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The effect of complementary units on the stability of higher fullerenes C_{84}

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We have studied the influence of so-called *complementary units* on the stability of the 24 IPR isomers of the fullerene C_{84}. The equilibrium geometries are obtained by optimization in the density functional theory scheme B3LYP using the basis set 3-21G. It was found by Hückel Molecular Orbital calculations, based on the values of the resonance integrals evaluated in the POAV/3D-HMO method, that the energy of higher fullerenes C_{84} increases with 5.1 kcal/mol for each β=18.0 kcal/mol of the HMO π-energy corresponding to the complementary units. It was attributed 8.7 kcal/mol to the π-energy for each isolated carbon atom C_1 part of the complementary units. We have established that the most stable C_{84} isomers have small planarity and that the complementary units do not contain isolated carbon atoms (C_1 units). We explain the exceptional stability of the two isomers of C_{84} confirmed experimentally by the low stabilization energies of their complementary units.

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1. Introduction

Since the discovery of the spherical cage-structure C_{60} cluster, several studies have been focused on the characterization of its electronic structure [1-2]. It is now evident that only a limited number of fullerenes can be extracted from carbon soot among many possible fullerene isomers. The most abundant higher fullerene systems extracted from carbon soot are C_{70}, C_{76}, and C_{84} [3-5]. In the case of C_{84}, only two isomers have been extracted [5], but yet the origins of this selection rule have not been established. Currently, three useful selection rules have been identified for the fullerenes larger than C_{60}: the "isolated-pentagon rule" (IPR) [5, 6], the "pentagon-pairing rule" (PPR) [7] and the "hexagon-neighboring rule" (HNR) [8]. The structures of IPR, PPR, and HNR are illustrated in Fig. 1, together with a new concept, so-called *complementary units* (CU) which are the main topic of this report.

In the first rule, Petrie [6] and co-workers explained that adjacent-pentagon fullerenes, like C_{56} and C_{58}, have a higher chemical reactivity than an isolated-pentagon fullerene, like C_{60}, because adjacent-pentagon fullerenes are substantially lower in their thermodynamic stability than isolated-pentagon fullerenes. In this case of IPR, the number of stable candidate isomers for C_{84} is reduced to 24 from 51,592 possible isomers.

The second rule known as the PPR was proposed by Saito and co-workers [7]. It is explained that π-states on a single pentagon form an open-shell electronic structure, whereas a pentagon dimer has a closed-shell electronic structure that is more stable than two separated pentagons.

By analyzing the isomers of C_{84}, Raghavachari has introduced the hexagon-neighboring rule (HNR) [8] which states that the fullerene has the maximum stability, for which each hexagonal ring has the same number of hexagonal neighbor rings.

However, the above rules are insufficient to identify extractable fullerenes. Under those conditions further study about higher fullerene isomers will be required. Accordingly, this study investigates the theoretical and geometric structures of the higher fullerene C_{84} using the concept of complementary units, which can be seen as the carbon atom networks remaining after the removal of the pentagonal rings from the fullerene. Computational results in this work will be compared with previous experimental available in the literature.

2. Methods

2.1. Calculations

The initial structures of all the 24 IPR isomers of C_{84} were produced using the ring-spiral algorithm [9]. They are labeled in accord to the scheme of Fowler and Manolopoulos [10]. For example, the notation $C_{84}(D_{2d})$-04 indicates the isomer of C_{84} with the symmetry D_{2d} and the index 4 in the Fowler-Manolopoulos scheme. The equilibrium geometries of the isomers C_{84} are established initially by the optimization within a semiempirical restricted Hartree-Fock method in the parameterization AM1 [11] and it is refined by additional optimizations using Density Functional Theory in the scheme B3LYP, using the small basis set 3-21G. Calculations are performed with the quantum chemistry code GAMESS

[12]. The eigenvectors obtained in the Hückel Molecular Orbital (HMO) [13] is used for a fast characterization of the CU fragments. To avoid using the empirical values of the Coulomb integrals α from HMO method, we report here the stabilization π-energy rather than the total π-energy, which is defined as the difference between the total π-energies of the analyzed n-atomic system and that of the isolated n carbon atoms ($n \cdot \alpha$). This energetic parameter is related to the resonance energy, which is smaller with $n \cdot \beta$. The stabilization π-energy is expressed in units of the resonance integral β. Different values are attributed to empirical parameter β depending on the fit of some experimental parameters, but a value of -18.0 kcal/mol is generally accepted.

