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We have proposed that the D_2-C_{84} has the chiral character by the model of C_{84}. The first—principle theoretical calculation results shown that the D_2- and D_{2d}-C_{84} have the similar cohesive energy and gap. And the shapes of the two isomers are similar. So the two isomers should have the same stability. Since the D_2-C_{84} has chiral character, the ratio of the two isomers is 2 : 1 in experiment. We have also discussed the stability and symmetry of the isomers of fullerene with C_{84}, and point out that not only the stable isomer should satisfied the closed electric shells, smallest cohesive energy and the largest gap, but a/so the curvature of the most stable isomer should be spreaded as uniformly over the cage as possible.

D_2-C_{84}的手征同素异形体

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摘　要　本文指出 D_2-C_{84}具有手征特性，这个结论可以很好地解释为什么实验上获得的 D_2-和 D_{2d}-C_{84}的产量之比为 2 : 1. 我们以 C_{84}为例就福勒烯(fullerene)的同素异形体(isomer)的结构、对称性及稳定性进行了定性的讨论。

关键词　福勒烯，C_{84}，手征

分类号　O561.1

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A Chiral Structure for the Fullerene D_2-C_{84}*

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Abstract A chiral structrure for the fullerene D_2-C_{84} is proposed. The conclusion explains why the formed ratio of D_2-to D_{2d}-C_{84} in the experiment is 2 : 1. The structure and symmetry and stability of fullerene isomer is discussed.

Key words Fullerene, C_{84}, chiral isomer

1 Introduction

Following the development of a method for bulk synthesis of C_{60}[1], the isolation of higher fullerenes ranging from C_{76} to C_{96} has been achieved using chromatographic techniques[2-4]. The structures of C_{60} and C_{70} have been determined[3]. Both conform to the fullerene pattern of three-connected polyhedral cage with n atoms (for $n \geqslant 20$) arranged in 12 pentagons and $(1/2)n-10$ hexagonal rings, and the n atoms are on the vertexes of the polyhedral. The results of theory and computer simulation show that the fullerene of n carbon atoms has many isomers based upon the different sets of the pentagons. For example C_{78} has two thousands isomers. Hence it is very difficult to determined which isomer is most stable for so many isomers by the first-principle calculation. Thus the stability of isomers is first discussed upon general chemical arguments. It is pointed out that the stable fullerene must satisfied[5,6]: (1) the covalent bond of the carbons in the fullerene must be similarly to sp^2 hybridized, thus the networks can form a cage structure, and the cage is constituted of pentagons and hexagons; (2) the pentagons are not abutted as possible; (3) closed electronic shells; (4) a small cohesive energy; (5) a large band gap between HOMO and LUMO; and (6) the geometric structure of the cage should be as little curvature as possible, so that the σ-skeleton achieves most nearly the ideal sp^2 geometry, and the overlap between adjacent π-like orbital is as large as possible. It is general thought that the fullerene satisfy criteria (1); the criteria (2) relates to the symmetry of fullerene; the criteria 3-5 must be determined by the first-prin-

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ciple calculation. The criteria (3) is the most important, because the fullerene is unstable if the criteria (3) is not satisfied. We will discussed the criteria (6) in the following. Fowler et. al[6]. have first proposed several formulae for determining the stability of the fullerene by geometry theory and Huckle molecular orbital theory. However, their theory can not firmly predict the most stable isomer in the isomers. For example, the Fowler's theory predicts that the stable isomers of C_{84} are successively T_d-, D_{6h}-, C_{2v}-, D_{2d}-, D_2- and helical D_2-C_{84}. In fact the most stable isomers are the D_{2d}- and D_2-C_{84}. We point out that the D_2-C_{84} has chiral struchure, which means the D_2-C_{84} has two isomers, and we also discussed the stability and symmetry of the isomers of fullerene upon the geometry structure.

