Density Functional and Multireference Perturbation Theory Calculations of Bis-nitronyl Nitroxide Biradical

Ohyun Kwon[*] and Gyusung Chung[†,*]

Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Korea. [*]E-mail: tigertom@dreamwiz.com
[†]Department of Chemistry, Konyang University, Chungnam 320-711, Korea. [*]E-mail: gschung@konyang.ac.kr

The electronic structure of bis-nitronyl nitroxide biradical has been investigated by using density functional theory (DFT) and *ab initio* multireference (MCSCF and MCQDPT2) methods. The broken-symmetry DFT approach has been applied to the open-shell singlet biradical at the BLYP, B3LYP, and BHandHLYP levels. DFT and MCSCF calculations show that the singlet biradical state is slightly more stable than the triplet state, which is refined at the MCQDPT2 level. The dependence of the singlet-triplet energy gap on the conformational change between two monoradicals is discussed. The results indicate that the choice of the theoretical model plays an important role in understanding the electronic nature of the organic biradicals.

Key Words : Organic biradical, Density functional theory, MCSCF, MCQDPT2

Introduction

Molecular organic magnets have attracted considerable interest for the past few decades due to the advantages of easy fabrication, mechanical flexibility, and low cost, possibly leading to active elements in organic devices.[1-4] The magnetic properties of organic materials highly depend on the intramolecular magnetic exchange coupling constants and the intermolecular interaction governed by the structural phase of a molecular crystal.[1,4] Among them, some nitroxide biradical species have been intensively investigated since they generally show the exceptional stability, easy preparation method, flexibility in coordination, and ability to produce and control cooperative magnetic properties.[5-7]

These biradicals can exist either in an open-shell singlet state or in a triplet state, and their electronic structures play a key role in determining molecular geometries and energetics. A previous experimental study of bis-nitronyl nitroxide concluded that the open-shell singlet state with twisted conformation (dihedral angle of two nitroxide units = 55º) is 0.89 kcal/mol lower in energy than the triplet state.[8] Castell et al. reported *ab initio* calculations of bis-nitronyl nitroxide where methyl groups were substituted by hydrogen atoms, showing that the open-shell singlet state is 1.04 kcal/mol lower in energy than the triplet state.[9] Recently, theoretical calculations by Ali *et al.* showed that the dihedral angle between two nitroxide units was calculated to be 78º, and the singlet-triplet (S-T) energy gap was 0.188 kcal/mol at the UB3LYP/6-311+G(d,p)//ROHF/6-31G(d,p) level.[10] The S-T energy gap was also calculated to be 0.818 kcal/mol at the optimized geometry with the fixed dihedral angle of 55º in order to compare with the crystal structure conformation.[10] Nevertheless, more accurate calculations are still necessary to examine their electronic structures and conformational behavior in a systematic way. In general, the computations of reliable geometries and physiochemical properties of open-shell electronic structures require higher levels of theory with a significant amount of electron correlation. Since the S-T energy gap is directly related to the spin-spin interaction in the two nitroxide units, accurate calculations of energetics for open-shell singlet and triplet states should be critical to understand the magnetism of the bis-nitronyl nitroxide species.

It is the aim of present study to investigate the structural features, electronic structures, and S-T gaps of bis-nitronyl nitroxide biradical by using high level *ab initio* multireference methods as well as density functional theory (DFT)[11,12] with various basis sets. The effects of basis set size and the levels of theory on the nature of biradical electronic structures have been thoroughly considered.

Computational Details

The Gaussian 98 program[13] was used for DFT calculations, and all multireference calculations were done using the GAMESS program.[14] For computational simplicity, the methyl groups in bis-nitronyl nitroxide biradical were replaced by hydrogen atoms. DFT calculations were performed at the level of BLYP, B3LYP, and BHandHLYP functionals,[15] where the Hartree-Fock (HF) exchange is varied from 0% (BLYP), 20% (B3LYP), and 50% (BHandHLYP) to probe the role by the HF exchange and draw conclusions of general applicability. It has been known that molecular geometries, energetics, and spectroscopic properties are highly dependent on the inclusion of some HF exchange in gradient-corrected functionals.[16-19] Using the DFT functionals mentioned above, molecular geometries of the biradical singlet and triplet states of bis-nitronyl nitroxide were optimized within the constraint of C_2 symmetry using Pople-type basis sets from 6-31G(d) up to 6-311+G(3df). All geometries were analyzed by computing vibrational frequencies and characterized as minima with no imaginary frequencies for open-shell singlet and triplet species.

