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A Quantum Chemical of Frontier Molecular Orbit of 4-Amino-Cobalt Phthalocyanine†

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Using the B3LYP/3-21G* of the density functional method,quantum chemical study of the charge, bond length and frontier molecular orbit of CoTAPc (4-amino-cobalt phthalocyanine) has been performed. The results show that the nitrogen atoms have strong nucleophilic activity while the hydrogen atoms have strong electrophilic activity in CoTAPc. Secondly, the two nitrogen atoms of N5 and N10 can form covalent bonds with Co atom and the N13 and N18 can connect with Co atom by the coordinate bonds. Thirdly, the composition of the highest occupied molecular orbital (HOMO) of the CoTAPc mainly comes from the contribution of carbon atoms and nitrogen atoms, while the constitution of the lowest unoccupied molecular orbital (LUMO) mainly comes from the contribution of carbon, nitrogen and cobalt atoms. The oxidation of CoTAPc mainly occurs on the C-C bond while its deoxidization mainly happens on the C-C, C-N and Co-N bonds.

Keywords: CoTAPc, Density functional design, Frontier molecular orbit, Quantum chemistry.

INTRODUCTION

The phthalocyanine compound has a highly distant 18 π electronic large ring conjugate system. On this ring, an electronic cloud is evenly distributed and all the C-N bonds have the same length and other properties like optic and electromagnetic properties[1]. The cavity inside the ring of metal-free phthalocyanine has a diameter of 27 nm (Fig. 1). It can compound with many metals to form metal phthalocyanine. Also,various compounds with different properties can be formed by introducing different kinds of sub-chain substitutes to the benzene ring of the phthalocyanine ring. A variety of structures and properties of phthalocyanine compounds make them widely applied in photoelectric material field. Thus,the phthalocyanine compounds are the promising catalysts for visible light[2,3].

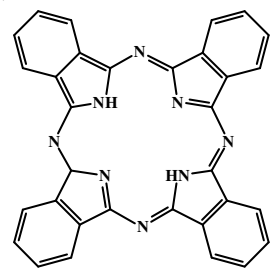

Fig. 1. Molecular structure of metal-free phthalocyanine

Phthalocyanine and metal phthalocyanine (Mpc) are known as promising catalysts for visible light. Due to their unique molecular structure, they have strong absorption for visible light[4]. Also,they have high chemical stability and simple preparation process as well as low production cost. Therefore, since 1990s there have been an active research on the phthalocyanine compounds, such as their computer simulation, photocatalytic oxidation and optoelectronic materials[5-8] and some breakthroughs have been made.This makes the phthalocyanine compounds be widely used in environmental, health care and photoconductive materials[9-11].

With the rapid development of the computer industry and quantum chemistry, the computer simulation and calculation of molecule has been achieved. The calculation results fit molecule's structural properties and reactivity a lot. Since the theoretical research of the CoTAPc (4-amino-cobalt phthalocyanine) has not been performed,the study of its structural properties and reactivity can act as an important complement, which also have a potential guidance for the future experiments and applications. Fig. 1 is the molecular structure of metal-free phthalocyanine.

COMPUTATIONAL METHOD

It is the first time to use the density functional B3LYP/3-21G* method to optimize the structures of X-Z, X-Y and their

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isomers, respectively. Then through comparing their energy and energy gaps, the X-Y isomers are turned out to be the most stable form of CoTAPc. According to a study in the literature[12], the most stable configuration of CoTAPc can be obtained as the X-Y isomers by using the B3LYP/3-21G* of the density functional method. Based on this configuration, the B3LYP/3-21G* of the density functional method is used to perform some quantum chemical study of the charge, bond length and frontier molecular orbital of the CoTAPc. Fig. 2 is the structure and atom numbering of the four amino cobalt phthalocyanine X-Y isomers.

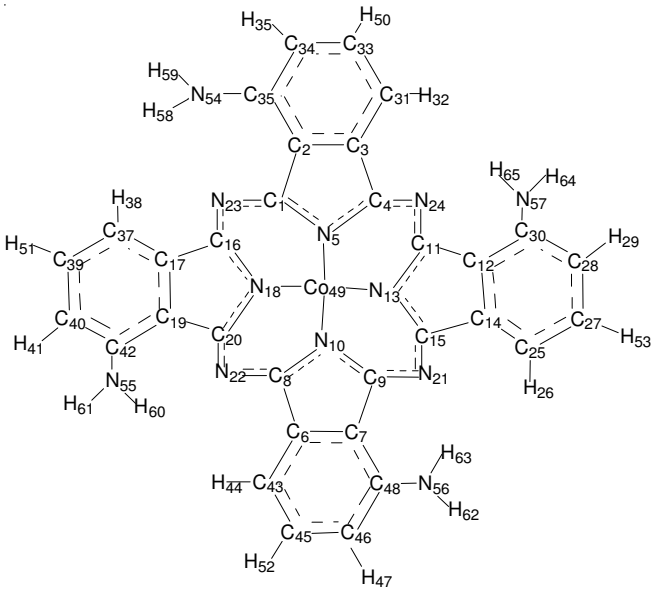


Fig. 2. Structure and atom numbering of the four amino cobalt phthalocyanine XY isomers