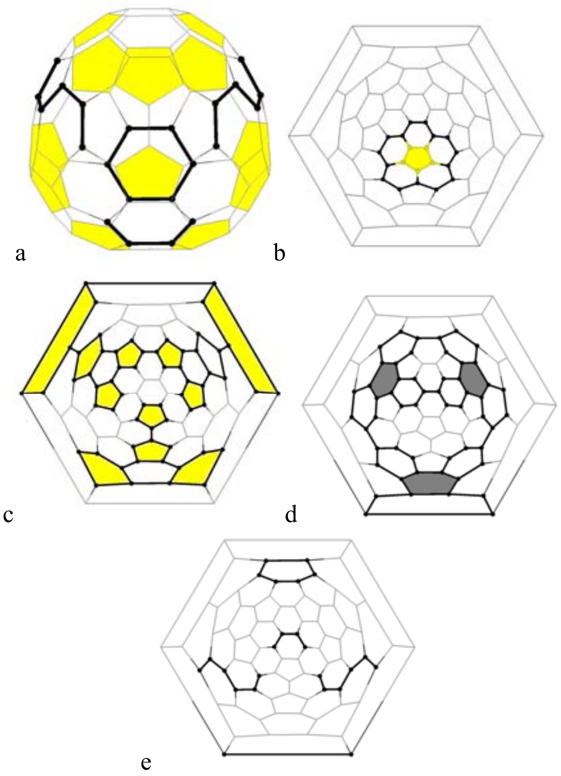


Fig. 1. (color online) The exemplification in 3D (a) and Schelegel diagrams (b-e) of the four rules for one of the C84 isomers, with the symmetry Cs and index 14 in accord to the scheme of Fowler and Manolopoulos: (a) the 3D representation of the isomer where the pentagonal rings are colored and the carbon network in the complementary units is indicated by bold lines and small spheres, (b) the isolated pentagonal rule, (c) the pairs of pentagons rule, (d) the hexagonal-neighboring rule and (e) the elements of the complementary units. The pentagonal rings are lightly colored.

The sphericity or planarity of the fullerene is characterized by the pyramidality of their atoms which can be efficiently quantified by the angle formed by π-orbital axis vector (POAV) [13] with the sigma bonds formed between the investigated carbon atom and its neighbors. The pyramidal angle is 90^o for planar systems, 108.9^o for a tetrahedral carbon atom and about 110.9^o for C_{20} corresponding to the smallest ball-shaped fullerene. The values of the resonance integral β are corrected for the non-planarity of the system witin the POAV/3D-HMO (3-dimensional Hückel Molecular Orbital Theory) method [14] with the help of the code QCPE 044 [15].

Because the POAV1 and the POAV2 analyses give very similar values for various parameters corresponding to the CUs of C_{84} IPR isomers, we report here only the values derived in the POAV1 scheme. The values corresponding to the carbon atoms in the pentagonal rings are only slightly different in the two schemes.

2.2. Theory

An analysis based on the Euler formula [16] of a polyhedron formed by pentagonal and hexagonal rings shows that a higher fullerene C_n ($n \geq 20$, the number of the carbon atoms) consists of exactly 12 pentagonal rings and n/2-10 hexagonal rings (except for n=22 which does not exist). The most abundant fullerene in the mass spectra experiments is found to be the C_{60} one, which consist in 12 pentagonal and 20 hexagonal rings. From 1,812 possible isomers only the one with the icosahedral symmetry satisfy the IPR: (i) the pentagonal rings have neighbors only as hexagonal rings (IPR is satisfied), (ii) each one is connected by a carbon-carbon bond to other five pentagons (PPR is accomplished, with each pentagon being connected to other five pentagons by C-C bonds), and (iii) each hexagon shares his edges with three pentagonal and three hexagonal intercalated rings (HNR is satisfied). The higher fullerenes (C_n for $n > 60$) consist of 12 pentagonal rings (C_{60}) plus a rest of n - 60 carbon atoms arranged in different pieces of rings (C_{n-60}). We define the complementary units as the pieces of the carbon network remaining after the removal of the 12 pentagonal rings from the structure. The CU is null for C_{60} and it consists of 24 carbon atoms which are forming short networks in the case of C_{84}. The most compact CU of C_{84} is found in one isomer with the symmetry D_2 where the CU consists in two identical groups of two interconnected hexagons $2C_{12}$ ($C_{60}+2C_{12}=C_{84}$) (see Fig. 2).

