Applied Chemical Engineering (2021) Volume 4 Issue 2
doi:10.24294/ace.v4i2.1343

ORIGINAL RESEARCH ARTICLE

Adsorption behavior between thiophene and M = (Mo, Pd, Sn) by quantum chemistry method

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ABSTRACT

Based on the existing experiment, Gaussian 03 package to study the adsorption microscopic behavior between thiophene molecules and three transition metals M = (Mo, Pd, Sn) were used, which combine with the quantum chemistry method and the genecp basis set. It is showed there are many different molecular adsorption patterns between the different transition metal atoms thiophene. The transition metal Mo is given more priority to occur the β and θ adsorbing model, and the decreased energy was 328.795 kJ/mol and 327.868 kJ/mol respectively. Transition metal Pd is given more priority to occur the δ adsorbing model, and the decreased energy as high as 380.654 kJ/mol; transition metal Sn is given more priority to occur the α and δ adsorbing model, and the decreased energy was 272.514 and 512.130 kJ/mol, respectively. The correction of zero energy should be considered in the calculation of adsorption energy. B3LYP method is more advantage about optimization and energy calculation.

Keywords: Thiophene Cracking; Transition Metal; Quantum Chemistry; Adsorption Behavior

ARTICLE INFO

Received: 25 April 2021
Accepted: 16 June 2021
Available online: 21 June 2021

1. Introduction

As a traditional fossil energy, petroleum plays an irreplaceable role in global industry[1]. Petroleum processing has always been a hot and difficult point in scientific research, and clean energy and environmental protection have attracted more and more attention of mankind all over the world[2]. Therefore, how to deeply process fossil energy so that it will not pollute the environment is an urgent chemical process goal[3]. During the industrial revolution, human beings have made extensive use of fossil energy, resulting in excessive SO_2 gas discharged into the atmosphere to form acid rain, which seriously endangers the survival of organisms on the earth. It can be traced back to the improper treatment of coal containing compounds[4]. There are many kinds of sulfur-containing compounds, and their desulfurization process is complex and cannot be unified, resulting in the desulfurization technology of sulfur-containing compounds has not been mature, and the human survival requirements of environmental protection and sustainable development need to focus on the catalytic conversion process of sulfur-containing organic compounds[5].

The desulfurization of organic sulfur-containing compounds is difficult[6]. Many organic compounds contain the ring structure of S atom, and their molecules are very stable, and the conjugation effect in the ring is very strong, so the conventional desulfurization methods cannot play a role. Thiophene, as a typical representative of organic sulfur compounds, occupies a large proportion of organic sulfur compounds, its molecules have a very stable ring structure, its desulfurization process is complex. Recently, transition metals have attracted the attention of the scientific community because of their good catalytic performance. Good results have been achieved through the desulfurization of thiophene molecules catalyzed by transition metals[3].

As early as 2008, Yu *et al.* compared the catalytic performance of Co/Ni/Mo supported on carbon nanotubes for thiontly[7]. Eduardo *et al.* showed that transition metal Mo doped in Ni can play a strong catalytic effect for thiophene desulfurization and pointed out that transition metal Mo is the best catalytic metal for thiophene desulfurization[8]. ZdeněK *et al.* pointed out through experiments that transition metal Pd or Pd-Pt can play a good catalytic effect on thiophene[9]. Valeria *et al.* proposed that hydrogen addition catalyzed by transition metal Pd-Au can better promote thiophene desulfurization[10]. In addition, Biswajit *et al.* experimentally found that the transition metal Sn can also exert a strong catalytic activity against the desulfurization of thiophene[11]. Chinese scholars Zhang *et al.* also explored the efficient catalytic desulfurization process of ZnO as Mo, Pd, Sn on thiophene, and proposed that they have strong catalytic activity on the desulfurization of thiophene[12]. Although there are many literatures on the desulfurization process of thiophene catalyzed by other transition metals[10,13]. However, its catalytic activity is uneven and cannot form a unified desulfurization mechanism.

