Basis Set Effects in Density Functional Calculations and BSSE-corrected on the Molybdate-Phosphonic acid Complex

M. H. Ghorbani[2] , M. R. Talei-Bavil-Olyai[2] and H. Aghaie[1*]

1. Department of Chemistry, Science and Research Campus, Islamic Azad University, Poonak, Hesarak, Tehran, Iran,P.O. Box: 14515-775
2. Department of Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran, P. O. Box: 11365-4435.

ABSTRACT

In this research, this possibility was investigated the relative stablilty geometry and binding energies of the hydrogen bonds of Molybdate-Phosphonic Acid (MPA) complex in gas phase on the basis of result of ab initio and DFT calculations. Three DFT methods have been applied 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 Mo and Phosphorus in which the basis set superposition error correction is also considered. At the B3LYP theory level, it is found that the best results for energetics and geometry of the ground state was obtained. The BSSE begins to converge for all of Methods/basis sets. For hydrogen-bonded systems, most levels of theory seem to give reasonable estimates of the known binding energies, but here, the binding energies after correction for BSSE are rather stable.

Keywords: Molybdate-Phosphonic Acid; DFT; BSSE

INTRODUCTION

Among noncovalent interactions [1], hydrogen bonding [2] is of paramount significance. A vast vary supermolecular assemblies owe their well-defined structure to the existence of adjacent hydrogen-bond-donor and –acceptor units at complementary constituent parts [2,3]. The investigation of hydrogen bonding is also important for many practical applications, such as the design of antibiotics [4,5] and the development of new materials with programmed properties, e.g., ordered nanocomposites [5], photoresponsive sensors [5,6].

The ability to understand and predict the stability of hydrogen-bonded systems is of importance for the rational development of these chemical technologies. A number of experimental and theoretical methods have been applied for analysis of the hydrogen-bonded systems [2] to obtain simple reliable models for interpreting their stabilities. Bader's "atoms in molecules" theory that describes any chemical bond by partitioning its electron density [7] has been very seminal in formulating several models allowing the linear [8,9] and nonlinear [10-14] correlations

---

*. Corresponding author: hn_aghaie@yahoo.com

between electron density at the bond critical point and bond distance and thus the bond strength. The groups of Elguero [13,14] and Mó [15-17] as well as other authors [18] have shown the usefulness of the latter models in interpreting the strength of some simple hydrogen-bonded systems such as methanol-water, phosphonic acid, and phosphinoxides and aminoxides. The basis set superposition error (BSSE) begins to converge for all of Methods/basis sets. Model calculations of the counterpoise correction for configurational energy differences show that the size of the BSSE correction is strongly dependent upon molecular structure [19].

In this paper we investigate the hypothesis of rationalizations of stabilities of hydrogen-bonded species and hydrogen-bonded building blocks by means of DFT methods. DFT calculations of hydrogen-bonded at the B3LYP, BP86 and B3PW91 methods with two series of basis sets: D95** and 6-31+G (d,p) for hydrogen and oxygen atoms; LANL2DZ for Mo and Phosphorus have been carried out. The question of the nature of a hydrogen bond is not addressed in the present work. Hydrogen bonding will be discussed in terms of observable properties such as geometry and interaction energy. Earlier ab initio studies of the structures and stabilities of hydrogen-bonded assemblies of nucleic acid basis carried out [20-27] and show that quantum chemical techniques could now be used to perform calculations on molecular systems of practical significance.

THE DENSITY FUNCTIONAL MODEL

In the last few years the Density Functional Theory (DFT) raised as one of the most powerful tools in computational chemistry. Actually, an increasing amount of studies deals with DFT theory, either in the field of pure theoretical developments or in the wide framework of chemical applications. There are several reasons for this success. First of all, methods rooted in DFT take into account a significant amount of the electron correlation, providing accurate numerical results. As a matter of fact, recent implementations of DFT perform at least as well as many body perturbation methods, and sometime even better.

