The Reactivities In Different HgCl Substitution Sites Of PCDDs/PCDFs

Zhengyang Gao [1,a], Peng Ji [1,b]

[1]School of Energy and power Engineering, North China Electric power University, Baoding 071003, China

[a]gaozhyang@163.com,[b]1136139858@qq.com

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Abstract. PCDD/Fs and mercury are contaminants with high toxicity and heavy harm in power plants especially in waste incineration plants, and they could produce polychlorinated and mercury chloride based Dioxins under the environment of high temperature and high pressure. PeCDD, which replaces the positions of 1, 2, 3, 6, 7 sites on PCDDs, has widely sources and high toxicity. Polychlorinated and mercury chloride based Dioxins are dioxin-like substances. DFT (Density Functional Theory) is used to optimize the structures and then calculate HOMO/LUMO and the electrostatic potential energy extreme value is calculated in Multiwfn. By analyzing the bond length and bond angle, HOMO/LUMO and electrostatic potential energy extreme points, it is known that the Cl on HgCl groups is easy to lose electron, known as nucleophilic reaction. All the atoms but the HgCl group and the H atoms are able to adsorb electron, and the Cl atom on C-Cl bond is most likely to react electrophilically.

1. Introduction

Dioxins are recognized as the Persistent Organic Pollutant (POPs). The dioxins, in the atmospheric environment, have complex origins, such as the coal-fired power plants and waste incineration plants which are so close to our daily life [1]. At the same time, there are many Dioxin-like substances in the air except the typical PCDD/Fs, such as the polychlorinated and mercury chloride based dioxins. Their structures and properties are closed to the PCDD/Fs, and more and more researches show that the Dioxin-like substances have a great influence on the environment and especially on human, which is beyond our imagination [2-5].

Dr. Zhang, Gang et al [6] have researched that the contents of Hg and PCDD/Fs in the contaminants from the waste incineration plants occupy a large proportion. The emission range of Dioxins in the typical waste incineration power plants in china is 0. 0042～7. 90ng I-TEQ/ nm^3, and the average value is 0. 561ng I-TEQ/ nm^3, and there is about 85% of the emissions in the waste incineration power plants conform to the limiting value 1. 0ng I-TEQ/nm^3 which is decided by Living Garbage Burning Pollution Control Standards (GB18485-2014). It can be inferred that there has some reactions between Hg and PCDD/Fs. Hu[7] et al have assessed the emission factor of atmospheric mercury is (126. 7± 109. 0) μg · kg^{-1} in the waste incineration plants of many different cities in china, which is calculated by the mercury removal efficiency and the level of Hg in Flue gas mercury facilities . Emissions atmospheric mercury can be extrapolated in the waste incineration plants in 2010, which is 6.1t, and the emission of organic mercury is about 0. 19t. Many researches are revealed that the emissions of Hg in the waste incineration plants increases by years. The limit of the Hg emissions from waste incineration power plants is decided by the Living Garbage Burning Pollution Control Standards (GB18485-2014), which is 1. 0mg/m^3. So the problem of Hg emissions in the plants is really serious [8].

Chen, Tong et al [9] have studied that PCDDs have a negative correlation with the heavy metal elements and PH, which means that they may have a good correlation, so that they can produce the polychlorinated and mercury chloride based dioxins in a series of reactions. Jensen [10] from Sweden have proved that the Hg^{2+} from the power plants can change into methyl mercury after a series of reactions, and the methyl mercury may change into 2-(Chloromercurio) phenol. In the formation

mechanism of PCDDs, Gao Rui et al. have researched that halogenated phenol can be the precursor of PCDDs, and these precursors play a very important role in producing PCDDs, and almost all of the PCDDs are produced by this way. Polychlorinated and mercury chloride based dioxins are a kind of dioxin-like substances, they have the same characters. So 2-(Chloromercurio) phenol may be one of the precursors of the polychlorinated and mercury chloride based dioxins. By the same time, 2-(Chloromercurio) phenol is also a kind of highly toxic pesticides, so there may produce the polychlorinated and mercury chloride based dioxins in the soil. By this way, polychlorinated and mercury chloride based dioxins are very likely to accumulate in human's bodies. Once they can be produced in soils, the society will face a huge crisis. So studying the character of them becomes very important.

