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Quantum chemical HF/4-31G calculations on buckminsterfullerene intermediates

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Quantum chemical *ab initio* (U)HF/4-31G investigation on buckminsterfullerene and some proposed intermediates in its formation is carried out in this study with a view to better understanding how small carbon species carry out self-assembly to form fullerenes. The calculations on 19 carefully designed fullerene intermediates reveal that the core of an intermediate, rather than the number of its dangling bonds or abutting pentagon rings, has an intrinsic effect on its energy. The computational results show that hexagonal-core structures have lower energies than pentagonal-core structures. In addition, the pentagonal core enclosed completely by hexagonal rings has the highest energy. The UHF/4-31G results also suggest that some intermediates such as C_{18}, C_{21} and C_{30} with hexagonal cores have unusually low energies in comparison with their isomers or neighbours. Based on these calculated results, we outline the possible pathways from precursor to intermediates to fullerenes, subject to synthesis conditions and raw materials. These pathways support some existing proposals, such as medium monocyclic ring stacking and small ring polymerization mechanisms. However, our results do not suggest that the numbers of dangling bonds or abutting pentagonal rings have the highest impact on fullerene formation. The calculated thermodynamic parameters of the dimerization and addition reactions between two bowl-shaped intermediates suggest that these reactions are favorable to fullerene formation, and that the concentration of bowl-shaped fullerene intermediates should be very low in all detectable carbon species.

Introduction

The hollow buckminsterfullerene (C_{60}-I_h) **1a** was first detected and suggested as a product arising from laser-ablated graphite vapor by Kroto *et al.* in 1985.[1] Tremendous progress has been made in fullerene chemistry since this discovery, especially in elucidating their structural, physical and chemical properties.[2–6] Fullerenes are now recognized as attractive new materials, and numerous reports regarding their applications have been proposed. For example, an experimental study on the fullerene C_{36} showed that this low-mass fullerene may exhibit some unusual electronic and structural properties.[3] However, it is still a mystery as to how small carbon species condense and self-assemble to form a symmetric hollow cage structure. A better understanding of buckminsterfullerene formation mechanisms should be helpful to the syntheses and applications of fullerenes and their compounds. There have been several proposals to describe the possible pathway of buckminsterfullerene formation from small carbon species.[7–16]

Heath *et al.*[8] tried to account for buckminsterfullerene growth by imposing the constraint that developing clusters minimize their number of dangling bonds by incorporating a maximal number of non-abutting pentagonal rings; meanwhile this incorporation allows the sheet to minimize energy by curling up. This is well known as the Pentagon Road, PR. Smalley[9] proposed that, initially, fullerenes form with cluster sizes of about forty atoms and grow by the addition of small carbon molecules, *e.g.* C_2, until C_{60} is reached. Taylor and Langley suggested that C_{10} fragments from naphthalene condense to give polycyclic aromatic hydrocarbons containing C_{20}, C_{30}, C_{40}, C_{50}, C_{60} and C_{70} frameworks, followed by hydrogen elimination to produce fullerenes.[10] Wakabayashi and Achiba suggested a kinetic-ring stacking model where buckminsterfullerene can be constructed by stacking appropriately-sized carbon rings.[11,12] Dias proposed a qualitative circumscribing algorithm based on a graph theoretical footing that is really akin to the kinetic-ring stacking model.[13] Jarrold's group proposed that buckminsterfullerene is the product of the coalescence of monocyclic rings.[14,15] Klein and Schmalz described a pathway from chain to single ring to bowl-like shape intermediates to buckminsterfullerene.[16]

Although a few proposals have argued that there is no need to invoke cup-shaped intermediates in the process of buckminsterfullerene formation,[15,17] we notice that most of these suggestions assume that there are intermediates on the way to the formation of hollow cage structures. However, different suggestions may have different intermediates, even if their intermediates are composed of the same number of carbon atoms. As detailed experimental studies of these possible intermediates are excessively difficult at present, theoretical investigation of these intermediates is essential for us to obtain insight into the rationality of these proposals. There are many publications that are related to theoretical investigations of buckminsterfullerene formation mechanisms;[6,18–22] we focus our interest here on the possible intermediates composed of up to 39 carbon atoms, especially for intermediates C_{30}. This is because an intermediate C_{30} might be a very important intermediate leading to the formation of buckminsterfullerene C_{60}.