By summarizing the experimental research on the catalytic desulfurization process of transition metals in thiophene, it is found that metals M = (Mo, Pd, Sn) have ideal catalytic activity compared with other transition metals[14]. Because thiophene itself is toxic and the transition metal is expensive, it is difficult to study the catalytic effect of thiophene experimentally. The author chose quantum chemical method to study the adsorption behavior of transition metal M = (Mo, Pd, Sn) and thiophene molecules. In this regard, although there are relevant reports, for example, Zheng Kewen *et al.* proposed that thiophene is easy to form intermediates with positive carbon ions on molecular sieve by quantum chemical method, and then desulfurization reaction occurs with olefin addition to produce hexene[15]. Xu Kun *et al.* proposed the mechanism of hydrodesulfurization reaction of thiophene on the γ-Mo_2N (100) surface using density functional theory, but these theoretical studies are one-sided and insufficient[16]. Based on the author's research basis and experience in this field, the quantum chemistry research method is selected to explore the specific adsorption behavior of three different transition metal atoms on thiophene molecules through calculation, which can provide scientific and reasonable guidance for further experiments and has important research significance[17,18].

2. Calculation method

Firstly, the B3LYP method in Density Functional Theory (DFT) is used to study the relationship between thiophene and transition metals M = (Mo, Sn, Pd). The adsorption model of atoms is studied, and then the energy accuracy is verified by quantitative methods such as HF, MP2 and CCSD. For transition metal atoms, the pseudopotential basis group lanl2dz is used, while other atoms choose 6-311+G(d,p). During the calculation, genecp method is used to fit the basis set. B3LYP method is used to optimize the geometric configuration and frequency analysis of each species. It is found that all vibration frequencies are positive, indicating that each species before and after adsorption is a minimum point on the potential energy surface. In order to improve the accuracy of energy, the zero energy is corrected at the same time of frequency analysis. The correction factor is 0.97, and the corresponding different relative energy data and adsorbed energy are obtained. Adsorbed energy $\Delta E_{\text{abs}} = (E_{\text{product}} + E_{\text{zpe}}) - (E_{\text{reactant}} + E_{\text{zpe}})$, among which the E_{product} is the energy to form a stable intermediate after adsorption, E_{reactant} is the sum of energy of adsorption thiophene molecules and transition metal atoms, and E_{zpe} is the zero-point energy correction value; ΔE is the relative energy after the zero-point energy correction. All the above work was done with the Gaussian 03 program[19] on a computational chemistry microcomputer of University of South China.

3. Results and discussion

3.1 Absorption behavior modes

Thiophene molecules, typical representative of sulfur-containing organic compounds, have a C_4–S ring, data of partial key length (unit: Å) and key angle (unit: °) are shown in **Figure 1(a)**, the length of C=C double bond on both sides of the molecule is significantly shorter than that of C–S bond by 0.369 Å, which is the main feature of C=C double bond. The length of C-C single bond at the bottom of the molecule is 0.04 Å longer than that of the double bond. The length of C–H bond in the molecule is about 1.082 Å, and the nine atoms in the molecule are almost in the same plane. The included angle of C–S–C is 91.5°, which fully indicates that the molecular configuration is not a regular pentagon. The data of C–C–C bond angle in the molecule is large and asymmetric, indicating that the molecule has a certain polarity. **Figure 1(b)** is the Homo molecular orbital of thiophene molecule, and the electron cloud occupying the lowest orbital is mainly concentrated on the symmetrical double bond, indicating that the electron density on the C=C bond is large, which can provide electrons for electrophilic reaction. **Figure 1(c)** is the LUMO molecular orbital of thiophene molecule, indicating that the anti-bond of each atom in the ring makes a great contribution to the unoccupied empty orbital of the molecule, and there are empty orbitals on the C–H single bond, indicating that the atoms on the molecular ring can be used as the reaction active site. The Mulliken charge layout in **Table 1** shows that the S atom in the thiophene molecular ring is positively charged. The C atom has negative charge, and the carbon atom near the S atom has more negative charge, which indicates that the intramolecular ring has a very strong conjugated electron effect. Most of the transition metal atoms have many 3d empty orbitals, and the single electron on the outermost orbital of some transition metal atoms is easy to be given. Considering the effect of lone pair electrons on S atom, the adsorption and binding mode of thiophene molecule and transition metals M = (Mo, Pd, Sn) is designed, as shown in **Figure 1(d)** adsorption model. α refers that the transition metal M mainly attacks the S atom and forms a bond with it; β indicates that the transition metal M mainly absorbs the electron cloud on the S–C bond; γ indicates that the transition metal M mainly absorbs the electron cloud on the right C=C bond; δ indicates that the transition metal M mainly attacks the lower C–C bond, which may be the anti-bond empty orbit that obtains electrons or releases electrons to the C–C bond; θ indicates that the transition metal M is close to the ring from the vertical upper center of the ring plane. Due to the ring structure of thiophene, the electron cloud may have a conjugation effect. It should be noted that this is also a mode in which transition metal M atoms attack thiophene molecules. The adsorption of H atoms on the surface of transition metals also exists, but Zhang Lianyang *et al.* have done detailed research and reported about it[20]. So the adsorption of H atoms on the surface of transition metal M atoms will not be repeated here. In this paper, four adsorption sites are considered for the transition metal M thiophene molecular loop.