2. Computing Method

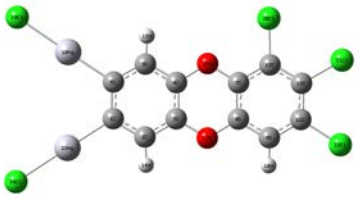
2.1 Theoretical Method.

As there are few researches on polychlorinated and mercury chloride based dioxins, there is a little knowledge on the structure, stability and the active sites of this substance. According to Zhao Jian-Ying's research[12], structures are calculated by using B3LYP/6-31+G(d，p) for the C, H, O, CL and SDD for the Hg in Gaussian 09, which is precise and rapid. Then the HOMO/LUMO comes out. By the same time, the electrostatic potential energy extreme values and their positions are calculated by multiwfn. The structural characteristics and reactivity points of polychlorinated and mercury chloride based dioxins can be inferred.

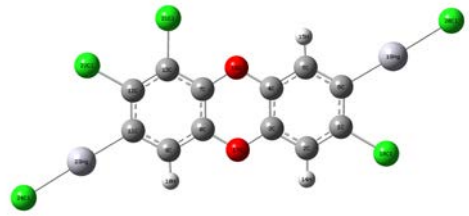
2.2 Theoretical Method.

Polychlorinated and mercury chloride based dioxins have a lot of homogeneous forms like PCDDs, which are changed with the attached positions and the number of HgCl groups and chorine groups. Among the 210 kinds of different structures in PCDDs, PeCDD has the characters of high toxicity, widely distribution. So 1, 2, 3, 6, 7-PCDDs have a good representative and universality. The homogeneous forms which take the place of these four positions can be regard as the typical structure of polychlorinated and mercury chloride based dioxins, the characters can be inferred from polychlorinated and mercury chloride based dioxins from this kind of structure.

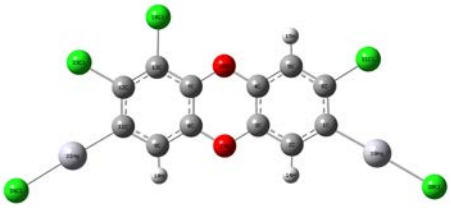
The electrons orbits and the electrostatic energy points are studied for two HgCl groups. There are 10 situations when there are two HgCl groups, shown in picture 1