Another major advantage of DFT is its scalability with the size of the system under investigation. The Kohn-Sham (KS) approach, the most common route to DFT, rests on equations which are close to those developed for the Hartree-Fock (HF) theory. It was therefore quite easy to implement this model in several commercial quantum-mechanical codes using already existing facilities. Algorithms like Fast-Multipole Methods (FMM) or fast assembly of the Hamiltonian matrix have been successfully applied to the DFT methods, essentially without any modification. So, the asymptotic linear scaling has been obtained, and sizeable systems (up to several hundreds of atoms) can be handled by this quantum mechanical tool.

The weakness of the DFT approach is represented by the non-classical part of the Hamiltonian, the so-called exchange-correlation contribution. This part is expressed by a functional of the electron density, whose form is a priori unknown. A huge number of forms for exchange and correlation have been proposed, each specific functional providing different numerical performance [2].

METHODS

All DFT calculations were carried out with the Gaussian 03 program [28]. 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:

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

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

This level that makes use of Becke-Style density functional theory [29] with the various correlation functionals (LYP, P86 and PW91) [30]. The double-ζ basis set adds two sizes of orbitals functions on heavy atoms and

hydrogens, respectively, as well as diffuse functions on both.

The standard A and B basis sets were used in all calculations. Literature analysis [25, 27,31] shows that the geometries, relative stabilities, and frequencies of the structures calculated at the B3LYP/6-31+G(d,p) level are in a good accord with experimental data. Pople et al. have shown that the absolute deviations for the bond lengths and angles are smaller than corresponding values obtained at such levels of theory as MP2/6-31G(d) and QCISD/6-31G(d) [32]. The earlier studies of hydrogen binding in nucleic acid bases indicate that the B3LYP method yields reliable interaction energies that correspond to the MP2/6-31G(d,p) level data [21]. Therefore, the B3LYP, BP86 and B3PW91 methods were applied in the all of calculations reported in this paper.

The interaction energies of the counterparts estimated as the energy difference between the complex and the isolated components and were corrected for the basis set superposition error (BSSE). All investigated metal basis sets, being at least TZ for 3d and DZ for 4s are adequate. It is remarkable that for the metal-metal bond, but not for the metal-ligand bond, there is for all pure s, p ligand bases after correction for the BSSE a discernible basis set incompleteness error (ca. 15 kJ/mol), which only disappears after adding at least one polarization function.

The Boys-Bernardi counterpoise method [33], applied at the MPA complex geometry, is used to account for BSSE. According to this method:

$$E_{Corr.} = E_{Interaction} + \Delta E_{BSSE}$$

Where $E_{Corr.}$ is corrected-interaction energies. And:

$$\Delta E_{BSSE} = [E^*_{Molybdate\ Ion} - E_{Molybdate\ Ion}$$
$$(Complex)] + [E^*_{Phosphonic\ Acid} - E_{Phosphonic\ Acid}$$
$$(Complex)]$$

Where E^* indicates that the energy of components at complex geometry calculated of various Methods/Basis sets of complex geometry. DFT optimizations of three methods with A and B basis sets resulted in very close geometries in each series of basis sets and also values of interaction energies as those obtained are closed.

RESULTS

Theoretical results of the calculated hydrogen-bond geometries for structure of MPA complex is given in Table 1 and the equilibrium structure obtained in the B3LYP/(H,O):6-1+G**+(Mo,P):LANL2DZ is shown in Scheme 1.Table 1 indicates the hydrogen-bond parameters in the species calculated by the DFT methods for B3LYP/A & B and B3PW91/A & B are closer than the values obtained by the BP86/A & B and Figures 2 and 3 show these trends. Also, Leszcynski et al. have shown that the better agreement with experimental data and their literature reports cited [34]; the discussion relies mostly on the DFT results.

Table1. Theoretical Data on Hydrogen-Bond Geometries (Å, Deg) in MPA Complex

Method	Basis Set	Bond Length		Angle	Bond Length		Angle
		H11...O2	H11-O8	O2-H11-O8	H12...O10	H12-O4	O4-H12-O10
B3LYP	A[a]	1.779	0.993	175.0	1.554	1.025	178.1
B3LYP	B[b]	1.885	0.986	175.6	1.628	1.014	179.5
BP86	A	1.671	1.017	175.5	1.456	1.066	176.8
BP86	B	1.763	1.008	174.1	1.530	1.045	177. 0
B3PW91	A	1.747	0.994	175.1	1.525	1.030	178. 0
B3PW91	B	1.844	0.987	175.7	1.587	1.019	179.67