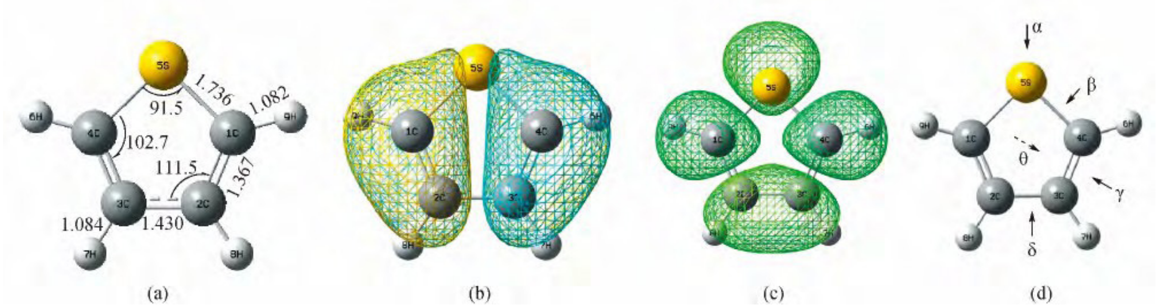

Figure 1. Geometric structure, molecular orbital and adsorption mode of thiophene molecule.

Table 1. The atomic Mulliken charge distribution of thiophene molecule

Atoms	Mulliken charge	Atoms	Mulliken charge
1C	–0.4032	6H	0.1870
2C	–0.1814	7H	0.1700
3C	–0.1373	8H	0.1514
4C	–0.3765	9H	0.1939
5S	0.3961		

3.2 Adsorption behavior between Mo with thiophene

Studies show that there are five stable adsorption modes between transition metal Mo and thiophene molecules, such as α, β, γ, δ, θ. Its extranuclear electron arrangement is $4d^5 5s^1$. 4d-orbit has five single electrons and its d-orbit is semi-filled structure, while the only electron on the 5s orbit is very easy to give, and it binds easily to thiophene molecules. Because the transition metal Mo has a large atomic radius, it is still subject to a large steric effect when it is close to thiophene molecules. As shown in **Figure 2**, when α site adsorption occurs, the distance between transition metal Mo and S atom is 2.438 Å, and the bond length of C–S bond is lengthened to 0.036 Å, while the included angle of C–S–C is basically unchanged. When β site adsorption occurs, the transition metal Mo atom directly destroys the C–S bond in the molecule, which is caused by the strong electron donor effect; when γ site adsorption occurs, the transition metal Mo atom does not destroy the sub ring structure, but forms a bond with C atom. Due to its d-orbital half-filled structure, it can still form a bond with H atom. The δ adsorption is similar to the occurrence of β adsorption, which indicates that it is easy to destroy the C–C single bond and difficult to attack the C=C double bond. When θ adsorption occurs, transition metal Mo atoms range from approximately 2.081 to 2.106 Å from the C atom in the molecule. In this case, the transition metal Mo atom is directly above the thiophene ring molecule. After adsorption, the basic structure of the ring molecule in the thiophene remains unchanged, and the bond length of the C–C bond is elongated to 1.443 Å, which indicates that the transition metal Mo atoms are constantly approaching the molecular ring, and the huge repulsion force makes the thiophene ring expand.

