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A Density Functional Theory Study of Structure of Phosphonic Acid

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ABSTRACT

The molecular structure of the stable conformation of phosphonic acid in gas phase has been computed by employing complete geometry optimization in Density Functional Theory (DFT) methods. The methods used for calculations are B3LYP, BP86 and B3PW91 that have been studied in two series of basis sets: D95** and 6-31+G(d,p) for hydrogen and oxygen atoms; LANL2DZ for phosphorus. Bond lengths and angles generally agree with the limited prior theoretical and experimental values. Phosphonic acid exhibits a minimum-energy conformation in which the acidic hydrogens are oriented toward the phosphoryl oxygen and the distance from it, nearly 2.7-2.8 Å. The conformation of phosphonic acid may be described on the basis dipole-dipole interactions plus relatively small internal hydrogen bonding and steric effect. In contrast to earlier studies, little conformational evidence of "anomeric" effects is found in this compound.

Keywords: Density Functional They ; Conformation ; Hydrogen bonding ; phosphonic acid

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INTRODUCTION

The oxyacids of phosphorus such as phosphonic acid have long been the subject of theoretical study, due to the role played by the phosphates in biological systems. The most important single property of phosphonic acid is its detailed molecular structure. Yet determining this structure has often proven elusive due to the absence of experimental data on isolated molecule and the computational difficulties encountered in comprehensive theoretical treatments. As an example of the latter, all previously reported computations of this class of compound has employed basis sets in HF level and have not determined the complete minimal-energy structure. Yet it is now generally recognized that polarization functions on phosphorus are essential in determining correct bond lengths and angles involving that element [1], and it is probable that inaccuracies in structural parameters are reflected in accurate energies of various conformations.

If one would judge the efficiency of a method by the number of publications based upon it, Density Functional Theory (DFT) would definitely emerges as "Quantum Chemical Methods" of the last 10 years of the second millennium. An increasing number of scientists are applying approximate DFT to describe those properties of molecular and extended chemical systems.

For these reasons, we considered it essential to reexamine some of these systems using large basis sets with complete geometry optimization at each step. The recent development of analytical-gradient optimization techniques has provided an extremely important tool for investigations of this type [2].

As a first set of compounds for study, we have considered a simple tetracoordinate acid of phosphorus: phosphonic acid (H_3PO_3). This may be considered formally to be derived from the hypothetical phosphine oxide molecule, H_3PO, by replacement of two hydrogens by hydroxyl groups.

This compound has been the subject of some previous theoretical studies. Previously, Emsely et al. [3] computed the energy of phosphonic acid in a 4-31G basis, optimizing the structure of the P-O-H linkage only.

COMPUTATIONAL DETAILS

All DFT calculations were carried out with the Gaussian 98 program [45]. Geometry optimizations in the gas phase for all components and complex were performed at the DFT level with B3LYP, BP86 and B3PW91 functionals and with two series of basis sets:

i. Dunning basis set plus polarized functions (D95**) for hydrogen and oxygen atoms; LANL2DZ phosphorus. The effective core potential of Wadt and Hay is also included for P.

ii. Double-zeta valance basis set plus polarized and diffuse functions (6-31+G(d,p)) for hydrogen and oxygen atoms; LANL2DZ for phosphorus. The effective core potential of Wadt and Hay is also included for P.

This level that makes use of Becke-Style density functional theory [5] with the various correlation functionals (LYP, P86 and PW91) [6].

The double-ζ basis set adds two sizes of s and p functions on heavy atoms and hydrogens, respectively, as well as diffuse functions on both.

Optimization of molecular structures was continued until successive changes in each bond length were less than 0.0001 Å, in each torsional angle less than 0.005° and in each of the other angles less than 0.002°.

THE STRUCTURE OF PHOSPHONIC ACID

We have computed all of the structural parameters of phosphonic acid employing three methods (B3LYP, BP86 and B3PW91) and (H,O):D95**+(P):LANL2DZ and (H,O):6-31+G**+(P):LANL2DZ basis sets . The results are summarized in Table1.

and the equilibrium structure obtained in the BP86/(H,O):D95**+(P): LANL2DZ structural parameters trends are shown in Figures 1, 2 and 3.