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Computational details

Nineteen possible fullerene intermediates have been constructed and are shown in Fig. 1 (**1c** to **1u**). Their geometries were fully optimized at the UHF/4-31G level on a Power Challenge R-10000 supercomputer using GAUSSIAN98 software.[23] Based on the optimized structures, frequency calculations were carried out so as to verify whether these optimized structures were on the minimum points of their potential surfaces.

In order to estimate the thermodynamic parameters of the reaction between two bowl-shaped intermediates to form C_{36}-D_{6h}, the HF/4-31G method was used to perform the geometry optimization and frequency calculation of fullerene C_{36}-D_{6h}. But, for the analogous reaction forming buckminsterfullerene C_{60}-I_h, the frequency calculation at the HF/4-31G level cost too much computer resource, so just the geometry optimization was performed at the HF/4-31G level, and the frequency calculation was carried out using the AM1 method, based on the AM1 geometry.

Results and discussion

The calculated frequencies on all optimized structures except the fullerene C_{36}-D_{6h} had real frequencies, establishing that the optimized geometries were on minimum points of their potential surfaces. Table 1 summarizes the (U)HF/4-31G energy (E), HOMO and LUMO energies. The calculated E/n, where n is the number of carbon atoms in an intermediate, the HOMO–LUMO gap and the numbers of dangling bonds and abutting pentagonal rings are also presented in Table 1.

We performed an analysis on all calculated E/n, frontier orbital energies (HOMO, LUMO or HOMO–LUMO gap), the number of dangling bonds and the number of pairs of abutting pentagonal rings in these intermediates using traditional statistical and partial least square, (PLS) methods. After many attempts, we did not find any relationship among them. All the q^2 values released from PLS results were negative, suggesting that dangling bonds and abutting pentagons might not be the intrinsic factors affecting the energy of an intermediate.

Regarding the intermediates with 30 carbon atoms (**1d**–**1h**), the intermediate **1d** with the most dangling bonds has the lowest energy, while intermediate **1h** without any abutting pentagonal ring has the highest energy. The energy difference between them is 193.541 kcal mol^{-1}. In **1f**, there are 6 pentagonal rings with 6 abutments to each other, but its energy is lower than that of **1h**, in which there are 6 non-abutting pentagonal rings. Intermediate **1g** has 9 pentagons, which can be divided into three groups, each of which is composed of three adjacent pentagonal rings. Even so, the energy of **1g** is still lower than that of **1h** by 41.843 kcal mol^{-1}. These results are in agreement with the PLS result that the numbers of dangling bonds and of pentagonal rings are not intrinsic factors in the stabilization of an intermediate. Because **1e** and **1h**, rather than **1d**, could be the possible intermediates of the PR mechanism, it seems unlikely that the PR is the primary pathway to buckminsterfullerene.

Analyzing the structural characteristics of these five C_{30} intermediates, the difference between **1d** and the other four C_{30} intermediates is that none of the pentagonal rings in **1d** is thoroughly enclosed. Hence, we think that the core structure of an intermediate might have the highest impact on its energy.

In the case of the structures **1i** to **1o**, all have hexagonal cores. In contrast, the structures **1p** to **1u** have pentagonal cores (Fig. 1). It is clear from Table 1 that all the structures with a hexagonal core (**1i** to **1o**) have lower energies than do the structures with pentagonal cores (**1p** to **1u**), regardless of the number of atoms in the hexagonal-core structures, which may be more or less than that in the pentagonal-core structures.