Open-shell singlet biradicals can have a multideterminant

(multireference) character, indicating that single determinant methods such as HF theory or correlated methods based on a HF single determinant wavefunction can not describe appropriately these molecules. Since both nondynamic and dynamic electron correlations are not easy to apply for larger systems by using high level multireference methods with a large active space, DFT methods may be a good alternative. A general approach is to optimize open-shell singlet geometries with unrestricted DFT method (UDFT) where α and β spins are allowed to be mixed in order to destroy spatial and spin symmetries. UDFT solutions for singlet biradical structures (broken-symmetry open-shell solution) can be found with the aid of "guess=mix" option in Gaussian 98 where the spin-squared value ($<S^2>$) may approach 1.0 for a strong singlet biradical rather than the correct value of 0.0. It has been known that while geometries from DFT methods closely match experiment and those from more sophisticated levels,[19-22] relative energies are somewhat sensitive to the proportion of HF exchange in density functionals.[18,19] In addition, some previous studies[23,24] indicate that DFT methods still suffer from difficulties in obtaining accurate open-shell singlet energies.

The mutireference wavefunction calculations were applied to optimize the geometries of the lowest open-shell singlet and triplet states by using fully optimized reaction space (FORS) multi-configurational self-consistent field (MCSCF) level with 6-31+G(d) basis set. The active space in our MCSCF calculations can be denoted as (10,10) which includes all ten p orbitals and their electrons in this system. The MCSCF method can provide a reliable evaluation of spin exchange effects, but completely neglects dynamic electron correlation. Therefore, based on the MCSCF geometries, the multi-configurational quasi-degenerate second-order perturbation theory (MCQDPT2) single-point energy calculations using a (10,10) active space with 6-31+G(d) basis set were carried out to consider the dynamic correlation effects.

Results and Discussion

The molecular structure of bis-nitronyl nitroxide (denoted as **BNN**) is shown in Figure 1. In **BNN**, two monoradicals are directly connected without any coupler, which results in either triplet or open-shell singlet state. Table 1 collects calculated relative energies and dihedral angles between two NCN planes ($N_1C_5N_2$ and $N_3C_6N_4$) of open-shell singlet and triplet states of **BNN** at the various levels of theory. All levels of theory show that the open-shell singlet state is computed to be slightly more stable than the triplet state. It is likely that the ground state spin is significantly governed by the conformation of the molecule, particularly the amount of twist between two five-membered rings.[25,26] Nachtigall and Jordan performed CI and MCSCF calculations of the S-T energy gap dependence on the torsional angle of tetramethyleneethane (TME) which is similar to BNN, and the calculated S-T gap was quite small and very sensitive to the molecular symmetry and levels of theory.[27] Thus, it will be
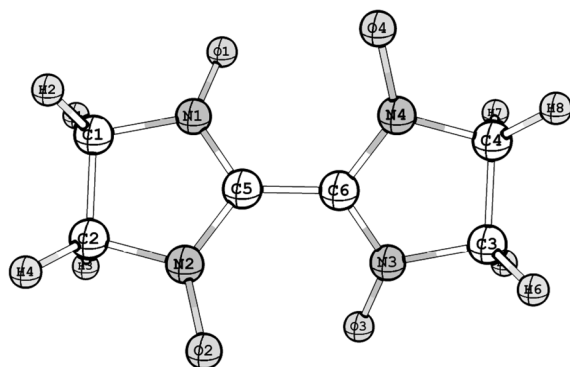

Figure 1. Molecular structure of bis-nitronyl nitroxide with atomic numbering.

important to discuss the dihedral angle between two NCN planes in **BNN**.