Table 1: Computed Structural Parameters[a] of Phosphonic Acid

Method	**B3LYP**		**BP86**		**B3PW91**	
Parameter	**A**[b]	**B**[c]	**A**	**B**	**A**	**B**
P=O	1.519	1.520	1.539	1.544	1.520	1.525
P-H	1.390	1.400	1.410	1.410	1.400	1.400
P-O	1.660	1.670	1.690	1.700	1.660	1.670
O-H	0.970	0.970	0.980	0.980	0.960	0.960
O=P-O	114.9	115.3	115.2	115.6	114.8	115.3
	114.9	115.3	115.2	115.6	114.86	115.36
O-P-O	105.0	105.1	105.5	105.6	105.0	105.1
P-O-H	111.6	112.4	110.0	110.8	111.2	112.0
	111.6	112.4	110.0	110.8	111.2	112.0
O=P-H	121.3	120.5	121.9	121.1	121.3	120.5
O-P-H	99.0	98.9	98.1	98.0	99.1	98.9
	99.0	99.0	98.1	98.0	99.1	98.9
H-O-P=O[d]	22.7	25.4	26.1	28.4	23.0	25.5
	-22.6	-25.3	-26.0	-28.3	-22.2	-25.4

[a] Bond lengths in Å, bond angles in degree.

[b] A: (H,O):D95** + (P):LANL2DZ

[c] B: (H,O):6-31+G(d,p) + (P):LANL2DZ

[d] Dihedral angle of the H-O-P plane with respect to the O-P=O plane.

It is important that the equilibrium structure obtained in the BP86/(H,O):6-31+G**+(P):LANL2DZ, exactly like to this figure. The optimized energies are listed in Table 2 and Figure 4 show these trends.

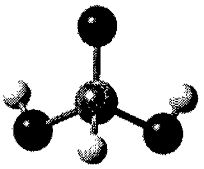

Figure 1. Structure of phosphonic acid computed in the BP86/(H,O):D95** + (P):LANL2DZ.

Both OH groups have a large deviation from O-P=O plane. In the lowest energy conformation, the resulting rotations

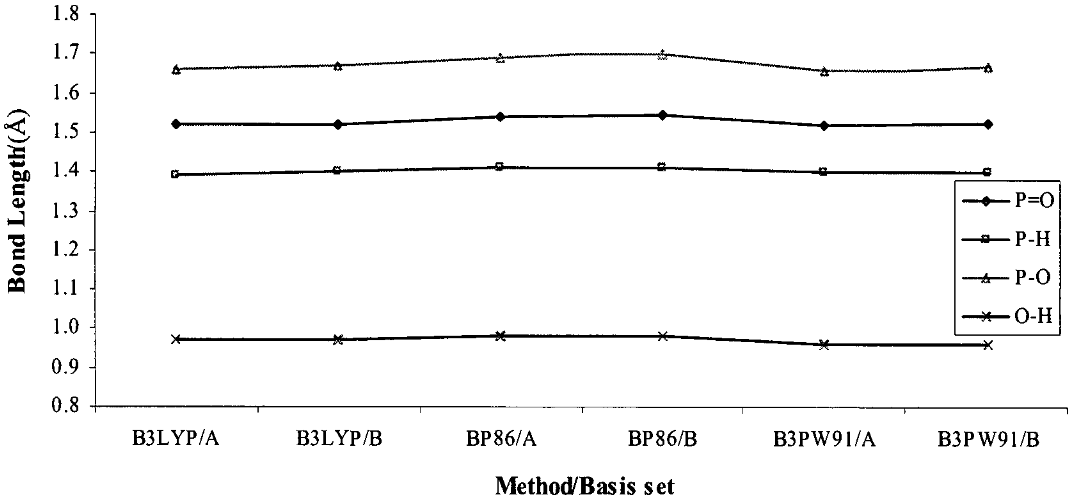

Figure 2. Bond Lengths for Phosphonic Acid for the indicated Method/Basis sets.