[a]A : (H,O):D95**+ (Mo,P):LANL2DZ
[b]B : (H,O):6-31+G**+(Mo,P):LANL2DZ
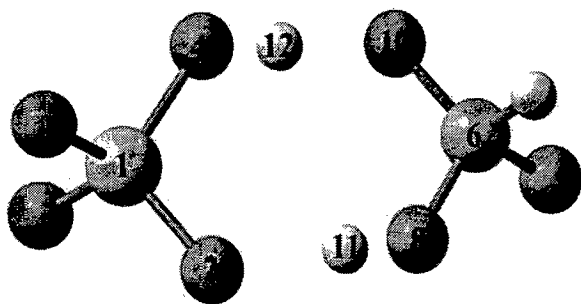
Scheme1. Equilibrium structure of MPA complex in the B3LYP/(H,O):6-31+G**+(Mo,P):LANL2DZ.
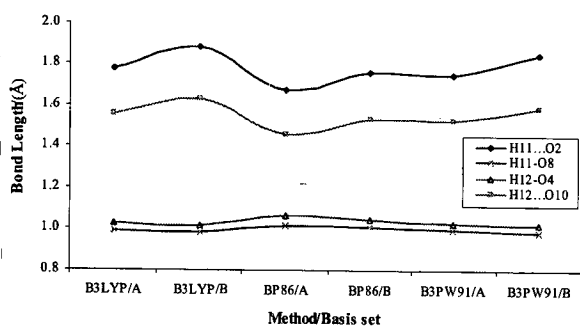

Figure2. Bond Lengths for MPA complex for the indicated basis sets.
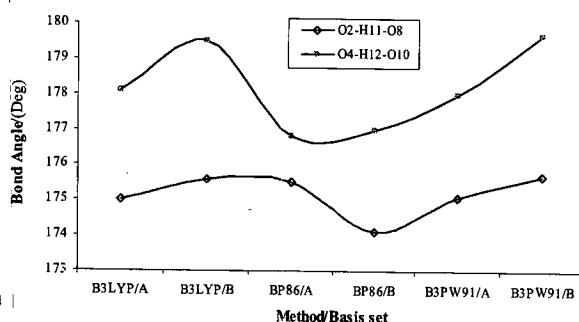

Figure3. Bond Angles for MPA complex for the indicated basis sets.

Interestingly, MPA complex, which according to the calculations are strongly bound species among the hydrogen-bonded systems have also the shortest hydrogen bonds and almost straight hydrogen-bond angles. The shorter hydrogen bonds and the straight hydrogen-bond angles do not necessarily reflect stronger binding. On contrary, with significantly high calculated interaction energies, display two O...H hydrogen bonds and deviation from 180° in the corresponding O-H...O angles.

There are several models evolved on the basis of Bader's theory showing linear or nonlinear relation between a bond length and electron density at the bond critical point. The latter value in turn reflects the strength of the bond. Therefore, the hydrogen-bond lengths can be used to some extent as indexes of the stabilization energy per hydrogen bond. Thus, the geometry analysis of hydrogen bonds in the calculated assemblies gives useful insights into internal cooperative effects regarding the complex stabilities but at the same time provides no general rules for any qualitative or semi-quantitative conclusions concerning the relative stabilities of the complex. On the other hand the hydrogen-bond geometry data could be profitable for the critical evaluation of particular level of theory by the calculated molecular parameters [35]. With these basis sets and theory algorithms, estimates of the basis set superposition error (BSSE) by the counterpoise method [33] are made for the equilibrium configuration. Table 2 reports the calculated interaction energies, EBSSE and ECorr.. The reported interaction energies and EBSSE are with respect to computations at the three methods of density functional theory as mentioned in the Methods section, with A and B basis sets.