At the DFT levels with 6-311+G(3df) basis set, the dihedral angle of open-shell singlet species is calculated to be 64.8° (BLYP), 61.5° (B3LYP), and 53.9° (BHandHLYP), whereas that of triplet species is 90° at the same levels of theory. The results indicate that adding diffuse functions increases the dihedral angle of open-shell singlet species considerably. The dihedral angle also increases with changing from double- to triplet-zeta basis set. It is likely that BLYP level is more sensitive to the size of the basis set compared to B3LYP and BHandHLYP. The optimized dihedral angle increases as the amount of HF exchange in DFT functionals decreases. At the MCSCF level, the dihedral angles of open-shell singlet and triplet species are calculated to be 77.9° and 90.0°, respectively. Since the triplet species is dominated by a single electronic configuration, there is a good agreement of the calculated dihedral angle between DFT and MCSCF results. However, the calculated dihedral angles for open-shell singlet state show some discrepancy between DFT and MCSCF. It might be because the MCSCF wavefunction is free from spin-contamination and it can control spin-polarization effectively. On the other hand, DFT geometries of open-shell singlet state by using the broken-symmetry approach are optimized for the 50:50 mixed singlet/triplet state, which may still suffer from spin-contamination. The optimized dihedral angle of the open-shell singlet at the BLYP/6-311+G(3df) level is the closest to that of MCSCF, and the $<S^2>$ value of BLYP is 1.027, which is compared to that of B3LYP ($<S^2>$ = 1.122) and BHandHLYP ($<S^2>$ = 1.371) levels. It is noted that there is a regular increase of $<S^2>$ value as the percentage of HF exchange is increased from 0 to 50%, which means that the pure functionals tends to show less spin symmetry breaking. In the crystal structure of **BNN**, the dihedral angle is measured to be 55°.[8] The difference of dihedral angle between experiment and theory may be due to the interaction of nitroxide units of neighboring **BNN** molecules giving rise to a crystal packing effect, which favors a smaller dihedral angle in the solid state. This is confirmed by the experimental measurement of the singlet-triplet separation, where the energy difference between open-shell singlet and triplet states (S-T

Table 1. Calculated Relative Energies (kcal/mol) of Singlet and Triplet States of **BNN** at the Various Theoretical Levels

Theoretical Level	Basis Set	Open-Shell Singlet State			Triplet State		
		Rel. Energy	$<S^2>^a$	φ^b	Rel. Energy	$<S^2>^a$	φ^b
BLYP	6-31G(d)	0.0	1.025	51.3	0.9	2.026	56.9
	6-31+G(d)	0.0	1.027	74.0	0.1	2.025	90.0
	6-311G(d)	0.0	1.026	56.9	0.001	2.026	90.0
	6-311+G(d)	0.0	1.027	70.4	0.2	2.025	90.0
	6-311+G(2d)	0.0	1.027	71.4	0.1	2.024	90.0
	6-311+G(df)	0.0	1.028	68.5	0.2	2.025	90.0
	6-311+G(2df)	0.0	1.027	66.7	0.2	2.025	90.0
	6-311+G(3df)	0.0	1.027	64.8	0.2	2.025	90.0
B3LYP	6-31G(d)	0.0	1.149	50.1	1.3	2.105	65.4
	6-31+G(d)	0.0	1.123	63.9	0.4	2.103	90.0
	6-311G(d)	0.0	1.139	54.9	0.9	2.105	74.8
	6-311+G(d)	0.0	1.125	63.3	0.001	2.104	90.0
	6-311+G(2d)	0.0	1.120	63.3	0.001	2.101	90.0
	6-311+G(df)	0.0	1.125	62.8	0.4	2.103	90.0
	6-311+G(2df)	0.0	1.122	62.2	0.5	2.101	90.0
	6-311+G(3df)	0.0	1.122	61.5	0.5	2.101	90.0
BHandHLYP	6-31G(d)	0.0	1.432	45.2	2.7	2.329	90.0
	6-31+G(d)	0.0	1.385	53.8	1.3	2.310	90.0
	6-311G(d)	0.0	1.420	48.0	0.004	2.323	90.0
	6-311+G(d)	0.0	1.391	53.6	1.4	2.313	90.0
	6-311+G(2d)	0.0	1.369	54.6	1.3	2.299	90.0
	6-311+G(df)	0.0	1.388	53.2	1.5	2.309	90.0
	6-311+G(2df)	0.0	1.372	53.8	1.4	2.299	90.0
	6-311+G(3df)	0.0	1.371	53.9	1.5	2.298	90.0
MCSCF (10,10)	6-31+G(d)	0.0		77.9	0.2		90.0
MCQDPT2 (10,10)^c	6-31+G(d)	0.0			0.4		