2 The chiral structure of D_2-C_{84}

Zhang et. al.[7,8] have detail calculated the probability stable isomer, which have preliminary sifted by Fowler, with first—principle theory. The calculated results are shown in table 1, here is the results for C_{84} only. It can be seen from table 1 that the order of the cohesive energy from large to small is D_2-, D_{2d}-, C_2-, D_{6h}-, T_d- and helical D_2-C_{84}; and the order of gap of energy from large to small is T_d-, helical D_2-, D_{6h}-, D_{2d}-, D_2-, and C_2-C_{84}. In spite of the results obtained with different method are different, the trend of the variety of the cohesive energy and gap is the same as shown in table 1. Only upon the table 1 it does not identify which isomer is the most stable. It is clear from table 1 that the isomer with smallest cohesive energy of is not with the largest gap. D_2 and D_{2d}-C_{84} are the most stable isomers by the cohesive energy. Recently the two isomers have been obtained in experiment and there structures have been determined by ^{13}C NMR[9]. The formed ratio of D_2- and D_{2d}-C_{84} is 2 : 1.

Table 1 Structural and electronic data for C_{84}(after ref[7])

Energy[a)]	ΔE[b)]	Symmetry	HOMO—LUMO[c)]	NMR[d)]
0.325		D_2	0.823	21
	0.033	D_{2d}	0.844	11
	0.263	C_2	0.660	42
	0.300	D_{6h}	1.140	5
	1.224	T_d	1.489	4
	1.902	D_2(helical)	1.277	21

* a) The energy here is the cohesive energy of the fullerene with respect to the 84 carbons graphite in the unit ev/atom.

b) ΔE is the cohesive energy of the isomer relative to the ground—state D_2-C_{84}.

c) HOMO—LUMO energy separation is in the unit of ev.

d) The value nuder NMR is the number of distinct of NMR lines.

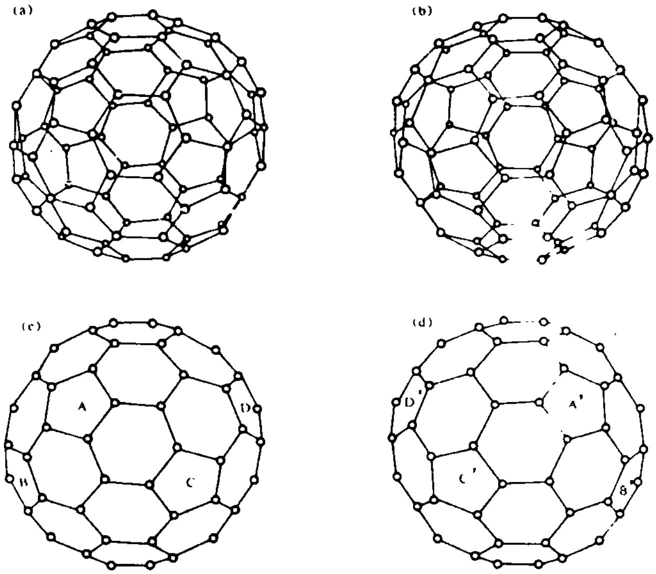

Fig. 1 (a) The geometry structure of D_2-C_{84}; (b) is the mirror image of (a); (c) and (d) are the projection of (a) and (b) on the paper respectively

On the other hand, we will note from table 1 that the cohesive energy and gap of D_2-and D_{2d}-C_{84} are almost same, which means that the two isomers have the same stability. So the output of the two isomers should be the same. In fact the ratio is 2 : 1. When we study the stability and symmetry of isomers, the chiral structure of D_2-C_{84} has been examined by the geometry model of the isomers as shown in fig. 1. Here the fig. (b) is the mirror image of (a). Fig. (c) and (d) are the projection of (a) and (b) on the paper respectively. For clear we denote the four pentagons in fig. (c) and (d) with A, B, C, D, and A′, B′, C′, D′ respectively. Here A′, B′, C′ and D′ are mirror image of A, B, C, D respectively. Since D_2-C_{84} has chiral characterization, it has two isomers and the stability of the two isomers are same. Thus it can be explained why the output ratio of D_2- and D_{2d}-C_{84} in experiment is 2 : 1.

