4. Other Research

Ionization Potentials for Polychlorinated Dibenzo-p-Dioxins: Ab initio Molecular Orbital and Density Functional Theory Studies

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Background

Polychlorinated dibenzo-p-dioxins (PCDDs) are typical environmental pollutants, which are often mutagenic or carcinogenic [1-3]. PCDDs have been accidentally produced in incinerators and detected as trace contaminants in incinerator fly ash, milk, and foods [4,5]. The differences in toxicity, such as receptor binding affinities, of PCDDs are dependent on their chlorine substitution pattern on the parent dibenzo-p-dioxin [1,2]. The parent structure for the PCDD is shown in Fig. 1 The numerals around benzene rings indicate the chlorine substituted positions. The chlorinated substituents that actually exist are 75 possible PCDDs. The highest degree of toxicity is shown in 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD).

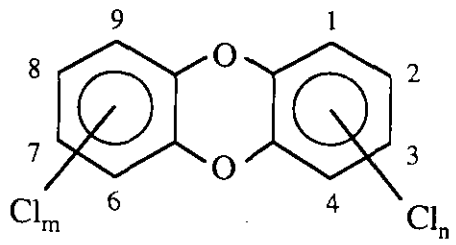

Fig.1 polychlorinated dibenzo-*p*-dioxin

The toxicity and induction responses of PCDDs have been proposed to involve binding of PCDDs to the aryl hydrocarbon receptor (Ah receptor) in cytosol that encoded by the aryl hydrocarbon gene [6]. This type of biological activity is allegedly related to the electronic structures of these compounds and their metabolites. In fact, it has been reported that PCDDs have charge-transfer interaction with the Ah receptor [7]. Our object is to use the IPs as an index of the effectiveness of the charge-transfer interactions in the binding process of PCDDs into the Ah receptor. In order to rationalize the binding affinities of a number of PCDDs with the Ah receptor, the relationships between ionization potentials (IPs) and reactivities toward DNA have also investigated experimentally and computationally [8,9]. It is, however, difficult to experimentally obtain the IPs for PCDDs due to the great number of PCDDs and the high toxicity of certain isomers. In the absence of experimental data, molecular orbital calculations have been used to provide vital information about these molecules to elucidate the charge-transfer interaction.

Koester and Hites [10] used the semiempirical modified neglect of diatomic overlap (MNDO) method to calculate the vertical IPs and the lowest unoccupied molecular orbital (LUMO) energies, which indicate the vertical electron affinities (EAs) of 49 PCDDs. Grebner and Neusser have obtained the experimental values of IPs for non-substituted DD, 2-monochlorinated (MC)DD, and 2,8-dichlorinated (DC)DD [11,12]. They have also calculated the IPs for DD and 8 PCDDs by using semiempirical AM1 method and compared with experimental values and theoretical ones. Kobayashi and coworkers employed semiempirical AM1 and PM3 calculations to determine the electronic structures of DD and 42 PCDDs [13].

However, the accuracy of these earlier semiempirical studies on PCDDs were not sufficient due to the computational limitations, so that, a theoretical systematic reexamination of this system is required. *Ab initio* MO and density functional theory (DFT) approaches to larger molecules are made possible by recent advances in supercomputer technology and methodology. Recently, the DFT study on PCDDs has been performed by Rauhut and Pulay [14]. They calculated the equilibrium geometries and the harmonic vibrational frequencies of 2,3,7,8-TCDD, 1,4,6,9-TCDD 1,3,7,8-TCDD, and 1,4,7,8-TCDD. Fraschini, Bonati, and Pitea reported molecular polarizabilities for DD, 2,3,7,8-TCDD, and 1,4,6,9-TCDD according to the coupled perturbational Hartree-Fock (CPHF) procedure [15].

In our previous study, we have carried out *ab initio* calculations for 2,3,7,8-TCDD at the HF level to analyze the planarity of TCDD. We have obtained the equilibrium geometry, the harmonic vibrational

frequencies, and potential energy curve (PEC) as a function of the folding angles (dihedral angles between the benzene planes) [16]. These results suggested that 2,3,7,8-TCDD has flexibility for bending motion although the most stable geometry is D_{4h} symmetrical planar conformation.

We have also estimated the vertical IPs of 2,3,7,8-TCDD based on the Koopmans' theorem [17]. All these *ab initio* calculations including our earlier calculation were limited by neglect of electron correlation and final state orbital relaxation effects. There is no report that gives reliable IPs including these effects. It is well known that the theoretical IP depends closely on the adopted wavefunction and basis set.