^{a}Spin-squared value at each DFT level before spin projection. ^{b}Calculated dihedral angle between two imidazole rings. The experimental value is 55 degree in the solid state [8]. ^{c}MCQDPT2 (10,10)/6-31+G(d)//MCSCF (10,10)/6-31+G(d) level.

energy gap) was estimated to be 311 and 292 cm^{-1} in the solid state and solution phase, respectively.[8] It means that the S-T energy gap of the solid state is larger than that of the solution. Calculations of S-T energy gaps with respect to the
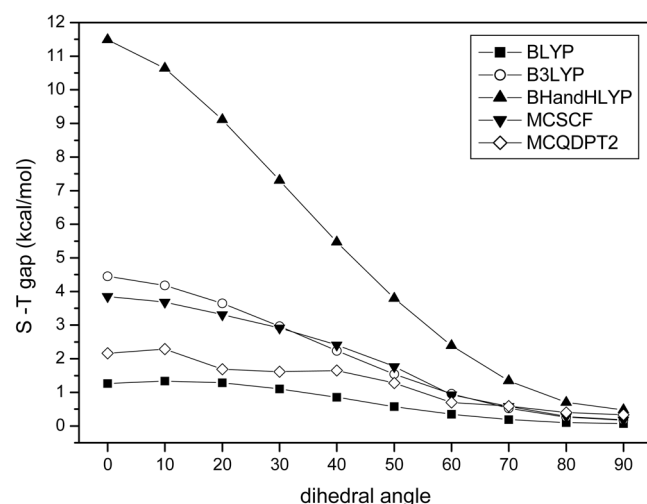
Figure 2. Calculated S-T energy gaps (kcal/mol) as a function of the dihedral angle between two NCN planes at the various theoretical levels.

dihedral angle between two NCN planes (See Figure 2) indicate that the S-T energy gap becomes smaller as the dihedral angle increases from 0° to 90°, which is in good agreement with the previous experimental data.[8]

Table 2 lists calculated geometrical parameters at the three DFT/6-311+G(3df) levels and the MCSCF/6-31+G(d) level. In general, the calculated bond distances and angles are in good agreement with the available solid state data.[8] The optimized bond distances deviate slightly from the experiment which may be due to the disorder of the NO groups in the solid state. The calculated bond distances at BLYP and B3LYP levels are very close to the experimental ones. The bond distances of the open-shell singlet state are very similar to those of the triplet state at all the theoretical levels. All the calculated angles are also in good agreement with the experimental ones except for $O_1N_1C_5$ bond angle which is again due to the known fact of the disorder of the oxygen atoms of **BNN** in the solid state.

As can be seen in Table 1, the relative energy differences between two minima corresponding to open-shell singlet and triplet states are sensitive to the choice of DFT functionals as well as the size of basis set. DFT calculations clearly show that considering diffuse functions is quite important to estimate the energy difference between open-

Table 2. Calculated Bond Distances (Å) and Angles (degree) of **BNN** Along with Available Experimental Data