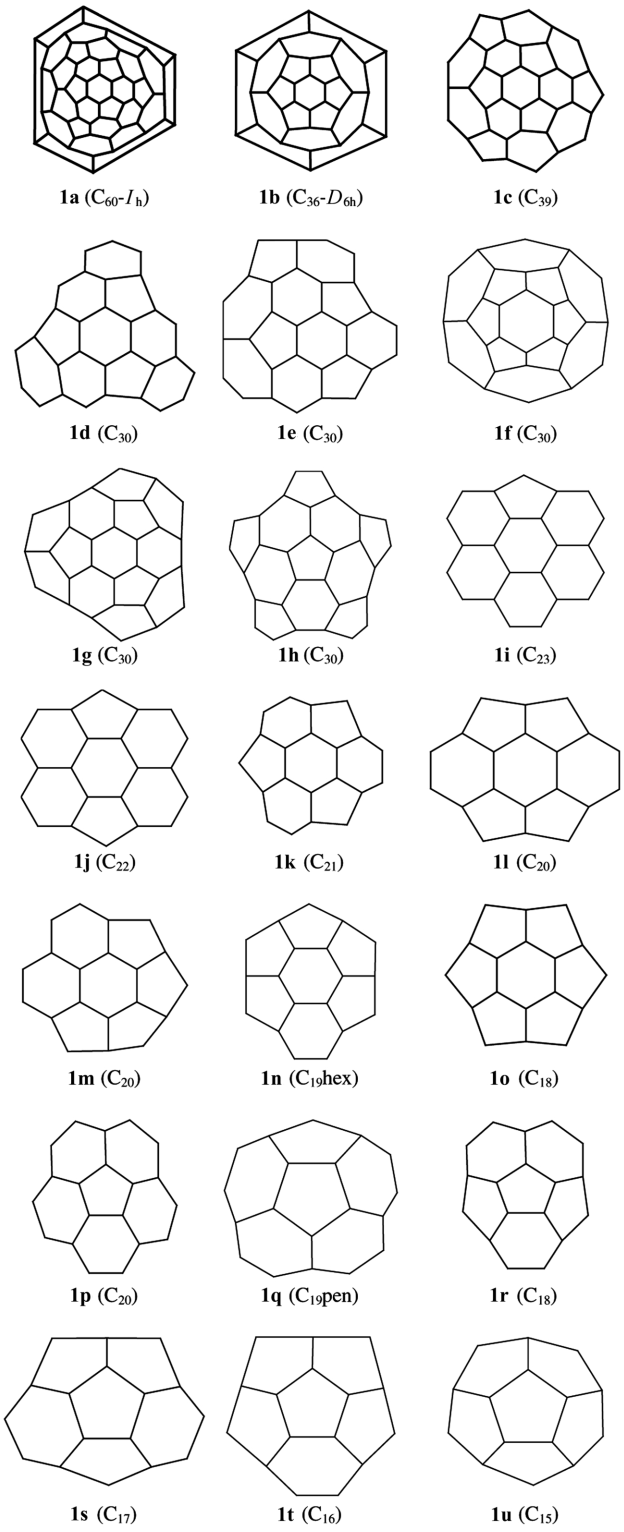
1a (C_{60}-I_h) **1b** (C_{36}-D_{6h}) **1c** (C_{39})
1d (C_{30}) **1e** (C_{30}) **1f** (C_{30})
1g (C_{30}) **1h** (C_{30}) **1i** (C_{23})
1j (C_{22}) **1k** (C_{21}) **1l** (C_{20})
1m (C_{20}) **1n** (C_{19}hex) **1o** (C_{18})
1p (C_{20}) **1q** (C_{19}pen) **1r** (C_{18})
1s (C_{17}) **1t** (C_{16}) **1u** (C_{15})

Fig. 1 Possible fullerene intermediates.

Hence, a pentagonal-core structure seems very unfavorable to the energies of intermediates. This result confirms our above supposition that the core pattern of an intermediate has an intrinsic impact on its energy. Accordingly, a hexagon, rather a pentagon, should be considered as a more probable precursor if the proposed pathway involves, initially, small ring structures, such as 5-membered and 6-membered rings, followed by coalescence around this precursor. This is consistent with the experimental[17] and quantum calculation results shown by Mishra and co-workers[20] and Raghavachari and Binkley.[24] However, there are obviously many possible ways to form the stable hexagonal-core intermediates, such as a large

Table 1 (U)HF/4-31G calculation results based on fully optimized geometries[a]