According to results that are shown in Table 2, the MPA complex has minimum energy configuration with similar interaction energies, differences between these energies that obtained by methods of DFT level as mentioned ratio to B3LYP/A are -0.223 (BP86/A) and 0.628 (B3PW91/A) kcal/mol and for B3LYP/B these differences are 1.456 (BP86/B) and -0.142 (B3PW91/B) kcal/mol, respectively. Using BSSE method and its effect in interaction energies have seen very different BSSE values especially for BP86 method. Therefore, differences between ECorr. ratio to B3LYP/A are 8.467 (BP86/A) and 1.185 (B3PW91/A) kcal/mol and for B3LYP/B are 5.274 (BP86/B) and 3.106 (B3PW91/B) kcal/mol, respectively. For hydrogen-bonded systems, most levels of theory seem to give reasonable estimates of known binding energies, but here, too, the BSSE overwhelms the

reliability of the binding energies for these methods and basis sets.

Analogues of results that have been shown in Table 1, Table 2 indicates that the interaction energies that calculated by three methods for B3LYP/A & B and B3PW91/A & B are closer than the values obtained by the BP86/A & B, but for the values of EBSSE have not shown this trends. Therefore, calculations of the counterpoise correction are strongly dependent upon molecular structure. Also, in this investigation the configuration calculated of these DFT methods, with B basis set has shown more stability than the A basis set.

Table 2: Calculated Interaction Energies, ΔE_{BSSE} and the Corrected-Interaction Energies of the MPA Complex

Method	Basis Set	Energy (kcal/mol)		
		$E_{Interaction}$	ΔE_{BSSE}	$E_{Corr.}$
B3LYP	A[a]	-77.0	93.6	16.6
B3LYP	B[b]	-72.2	65.8	-6.4
BP86	A	-77.2	102.2	25.0
BP86	B	-70.8	69.6	-1.1
B3PW91	A	-76.4	94.1	17.7
B3PW91	B	-72.4	69.1	-3.3

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

[b]**B :** (H,O):6-31+G**+(Mo,P):LANL2DZ

CONCLUSION

Our investigations clearly confirm that the geometry analysis of the hydrogen bonds can give useful insights into their cooperative effects affecting the complex stabilities. On the basis of the results of these studies we conclude the following:

(1) The ab initio calculations predicted binding energies of hydrogen-bonded interactions at the theory levels explored herein lies with inadequate basis set. According to previous studies, HF-optimized structures show essentially bigger deviations in hydrogen-bond lengths [34]. Second, as shown by Bickelhaupt et al., [35] the molecular environment in the crystal cell may cause significant disagreement between theory and experiment regarding hydrogen-bond lengths.

(2) Systems with more than 3 or 4 heavy atoms are too expensive to treat accurately reasons.

(3) The present study shows that the results obtained by the DFT methods for B3LYP/A & B and B3PW91/A & B are closer than the BP86/A & B.

(4) The optimization geometry have been computed using DFT and ab initio methods, the best results for energetics and geometry for this complex obtained by B3LYP/(H,O):6-31+G**+(Mo,P):LANL2DZ calculations.

(5) The longest hydrogen bonds correspond to O...H bonds present in MPA complex,

while small deviations of hydrogen-bond angles from 180° manifest themselves in complex of MPA.

(6) This study has also shown that the MPA complex has minimum energy configuration with similar binding energies, but very different BSSE values.

(7) In summary, we have described the results of DFT calculations on the intramolecular interaction involving hydrogen-bonded systems when BSSE is accounted for, the binding energies of hydrogen-bonded systems are remarkably insensitive to basis set and its effect for stability of MPA complex is very important and indicates that the BSSE overwhelms the reliability of the binding energies for these basis sets.

(8) We note that, after correcting for BSSE, the bonding energies computed in a small basis are reasonably close to the converged values.