A quantitative analysis of the planar property relative to the CU (C_{n-60}) is required. By calculating the π-energy of the CU, their quantitative value can be established. The 12 pentagons (C_{60} for a spherical unit) have a high degree of sp^3 characters, whereas the CUs have a high degree of sp^2 with only marginal sp^3 characters. Similarly, a sp^3 hybrid carbon tends toward a tetrahedral coordination, while a sp^2 hybrid carbon is inclined to a planar coordination. Since all CUs have a high degree of sp^2 characters, the π-orbitals are bonding to each other with exhibiting a tendency to be the flat structure.

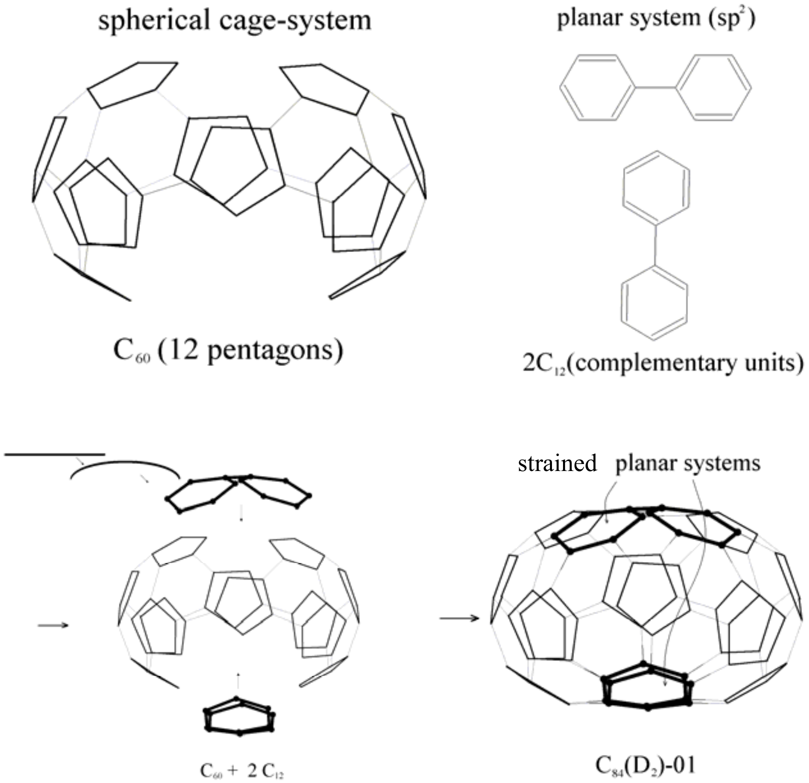


Fig. 2. The geometrical conflict between the spherical-cage system and the planar system.

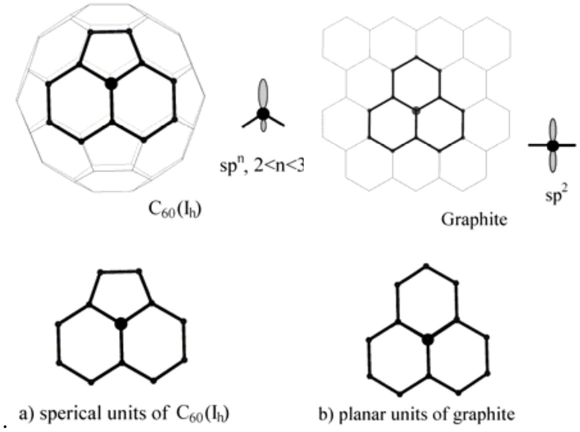


Fig. 3. The geometric structures of the spherical unit (a) and the planar unit (b).