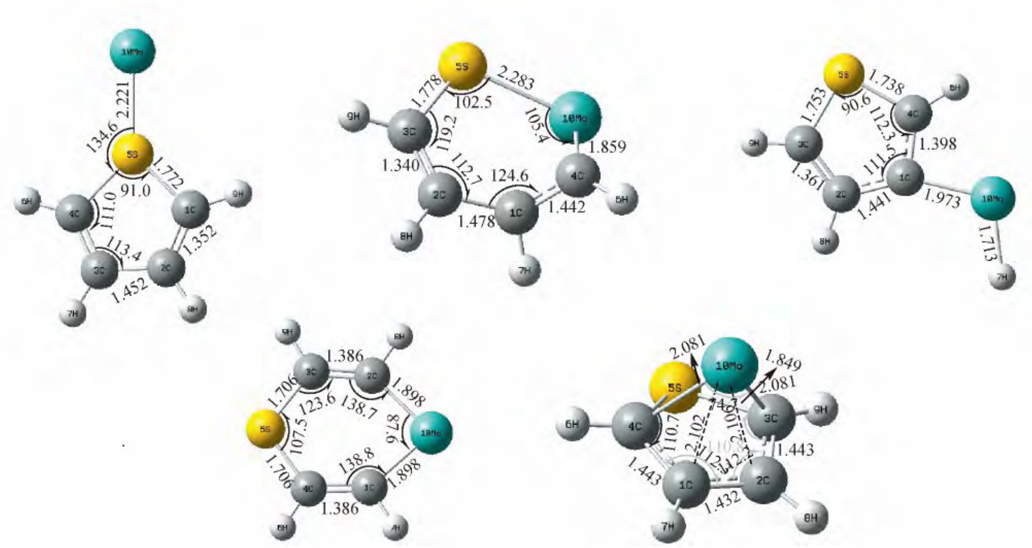

Figure 2. Five adsorption patterns between transition metal Mo and thiophene molecule.

Considering the adsorption energy at these 5 adsorption sites, the energy data are listed in **Table 2**. It is not difficult to find that the energy of the adsorbed products is lower than that of the reactants. ΔE_{abs} is the adsorption energy data without considering zero energy correction; $\Delta I'_{abs}$ is the adsorption energy data after considering zero energy correction, and ΔE is the relative energy of the two modes. The greater the negative value of adsorption energy is, the more stable the whole system is after adsorption. It can be seen from the comparative values that the system formed by transition metal Mo atom calculated by B3LPY method after the adsorption of thiophene molecules is relatively stable. Its energy is 328.795 and 327.868 kJ/mol lower than α adsorption respectively, indicating that transition metal Mo is more suitable for adsorbing thiophene in these two directions and catalytic cracking reaction. In order to further measure the accuracy of energy, HF, MP2, CCSD and other methods are used to calculate at the same base group level with the same geometric configuration. Corresponding ΔE is also listed in **Table 2**, which is basically consistent with the trend calculated by the B3LYP method.

Table 2. Energy of adsorption between Mo and thiophene molecule

Adsorption pattern	ΔE_{abs} /kJ·(mol)$^{-1}$	$\Delta E'_{abs}$ /kJ·(mol)$^{-1}$	ΔE /kJ·(mol)$^{-1}$	ΔE_{HF} /kJ·(mol)$^{-1}$	ΔE_{MP2} /kJ·(mol)$^{-1}$	ΔE_{CCSD} /kJ·(mol)$^{-1}$
α	–563.120	–562.716	0.000	0.000	0.000	0.000
β	–885.475	–891.511	–328.795	–319.817	–326.020	–328.843
γ	–730.902	–746.408	–183.692	–181.092	–180.987	–180.076
δ	–713.471	–729.401	–166.685	–167.031	–163.921	–166.342
θ	–888.727	–890.583	–327.868	–325.243	–321.760	–326.051

3.3 Adsorption behavior between Pd and thiophene

The calculation results show that the adsorption of thiophene molecule by transition metal Pd atom is different from that of Mo. The author has found four modes, namely β, γ, δ, θ. But its stable adsorption is only δ. The outermost electron arrangement of transition metal Pd atom is 4d^{10}. The electrons in the d-orbit are full, so the transition metal Pd atoms is low. The geometric structure of **Figure 3** shows that when the transition metal Pd atoms adsorb thiophene molecules from α, β, γ, and θ, it basically does not affect the molecular structure of the thiophene ring. While δ adsorption occurs, the ring structure of thiophene molecule is destroyed, and the C–C bond is interrupted by transition metal Pd atom to form a planar structure of a six membered ring. Similarly, when β and θ adsorption occur, the transition metal atoms are biased to one side, and are mainly close to and bonded with the C atom connecting the S atom above or below the molecular ring plane. This irregular and unstable adsorption is mainly due to the lack of single electrons in the outermost layer. The relevant adsorption energy data are shown in **Table 3**. It is found that the energy of adsorption only at δ position decreases greatly, indicating that it is a stable adsorption mode. The energy after adsorption decreases by 380.654 kJ/mol, while the energy after adsorption at other positions increases, which may