On this report, we, therefore, discuss the correlation effects and basis set dependency of theoretical IPs for PCDDs in order to reproduce reliable vertical and adiabatic IPs. We furthermore evaluated the Koopmans' IPs for all 75 PCDD substituents at the HF/DZ+P and the correlated B3LYP/DZ+P levels because only a part of IPs for PCDDs was reported on earlier theoretical studies. Our correlated values of IPs are compared with experimental results. The goal of this work is to derive converged values for the IPs of PCDDs through a systematic series of extended basis set calculations using an assortment of correlated wavefunctions.

Computational Methods

All computations were performed with the Gaussian 94 program package [18] on the NEC SX-3 and SX-4 supercomputer systems at the National Institute of Environmental Studies (NIES). Molecular geometries were fully optimized at the non-correlated HF and the Becke's nonlocal three-parameter exchange and correlation functional in conjunction with the Lee-Yang-Parr correlation function (B3LYP) [19,20] levels. We assumed that the parent rings of all PCDD substituents are planar structures. The calculations for the Koopmans' IPs for DD and 75 PCDDs were carried out at the HF/DZ+P level [21]. The standard Dunning-Huzinaga's double zeta plus polarization (DZ+P) basis sets [22,23] were mainly employed. The vertical IPs were also evaluated by using the HF and the B3LYP methods according to the ΔSCF method. The total energies of the cation radicals were calculated at the optimized geometries of corresponding neutral species at the same level. In the case of calculating the adiabatic IPs, the geometries were optimized at the B3LYP/DZ+P level for both neutral molecules and cation radicals. Single point calculations for energy refining were performed by using (second order) Mϕller-Plesset perturbation theory (MP2), MP4(SDQ), and configuration interaction with single and double excitations (CISD) correlated wave functions in addition to the above mentioned methods. We also tested Pople's 6-31G* basis sets [24-27] and Dunning's correlation-consistent basis set, polarized valence double-zeta (cc-pVDZ) [28,29]

Results and Discussion

1. Koopmans' IP

We have obtained the IPs for DD and all 75 PCDD substituents on the basis of the Koopmans' theorem, that is, the negatives of the one-electron energies of filled molecular orbitals conventionally give vertical IPs. A value for the first IP of the molecule is derived from the energy of the highest occupied molecular orbital (HOMO).

The Koopmans' IPs and EAs for DD and all 75 PCDD substituents are listed in Table I. The IPs rise with increasing in the total number of chlorine atoms substituted at DD. This situation is clearly shown in Fig.2. These results suggest that the stability of cation is in inverse proportion to increasing the number of substituted chlorine atom. The similar tendency is shown in Fig. 3 at the case of the EAs.

We have investigated ring puckering effects on the HOMO and LUMO. It was found that the difference in the Koopmans' IP is very small by scanning the folding angle for ring puckering. Actually, when the changing of folding angle is 5 degrees, the Koopmans' IP increases only 0.010 eV while the corresponding EA is 0.005 eV. These results suggest that geometries can be assumed to be planar when the IPs and EAs are determined. We therefore performed all geometry optimizations at the Cs symmetries. [12].

The IPs obtained at this work are in more agreement with experimental ones rather than previous theoretical studies. For example, our calculated value of IP for DD at the HF/DZ+P level is 7.916 eV, which agrees with experimental IP, 7.598 eV. (While the Koopmans' IP using AM1 method is 8.59 eV [12].) In the case of 2,3,7,8-TCDD, the Koopmans' IP is 8.582 eV by the HF/DZ+P method, while the corresponding ones are 9.00 eV and 9.148 eV by the AM1 [12] and MNDO methods [11], respectively. We ,however, cannot compare these theoretical IPs with experimental results because of lacking experimental studies for 2,3,7,8-TCDD.

The PCDDs that have chlorine atoms on neighboring positions have lower IP values by comparing the IP values of PCDDs that have the same number of chlorine atoms. Especially, the IP of 1,2,3,4-TCDD is the lowest value among TCDDs. Furthermore, PCDDs that have chlorine atoms on 1,4,6,9-positions are unstable at the planer geometries.