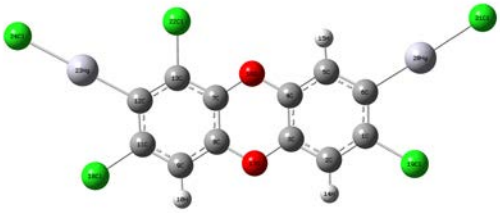
D1: 1, 2, 3-Cl 6, 7-HgCl PCDD



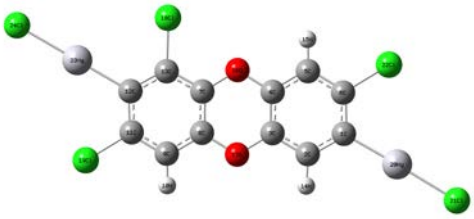
D2: 1, 2, 6-Cl 3, 7HgCl PCDD



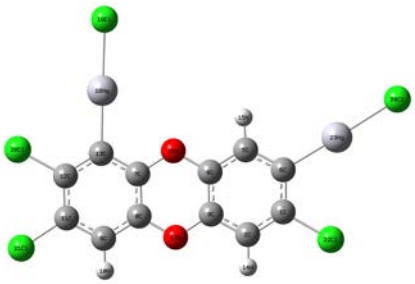
D3: 1, 2, 7-Cl 3, 6-HgCl PCDD



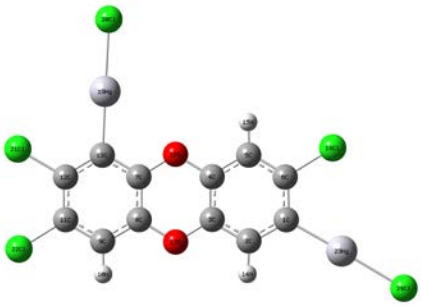
D4: 1, 3, 6-Cl 2, 7HgCl PCDD



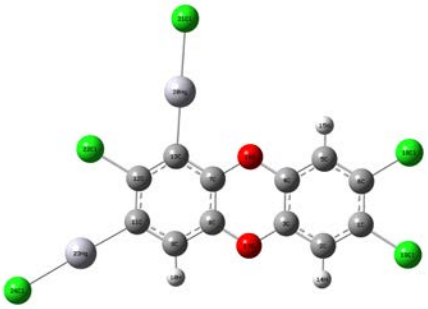
D5: 1, 3, 6-Cl 2, 7-HgCl PCDD



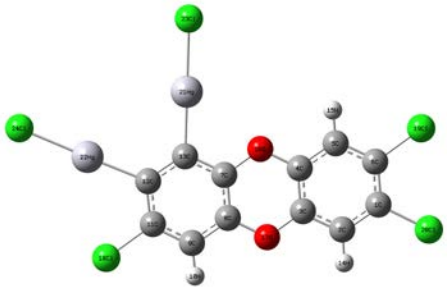
D6: 2, 3, 6-Cl 1, 7HgCl PCDD



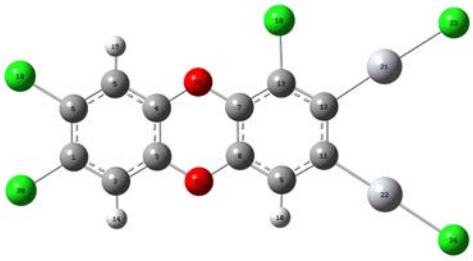
D7: 2, 3, 7-Cl 1, 6-HgCl PCDD



D8: 2, 6, 7-Cl 1, 3-HgCl PCDD



D9: 3, 6, 7-Cl 1, 2-HgCl PCDD



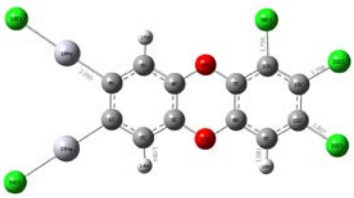
D10: 1, 2, 6-Cl 3, 7HgCl PCDD

Fig1. 3cl-2HgCl-Dioxins

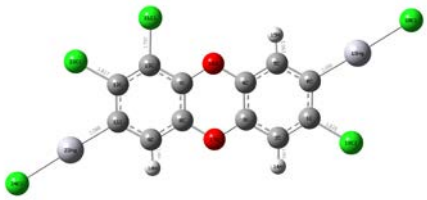
3. Result And Analysis

3.1 Physical Structure.

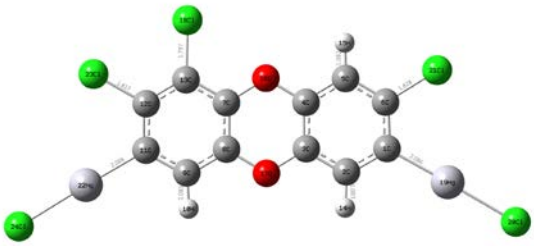
1, 2, 3, 6, 7-Dioxins have widely sources and highly toxic. The influence on electrostatic energy and HOMO/LUMO are studied for HgCl groups in different attached positions. The atomic separations for the optimized structures have shown in picture 2.