	BLYP[a]		B3LYP[a]		BHandHLYP[a]		MCSCF[b]		Exptl.[c]
	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet	
$r(C_1C_2)$	1.542	1.543	1.533	1.534	1.525	1.527	1.537	1.537	
$r(C_1N_1)$	1.506	1.506	1.485	1.485	1.467	1.467	1.467	1.467	1.507(2)
$r(N_1C_5)$	1.363	1.360	1.350	1.346	1.342	1.335	1.341	1.340	1.343(2)
$r(N_1O_1)$	1.275	1.275	1.259	1.259	1.243	1.244	1.242	1.243	1.275(2)
$r(C_5C_6)$	1.448	1.455	1.440	1.449	1.427	1.444	1.451	1.453	1.444(4)
$\angle C_1N_1O_1$	122.2	122.1	122.2	122.2	122.3	122.3	122.1	122.1	123.0(2)
$\angle O_1N_1C_5$	127.5	127.6	127.3	127.4	127.0	127.0	126.8	126.8	97.4(1)
$\angle N_1C_5C_6$	124.1	124.0	124.2	124.0	124.5	124.1	124.5	124.4	125.3(2)
$\angle N_1C_5C_6N_4$	64.8	90.0	61.5	83.7	53.9	90.0	77.9	90.0	55.0

[a]6-311+G(3df) basis set at each DFT level. [b]6-31+G(d) basis set at MCSCF level. [c]From solid structural parameters [8].

Table 3. Calculated Singlet-Triplet Energy Gaps (kcal/mol) of Conformers of **BNN** (Dihedral Angle = 0, 50, 60, 70°) at the Various Theoretical Levels

dihedral angle	BLYP /6-311+G(3df)	B3LYP /6-311+G(3df)	BHandHLYP /6-311+G(3df)	MCSCF(10,10) /6-31+G(d)	MCQDPT2(10,10) /6-31+G(d)[a]
0°	1.261	4.453	11.485	3.852	2.163
50°	0.578	1.544	3.794	1.769	1.275
60°	0.347	0.956	2.386	0.929	0.703
70°	0.186	0.524	1.341	0.579	0.587

[a]MCQDPT2 (10,10)/6-31+G*//MCSCF (10,10)/6-31+G* level.

shell singlet and triplet species. The triple-zeta basis sets with diffuse functions and f-type polarization functions have a large impact on this energy difference since spin-polarization and delocalization play an important role in the electronic structures of open-shell species. These energy differences increase when a larger proportion of HF exchange in DFT functionals is included. For instance, this energy difference is calculated to be 1.5, 0.5, and 0.2 kcal/mol at the BHandHLYP (50% HF exchange), B3LYP (20%), and BLYP (0%) levels with 6-311+G(3df) basis set, respectively. It appears that the spin-contamination grows larger with the introduction of HF exchange in both the open-shell singlet and triplet species as shown in Table 1. Since the considerable spin-contamination of the open-shell wavefunction results in an overestimation of the spin-polarization, the BHandHLYP results show the largest energy difference among the DFT functionals considered here. Cramer and co-workers have previously reported that pure density functionals are much more accurate for modeling singlet biradicals than hybrid functionals.[19]

The MCSCF energy difference is computed to be 0.2 kcal/mol, which is refined as 0.4 kcal/mol when the dynamical correlation effect is considered at the MCQDPT2 level. It should be noted that the energy difference between open-shell singlet and triplet states of multireference methods cannot be directly compared with that of DFT methods since the calculated dihedral angles of two methods are different from each other (See Table 1). However, the energy difference dependence on the dihedral angle at the multireference and DFT methods will be discussed in the next paragraph.

Figure 2 shows the changes of the S-T energy gap with respect to the dihedral angle between two NCN planes in **BNN**. The S-T energy gaps at several points of dihedral angle are also listed in Table 3. It is clear that the open-shell singlet state is slightly more stable than the triplet state at all the levels of theory. The magnitude of S-T energy gap significantly decreases as the dihedral angle increases. This is because the planar conformation (dihedral angle = 0°) leads to the maximum π-overlap between two nitroxide units, while the perpendicular conformation (dihedral angle = 90°) results in the minimum conjugation between two π-systems. The unpaired electron in each nitroxide unit becomes strongly localized at the perpendicular conformation, leading to a strong spin-polarization.