RESULTS AND DISCUSSION

Analysis of the charge and bond length: From the atoms' NBO charge distribution of the X-Y isomers of CoTAPc shown in Table-1, it can be seen that the nitrogen atoms of CoTAPc have the negative charge, the hydrogen atoms have positive charge and the carbon atoms have both positive and negative charge. So the nitrogen atoms have strong nucleophilic activity and the hydrogen atoms have strong electrophilic activity. The bond length of atoms and the interaction force of the nearby atoms play the decisive factor on the atom charge during the calculation.From the calculation result, it can be seen that the bond length of N55-H61 and N57-H64 on the CoTAPc are the shortest, about 1.0111; while the bond length of N13-Co49 and N10-Co49 are the longest, about 1.8919.

Table-2, showed, in the CoTAPc molecule, the charge number of Co atom is 1.113058, which indicates that the Co atom and phthalocyanine atom are combined by covalent bond, not combined totally by ionic bond. This is because the nitrogen atom has a high electronegativity that can cause charge accumulation. As shown in Table-1, the electronegativities of N5 and N10 are approximately equal, while the electronegativities of N18 and N13 are higher than N5 and N10. So the four nitrogen atoms on the CoTAPc can be classified into two kinds. One kind is the nitrogen atoms with same-length C-N bonds. These two nitrogen atoms are connected with the Co atom by covalent bonds, such as N5 and N10. The other kind is the nitrogen atoms with different-length C-N bonds. These two nitrogen atoms are connected with Co atom by coordinate bond, such as N13 and N18. Just because of the covalent bonds are formed between N13, N18 and the Co atom on the CoTAPc, MLCT and LMCT are generated between the Co atom and the ligands, which influences the transition of the Q zone of the CoTAPc.

TABLE-1
FOUR AMINO COBALT PHTHALOCYANINE
NBO CHARGE DISTRIBUTION DATA

Atoms	Charge	Atoms	Charge	Atoms	Charge
1C	0.640887	2C	-0.030941	3C	-0.000020
4C	0.595866	5N	-0.834979	6C	-0.000021
7C	-0.030943	8C	0.595901	9C	0.640918
10N	-0.834989	11C	0.630391	12C	-0.024267
13N	-0.835098	14C	-0.007556	15C	0.612396
16C	0.612333	17C	-0.007542	18N	-0.835113
19C	-0.024277	20C	0.630448	21N	-0.716846
22N	-0.714238	23N	-0.716876	24N	-0.714273
25C	-0.226084	26H	0.177650	27C	-0.179037
28C	-0.171653	29H	0.173709	30C	0.335248
31C	-0.229474	32H	0.178321	33C	-0.176126
34C	-0.174290	35H	0.173428	36C	0.339939
37C	-0.226078	38H	0.177649	39C	-0.179037
40C	-0.171654	41H	0.173708	42C	0.335236
43C	-0.229474	44H	0.178328	45C	-0.176126
46C	-0.174284	47H	0.173433	48C	0.339944
49Co	1.113058	50H	0.186750	51H	0.185487
52H	0.186755	53H	0.185487	54N	-0.876350
55N	-0.877649	56N	-0.876353	57N	-0.877647
58H	0.342949	59H	0.302824	60H	0.341431
61H	0.300804	62H	0.302826	63H	0.342956
64H	0.300806	65H	0.341429	–	–

TABLE-2
OPTIMIZATION OF THE GEOMETRY PARAMETERS
OF FOUR-COBALT PHTHALOCYANINE

Atoms	Charge	Bond length
Co	1.113058	–
N5	-0.834979	R(C1, N5) 1.4046
		R(C4, N5) 1.4002
N10	-0.834989	R(C8, N10) 1.4002
		R(C9, N10) 1.4046
N13	-0.835098	R(C11, N13) 1.4047
		R(C15, N13) 1.4006
N18	-0.835113	R(C16, N18) 1.4007
		R(C20, N18) 1.4045

Frontier molecular orbit analysis: To explore the electronic structure and the bonding properties of the CoTAPc, study its molecular orbital, the B3LYP method of DFT, the 3-21G* calculation basis set were used to do the frontier molecular orbital calculations. The result shows that the CoTAPc has 465 molecular orbitals, of which 162 occupied molecular orbital and 303 unoccupied molecular orbital. The HOMO of the CoTAPc is -422.54793 kJ/mol and the LUMO is -247.11204 kJ/mol. The orbital energy level difference between HOMO and LUMO plays an important role when explaining the Q zone of electronic absorption spectrum. It reflects that the energy an electron needs when it transfer from HOMO to LUMO is 175.43589 kJ/mol on the CoTAPc.