The rotation angles are more nearly the same in the variety of basis sets. The energy surface was systematically searched for local minima with the two larger basis sets. No clearly defined high-energy minima could be found.

However, analysis of the energies calculated with the 6-31+G** basis indicated the presence of two relatively flat regions in the energy surface which may contain very shallow minima.

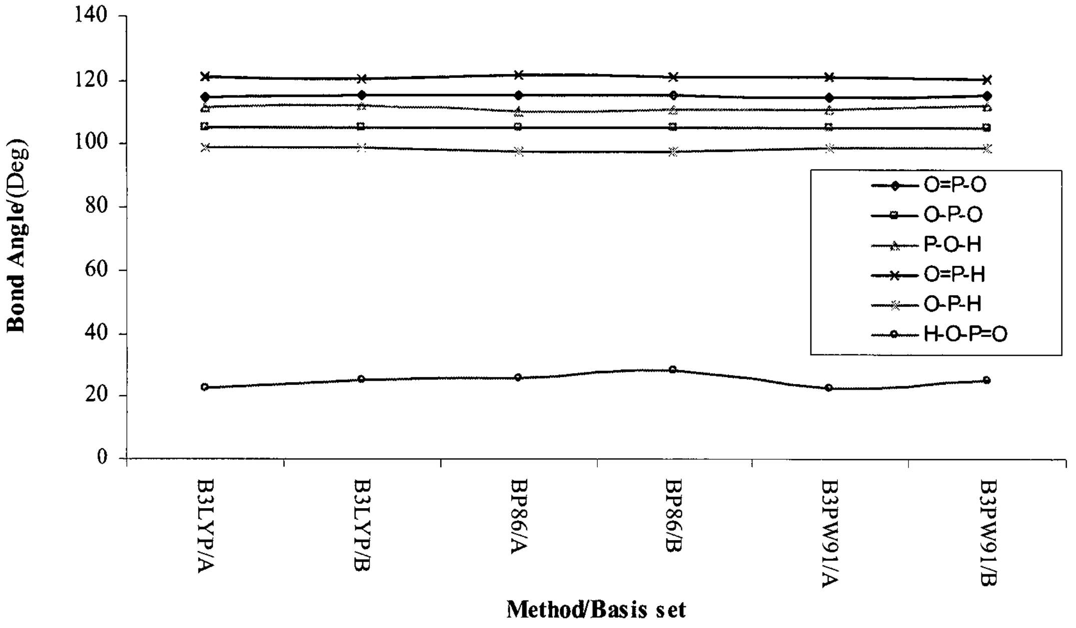

Figure 3. Bond Angles for phosphonic acid for the indicated Method/Basis sets.

Interpretation of the torsional potential function is difficult for this molecule, duo to the presence of more internal degrees of freedom and the lower symmetry of the torsional potential function. Attempts to analyze the potential in terms of Fourier series generally have required many additional terms in the expansion, the physical significance of each term becoming quiet unclear [8]. However, the general features of the conformations are again consistent with stabilization by dipole-dipole interactions.

Table 2 indicates that the D95** basis set for various methods are shown more minimum energy than the other basis set, 6-31+G(d,p), and in this investigation BP86/(H,O):D95**+(P):LANL2DZ shows minimum energy. However, the data of Table 1 show that the structural parameters have been calculated with B3LYP method are in a good accord with experimental data that obtained by X-ray diffraction studies of phosphonic acid crystal.

