The Structure and Electronic Properties of C_{80} Carbon Nanotube

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Abstract. The possible geometrical and electronic structures of C_{80} carbon nano-tube (CNTs) are optimized by using the density functional theory at B3LYP/6-31G level. The stability of the ground state structure has been studied, and its electronic properties have been calculated. The calculate results showed that C atoms are sp^2 hybridization, but the coalescent between the two C atoms includes covalent bond and a spot of electrovalent bond. The molecular orbitals of C_{80} Carbon Nanotube had obvious delocalization characteristics.

Introduction

Carbon nanotubes attracted scientist's great interests[1-5] since it was firstly found by Japanese researcher Iijima[6] in 1991. In 1993, single-walled carbon nanotubes have been successfully synthesized by Iijima and Ichihashi[7]. Carbon nanotubes also had particular electric characteristics because Dad[8] found that the radial resistance of carbon nanotubes is greater than the axial resistance, and the anisotropy of resistance increased with decreasing temperature. The theoritical computation and measured results of Mintmire etc.[9], Ebbesent etc.[10] and Huang etc.[11] showed that C_{80} carbon nanotubes had various characteristics such as semiconductor, conductor and superconductor because of the different structures. Many potential applications have been proposed for carbon nanotubes, including nanometer-sized semiconductor devices, probes, high-strength composites, energy storage and energy conversion devices and catalysts support, and we know that the applications is based on their good thermal conductivity , the special mechanical property, the high aspect ratio and hollow structure with nano-scale of carbon nanotubes. But people have few studies on the small carbon nanotubes. This paper is the study of the structure and electronic properties of small C_{80} carbon nanotubes with density functional theory. This study can provide theoretical basis for synthesis of small carbon nanotubes in the future and in favor of people knowing more about small C_{80} carbon nanotubes

Calculation Methods

In order to find the structure of C_{80} carbon nanotube with lowest energy, we took a large number of possible initial configurations into consideration. We got the stable configuration of C_{80} carbon nanotube through optimizing its structure at B3LYP/6-31G level. We knew that they don't have imaginary frequency after analyzing the frequency of the optimized structures. We got the stable structure of C_{80} carbon nanotube and determined the basic structure of clusters based on their energy at the premise of considering their spin multiplicity. All calculations were completed by the Gaussian03 program.

Results and Discussion

Ground-state Configuration

Carbon nanotubes are not always straight, but anomalistic in the local area. This is due to the

appearance of five-membered rings or seven-membered rings when six-membered rings braided. Five-membered rings or seven-membered rings also play an important role in carbon nanotubes. On the one hand, carbon nanotubes become convex when five-membered rings arise with the six-membered rings gradually extended. On the other hand, carbon nanotubes become concave when seven-membered rings arise. Ground-state configuration of C_{80} carbon nanotubes through optimizing its structure is shown in figure 1. C_{80} carbon nanotube is composed of thirty six-membered rings and twelve five-membered rings, and there is no seven-membered rings, the C_{80} carbon nanotubes belong to standard straight carbon nanotubes. Each carbon atom bonds with the three surroundings, and the length of C-C single bond in C_{80} carbon nanotube is between 0.145nm and 0.150nm, the changed length of C=C double bond is between 0.139nm and 0.145nm. In this paper, ground-state structure's symmetry is C_1.

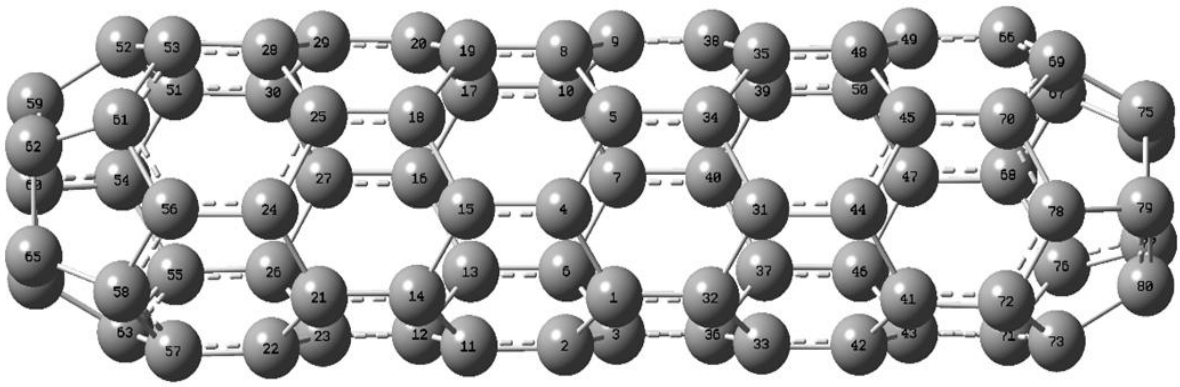

Fig.1 Ground-state Structure of C_{80} carbon nanotubes

NBO Analysis of C80 Carbon Nanotubes

In order to study the bonding character and charge distribution of nanotubes, we had population analysis for optimized C_{80} carbon nanotubes by means of Natural Bond Orbitals（NBO）. Table 1 lists out natural electron configuration and net charge of each carbon atom (The carbon atomic ordinal numbers in table.1 are consistent with that in Fig.1).