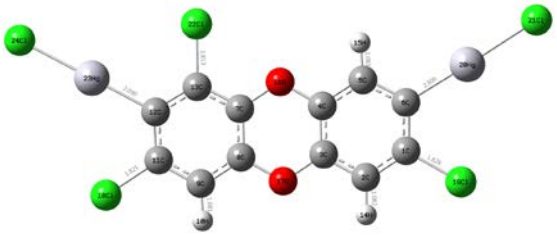
D1: 1, 2, 3-3Cl 6, 7-2HgCl PCDD



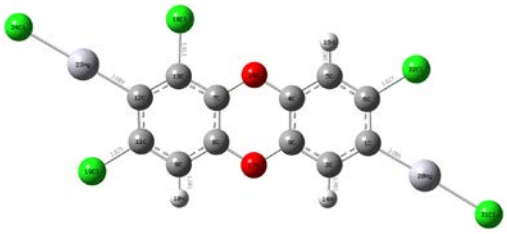
D2: 1, 2, 6-3Cl 3, 7-2HgCl PCDD



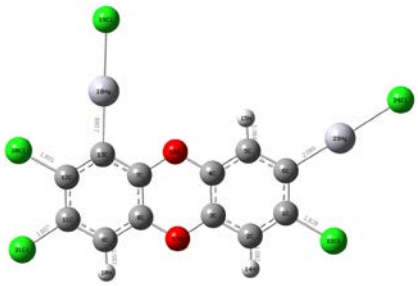
D3: 1, 2, 7-3Cl 3, 6-2HgCl PCDD



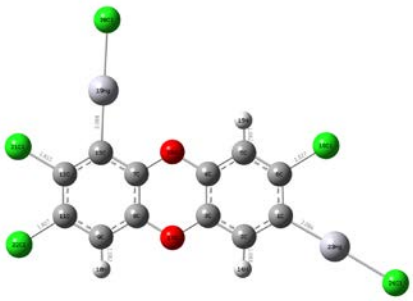
D4: 1, 3, 6-3Cl 2, 7-2HgCl PCDD



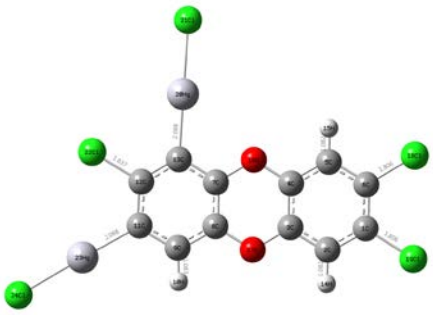
D5: 1, 3, 6-3Cl 2, 7-HgCl PCDD



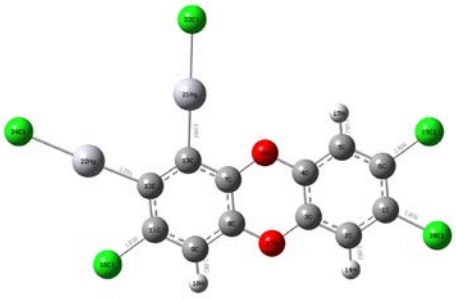
D6: 2, 3, 6-Cl 1, 7-2HgCl PCDD



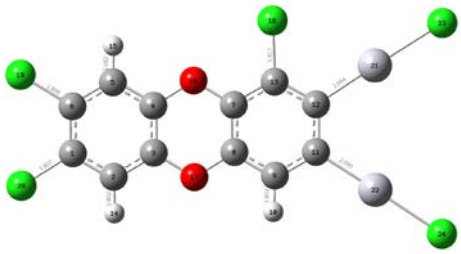
D7: 2, 3, 7-3Cl 1, 6-2HgCl PCDD



D8: 2, 6, 7-3Cl 1, 3-2HgCl PCDD



D9: 3, 6, 7-3Cl 1, 2-2HgCl PCDD



D10: 1, 2, 6-3Cl 3, 7-2HgCl PCDD

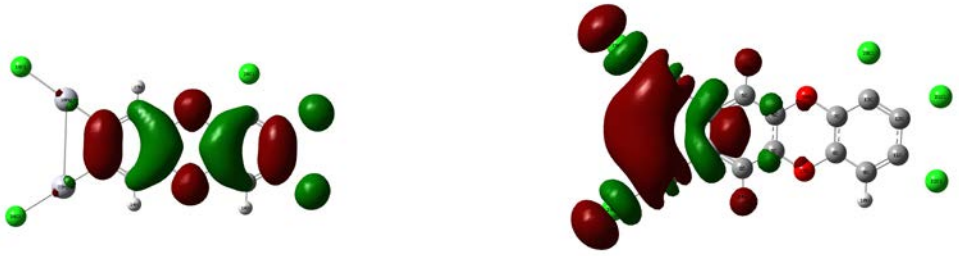
Fig2. : The atomic separation and angle in optimized 2cl-2HgCl-Dioxins