Table I : Koopmans' Ionization Potentials, Electron Affinities, and Total Energies for PCDDs

	IP (eV)	EA (eV)	Total Energy (hartree)
DD	7.916	-3.143	-608.89994548
1-MCDD	8.141	-2.897	-1067.78266855
2-MCDD	8.110	-2.874	-1067.78616546
1,2-DCDD	8.269	-2.683	-1526.66319099
1,3-DCDD	8.317	-2.652	-1526.66760068
1,4-DCDD	8.347	-2.649	-1526.66437662
1,6-DCDD	8.370	-2.671	-1526.66515872
1,7-DCDD	8.324	-2.670	-1526.66858202
1,8-DCDD	8.323	-2.669	-1526.66848152
1,9-DCDD	8.362	-2.680	-1526.66449810
2,3-DCDD	8.269	-2.636	-1526.66678719
2,7-DCDD	8.295	-2.649	-1526.67203222
2,8-DCDD	8.287	-2.671	-1526.67198931
1,2,3-TriCDD	8.417	-2.492	-1985.54232862
1,2,4-TriCDD	8.462	-2.448	-1985.54382398
1,2,6-TriCDD	8.486	-2.479	-1985.54546369
1,2,7-TriCDD	8.448	-2.473	-1985.54883827
1,2,8-TriCDD	8.439	-2.478	-1985.54871361
1,2,9-TriCDD	8.478	-2.487	-1985.54476344
1,3,6-TriCDD	8.534	-2.451	-1985.54971395
1,3,7-TriCDD	8.483	-2.449	-1985.55314919
1,3,8-TriCDD	8.493	-2.446	-1985.55309758
1,3,9-TriCDD	8.526	-2.461	-1985.54918635
1,4,6-TriCDD	8.571	-2.450	-1985.54600617
1,4,7-TriCDD	8.518	-2.439	-1985.54990789
1,7,8-TriCDD	8.474	-2.503	-1985.54885633
2,3,7-TriCDD	8.441	-2.465	-1985.55233357
1,2,3,4-TCDD	8.551	-2.318	-2444.41701671
1,2,3,6-TCDD	8.625	-2.318	-2444.42427598
1,2,3,7-TCDD	8.581	-2.313	-2444.42767747
1,2,3,8-TCDD	8.581	-2.316	-2444.42759824
1,2,3,9-TCDD	8.618	-2.326	-2444.42370022
1,2,4,6-TCDD	8.675	-2.265	-2444.42528808
1,2,4,7-TCDD	8.630	-2.252	-2444.42911918
1,2,4,8-TCDD	8.620	-2.251	-2444.42908849
1,2,4,9-TCDD	8.675	-2.264	-2444.42521743
1,2,6,7-TCDD	8.601	-2.299	-2444.42557169
1,2,6,8-TCDD	8.637	-2.274	-2444.42975181
1,2,6,9-TCDD	8.675	-2.272	-2444.42607035
1,2,7,8-TCDD	8.586	-2.315	-2444.42887937
1,2,7,9-TCDD	8.640	-2.281	-2444.42921074
1,2,8,9-TCDD	8.586	-2.307	-2444.42481031
1,3,6,8-TCDD	8.694	-2.248	-2444.43398739
1,3,6,9-TCDD	8.722	-2.247	-2444.43033917
1,3,7,8-TCDD	8.629	-2.289	-2444.43317738
1,3,7,9-TCDD	8.674	-2.257	-2444.43353645
1,4,6,9-TCDD	8.775	-2.246	-2444.42668182
1,4,7,8-TCDD	8.659	-2.280	-2444.42995617
2,3,7,8-TCDD	8.582	-2.301	-2444.43241736
1,2,3,4,6-PCDD	8.756	-2.137	-2903.29828853
1,2,3,4,7-PCDD	8.708	-2.124	-2903.30210470
1,2,3,6,7-PCDD	8.728	-2.144	-2903.30416821
1,2,3,6,8-PCDD	8.774	-2.120	-2903.30834026
1,2,3,6,9-PCDD	8.806	-2.118	-2903.30470051
1,2,3,7,8-PCDD	8.716	-2.159	-2903.30752101
1,2,3,7,9-PCDD	8.765	-2.127	-2903.30787142
1,2,3,8,9-PCDD	8.723	-2.152	-2903.30355506
1,2,4,6,7-PCDD	8.780	-2.098	-2903.30517556
1,2,4,6,8-PCDD	8.814	-2.073	-2903.30937381
1,2,4,6,9-PCDD	8.866	-2.074	-2903.30574180
1,2,4,7,8-PCDD	8.760	-2.100	-2903.30895287
1,2,4,7,9-PCDD	8.827	-2.074	-2903.30933735
1,2,4,8,9-PCDD	8.770	-2.096	-2903.30508113
1,2,3,4,6,7-HCDD	8.852	-1.973	-3362.17802356
1,2,3,4,6,8-HCDD	8.896	-1.951	-3362.18221662
1,2,3,4,6,9-HCDD	8.940	-1.952	-3362.17863224
1,2,3,4,7,8-HCDD	8.838	-1.976	-3362.18180004
1,2,3,6,7,8-HCDD	8.854	-1.994	-3362.18258613
1,2,3,6,7,9-HCDD	8.898	-1.951	-3362.18360647
1,2,3,6,8,9-HCDD	8.901	-1.950	-3362.18354305
1,2,3,7,8,9-HCDD	8.848	-2.001	-3362.18207283
1,2,4,6,7,9-HCDD	8.963	-1.912	-3362.18464375
1,2,4,6,8,9-HCDD	8.949	-1.910	-3362.18461601
1,2,3,4,6,7,8-HeptaCDD	8.972	-1.831	-3821.05632926
1,2,3,4,6,7,9-HeptaCDD	9.026	-1.794	-3821.05739379
1,2,3,4,6,7,8,9-OCDD	9.094	-1.679	-4279.93006525