Structure	E	E/n	HOMO	LUMO	Gap	DB[b]	AP[c]
1a (C_{60}-I_h)	−2268.519649	−37.808661	−0.2928	−0.0126	0.2801	—	—
1b (C_{36}-D_{6h})	−1360.501779	−39.791716	−0.2163	−0.0816	0.1347	—	—
1c (C_{39})	−1474.046549	−37.796065	−0.2976	0.0251	0.3227	9	0
1d (C_{30})	−1133.778248	−37.792608	−0.3301	0.0476	0.3777	12	0
1e (C_{30})	−1133.684515	−37.789484	−0.3090	0.0343	0.3433	10	0
1f (C_{30})	−1133.576447	−37.785882	−0.3449	0.0424	0.3873	6	6
1g (C_{30})	−1133.536501	−37.784550	−0.3372	0.0305	0.3677	6	9
1h (C_{30})	−1133.469821	−37.782327	−0.3114	0.0301	0.3415	10	0
1i (C_{23})	−868.985580	−37.781982	−0.3329	−0.0100	0.3428	11	0
1j (C_{22})	−831.251447	−37.784157	−0.3238	0.0422	0.3660	10	0
1k (C_{21})	−793.426830	−37.782230	−0.3152	0.0301	0.3453	9	0
1l (C_{20})	−755.621334	−37.781067	−0.3152	0.0529	0.3681	8	2
1m (C_{20})	−755.596676	−37.779834	−0.3408	0.0351	0.3758	8	3
1n (C_{19}hex)	−717.762182	−37.776957	−0.3077	0.0356	0.3433	7	4
1o (C_{18})	−680.006889	−37.778160	−0.3542	0.0779	0.4321	6	6
1p (C_{20})	−755.529418	−37.776471	−0.3139	0.0203	0.3342	10	0
1q (C_{19}pen)	−717.758710	−37.776774	−0.3418	0.0286	0.3704	9	1
1r (C_{18})	−679.976524	−37.776474	−0.3193	0.0427	0.3620	8	2
1s (C_{17})	−642.161342	−37.774197	−0.3236	0.0440	0.3676	7	4
1t (C_{16})	−604.370507	−37.773157	−0.3351	0.0682	0.4033	6	7
1u (C_{15})	−566.542478	−37.769499	−0.3557	0.0748	0.4306	5	10
C_{10} (naphthalene ring)	−377.533520	−37.753352	−0.3055	−0.0377	0.3432	8	0
C_6 (benzene ring)	−226.397294	−37.732882	−0.3262	0.0326	0.3588	6	0

[a] Energies are presented in units of hartree. [b] The number of dangling bonds. [c] The number of abutting pentagonal rings.

single ring joined with smaller clusters, which may result in hexagonal-core fragments.[25]

There were 3 structures that were composed of 20 carbon atoms: **1l**, **1m** and **1p**. Compared with **1p**, which has only one pentagon ring, structure **1m** has 4 abutting pentagonal rings. But, the energy of **1m** is still lower than **1p**, suggesting once again that the pentagonal core is an unstable structure. Furthermore, regarding the structures **1p**, **1q** and **1r**, as the number of carbon atoms in them decreases, their E/n should be increased. However, structure **1p** has the highest E/n value, suggesting that a pentagonal core enclosed completely by hexagonal rings is energetically unfavorable as a route to the formation of fullerene. This is consistent with Fowler and Mitchell's MNDO results,[26] which showed that those isomers with enclosed pentagonal-core structures have higher energies than the structures in which the pentagonal rings are located at their rim in 30 indacenoid isomers of $C_{30}H_{12}$.

The UHF/4-31G result showed that the structures **1d**, **1k** and **1o** have lower E/n values in comparison with their isomers or neighbours (Fig. 1 and Table 1), suggesting that the growth of fullerene precursors might not proceed through the addition of carbon atoms one by one. Furthermore, we would like to think that intermediates **1d**, **1k** and **1o**, which have unusually low energies, might play an important role on the way to the formation of fullerenes.

The possible fullerene formation pathway

Based on the calculated lower energy intermediates and the possible precursor structures, we outline possible pathways from precursor to fullerenes as shown in Fig. 2. Fig. 2(a) depicts the formation of buckminsterfullerene C_{60} with symmetry of I_h, Fig. 2(b) the formation of fullerene C_{36} with symmetry of D_{6h}.