Table 2: Total Energies of phosphonic acid[a]

Method	Basis Set	Energy
B3LYP	A[b]	-234.01
B3LYP	B[c]	-233.97
BP86	A	-234.04
BP86	B	-234.00
B3PW91	A	-233.94
B3PW91	B	-233.89

a At the optimized molecular structure, in hartrees.
b A: (H,O):D95** + (P):LANL2DZ
c B: (H,O):6-31+G(d,p) + (P):LANL2DZ

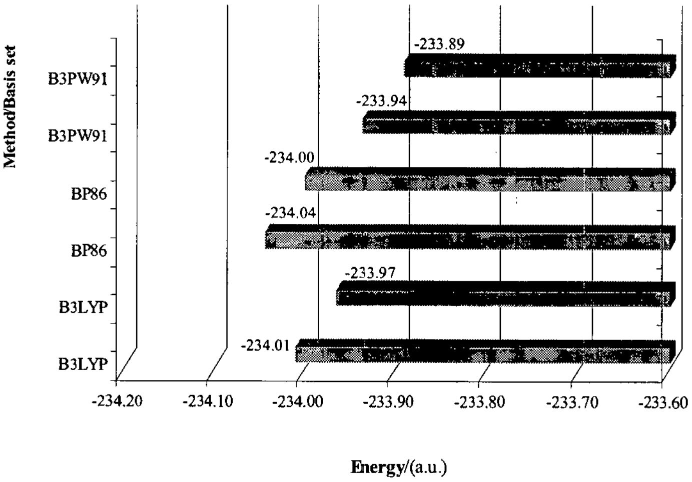

Figure 4. Binding energies for phosphonic acid for the indicated Method/Basis sets.

DISCUSSION

Our computed structure of phosphonic acid may be compared with it's obtained by X-ray diffraction studies of its crystal.

Phosphonic acid crystal has a P=O bond length of only 1.485 Å and P-O bond lengths of 1.544 and 1.552 Å [7], in agreement with the values we obtained.

In attempting to identify the origin of the conformational preferences of this molecule, Lehn and Wipf [9] assumed that since the OH groups are rotated away from the P=O bond, this is evidence of stereoelectronic effects. However, their argument was based on a questionable description of the spatial arrangement of the oxygen lone-pair orbitals [10]. Also, this computed structure displays the same P=O...H distance regardless of the values of other structural parameters. The nonbonded P=O...H distances are listed in Table 3 and Figure 4 shows these distances. It is not reasonable to assume that any property of the P-O or P=O bonds alone would have precisely this effect.

The system that we have studied, employing each of the two series of basis sets, exhibits a preferred equilibrium conformation that may be explained entirely on the grounds of dipole-dipole interaction plus steric repulsion by the phosphoryl oxygen.

This is exactly the direction of change predicted by the anomeric effect resulting from the mixing of oxygen lone pairs into the P=O □* orbital when a hydrogen is adjacent to the P=O bond. However, the changes are considerably smaller than analogous values in carbon acids, which may be a few hundredths of an angstrom. Also it should be noted that most of the other structural parameters show similar trends. This suggests that although stereoelectronic effects are present, they are relatively small and more complicated than has thus far considered by proponents of the anomeric effects.

The data shown in Table 3 are also clearly consistent with the formation of internal P=O...H-O-P hydrogen bonds.

Table 3: Nonbonded P=O...H Distance (Å)

Method	Basis set	Distance
B3LYP	A[a]	2.744
B3LYP	B[b]	2.783
BP86	A	2.777
BP86	B	2.814
B3PW91	A	2.836
B3PW91	B	2.774