Koopmans' IP = - ε HOMO Koopmans' EA = - ε LUMO (Geometries optimized at the HF/DZ+P)

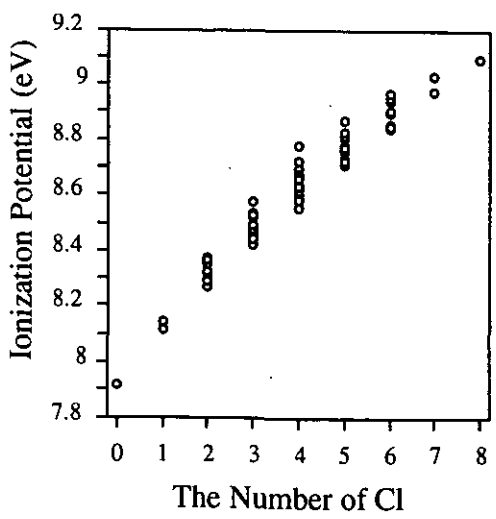

Fig 2. Relation between ionization potentials and the number of Cl for PCDDs

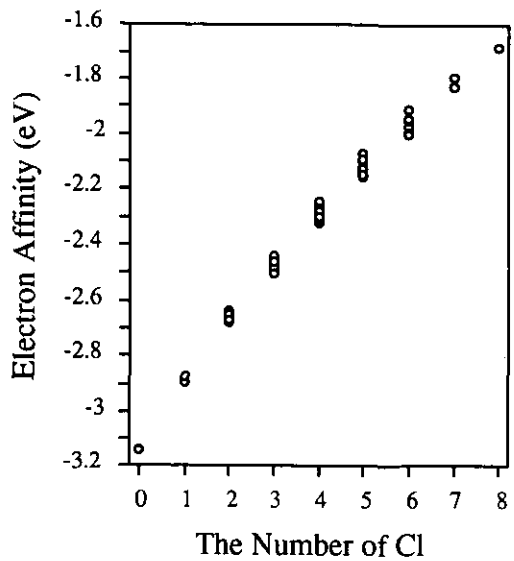

Fig 3. Relation between electron affinities and the number of Cl for PCDDs

2. Vertical and adiabatic IPs

The first IPs were also computed as the energy difference between the cation radical and the neutral molecule (ΔSCF method). At this method, the IP is defined as the energy required to remove an electron from the neutral molecule. We show the calculated vertical and adiabatic Ips by using the ΔSCF method for DD and 20 PCDDs in Table II.

In generally, the ΔSCF method leads to too small IPs. On the other hand, the Koopmans' theorem leads to too large values because the theorem assumes that the orbitals do not relax upon ionization. The theoretical IPs approach to exact values as including electron correlation effects. Actually, the vertical IPs that obtained at the B3LYP level are higher than the values at the HF level and lower than Koopmans' IPs.

We optimized geometries for cations of PCDDs in order to obtain the adiabatic IPs. The equilibrium geometries of DD and 2,3,7,8-TCDD have D_{4h} symmetry in neutral, but in the case of radical cations (and anions), the geometries with D4h symmetry are about 0.2 eV higher in the total energy. This is because the instabilities are caused by the Renner-Teller distortions at the HF level. While, at the correlated B3LYP and MP2 level, the symmetrized geometries of radical cations are more stable than symmetry broken geometries.