3 The stability and symmetry of isomer

From table 1 we have pointed above that the smallest cohesive energy and the

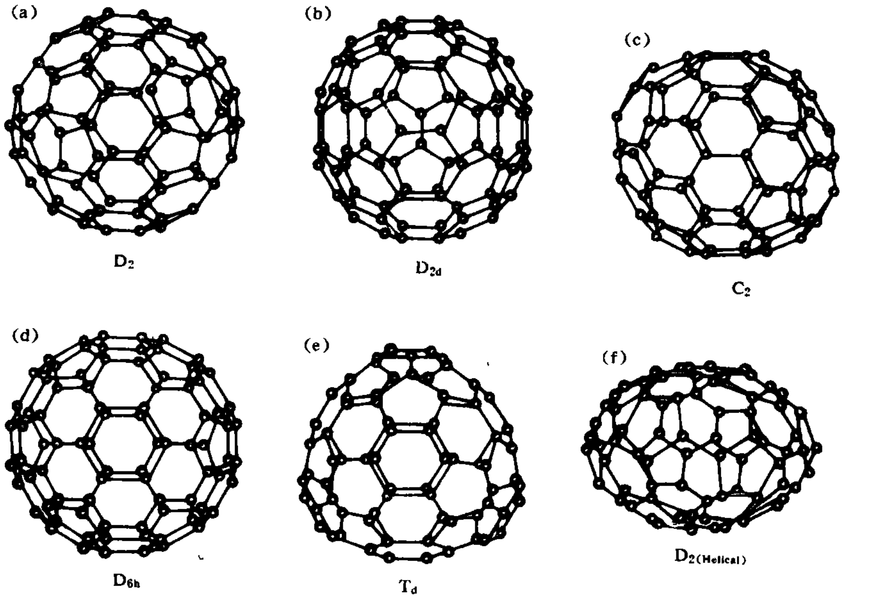

Fig. 2 The structure patterns of six isomers for C_{84} (after ref. [7])

largest gap could not satisfied simultaneously. Thus it is difficulty to determent which isomer is the most stable by the firt-principle calculation. It was pointed that the stable isomer should have as higher symmetry as possible[5]. In fact it is not true. We point here that the curvature of the geometry structure of a stable isomer should be as well—distributed as possible. In the isomers of C_{60}, I_h-C_{60} with highest symmetry is the most stable one[10]. But in C_{84} the situation is different. It is seen from table 1 that the D_2- and D_{2d}-C_{84} would be the most stable isomers upon the cohesive energy, but the T_d- and D_{6h}-C_{84} should be the most stable upon the gap. The experiment results shown that the D_2- and D_{2d}-C_{84} are the most stable. Thus the isomers of C_{84} with higher symmetry may not be the most stable. Here we discuss the stability of isomer of C_{84} upon the shape of isomer. The shape of isomer D_2-, D_{2d}-, D_2-, D_{6h}-, T_d- and helical D_2-C_{84} are shown in fig. 2. It is ease seen from the models of these isomers that the curvature of D_2- and D_{2d}-C_{84} are the most well—distributed and the shapes of the two isomers are similarly. The isomers with other symmetry have no such character. For example the shape of T_d-C_{84} is similar to the truncated icosahedron. The chemical bond of T_d-C_{84} at the edge of the icosahedron has larger curvature, and so the adding elastic potential energy is created. The shape of D_{6h}-C_{84} is similar to the thick dick, and the bond at the edge of the dick has larger curvature, so the adding potential energy is induced.

Because of the adding elastic potential energy, the isomer with the well—distributed curvature is more stable than that with the bad—distributed curvature. So the most stable isomer can be exact identified upon the first—principle theoretical calculation and the shape of the isomer. The quantity of analysis the effect of the difference of the isomer shape to the stability should be studied further.

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