Firstly, we analyzed the bonding styles between carbon atoms in C_{80} carbon nanotubes. Ground-state free carbon atom's electronic configuration of outer space is $2s^2 2p^2$ on the basis of the Pauli exclusion principle and the lowest energy principle. The data in table 1 show that there were 0.86~0.94 electron on each 2s orbital where should have two electron. It indicates that partly electron in 2s orbital transferred to 2p orbital, so there was only one electron in 2s orbital. Moreover, it was hybridization with two 2p orbital, and formed three sp^3 orbital were almost equivalent to each other. The three hybridization orbitals formed σ type bond with "head-to-head" linkage in C_{80} carbon nanotubes, and σ type bond composed the framework of C_{80} carbon nanotubes because it had stronger bond energy and stable structure. Then each carbon atom has one residual electron, and this electron formed π type bond which can't exist alone but attaching to σ type bond. In addition, π type bond occupied the leading position of electronic properties in C_{80} carbon nanotubes because it's easy to be broken and active chemistry.

Secondly, we analyzed charge distribution in atom orbital and electrical property. In C_{80} carbon nanotubes, 2s orbital lost electrons and its total electrons are between 0.86~0.94. Otherwise, 2p orbital gained electron and its total electrons are between 2.95~3.18, all atomic 3p orbital have the electronic from 0.01 to 0.02. From the global aspect, C_{80} carbon nanotubes are electroneutrality, but it hasn't equal electrons on each atom, and some atoms have more electron than others. This means that the coalescent between the two carbon atom includes covalent bond and a spot of electrovalent bond.