Table II. Vertical IP and Adiabatic IP for PCDDs

	HF/DZ+P		B3LYP/DZ+P	
	Koopmans' IP	Vertical IP	Vertical IP	Adiabatic IP
DD	7.916	6.968	7.256	7.150
1-MCDD	8.141	7.159	7.418	7.303
2-MCDD	8.110	7.153	7.366	7.254
2,8-DCDD	8.287	7.320	7.472	7.346
1,2,4-TriCDD	8.462	7.450	7.616	7.490
2,3,7-TriCDD	8.441	7.482	7.547	7.422
1,2,3,4-TCDD	8.551	7.541	7.636	7.514
1,2,7,8-TCDD	8.586	7.597	7.637	7.515
1,3,6,8-TCDD	8.694	7.675	7.749	7.616
1,3,7,8-TCDD	8.629	7.632	7.678	7.545
1,4,6,9-TCDD	8.775	7.698	7.850	7.720
2,3,7,8-TCDD	8.582	7.625	7.617	7.489
1,2,3,4,7-PCDD	8.708	7.710	7.730	7.595
1,2,3,7,8-PCDD	8.716	7.737	7.708	7.574
1,2,4,7,8-PCDD	8.760	7.731	7.771	7.633
1,2,3,4,7,8-HCDD	8.838	7.835	7.784	7.653
1,2,3,6,7,8-HCDD	8.854	7.852	7.791	7.659
1,2,3,7,8,9-HCDD	8.848	7.845	7.784	7.652
1,2,3,4,6,7,8-HeptaCDD	8.972	7.952	7.874	7.732
1,2,3,4,6,7,8,9-OCDD	9.094	8.051	7.940	7.807

3. Electron Correlation Effect for Adiabatic IPs

The adiabatic IPs at various levels and the comparison with known experimental values are listed in Table III(where "//" means "at the geometry of"). The effects of electron correlation and basis set dependency on IP have been studied for non-substituted DD. Calculations with the larger cc-pVDZ and DZ+P basis set give the larger values of IP when the same wave functions are used. This result indicates that the larger basis sets improve the values of IP. Especially, DZ+P is the most effective in the used basis sets to calculate here for IP. The theoretical value of the adiabatic IP approaches the experimental one with higher electron correlated calculation, in the order of B3LYP, MP2, MP4(SDQ), but the IP calculated with the CISD method is not so good, compared with experimental one.

Table III. Adiabatic Ionization Potentials for Non-Substituted DD

Method	Basis set	Adiabatic IP
HF	6-31G*	6.612
HF	cc-pVDZ	6.697
HF	DZ+P	6.754
B3LYP	6-31G*	6.999
B3LYP	cc-pVDZ	7.132
B3LYP	DZ+P	7.150
MP2	6-31G*	7.021
MP2	cc-pVDZ	7.186
MP2	DZ+P	7.202
MP4(SDQ)	cc-pVDZ//	7.274
MP4(SDQ)	DZ+P//	7.288
CISD	cc-pVDZ//	7.022
Experimental		7.598 a)

a) Ref.11
// : geometries optimized at the B3LYP/DZ+P level

In the same way, 2,8-DCDD, and 2,3,7,8-TCDD have been investigated. The results of correlated calculations for these PCDDs are listed in Table IV. We could not obtain their IPs with the CISD method and the IP for 2,3,7,8-TCDD with the MP4(SDQ) because the computations required too much disk spaces of I/O files. The improvements are similarly realized with the large basis sets and electron correlated wave functions.

Table IV. Adiabatic Ionization Potentials for 2,8-DCDD and 2,3,7,8-TCDD

Method	Basis set	2,8-DCDD	2,3,7,8-TCDD
HF	6-31G*	6.817	7.349
HF	DZ+P	6.884	7.391
B3LYP	6-31G*	7.259	7.444
B3LYP	DZ+P	7.346	7.489
MP2	cc-pVDZ//	7.437	7.546
MP2	DZ+P//	7.443	7.553
MP4(SDQ)	cc-pVDZ//	7.542	-
MP4(SDQ)	DZ+P//	7.546	
Experimental		7.802 a)	

a) Ref.12
// : geometries optimized at the B3LYP/DZ+P level

Concluding Remarks

The *ab initio* MO calculations including the electron correlations for PCDDs have been proved to be very useful in order to reproduce the reliable Ips. The Koopmans' Ips for all PCDD substituents have been obtained. The IPs strongly depend on the number of chlorine atoms and the substituted sites. The values of the IP for 2,3,7,8-TCDD is estimated to be 8.0 eV by the correlated calculations It should be noted that the theoretical IPs evaluated by using the post-HF calculations for DD and 2,8-DCDD are closely agreement with experimental values.