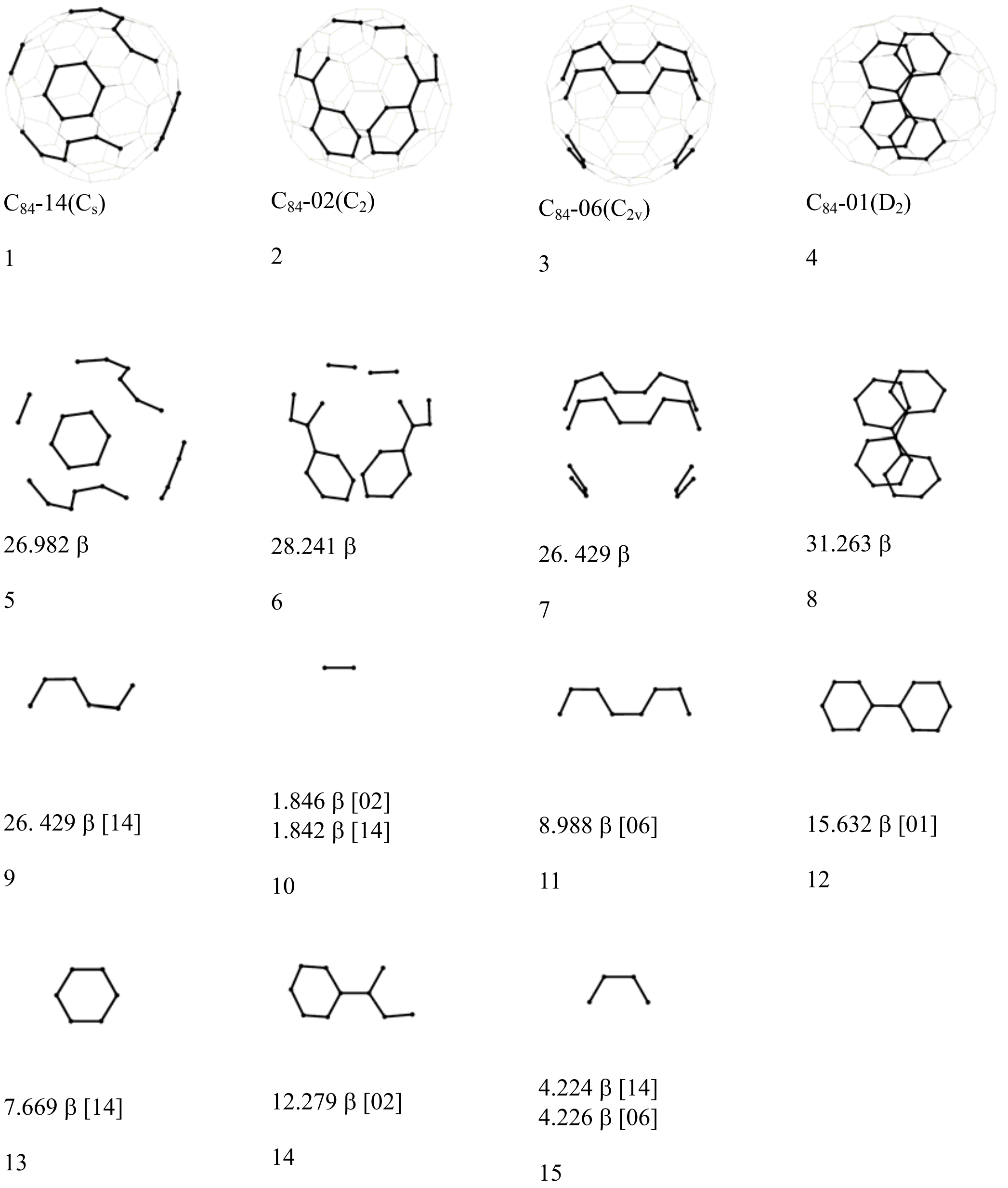
As the pentagonal rings introduce the sphericity and the hexagonal rings gives the planarity of the fullerene, the properties of the 12 pentagons are different from those of the CU, i.e., the 12 pentagons show a tendency to form a spherical cage-structure (spherical units), while the CU show a tendency to be flat (planar units). Since the 12 pentagons are apt to construct a spherical cage-structure and the CU is apt to construct a plane, the CU places a strain on the spherical cage-structure with interrupting the construction of spherical cage-structures. Larger CUs introduce larger deviations of the fullerene shape from the spherical shape by inducing the high tension in the interface of planar and spherical areas. In Fig. 3(a), we illustrate the only structural features found on the surface of C_{60} with two hexagons and one pentagon. Higher fullerenes contain structural features of types (a) and (b), whereas the graphite has the lowest deviation from the planarity [17]. Thus, the most sphere-like C_{60} has all the structural features of type (a), whereas the perfect planar graphite has all the structural features of type (b).

3. Results and discussion

3.1. Stabilization π-energy of CUs

24 carbon atoms form the complementary units in the fullerenes C_{84}. We exemplify the CUs (9-15) for four IPR isomers of C_{84} (1-4) in Fig. 4. The unit C_2 has the smallest resonance energy (about 1.840 β), while C_{12} has the largest resonance energy (15.632 β).