We postulate that there might be two ways for a precursor to grow. One is the addition of medium-sized monocyclic carbon species to a precursor to form fullerene intermediates (indicated by full-line arrows in Fig. 2), the other is the addition of small carbon species to a precursor (dashed arrows in Fig. 2). Whilst the former is similar to the ring stacking model,[11–13] the latter is nearer the chain addition and ring polymerization mechanism.[10] For example, the addition of the monocyclic structure C_{15} to the precursor C_6 to form intermediate **1k**, and of the monocycle C_{18} to **1k** to form **1c** (Fig. 2(a) full-line arrows) and the addition of the monocycle C_{12} to precursor C_6 or to **1o** to form **1o** or **1f** (Fig. 2(b) full-line arrows) constitute the first pathway. The addition of small carbon-chain species C_n, $n = 1–5$, to precursor C_6 to form **1k**; to **1k** to form **1d** or **1e** and the polymerization of naphthalene to form **1d** constitute the second pathway (with dashed arrows in Fig. 2(a)). Accordingly, the growth of the precursor might be very complicated, with a lot of alternative pathways leading to the same intermediate. Whether the route follows monocyclic ring stacking or small chain addition and a ring-polymerization pathway depends on the synthesis conditions and raw materials. Different reactants and conditions may give rise to different growth pathways. However, based on our calculations, we find that there is no need to impose the constraint of minimizing the numbers of both dangling bonds and abutting pentagonal rings. In addition, we think that medium-sized monocyclic ring addition or small ring polymerization is a shortcut to forming fullerene, for it needs fewer steps than the small chain addition mechanism.

The last step of fullerene formation could be the dimerization of bowl-shaped intermediates, or the addition of a precursor or a smaller intermediate to an existing bowl-shaped intermediate. For instance, the dimerization of intermediate C_{30} could form buckminsterfullerene C_{60}-I_h, and the dimerization of intermediate C_{18} could form fullerene C_{36}-D_{6h}. The addition of intermediate **1k** to **1c** (Fig. 2(a)) could also form buckminsterfullerene C_{60}-I_h, and the addition of precursor C_6 to **1f** (Fig. 2(b)) could also form fullerene C_{36}-D_{6h}.

Table 2 summarizes the calculated thermodynamic parameters of these possible reactions to form fullerenes C_{60}-I_h and C_{36}-D_{6h}. The estimated energy change, change of free energy and equilibrium constant suggest that dimerization or addition reactions are a very favorable means of fullerene formation. For example, the calculated equilibrium constants for those 7 possible dimerizations and addition reactions range from 10^{177} to 10^{647} at 298.15 K. Thus, the concentration of these bowl-shaped intermediates must be very low. Hence, if dimerization and addition reactions are possible pathways to fullerene formation, it is easy to account for the very low concentrations of carbon species with 23–35 atoms and the precursor C_6 in early clustering systems.[17] Then, not only can we understand why bowl-shaped intermediates are hard to observe

Table 2 The thermodynamic parameters of fullerene formation reactions

Reaction type	Reactants	Product	ΔE^a/kcal mol^{-1}	ΔH^b/kcal mol^{-1}	ΔG^c/kcal mol^{-1}	$K_f^{298\ d}$
Dimerization	**1d** + **1d**	C_{60}-I_h	−604.388	−509.638^e	−472.988^e	$4.56 \times 10^{346\,e}$
Dimerization	**1e** + **1e**	C_{60}-I_h	−722.025	−632.589^e	−599.416^e	$2.09 \times 10^{439\,e}$
Dimerization	**1h** + **1h**	C_{60}-I_h	−991.470	−917.101^e	−882.974^e	$1.39 \times 10^{647\,e}$
Addition	**1k** + **1c**	C_{60}-I_h	−656.545	−580.792^e	−547.974^e	$4.15 \times 10^{401\,e}$
Dimerization	**1o** + **1o**	C_{36}-D_{6h}	−306.225	−270.230	−242.180	3.14×10^{177}
Dimerization	**1r** + **1r**	C_{36}-D_{6h}	−344.334	−310.447	−280.583	8.15×10^{205}
Addition	**1f** + C_6	C_{36}-D_{6h}	−331.350	−303.001	−278.859	1.71×10^{204}

^{a} $\Delta E = E_{\text{fullerene}} - \Sigma(E_{\text{intermediate}})$. ^{b} $\Delta H = \Delta E + \Delta E_{\text{therm}} - RT$. ^{c} $\Delta G = \Delta H - T\Delta S$. ^{d} $\Delta G = -RT\ln K_s^{298}$. ^{e} The E_{therm} and S of intermediate C_{39} (**1c** in Fig. 1) and buckminsterfullerene C_{60}-I_h are estimated using the AM1 method.