There are some conclusions which are obtained from the data of four Dioxins' bond length in Fig4, the length of c-cl bond is 1. 795～1. 837Å, The bond lengths of c-cl change a lot with the different positions of c-hg bond, the bond length will increase when it is close to c-hg bonds, and the bond energy is lower, which means that the bond of c-hg bond influence the stability of c-cl bond. The reason of this problem may be that the c-hg bonds have interferences on the structure stability, so that c-cl bonds have lower bond energy. The bond length of c-hg is 2. 086～2. 090Å, and there is a little gap between every different structure. The c-hg bond length increase only when c-hg bonds are closed to the oxygen bridge, and its bond energy is lower.

3. 2 HOMO/LUMO.

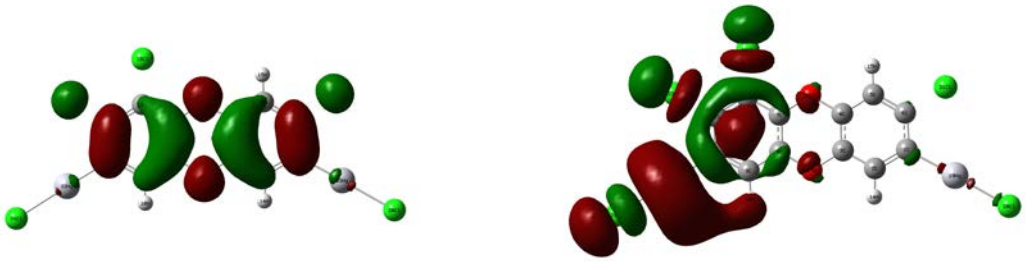
HOMO represents Highest Occupied Molecular Orbital, and LUMO represents Lowest Unoccupied Molecular Orbital. According to the frontier orbital theory, they are all frontier orbitals. HOMO and LUMO influence the active sites of chemical reactions, the other energy molecular orbitals have so little influence which can be ignored.

Optimizing the structures of polychlorinated and mercury chloride based dioxins on Gaussian 09 by the base of B3LYP/6-31G and SDD, then HOMO and LUMO come out, the sizes and locations of electrostatic potential extreme values are calculated after putting the optimized structure into Multiwfn. The HOMO/LUMO of polychlorinated and mercury chloride based dioxins show in the picture 3.

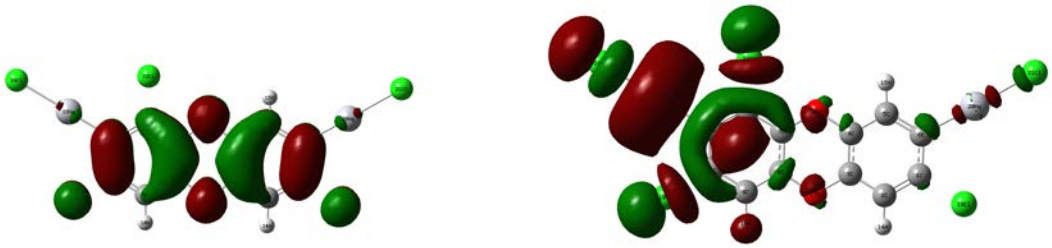


D1: (HOMO/LUMO)

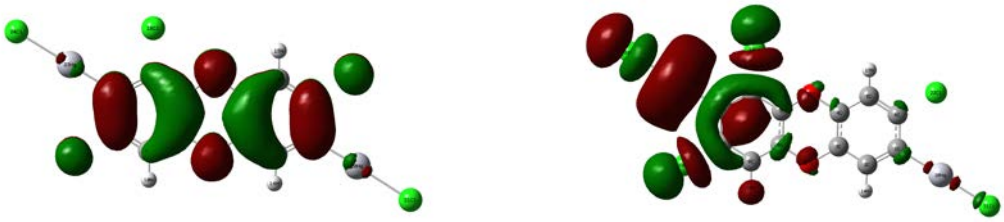
D2: (HOMO/LUMO)