References

[1] Bumb, R. R.; Crummett, W. B.; Cutie, S. S.; Gledhill, J. R.; Hummel, R. H.; Kagel, R. O.; Lamparski, L. L.; Luoma, E. V.; Miller, D. L.; Nestrick, T. J.; Shadoff, L. A.; Stehl, R. H.; Woods, J. S. Science 1980, 210, 385

[2] Poland, A.; Kuntsun, J. C. Ann. Rev. Pharmacol. Toxicol. 1982, 22, 517.

[3] Poland, A.; Glover, E.; Kende, A. S. J. Biol. Chem. 1976, 251, 4936-4946; Burbach, K. M.; Poland, A.; Bradfield, C. A. Proc. Natl. Acad. Sci. USA 1992, 89, 8185-8189.

[4] Aitio, A.; Hesso, A.; Luotamo, M.; Rosenberg, C. Chemosphere 1993, 27, 516.

[5] Mason, G.; Farrell, K.; Keys, B.; Piskorska-Pliszczynska, J.; Safe, L.; Safe, S. Toxicology, 1986, 41, 21-31; ibid, 1985, 37, 1.

G. Mason, K. Farrell, B. Keys, J. Piskorska-Pliszczynska, L. Safe and S. Safe, Toxicology, 41, 21-31 (1986)

[6] Nebert, D. W.; Eisen, H. J.; Negishi, M.; Lang, M. A.; Hjelmeland, L. M. Ann. Rev. Pharmacol. Toxicol. 1981, 21, 431-462.

[7] Miller, G.; Sontum, S.; Crosby, D. G. Bull. Environ. Contam. Toxicol. 1977, 18, 611.

[8] J. Phys. Chem. 1993, 97, 2385.
[9] Chem. Research Toxicol., 1992, 5, 346.
[10] Koester, C. J.; Hites, R. A. Chemosphere 1988, 17, 2355.
[11] Zimmermann, R.; Boesl, U.; Lenoir, D.; Kettrup, A.; Grebner, Th. L.; Neusser, H. J. Int. J. Mass Spectrum. Ion Processes 1995, 145, 97.
[12] Grebner, Th. L.; Neusser, H. J.; Ernstberger, B. Int. J. Mass Spectrum. Ion Processes 1994, 136, 101.
[13] Kobayashi, S.; Sameshima, K.; Ishii, Y.; Tanaka, A. Chem. Pharm. Bull. 1995, 43, 1780.
[14] Rauhut, G.; Pulay, P. J. Am. Chem. Soc. 1995, 117, 4167.
[15] Fraschini, E.; Bonati, L.; Pitea, D. J. Phys. Chem.. 1996, 100, 10564.
[16] Fujii, T.; Tanaka, K.; Tokiwa, H.; Soma, Y. J. Phys. Chem. 1996, 100, 4810.
[17] Koopmans, T. Physica 1934, 1, 104.
[18] Gaussian 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
[19] Becke, A. D. J. Chem. Phys. 1993, 98, 5648.
[20] Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. 1988, B 41, 785.
[21] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.
[22] Huzinaga, S. J. Chem. Phys. 1965, 42, 1293.
[23] Dunning, T. H. J. Chem. Phys. 1970, 53, 2823.
[24] Pople, J. A.; Head-Gordon, M.; D. J. Fox, D. J.;. Raghavachari, K.; Curtiss, L. A. J. Chem. Phys. 1989, 90, 5622.
[25] Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. J. Chem. Phys. 1990, 93, 2537.
[26] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. J. Chem. Phys. 1991, 94, 7221.
[27] Curtiss, L. A.; Raghavachari, K.; Pople, J. A. J. Chem. Phys. 1993, 98, 1293.
[28] T. H. Dunning, Jr., J. Chem. Phys. 90, 1007 (1989)
Dunning, T. H. J. Chem. Phys. 1989, 90, 1007.
[29] David E. Woon and Thom H. Dunning, Jr., J. Chem. Phys. 98, 1358 (1993)
Woon, D. E.; Dunning, T. H.; J. Chem. Phys. 1993, 98, 1358