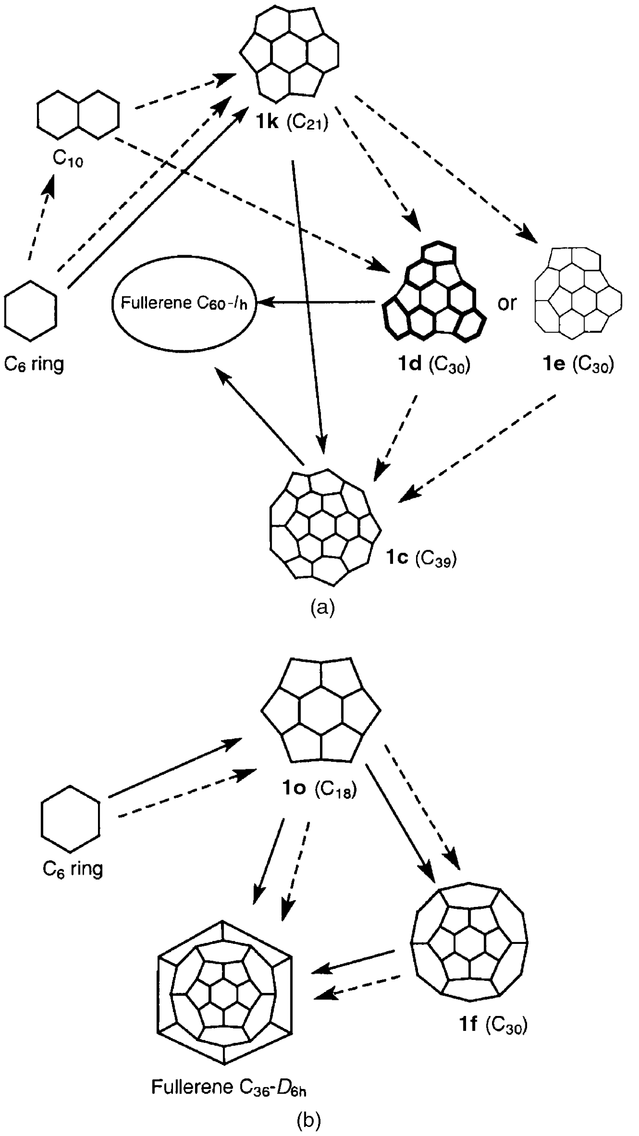

Fig. 2 Possible fullerene formation pathways: (a) to fullerene C_{60}-I_h; (b) to fullerene C_{36}-D_{6h}. Full-line arrows indicate addition of medium-sized monocyclic carbon species (along the lines of the ring stacking model) while dashed arrows indicate the addition of smaller carbon species (roughly corresponding to the chain addition and ring polymerization models).

in of mass spectrum and ion mobility experiments,[17] but we also can understand why the atom numbers of the clustering products larger than ~40 carbon atoms are generally even.[27]

Conclusion

We have performed quantum chemical *ab initio* (U)HF/4-31G calculations on 19 fullerene intermediates with up to 39 carbon atoms and fullerenes C_{60}-I_h and C_{36}-D_{6h} in order to get deeper insight into fullerene formation mechanisms. This study suggests that a pentagonal-core structure has higher energy than a hexagonal-core structure. Among all possible pentagonal-core structures, the one in which the pentagonal core is enclosed entirely by hexagonal rings has the highest energy. The UHF/4-31G calculations suggest that the energies of fullerene intermediates mainly depend on the core pattern rather than the number of dangling bonds or the occurrence of abutting pentagonal rings. We also find that some bowl-shaped intermediates such as **1d**, **1k** and **1o** (Fig. 1) have unusually low energies in comparison with their isomers or neighbours. Based on these lower energy intermediates, we get a clear picture of a pathway from precursor to bowl-shaped intermediates to fullerenes, indicating that fullerene formation, depending on its synthesis conditions and raw materials, might have many different pathways. This picture supports some existing proposals, such as the ring-stacking and ring polymerization mechanisms. But, UHF/4-31G results do not show that it is necessary to impose the constraint of minimizing the numbers of dangling bonds and abutting pentagonal rings on the pathway from precursor to fullerenes. The calculated energy change, the change of enthalpy and the change of free energy suggest that dimerization and addition reactions between bowl-shaped intermediates could occur to form fullerenes. The estimated reaction equilibrium constants could account for the low experimental concentrations of the intermediates with 23–35 carbon atoms.

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