As mentioned above, previous study reported that the pure functional approach promises us much better energy result for singlet biradicals than the hybrid functionals.[19] The present DFT calculations is well consistent with the previous study. At the planar conformation (dihedral angle = 0°), the S-T energy gap is calculated to be the largest (11.5 kcal/mol) at the BHandHLYP level, and the smallest value (1.3 kcal/mol) at the BLYP level. This energy gap is predicted to be 3.9 kcal/mol at the MCSCF level. The inclusion of the dynamical correlation at the MCQDPT2 level reduces this value into 2.2 kcal/mol. From the comparison of S-T energy gaps, BLYP level shows the best performance compared to MCQDPT2 level.

Conclusion

The electronic structures of open-shell singlet and triplet states for bis-nitronyl nitroxide biradical have been investi-

gated by using multireference (MCSCF, MCQDPT2) methods and DFT methods with the variable proportion of HF exchange ranging from 0% to 50%. The dihedral angle between two NCN planes of the open-shell singlet state is very sensitive to the choice of level of theory as well as the size of basis set. DFT methods show that the dihedral angle is calculated to be smaller as the mixing of HF exchange becomes larger: BLYP (65°, 0% HF exchange), B3LYP (62°, 20%), BHandHLYP (54°, 50%) with 6-311+G(3df) basis set, whereas the MCSCF geometry shows 78° of the dihedral angle. At the same time, both DFT and MCSCF geometries for the triplet state show 90° of the dihedral angle. Both DFT and multireference methods confirm that the open-shell singlet state is slightly more stable than the triplet state. It is noted that the mixing ratio of HF exchange in the DFT functionals significantly affects the S-T energy gap in the nitroxide biradicals: S-T energy gap increases when a larger portion of HF exchange is introduced. Among the studied DFT methods, the S-T energy gap of the BLYP level is the closest to that of the MCQDPT2 level. The overall results indicate that the choice of the theoretical model plays an important role in understanding the electronic nature of organic biradical systems.

References

1. Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
2. Goodenough, J. B. *Magnetism and the Chemical Bond*; Interscience: New York, 1963.
3. Coronado, E.; Delhaè, P.; Gatteschi, D.; Miller, J. S. *Molecular Magnetism: From Molecular Assemblies to the Devices*, NATO ASI Series E, Applied Sciences; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1996; Vol. 321.
4. Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.
5. Ullman, E. F.; Boocock, D. G. B. *J. Chem. Soc., Chem. Commun.* **1969**, *20*, 1161.
6. Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.
7. Ali, M. E.; Vyas, S.; Datta, S. N. *J. Phys. Chem. A* **2005**, *109*, 6272.
8. Alies, F.; Luneau, D.; Laugier, J.; Rey, P. *J. Phys. Chem.* **1993**, *97*, 2922.
9. Castell, O.; Caballol, R.; Subra, R.; Grand, A. *J. Phys. Chem.* **1995**, *99*, 154.
10. Ali, M. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 2776.
11. Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley & Sons: New York, 2000.
12. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., 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.; Baboul, A. G.; 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.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
14. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, K.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
15. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
16. Dierksen, M.; Grimme, S. *J. Phys. Chem. A* **2004**, *108*, 10225.
17. Zhang, Y.; Lin, W.; Li, Y.; Ding, K.; Li, J. *J. Phys. Chem. B* **2005**, *109*, 19270.
18. Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48.
19. Lewin, J. L.; Heppner, D. E.; Cramer, C. J. *J. Biol. Inorg. Chem.* **2007**, *12*, 1221.
20. Kwon, O.; Almond, P. M.; McKee, M. L. *J. Phys. Chem. A* **2002**, *106*, 6864 and references therein.
21. Kang, D. B. *Bull. Korean Chem. Soc.* **2008**, *29*, 963.
22. Chung, G.; Lee, D. *Bull. Korean Chem. Soc.* **2006**, *27*, 2051.
23. Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664.
24. Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 329.
25. Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273.
26. Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.
27. Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 270.