Saito reported that fullerenes with a C_6-ring unit have not been extracted yet, partly because the C_6-ring may be related to the degree of solubility during the extraction process [7]. However, the geometric strain of the CU would appear to be a more accurate reason. For example, the presence of a unit C_6-ring in higher fullerenes involves about six more surrounding hexagons in the network, thereby forcing the adjacent area to be flattened in concordance with HNR. The resulting strain means that higher fullerenes cannot be extracted. Although the C_6-ring unit creates a substantial geometric strain on the spherical cage-structure, the C_{10} (12.279 β in $C_{84}(C_2)$-02) and C_{12} (15.632 β in $C_{84}(D_2)$-01) units (see Fig. 4) create an even larger geometric strain than the C_6-ring (7.669 β in $C_{84}(D_s)$-14, 8.898 β in $C_{84}(D_2)$-05, 8.988 β in $C_{84}(D_{2v})$-06 and 9.009 β in $C_{84}(C_{2v})$-07) unit. In contrast, because the planarity of the C_2 unit is very small, it does not interfere with the construction of the spherical cage-structure. The degree of strain created by the CU corresponds to the π-energy, respectively to the resonance energy. Extractable fullerenes $C_{84}(D_2)$-22 and $C_{84}(D_{2d})$-23 only have even-atoms as their structural units, whereas unextracted fullerenes ($C_{84}(D_2)$-21), ($C_{84}(C_s)$-10) have several isolated C_1 units.



C_{84}-14(C_s) 1

C_{84}-02(C_2) 2

C_{84}-06(C_{2v}) 3

C_{84}-01(D_2) 4

26.982 β 5

28.241 β 6

26. 429 β 7

31.263 β 8

26. 429 β [14] 9

1.846 β [02]
1.842 β [14] 10

8.988 β [06] 11

15.632 β [01] 12

7.669 β [14] 13

12.279 β [02] 14

4.224 β [14]
4.226 β [06] 15

Fig. 4. Four C_{84} isomers (1-4), their complementary units (5-8), and the elements (9-15) of the complementary units of respective C_{84} isomers. The values expressed in β unit represent the POAV/3D-HMO stabilization energy of the CUs that are components of the C_{84} isomers indicated in square parenthesis.

As such, the CUs of stable and extractable higher fullerenes have closed electronic structures. In the case of fullerenes including the CU with C_1 units, the distance between two C_1 units can be an important factor in their stability [18, 19]. Accordingly, if a fullerene satisfies the PPR with CUs having the lower stabilization π-energy, it should be extractable.

Table 1. The elements of the complementary units, the band gap, and the relative energy of the isomers to the most stabile one in the calculation scheme B3LYP/3-21G together with the resonance energy of the CU in $C_{84}(D_{2d})$-23 using the resonance integrals calculated with the POAV1/3D-HMO method.

Order Index	IPR Index	Symmetry	Elements of the complementary units	Relative Energy B3LYP/3-21G [kcal/mol]	POAV1 Stabilization π-energy [i] [β]	Corrected POAV1 Stabilization π-energy [ii] [β]
1	23	D_{2d}	$4C_2$, $4C_4$	0.00	24.39	24.39
2	22	D_2	$4C_2$, $4C_4$	2.27	24.38	24.38
3	24	D_{6h}	$6C_2$, $2C_6$-ring	8.10	26.55	26.55
4	16	C_s	$3C_2$, $3C_4$, $1C_6$-ring	8.77	25.94	25.94
5	11	C_2	$1C_2$, $4C_4$, $1C_6$	8.94	25.37	25.37
6	19	D_{3d}	$6C_4$	10.53	25.33	25.33
7	15	C_s	$2C_1$, $3C_2$, $1C_4$, $2C_6$	13.09	23.07	40.47
8	12	C_1	$2C_1$, $2C_2$, $3C_4$, $1C_6$	14.01	23.04	40.44
9	14	C_s	$1C_2$, $1C_4$, $2C_6$, $1C_6$-ring	14.51	26.98	26.98
10	4	D_{2d}	$4C_6$	15.03	26.53	26.53
11	18	C_{2v}	$2C_2$, $2C_4$, $2C_6$	15.28	27.52	27.52
12	6	C_{2v}	$2C_4$, $2C_8$	16.02	26.43	26.43
13	5	D_2	$4C_2$, $2C_8$	16.43	25.19	25.19
14	21	D_2	$4C_1$, $4C_2$, $2C_6$	19.17	20.72	55.52
15	17	C_{2v}	$2C_1$, $4C_4$, $1C_6$-ring	22.08	24.58	41.98
16	8	C_2	$2C_1$, $2C_2$, $3C_6$	23.65	23.60	41
17	7	C_{2v}	$4C_1$, $2C_2$, $2C_8$	25.63	21.76	56.56
18	13	C_2	$4C_1$, $2C_4$, $2C_6$	26.21	21.69	56.49
19	3	Cs	$2C_1$, $1C_2$, $2C_6$, $1C_8$	27.81	24.13	41.53
20	20	T_d	$4C_6$-ring	27.93	30.69	30.69
21	9	C_2	$2C_1$, $4C_4$, $1C_6$	28.08	23.56	40.96
22	2	C_2	$2C_2$, $2C_{10}$	30.18	28.24	28.24
23	10	C_s	$4C_1$, $2C_2$, $1C_4$, $2C_6$	31.80	21.22	56.02
24	1	D_2	$2C_{12}$ [iii]	44.86	31.26	31.26