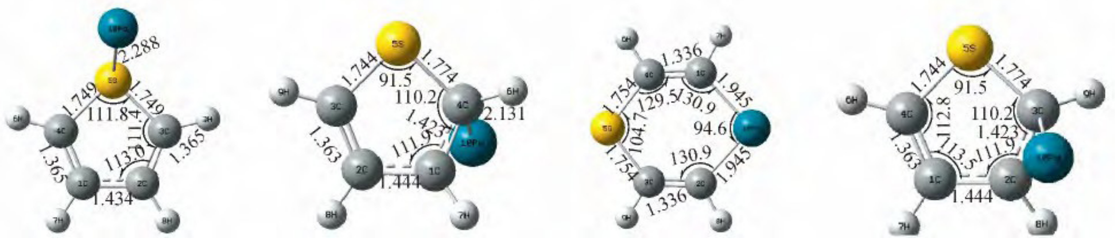

Figure 3. Four adsorption patterns between Pd and thiophene molecule.

Table 3. Energy of adsorption between Pd and thiophene molecule

Adsorption pattern	ΔE_{abs} /kJ·(mol)$^{-1}$	$\Delta E'_{abs}$ /kJ·(mol)$^{-1}$	ΔE /kJ·(mol)$^{-1}$	ΔE_{HF} /kJ·(mol)$^{-1}$	ΔE_{MP2} /kJ·(mol)$^{-1}$	ΔE_{CCSD} /kJ·(mol)$^{-1}$
β	967.926	969.695	683.685	684.029	690.331	683.076
γ	312.105	313.042	27.032	26.987	25.031	27.009
δ	–373.754	–380.654	–666.664	–659.098	–661.703	–666.523
θ	285.062	286.010	0.000	0.000	0.000	0.000

be due to the resistance between the lone pair electron pair of S atom and the 4d half-filled electron orbit of transition metal. In order to further measure the accuracy of energy, HF, MP2, CCSD and other methods are used to calculate with the same geometric configuration at the same basis group level. The obtained Δ*E* is also listed in **Table 3**, which is basically consistent with the calculation trend of B3LYP method, and improves the reliability of calculation.

3.4 Adsorption behavior between Sn and thiophene

The calculation results show that there are four modes for the adsorption between thiophene molecules and transition metal Sn, namely α, β, δ, θ. But its stable adsorption is only α and δ. Because the electron arrangement on the outermost orbital of the transition metal atom is $4d^{10}5s^{2}5p^{2}$, four electrons can be given. Therefore, the transition metal Sn atoms give a strong adsorption capacity of electron and thiophene molecules. Except for the adsorption behavior of γ with C=C double bonds, the transition metal Sn atoms can better bond to thiophene molecules. The geometric structure of **Figure 4** shows that when the transition metal Sn atoms adsorb thiophene molecules from α and θ, they basically do not affect the molecular structure of the thiophene ring. Unlike the front, the transition metal Sn atoms at α are not in the same plane as the thiophene ring, but the adsorption in the δ position direction distorts the ring structure of the thiophene molecule to a certain extent. On the other hand, because there are already two electrons in the 5p orbital of Sn atom, it cannot accept two electrons at the same time, so it cannot form a stable bond with S atom. So, the Sn–S spacing in the adsorption α is 2.580 Å. The β adsorption pattern of steric instability shows that the transition metal Sn is close to the back of the thiophene ring and forms a bond with two C atoms. At the same time, S atoms are excluded, so that the thiophene ring is no longer planar structure but distorted, which is difficult to occur adsorption. The δ adsorption mode pattern shows that, like the above two transition metal atoms, Sn can attack the C–C single bond, thus destroying the molecular structure of thiophene. When θ adsorption occurs, the distance between the transition metal Sn atom and the C atom in the molecule is about 2.373–2.453 Å, which indicates that after the adsorption of the transition metal Sn atom directly above the thiophene ring molecule, the basic structure of the thiophene ring molecule remains unchanged, while the bond length of the C–C bond is slightly elongated. The energy data of the four adsorption patterns are shown in **Table 4**, the energy data of α and δ adsorption is negative, indicating that they have two kinds of adsorption sites, the stability of molecules is enhanced. The energy decrease after the occurrence adsorption was greatest, up to 512.130 kJ/mol. The β and θ adsorption are unstable adsorption because the energy of the system increas-

