acid derivatives. They estimate that for phosphoric acid derivatives this shift should be approximately +7 kcal/mol per P—O—C linkage. Assuming that this approximation holds for the enthalpy as well, this would shift our computed values precisely into the experimentally observed range.

Dipole Moments. Finally, we note that our computed forms of trimethyl phosphate are consistent with the limited experimental data on this compound in that we obtain two conformations of comparable energy.²⁰ As shown in Table VIII, we have computed dipole moments for the lower and higher energy forms of 4.14 and 0.15 D, respectively. Assuming that our computed dipole moments are correct, use of the Boltzmann equation shows conformation 2 to be higher in energy than conformation 1 by 0.68 kcal/mol. Conversely our computed energy difference would similarly predict a total dipole moment averaged over the two forms of 3.52 D—a number to be compared with experimental values (in nonpolar solvents at room temperature) typically around 3.19 D.²⁹ As can be seen from Table III, this agreement is in accord with the level of accuracy to be expected with an ab initio calculation at the level of approximation employed.

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Office of Scientific Research under Grant AFOSR-82-0100. The computations were carried out on the conjoined set of DEC-10 central processors at the Vanderbilt 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.

Registry No. $\text{H}_2\text{PO}(\text{OCH}_3)$, 14684-31-2; $\text{HP}=\text{O}(\text{OCH}_3)_2$, 868-85-9; $\text{P}=\text{O}(\text{OCH}_3)_3$, 512-56-1; $\text{HP}=\text{O}(\text{OH})_2$, 13598-36-2; phosphoric acid, 7664-38-2.

Why Are Organic Acids Stronger Acids than Organic Alcohols?

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Abstract: Comparison of experimental gas-phase acidities and oxygen core-ionization energies of acetic acid and phenol with those of aliphatic alcohols provides insight into the reasons for the acidity of acetic acid and phenol. Contrary to the generally accepted view, resonance delocalization of negative charge in the anion plays only a minor role in determining the relative acidity of these compounds. The higher acidity of the acids arises principally because the electrostatic potential at the acidic hydrogen is more positive in the neutral acid molecule than in a similar alcohol. Quantum mechanical calculations of the initial-state potential and final-state relaxation in phenol, acetic acid, cyclohexanol, and 2-propanol support this view.

As is well known, carboxylic acids and aromatic alcohols are more acidic than aliphatic alcohols. The usual explanation¹ for this difference is that resonance stabilization is greater for acidic anions than for the un-ionized acids. This leads to a lower energy of ionization for the acids than for aliphatic alcohols, where no resonance stabilization is possible for either the anion or the neutral molecule. In this description, the important factor is the electronic rearrangement that takes place after proton removal. This is thought to be greater (and hence, more stabilizing) for acidic anions than for anions derived from alcohols.

We present here both experimental and theoretical evidence that the difference in final-state relaxation between the two types of anion is, in fact, small and has only a minor effect on the relative acidities. We find that the major difference between alcohols and acids is in the charge distribution of the neutral molecule, which establishes a potential at the hydroxyl proton that is more positive (and, hence, less attractive) in acids than in alcohols.

Basic Considerations

Many chemical phenomena depend on the ability of a molecule to accept charge at a particular site. Among these are acidity, basicity, ionization energy, hydrogen bonding, and rates of acid- and base-catalyzed reactions. It is useful to divide the energy for such processes into two parts: an initial-state (potential) energy, which is due to the charge distribution in the original molecule, and a final-state (relaxation) energy, which arises from the rearrangement of valence electrons in response to the newly added charge.

At first glance, this division may appear to be artificial, since it is not obvious how one would sort out the contributions of the two effects: initial-state charge distribution and final-state charge rearrangement. However, the energies involved in these two phenomena can be given a clear theoretical definition and can be experimentally measured by the comparison of core-ionization energies with either gas-phase acidities or Auger energies. A simple classical argument, outlined in the following paragraphs, illustrates the underlying physical principles. These ideas have been developed more fully and quantum mechanically elsewhere.²⁻⁶

A quantum mechanical derivation of the relationship between acidity and initial- and final-state properties is given in the Appendix of this paper.

In the classical model, the molecule is treated as a polarizable medium containing an atom of charge qe . To this atom is added one unit of charge (positive or negative), giving a new localized charge of $(q \pm 1)e$. Before the charge is changed, the atom is subject to some electric potential, Φ_q , which arises from the distribution of charges in the surrounding medium. We can write

$$\Phi_q = \Phi_0 - \alpha'qe \quad (1)$$

In this expression Φ_0 represents the potential due to the charge distribution that would exist if $q = 0$, and there is, therefore, no polarization of the surroundings. The second term shows the change in potential due to the polarization of the medium by the charge q ; the constant α' is closely related to the polarizability of the surroundings. The minus sign reflects the fact that a positive charge will induce a local negative field and a negative charge will induce a local positive field.

As additional charge edq is introduced at the site of interest there will be a change in energy

$$dE = \Phi_q edq \quad (2)$$

Integrating from q to $q + 1$ gives ΔE_+ , the energy needed to remove an electron.

$$\begin{aligned} \Delta E_+ &= \Phi_0 e - \alpha'qe^2 - \alpha'e^2/2 \\ &= \Phi_q e - \alpha'e^2/2 \\ &= V_q - \alpha/2 \end{aligned} \quad (3)$$

In the last line of eq 3, we have set $\Phi_q e$ equal to V_q and have replaced $\alpha'e^2$ with α . By similar arguments, ΔE_- , the energy to remove a proton, is given by

$$\Delta E_- = -V_q - \alpha/2 \quad (4)$$

(Note that the quantity V_q appearing in eq 3 and 4 has a different value in these two different situations. Since the original molecule is neutral the potential at a bound electron must be positive and that at a bound proton must be negative. Thus ΔE is positive in both cases. We will, however, only be concerned with *changes*

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