REFERENCES

1. Müller-Dethlefs, K.; Hobza, P. Chem. Rev. 2000, 100, 143.
2. (a) Jeffrey, G. A. An Introduction to Hydrogen Bonding; Oxford University Press: New York, 1997. (b) Scheiner, S. Hydrogen Bonding: A Theoretical Perspective; Oxford University Press: New York, 1997. (c) Desiraju, G. R.; Steiner, T. To Weak Hydrogen Bond; Oxford University Press: Oxford, 1999.
3. A recent review on multiply hydrogen-bonded synthetic systems: Sherrington, D. C.; Taskinen, K. A. Chem. Soc. Rev. 2001, 30, 83.
4. Bohler, C.; Nielsen, P. E.; Orgel, L. E. Nature 1995, 376, 578.
5. Bong, D. T.; Clark, T. D.; Gronja, J. R.; Ghadiri, M. R. Angew. Chem., Int. Ed. 2001, 40, 988.
6. (a) Sessler, J. L.; Wang, B.; Springs, S. L.; Brown, C. T. In Comprehensive Supermolecular Chemistry; Murakami, Y.; Ed.; Pergamon: New York 1996; Vol 4; pp 311-366. (b) Sessler, J. L.; Sathiosatham, M.; Brown, C. T.; Rhodes, T. A.; Wiederrecht, G. J. J. Am. Chem. Soc. In Press.
7. Boyd, R. J.; Choi, S. C. Chem. Phys. Lett. 1985, 120, 80.
8. Boyd, R. J.; Choi, S. C. Chem. Phys. Lett. 1986, 129, 62.
9. Knop, O.; Boyd, R. J.; Choi, S. C. J. Am. Chem. Soc. 1988, 110, 7299.
10. Roversi, P.; Barzaghi, M.; Merati, F.; Destro, R. Can. J. Chem. 1996, 74, 1145.
11. Alkorta, I.; Rozas, I.; Elguero, J. Struct. Chem. 1998, 9, 243.
12. Alkorta, I.; Elguero, J. J. Phys. Chem. A 1999, 103, 272.
13. Alkorta, I.; Barrios, L.; Rozas, I.; Elguero, J. J. Mol. Struct. (THEOCHEM) 2000, 496, 131.
14. González, L.; Mó, O.; Yáñez, M.; Elguero, J. J. Chem. Phys. 1998, 109, 2685.
15. González, L.; Mó, O.; Yáñez, M. J. Chem. Phys. 1998, 109, 139.
16. González, L.; Mó, O.; Yáñez, M. J. Org. Chem. 1999, 64, 2314.
17. Popelier, P. L. A. J. Phys. Chem. A 1998, 102, 1873.
18. (a) Jorgensen, W. L.; Pranata, J. J. Am. Chem. Soc. 1990, 112, 2008. (b) Pranata, J.; Wierschke, S. G.; Jorgensen, W. L. J. Am. Chem. Soc. 1991, 113, 2810. (c) Jorgensen, W. L.; Severance, D. L. J. Am. Chem. Soc. 1991, 113, 209.
19. Rappé, A. K.; Bernstein, E. R. J. Phys. Chem. A 2000, 104, 6117.
20. Florián, J.; Leszcynski, J. J. Am. Chem. Soc. 1996, 118, 3010.
21. Šponer, J.; Leszcynski, J.; Hobza, P. J. Phys. Chem. 1996, 100, 1965.
22. Šponer, J.; Leszcynski, J.; Hobza, P. J. Phys. Chem. A 1997, 101, 9489.
23. Zhanpeisov, N.; Šponer, J.; Leszcynski, J. J. Phys. Chem. A 1998, 102, 10373.
24. Padolyan, Y.; Rubin, Y.; Leszcynski, J. J. Phys. Chem. A 2000, 104, 9964.
25. Gu, J.; Leszcynski, J. J. Phys. Chem. A 2000, 104, 7353.
26. Gu, J.; Leszcynski, J. J. Phys. Chem. A 2000, 104, 1898.
27. Gu, J.; Leszcynski, J. J. Phys. Chem. A 2000, 104, 6308.
28. Gaussian 03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T.

Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

29. Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
30. Lee, C.; Yang, W.; Parr, R.G. Phys. Rev. B 1988, 37, 785.
31. Mebel, A. M.; Morokuma, K., Lin, C. M. J. Chem. Phys. 1995, 103, 7414.
32. Johnson, B. G.; Gill, P. M. W.; Pople, J. A. J. Chem. Phys. 1995, 98, 5612.
33. Boys, S. F.; Bernardi, F. Mol. Phys. 1970, 19, 533.
34. Oleg, L.; Leszcynski, J. J. Phys. Chem. A 2002, 106, 6775.
35. Guerra, C. F.; Bickelhaupt, F. M.; Snijders, J. G.; Baerends, E. J. J. Am. Chem. Soc. 2000, 122, 4117.