Tab.1 The natural electron configuration of C_{80} CNTs

No.	Natural Electron Configuration	Net Charge	No.	Natural Electron Configuration	Net Charge
1	2S(0.86)2p(3.13)3p(0.01))	-0.005	41	2S(0.88)2p(3.07)3p(0.01)	0.039
2	2S(0.86)2p(3.13)3p(0.01)	-0.009	42	2S(0.86)2p(3.16)3p(0.01)	-0.030
3	2S(0.86)2p(3.13)3p(0.01)	-0.002	43	2S(0.88)2p(3.06)3p(0.01)	0.054
4	2S(0.86)2p(3.13)3p(0.01)	-0.005	44	2S(0.86)2p(3.15)3p(0.01)	-0.024
5	2S(0.86)2p(3.13)3p(0.01)	-0.005	45	2S(0.87)2p(3.11)3p(0.01)	0.012
6	2S(0.86)2p(3.13)3p(0.01)	-0.003	46	2S(0.86)2p(3.19)3p(0.01)	-0.058
7	2S(0.86)2p(3.13)3p(0.01)	-0.003	47	2S(0.88)2p(3.05)3p(0.01)	0.057
8	2S(0.86)2p(3.13)3p(0.01)	-0.005	48	2S(0.86)2p(3.15)3p(0.01)	-0.027
9	2S(0.86)2p(3.14)3p(0.01)	-0.009	49	2S(0.88)2p(3.08)3p(0.01)	0.032
10	2S(0.86)2p(3.13)3p(0.01)	-0.002	50	2S(0.86)2p(3.16)3p(0.01)	-0.029
11	2S(0.86)2p(3.16)3p(0.01)	-0.025	51	2S(0.88)2p(3.16)3p(0.01)	-0.054
12	2S(0.86)2p(3.12)3p(0.01)	0.004	52	2S(0.92)2p(3.03)3p(0.01)	0.041
13	2S(0.86)2p(3.15)3p(0.01)	-0.020	53	2S(0.88)2p(3.18)3p(0.01)	-0.072
14	2S(0.87)2p(3.09)3p(0.01)	0.028	54	2S(0.93)2p(2.95)3p(0.01)	0.106
15	2S(0.86)2p(3.14)3p(0.01)	-0.008	55	2S(0.88)2p(3.17)3p(0.01)	-0.059
16	2S(0.87)2p(3.11)3p(0.01)	0.015	56	2S(0.88)2p(3.14)3p(0.01)	-0.032
17	2S(0.86)2p(3.15)3p(0.01)	-0.017	57	2S(0.88)2p(3.19)3p(0.01)	-0.075
18	2S(0.87)2p(3.10)3p(0.01)	0.025	58	2S(0.92)2p(2.97)3p(0.01)	0.096
19	2S(0.86)2p(3.15)3p(0.01)	-0.025	59	2S(0.94)2p(3.02)3p(0.01)	0.025
20	2S(0.86)2p(3.12)3p(0.01)	0.003	60	2S(0.94)2p(3.14)3p(0.02)	-0.091
21	2S(0.86)2p(3.15)3p(0.01)	-0.028	61	2S(0.92)2p(2.98)3p(0.01)	0.083
22	2S(0.88)2p(3.08)3p(0.01)	0.032	62	2S(0.94)2p(3.06)3p(0.01)	-0.008
23	2S(0.86)2p(3.15)3p(0.01)	-0.029	63	2S(0.92)2p(3.02)3p(0.01)	0.048
24	2S(0.87)2p(3.11)3p(0.01)	0.013	64	2S(0.94)2p(3.01)3p(0.01)	0.035
25	2S(0.86)2p(3.15)3p(0.01)	-0.024	65	2S(0.93)2p(3.08)3p(0.01)	-0.026
26	2S(0.88)2p(3.05)3p(0.01)	0.056	66	2S(0.88)2p(3.18)3p(0.01)	-0.074
27	2S(0.86)2p(3.19)3p(0.01)	-0.058	67	2S(0.92)2p(3.02)3p(0.01)	0.048
28	2S(0.88)2p(3.07)3p(0.01)	0.039	68	2S(0.88)2p(3.17)3p(0.01)	-0.058
29	2S(0.86)2p(3.16)3p(0.01)	-0.030	69	2S(0.92)2p(2.97)3p(0.01)	0.094
30	2S(0.88)2p(3.06)3p(0.01)	0.055	70	2S(0.88)2p(3.14)3p(0.01)	-0.031
31	2S(0.87)2p(3.10)3p(0.01)	0.025	71	2S(0.88)2p(3.16)3p(0.01)	-0.054
32	2S(0.86)2p(3.15)3p(0.01)	-0.025	72	2S(0.88)2p(3.18)3p(0.01)	-0.071
33	2S(0.86)2p(3.12)3p(0.01)	0.002	73	2S(0.92)2p(3.03)3p(0.01)	0.040
34	2S(0.86)2p(3.14)3p(0.01)	-0.007	74	2S(0.94)2p(3.01)3p(0.01)	0.033
35	2S(0.87)2p(3.09)3p(0.01)	0.027	75	2S(0.93)2p(3.07)3p(0.01)	-0.023
36	2S(0.86)2p(3.15)3p(0.01)	-0.017	76	2S(0.93)2p(2.95)3p(0.01)	0.105
37	2S(0.87)2p(3.11)3p(0.01)	0.015	77	2S(0.94)2p(3.14)3p(0.02)	-0.090
38	2S(0.86)2p(3.16)3p(0.01)	-0.025	78	2S(0.92)2p(2.98)3p(0.01)	0.083
39	2S(0.86)2p(3.12)3p(0.01)	0.004	79	2S(0.93)2p(3.06)3p(0.01)	-0.010
40	2S(0.86)2p(3.15)3p(0.01)	-0.020	80	2S(0.94)2p(3.02)3p(0.01)	0.026

The Energy Levels and Orbital of C80 Carbon Nanotubes

The frontier molecular orbital theory holds that: it only relates to frontier molecular orbital when the molecular carrying out chemical reaction, and electrons from one molecular HOMO orbital transferred to others LUMO orbital, so orbital nearby HOMO and LUMO determines the chemical properties of the molecule. HOMO orbital reflects the ability of loose electron in the clusters. According to Koopmanns theorem, the negative value of HOMO orbital shows the first ionization potential, and the higher of HOMO orbital energy, the lower of the first ionization potential. While

the value of LUMO orbital approximates with electron affinity, and the lower the LUMO orbital, the easier the molecular gain electrons. The HOMO and LUMO in C_{80} carbon nanotubes are -5.213eV and -4.330eV , and the energy gap of C_{80} carbon nanotubes is -0.883eV. We got the HOMO and LUMO orbital of C_{80} carbon nanotubes (in Fig.2, the left one is HOMO orbital and the right one is LUMO) to describe the orbital shape of C_{80} carbon nanotubes intuitive。