[i] The total π-energy is calculated by Hückel Molecular Orbital method using the relative resonance integrals calculated in POAV1/3D-HMO scheme. The values are expressed in β-units and the C-C resonance integral for ethane (usually chosen as 18 kcal/mol); [ii] The stabilization π-energy is corrected with 8.7 kcal/mol for each unit C_1; [iii] Two connected rings C_6.

3.2. Comparison of theoretical data based on CU and experimental data

Sun and Kertesz [20] reported that C_{84} includes two major isomers based on experimental data of ^{13}C NMR spectra (Fig. 5) [21]. The ratio of $C_{84}(D_2)$ to $C_{84}(D_{2d})$ is 2:1. The stability of 24 C_{84} isomers satisfying IPR was investigated using semi-empirical RHF/AM1 and RHF/PM3 methods [22-24] as well as B3LYP/6-31G* [24, 25]. $C_{84}(D_2)$ and $C_{84}(D_{2d})$ were found to have the lowest values of the formation energy. This result is consistent with Kikuchi's results [26]. Table 1 shows component parts of the complementary units, the B3LYP/3-21G relative energy of the isomers to the most stabile one, and the resonance π-energy of the CU in C_{84} determined using the resonance integrals calculated with the POAV1/3D-HMO method. The corrected resonance energies of the CU in C_{84} for the C_1 units, which are not considered in the calculation of the π-energy, are also presented in Table 1. The value of 1.902 β, as the contribution of the C_1 units, was established by the minimization of the mean square energy of the relative energies deviation from a linear fit.

As shown in Table 1, $C_{84}(D_2)$-22 and $C_{84}(D_{2d})$-23 indicate the least number of CUs and the smallest stabilization π-energy. Therefore, the CU in $C_{84}(D_2)$-22 and $C_{84}(D_{2d})$-23 do not interrupt the construction of the spherical cage-system.

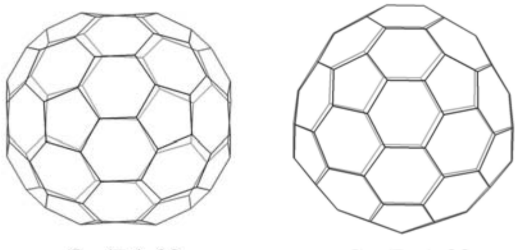

$C_{84}(D_2)$-22 $C_{84}(D_{2d})$-23

Fig. 5. Two extractable C_{84} isomers (in a ratio 2:1) in experiment.

It appears that $C_{84}(D_2)$-22 and $C_{84}(D_{2d})$-23 have the most stable geometric structure among the 24 C_{84} isomers, satisfying IPR in agreement with previous work [27]. In contrast, $C_{84}(D_2)$-01 has the largest CU ($2C_{12}$) and the highest resonance energy in the CU (6.918β and 8.000β). It becomes very stable electronic structures due to the strong π-bonding and the second largest HOMO/LUMO (highest occupied molecular orbital/lowest unoccupied molecular orbital) energy gap of 2.51 eV after $C_{84}(T_d)$-20. However, $C_{84}(D_2)$-01 has the strong π-bonding related to a strong planar property and this interrupts the construction of a cage-structure. Therefore, since it has the largest geometric strain among the C_{84} isomers, it cannot be extracted from the carbon soot.