D3: (HOMO/LUMO)

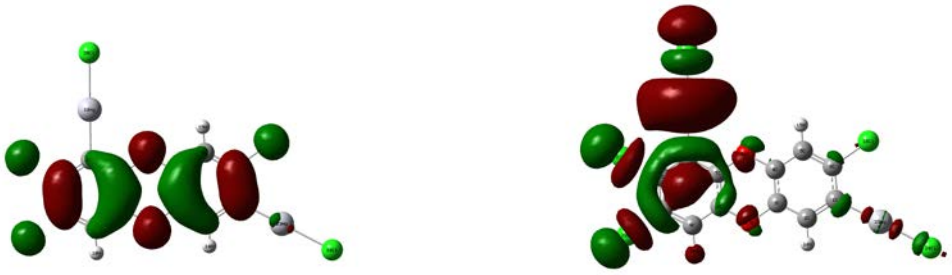


D4: (HOMO/LUMO)

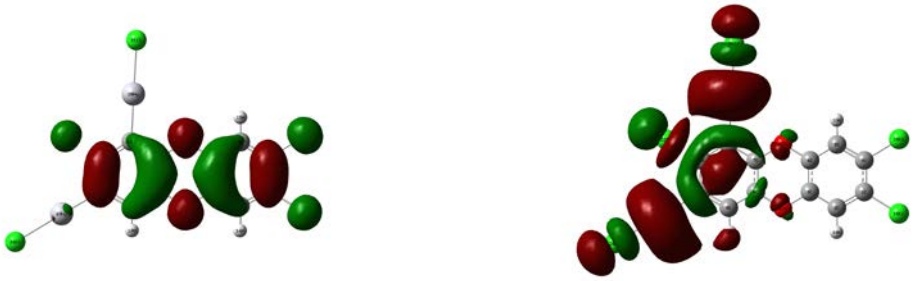


D5: (HOMO/LUMO)

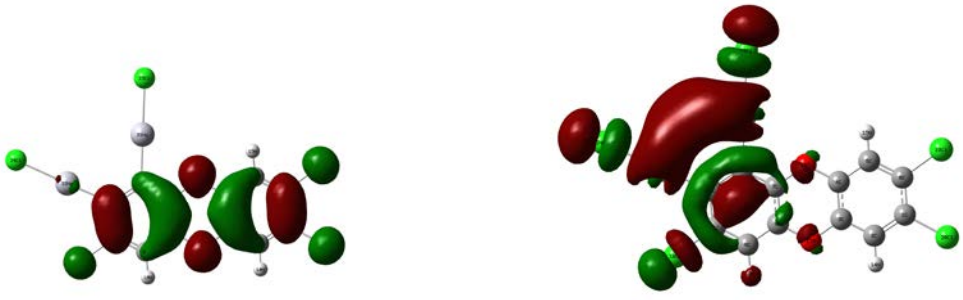
D6: (HOMO/LUMO)



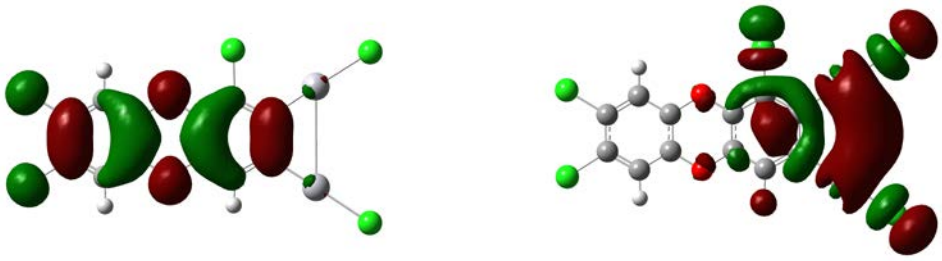
D7: (HOMO/LUMO)