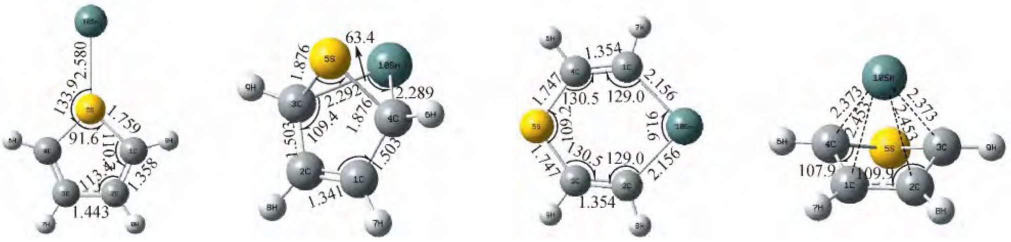

Figure 4. Four adsorption patterns between Sn and thiophene molecule.

Table 4. Energy of adsorption between Sn and thiophene molecule

Adsorption pattern	ΔE_{abs} /kJ·(mol)$^{-1}$	$\Delta E'_{abs}$ /kJ·(mol)$^{-1}$	ΔE /kJ·(mol)$^{-1}$	ΔE_{HF} /kJ·(mol)$^{-1}$	ΔE_{MP2} / kJ·(mol)$^{-1}$	ΔE_{CCSD} /kJ·(mol)$^{-1}$
α	–272.952	–272.514	–1018.500	–1016.323	–1015.684	–1018.492
β	1836.902	1835.316	1089.330	1086.465	1081.036	1089.292
δ	–507.488	–512.130	–1258.116	–1257.045	–1255.340	–1258.099
θ	747.054	745.986	0.000	0.000	0.000	0.000

es. Due to the steric hindrance effect, the energy of the system increases the most after β adsorption, indicating that this mode is the most unstable. In order to further measure the accuracy of energy, HF, MP2, CCSD and other methods are used to calculate with the same geometric configuration at the same basis group level. ΔE is also listed in **Table 4**, which is basically consistent with the calculation trend of B3LYP method, which improves the reliability of calculation.

4. Conclusion

Through the quantitative calculation of the adsorption patterns between thiophenes and three transition metals M = (Mo, Pd, Sn), it is found that different transition metals have different adsorption modes. By comparing the energy data of each adsorption mode, the best stable adsorption sites for different metals are found. It has positive significance for further research on the reaction mechanism:

1) There are five adsorption sites for transition metal Mo atoms, and the system energy decreases after each adsorption, but there are only a few adsorption sites for transition metals Pd and Sn. The energy data show that they have only one and two stable adsorption modes respectively.

2) The position of thiophene molecules adsorbed by transition metal Mo is mainly at β and θ. The adsorption energy decreased by 328.795 and 327.868 kJ/mol respectively. The position of thiophene molecules adsorbed by transition metal Pd is mainly at δ and the adsorption energy decreased by 380.654 kJ/mol. The position of thiophene molecules adsorbed by transition metal Sn is mainly at α and δ and the adsorption energy decreased by 272.514 and 512.130 kJ/mol respectively. The stable adsorption behavior was the decrease of system energy after adsorption.

3) Transition metal Mo has more adsorption sites for thiophene, indicating that it has greater reaction activity with thiophene molecules, can adsorb thiophene molecules in different directions, and then catalyze ring opening desulfurization, which is consistent with the reports in relevant experimental literature[8,11].

4) The influence of zero point energy correction should be considered in the calculation of adsorption energy. The adsorption energy deviation without zero point energy correction is large, which is an error that should be considered and eliminated in the energy superposition in quantitative calculation. Compared with other methods, the B3LYP method has higher accuracy and advantages in configuration optimization and energy calculation. The energy data calculated by the CCSD method is similar to that calculated by the B3LYP method.

Conflict of interest

No conflict of interest was reported by the author.

Acknowledgements

This work was supported by Hengyang Science and Technology Bureau (2013KJ23).

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