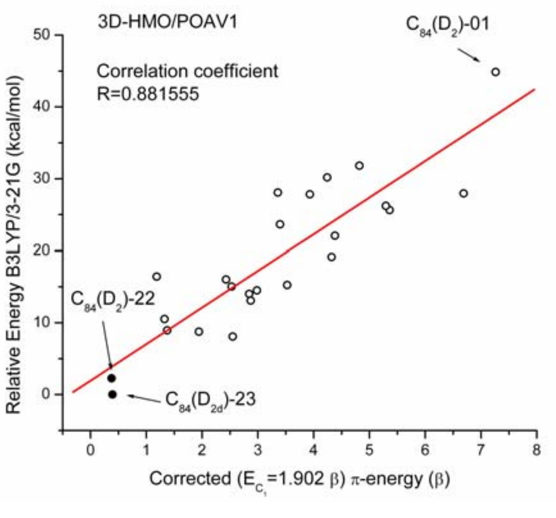


Fig. 6. The plot of the relative energy B3LYP/3-21G to the most stabile one versus the HMO stabilization π-energy. The value of stabilization energy corresponding to the fragments C_1 present in some C_{84} isomers was determined to be 1.902 β to reduce the deviation from a linear correlation. The filled symbols represent the extracted C_{84} fullerene isomers within experiment.

Fig. 6 shows the strain effect whereby the CU affects fullerenes. It can be seen that the higher the π-energy of the CU, the higher the geometric strain on C_{84}.

The relationship between the rehybridization of the CU and 12 pentagons was also investigated in this work. Fig. 7 shows the s-character regarding as the p_π-orbitals of $C_{84}(D_{2d})$-1 using the POAV1 method. The s-character of the 12 pentagons is 2-2.5 times higher than that of the CU. Since the 12 pentagons have high s-characters, it is easy to construct a spherical cage-structure. However, the CU interrupts the construction of a spherical cage-structure due to the high p-character. In addition, the theoretical reactivity around the CU in $C_{84}(D_{2d})$-22 can be deduced in this figure.

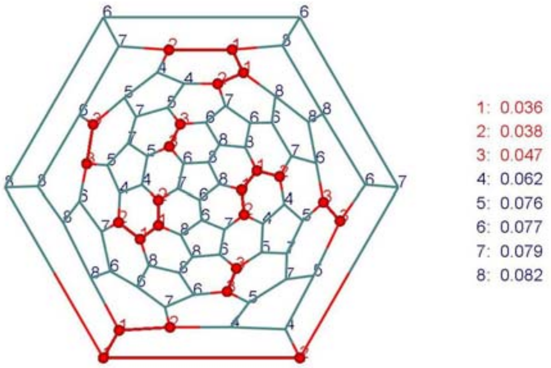
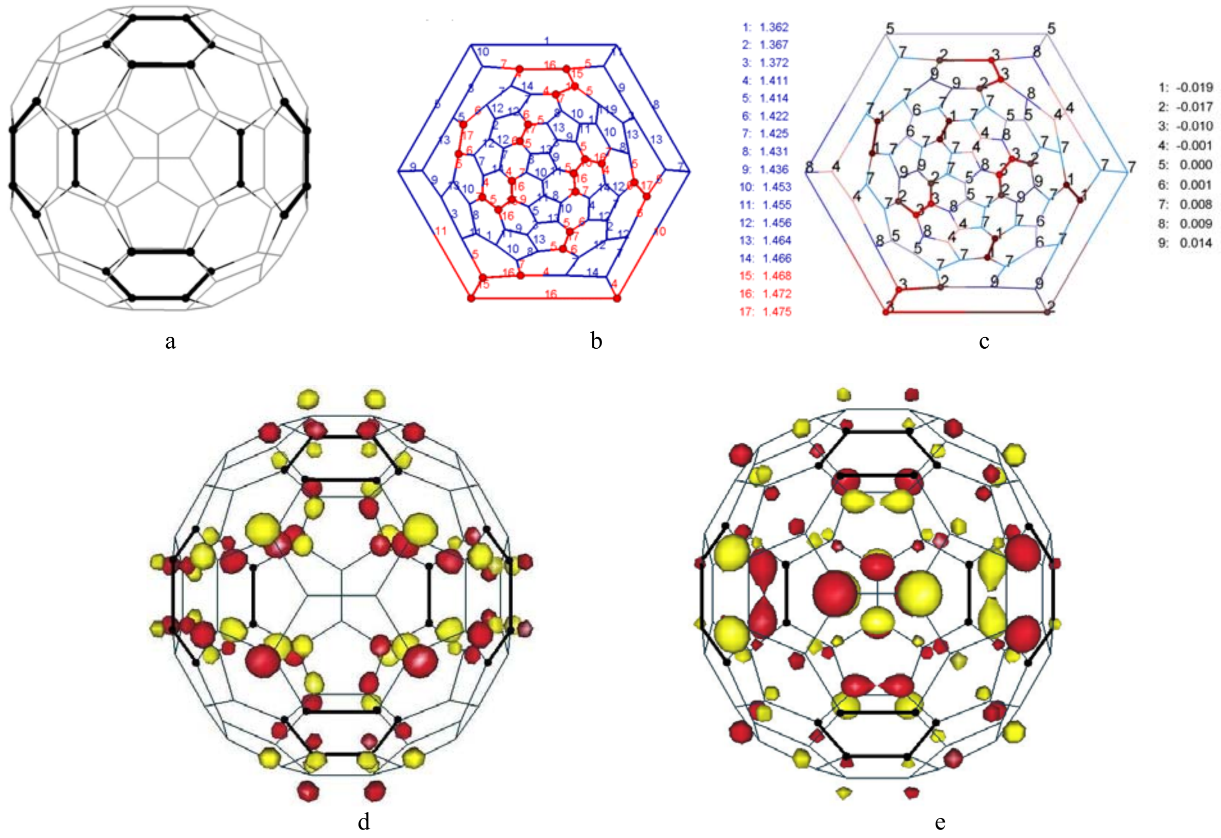