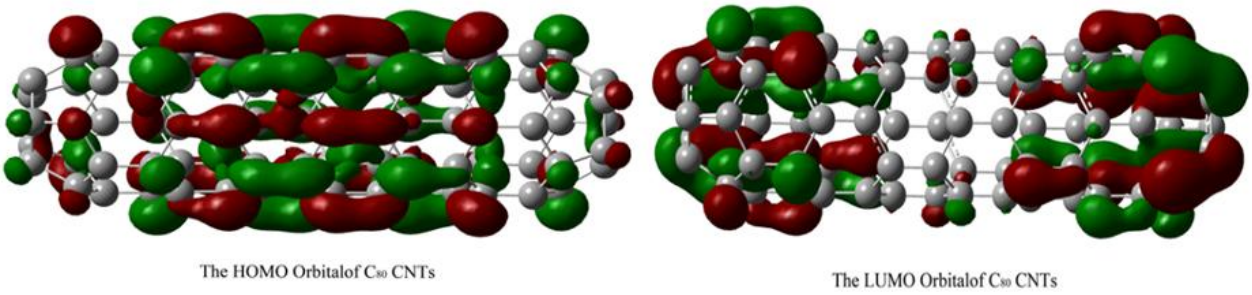

Fig.2 The HOMO and LUMO Oribita of C_{80} CNTs

From figure 2, we can see that the HOMO orbital is mostly composed of the middle atoms of C_{80} carbon nanotubes while the LUMO orbital is mostly composed of the two ends atoms, indicating that the middle atoms of C_{80} carbon nanotubes have higher chemical activity. Some electron clouds are around several atoms, this shows that the molecular orbitals of C_{80} carbon nanotube has delocalization characteristics, and the delocalization π bond make the molecular more stable.

Conclusion

The ground state structure of C_{80} carbon nanotubes has been studied and its electronic properties have been calculated by using the density functional theory at B3LYP/6-31G level.

1. C_{80} carbon nanotube is composed of thirty six-membered rings constituting a hollow tube and each of ends capped by half carbon cage (six five-membered rings).

2. From the NBO analysis of C_{80} carbon nanotubes, we can see that about one electron of 2s orbital transferred to 2p orbital, and formed three σ type bond by sp^2 hybridization. Besides, about one residual electron formed π type bond on the surface of C_{80} carbon nanotubes, and the coalescent between two C atoms includes covalent bond and a spot of electrovalent bond.

3. From the energy levels and orbital of C_{80} carbon nanotubes, we can see that the HOMO orbital is mostly composed of middle atoms in C_{80} carbon nanotubes while the LUMO orbital is composed of two terminal atoms, and the molecular orbitals of C_{80} Carbon Nanotube have obvious delocalization characteristics.

References

[1]Pan H, Li J, Feng Y P,. Carbon Nanotube for Supercapacitor [J]. Nanoscale Res Lett, 2010, 5: 654-668.

[2]Ppstm H W C, Teepen T, Yzo Zhen, et al. Carbon nanotube singleelectron transistors at room temperature [J]. Science, 2001, 293:76.

[3]Han Zhu, Li Guibao, Pu Guangzhe. Synthesis and growth mechanism of fullerene C60 carbon Nanotube [J]. Qingdao University of Science and Technology, 2010, 31 (2).

[4]Li Q, Zhang X, DePaula R F, et al. Sustained growth of ultralong carbon nanotube arrays for fiber spinning [J]. Advanced Materials, 2006, 18: 3160-3163.

[5]Zhang R, Zhang Y, Zhang Q, et al. Growth of half-meter long carbon nanotubes based on Schulz-Flory distribution [J]. ACS Nano, 2013, 7(7): 6156-6161.

[6]Iijima S. Helical microtubules of graphitic carbon. Nature, 1991, 354: 56–58.

[7]Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1 nm diameter. Nature, 1993, 363: 603–605.

[8]DAI H J, WONG E W, LIEBER C M. Procing electrical transport in nanomaterials: conductivity of individual carbon nanotubes[J]. Science, 1996, 272(526): 523-526.

[9]MINTMIRE J W, DUNLAP B I, WHITE C T. Are fullerene tubules metallic[J]. Physical Review Letters, 1992, 68(5): 631-634.

[10]EBBESEN T W, LEZEC H J, HIURA H, et al, Electrical conductivity of individual carbon nanotubes[J]. Nature, 1996, 382(6586): 54-5.

[11]HUANG Y, OKADA M, TANAKA K, et al, Estimation of superconducting transition temperature in metallic carbon nanotubes[J]. Physics Review B, 1996, 53(9): 5129.