From the frontier molecular orbit of the CoTAPc shown in Fig. 2, it can be seen that HOMO mostly distribute on the carbon atoms, which is connected with the nitrogen atoms. The four carbon atoms, on which the benzene ring of the different indole unit are and on the nitrogen atoms of the amino substituent. However, the Co atoms and the nitrogen atoms on the pyrrole or between the 4-isobenzazoles and other carbon atoms as well as the hydrogen atoms almost have no distribution of orbits. LUMO mostly distributes on the Co atoms, the 4-isobenzazoles, the nitrogen atoms between the 4-isobenzazoles and the nitrogen atoms which are on the amino substituent[13].

After squaring the molecular orbital coefficients of each atom, then through the normalization process, the rate contribution of HOMO and LUMO of each atom on the CoTAPc can be get, as shown in Table-3. Although the output file of molecular orbital calculation can show results with a precision of fifth decimal at most, it can be compared the size of results by looking at the fourth decimal. So the results are only needed to keep to fourth decimal when calculating the rate contribution of each atom in the molecular orbital.

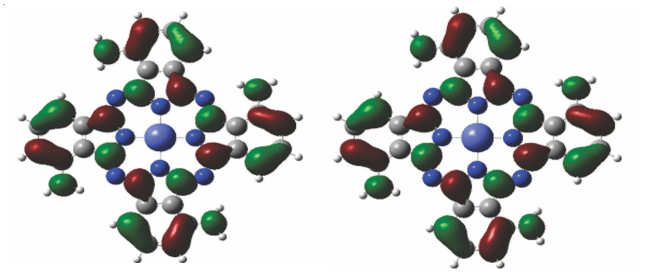
TABLE-3
CONTRIBUTION RATE OF EACH ATOM TO HOMO AND LUMO ORBITS (%)

Atoms	Contribution rate to HOMO (%)	Contribution rate to LUMO (%)
C	85.4696	65.3120
N	14.5124	33.0021
Co	0.0181	1.6864

Note: It can be ignored the orbital contribution when is less than 0.0001 %.

From Fig. 2 and Table-3 we obtain the following observations: (a) The HOMO constitution of CoTAPc mostly comes from the carbon atoms (of which the atomic contribution is 85.4694 %) and the nitrogen atoms (of which the atomic contribution is 14.5124 %). At the same time, the Co atoms have a very small contribution to the HOMO, about 0.0181 %. (b) The LUMO constitution mainly comes from the carbon atoms (of which the atomic contribution is 65.3120 %), the nitrogen atoms (of which the atomic contribution is 33.0021 %) and the Co atoms (of which the atomic contribution is 1.6864 %). (c) The hydrogen atoms have no contribution to the HOMO or the LUMO.

According to the molecular orbital theory, the frontier orbit (HOMO, LUMO) and the molecular orbit nearby have the significant influence to the activity of the compound. The HOMO and the molecular orbital nearby have a function of preferentially providing electrons. The LUMO and the empty orbit nearby play an important role in accepting electrons[14]. So it can be inferred that when the CoTAPc has an oxidizing reaction, the change of the bond length mainly happens on the C-C bonds while others almost have no or very little change. However, when they have a reduction reaction, the change of the bond length will happen on the C-C, C-N, Co-N. For the compound of CoTAPc, the C-H bonds will have no change in any reactions (Fig. 3).



: Carbon atoms; :Nitrogen atoms ; : Hydrogen atoms; : Cobalt atoms

Fig. 3. Frontier molecular orbital of the four amino cobalt phthalocyanine

Conclusion

Through the quantum chemistry calculation and the frontier molecular orbital analysis, we got the following conclusions: (a) All the nitrogen atoms on the stable configuration of CoTAPc have the negative charge, all the hydrogen atoms have positive charges, while the carbon atoms can have both negative charge and positive charge. (b) In the CoTAPc molecule, the two nitrogen atoms N5 and N10 form covalent bonds with Co atom, while the N13 and N18 connect with Co atom by the coordinate bonds. (c) The constitution of HOMO of the CoTAPc mainly comes from the contribution of carbon atoms and nitrogen atoms. The constitution of LUMO mainly comes from the contribution of carbon atoms, nitrogen atoms and Co atoms.

ACKNOWLEDGEMENTS

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