[a] A=(H,O):D95**+(P):LANL2DZ
[b] B=(H,O):6-31+G(d,p)+(P):LANL2DZ

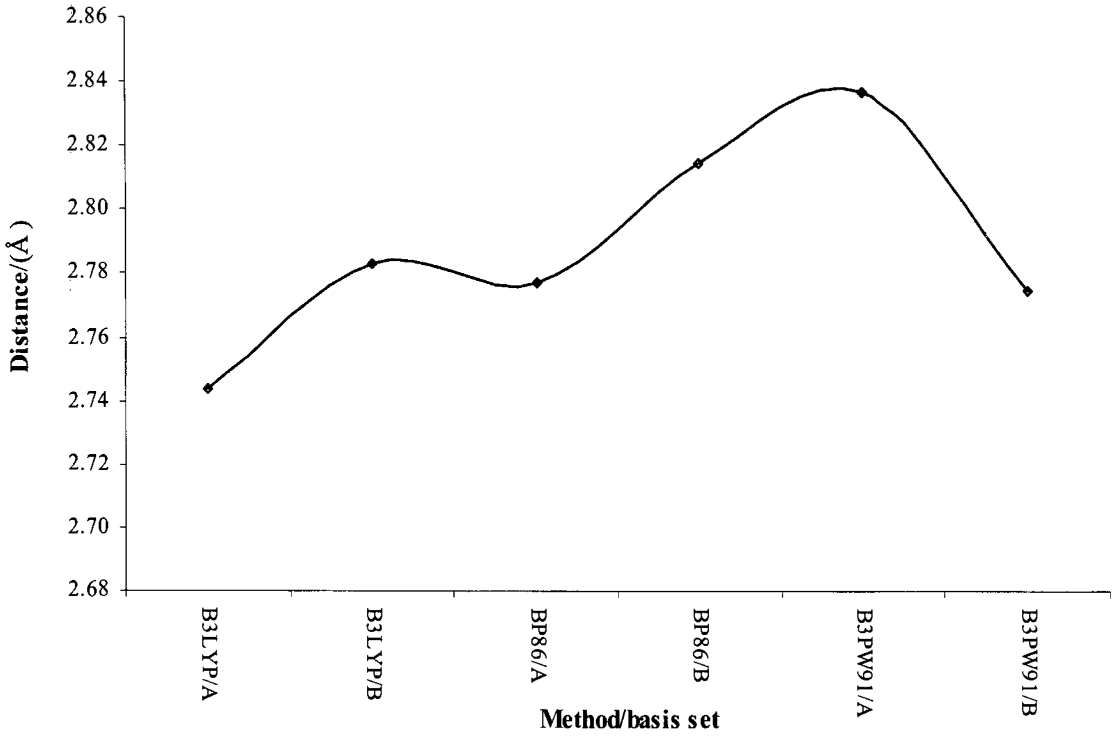

Figure 5. Nonbonded P=O...H Distance (Å) for phosphonic acid for the indicated Method/Basis sets.

These are predominantly electrostatic and very similar in nature to dipole-dipole interactions, so that it is difficult to distinguish between the two effects. The O...H distances shown in Table 3 are comparable to those found experimentally for intermolecular P=O...H-O bonds, which are in the range 2.48-2.84 Å [11]. However, if internal hydrogen bonds were to exist, they would be broken as the torsional dihedral angle goes from 0° to 90° and 180°.

For this system BP86/(H,O):D95**+(P):LANL2DZ has shown more minimum energy than the other Method/Basis set that are used and the structural parameters have been calculated with B3LYP method are in a good accord with experimental data.

In conclusion, we have attributed the bulk of the conformational forces to dipole-dipole interactions. Further computations, particularly on the esters of the title compounds, are required to resolve the relative importance of dipole-

dipole and hydrogen bond interactions with more certainty.

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REFERENCES

1. For example see: (a) Delaere, D.; Nguyen, M. T. *J. Organometallic Chem.* **2002**, *643-644*, 194. (b) Huang, N.; Mackiell, A. D. *J. Phys. Chem. A* **2002**, *106*, 7820. (c) Kleszczynska, H.; Sarapuk, J.; Dziamska A. *Celullar & Molecular Biology Let.* **2000**, *5*, 415. (d) Deemi, R. W.; Fettinger, C. J.; Knight, A. D. *J. Organometallic Chem.* **1997**, *538*, 257.
2. Schäfer, L. *J. Mol. Struct.* **1983**, *100*, 51.
3. Emsely, J.; Lucas, J.; Parker, R. J.; Overill, R. E. *Polyhedron* **1983**, *2*, 19.
4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S. and Pople, J. A.. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1988.
5. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
6. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785.
7. Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 1965.
8. Jeffrey, G. A.; Yates, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 820.
9. Lehn, J. M.; Wipff, G. *J. Chem. Soc. Chem. Commun.* **1975**, 800.
10. Kirby, A. J. "The Anomeric Effect and Related Stereoelectronic Effects at Oxygen"; Springer-Verlag: New York, 1982.
11. Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974.