D8: (HOMO/LUMO)



D9: (HOMO/LUMO)



D10: (HOMO/LUMO)

Fig3. Polychlorinated and mercury chloride based Dioxins' HOMO (front) and LUMO (behind)

There are some conclusions learning from the HOMO/LUMO. In the picture of D1 LUMO, the electronic orbits on HgCl functional groups are dense, which means the electrons on the frontier molecular orbital in this area focused. According to the HOMO, all the atoms except the HgCl groups and h atom have complete electronic orbits. They are easily to adsorb electrons, which has a big probability to have a nucleophilic reaction. The electrostatic potential energy minimal value point in this group is -22.35kcal/mol which is on the cl atom of Hg-Cl bonds. The electrostatic potential energy maximal value point is 30.09kcal/mol, which is on the middle position of oxygen bridges. In the same time, the electrostatic potential energy on h atom is 29.89kcal/mol, which is also high.

The HOMO and LUMO from D2 have different conclusions with D1.In LUMO of D2, there is a good orbit on the HgCl group which is close to the Cl nearing the oxygen bridge. The electrostatic potential energy minimal value point is -21.69kcal/mol, which is on the cl atom of HgCl groups. The electrostatic potential energy maximal value point is 36.72kcal/mol, which is on the middle position of two Hg atoms. The electrostatic potential energy on h atom is 28.52kcal/mol, which is also high.As for D3～D8, their HOMO and LUMO are similar with D2. The electrostatic potential energy minimal value points are -21.57kcal/mol, -21.97kcal/mol, -20.97kcal/mol, -21.34kcal/mol, -21.54kcal/mol and -20.69kcal/mol, which is on the cl atom of HgCl groups. The electrostatic potential energy maximal value points are 36.84kcal/mol, 37.12kcal/mol, 35.97kcal/mol, 36.87kcal/mol 37.01kcal/mol and 36.77kcal/mol which are on the Hg nearing oxygen bridges. The electrostatic potential energies on h atoms are 29.91kcal/mol, 28.71kcal/mol 28.96kcal/mol 29.75kcal/mol 29.91kcal/mol and 28.63kcal/mol, which are also high.

In LUMO of D9, D10, there are big frontier orbitals on the Cl atoms of HgCl groups, which are likely to release electrons to have a electrophilic reaction. In HOMO, there is probably to have a nucleophilic reaction on the c-cl bonds, there is a small orbit on HgCl groups and h atoms. The electrostatic potential energy minimal value point is -21.12kcal/mol, which is on the cl atom and hg atom in this group. The electrostatic potential energy maximal value point is 38.12kcal/mol, which is on the middle position of two Hg atoms. The electrostatic potential energy on h atom is 28.32kcal/mol, which is also high. It can be learned that both of two HgCl bonds on the same side have a big opportunity to release the electrons on cl atoms of HgCl groups, which can increase the reactivity of reaction.

4. Summary

1), The bond lengths of C-Cl bonds are 1.795～1.837Å, which are changed for C-Hg bonds' positions, the lengths increase when they close to the C-Hg bonds, which means the stability of C-Cl bonds can be influenced by C-Hg bonds. The C-Hg bonds may influence the bond energy of C-Cl bonds by affecting the structure stability. The bond lengths of C-Hg bonds are 2.086～2.090Å, which are invariant.

2), In HOMO, the electron orbits concentrate on HgCl groups especially the chlorine, which are likely to have nucleophilic reactions. In LUMO, there is a good frontier orbits on all but the HgCl groups and H atoms, especially on chlorine of C-Cl bonds, which is likely to adsorb electrons to have a electrophilic reaction.

3), The electrostatic potential energy minimal value is -22.35～-20.69kcal/mol on chlorine of HgCl groups; The electrostatic potential energy maximal value is 35.97～38.12kcal/mol on Hg of HgCl groups nearing H atoms. The electrostatic potential energies are also big on H atoms.

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