Fig. 7. The s character of the $C_{84}(D_{2d})$-23 isomer into the p_π-orbital (m value of s^mp by the POAV/3D-HMO method). The carbon atoms that are forming CU are represented by small balls.

Fig. 8 shows the interatomic distances, the Mülliken atomic charges of the carbon atoms and the frontier molecular orbitals (FMO) which are the highest occupied and the lowest unoccupied molecular orbitals determined in the DFT calculations B3LYP/3-21G. When the FMOs are visualized we can see that they are located mainly on the carbon atoms within pentagonal rings.

As a result, the 12 pentagons have a stronger reactivity than the CU. The reactivity of the CU is negligible because of small FMO coefficients. This will explain why several organic reactions for $C_{84}(D_{2d})$-22 can occur at the sites of the 12 pentagons (spherical units).

Generally, the absolute values of the charge population in the Mulliken analysis are sensible to the basis set but we are looking here to the relative values. We can see in Fig. 8 that the values of charges are very small but the charges on the carbon atoms from CU are negative (about 0.02 $|e^-|$), illustrating more significant indication of an electronic transfer from carbon atoms from the pentagonal rings.



a b c

d e

Fig. 8. Some properties of the pentagonal area and of the complementary units in the $C_{84}(D_{2d})$-23 isomer optimized in the B3LYP/3-21G calculations: (a) the 3D representation of the isomer where the CU is marked by bold bonds, (b) the interatomic distances, (c) the Mulliken atomic charges, (d) the HOMO and (e) the LUMO. The carbon atoms that are forming CU are represented by small balls. By red and yellow lobes are represented the positive and negative values of HOMO and LUMO, respectively.

In summary, extractable and stable fullerenes are investigated in the framework of a minimum planarity due to the presence of CUs. The structure of the CU is an important concept along with IPR and PPR, and fullerene isomers can be determined as stable or extractable based on the structure of their CUs. Consequently, the structures for the fullerenes C_{86}-C_{100} can be predicted without the need for higher-level electronic theory calculations.

4. Conclusions

The stability of fullerenes relative to the presence of the CU is in agreement with ^{13}C NMR spectra and with the quantum chemistry calculations. This result can be interpreted as a geometric conflict between a spherical system and a planar system. The 12 pentagons in higher fullerenes act as a spherical unit, whereas the CUs as a planar unit. The planarity of the CU is mainly caused by the strong π-bonding, and the geometric strain can be measured from the relative energy on the interaction of the π-orbitals. It is evaluated in the POAV analysis that the planarity of the CU is higher than that of the 12 pentagons. Moreover, the CUs are found to have ~~a~~ very low reactivity, based on a HOMO-LUMO analysis. As observed in this work, the planarity of the CU is an important concept along with IPR and PPR, and the resulting stability of the fullerene can be related to the size and structure of complementary units as well as their distribution and arrangement in the fullerene structure itself.

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