Quantum Chemical AM1 Treatment of the Circumscribing Algorithm: Fullerene Growth Mechanism

Rama K. Mishra,[†] Ying-Ting Lin, and Shyi-Long Lee*

Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi 62117, Taiwan

A graph theoretically formulated circumscribing algorithm for the fullerene growth mechanism has been analyzed using the quantum chemical AM1 method. Following different routes, two small fullerenes C_{28} (T_d and D_2) and C_{26} (D_{3h}) have been constructed from monocyclic/polycyclic precursors and circumscribed with appropriate carbon belts. The deformation energies (DE) and the average bond lengths $\langle R \rangle$ of the precursors have been computed. The DE values suggest that there is a chance of bond cleavage of the polycyclic precursors as the growth process proceeds toward the cage formation. On the other hand, the monocyclic precursors are found to have significantly lower deformation energies than the polycyclic precursors. Further, with analysis of $\langle R \rangle$ values of the polycyclic and monocyclic cases at different stages, it is observed that the $\langle R \rangle$ values of the polycyclic cases decrease gradually, depicting a shrinkage in the precursors which may be detrimental to the growth process, whereas monocyclic precursors tend to swell, corroborating the tendency of the system to grow which may be conducive for the growth process.

Low-mass fullerenes possessing high curvature and increased strain owing to the presence of adjacent pentagonal rings could lead to solids with unusual intermolecular bonding and electronic properties.[1] The recent synthesis[1] of macroscopic quantities of solid fullerene C_{36} might be viewed as another milestone in the study of fullerene chemistry. The C_{36} fullerene synthesis begs the question of a possible synthesis of even smaller fullerenes than C_{36}. After the epoch making discovery of C_{60} (Buckminsterfullerene[2]) in 1985, fullerene chemistry had to wait reluctantly for 6 more years until C_{60} was synthesized in bulk quantity for the full experimental characterization.[3] At that juncture the progress in the characterization of the lower fullerenes is considered to be only of theoretical interest. But, now with the synthesis of C_{36} by Piskoti et al.,[1] a new area in the lower fullerene domain has emerged. Though fullerene is now well-recognized as an attractive new material and numerous reports regarding its applications have been proposed, the mechanism of how such a symmetric hollow cage structure can be self-assembled has remained as an intriguing problem.

In recent years, several attempts have been made both theoretically and experimentally in order to unveil the mystery of fullerene growth mechanism. Experiments on resistive evaporation of two carbon rods with different degrees of enrichment in ^{13}C have revealed that the carbon vapor consists of smaller clusters before the process of fullerene formation starts.[4] Further, experimental gas ion chromatography studies of the structure of the carbon clusters lead to the formation of the possible paths of fullerene formation through the coagulation of monocycles and gradual transformations of polycyclic structures into fullerene cages.[5−7] These elementary carbon clusters such as monocyclic rings or polycyclic rings are termed as precursors[5,6] from which

the fullerenes are supposed to be formed by the successive stacking/circumscribing with the different carbon belts.[8,9] It is quite natural to presume that the fullerene cages must have been generated from appropriate precursors. Wakabayashi and Achiba[8] have suggested a kinetic-ring stacking model where fullerenes can be constructed by stacking proper-sized carbon rings. Dias[9] has proposed a qualitative circumscribing algorithm based on the graph theoretical footings which is really akin to the kinetic-ring stacking model. This algorithm can be stated as a method of encircling a monocyclic/polycyclic precursor (known as the base excise internal structure (EIS)) with appropriate carbon belts in order to generate the fullerene cage structures. It has been further mentioned that successive circumscribing of qualified conjugated hydrocarbons with a combination of pentagonal and hexagonal rings terminates at fullerenes when the number of pentagonal rings reaches 12 or terminates at systems that can be capped to give fullerenes with 12 pentagonal rings.[9]

Here, in this study, we have not tried to broach an analysis of the circumscribe algorithm but concentrated on the different precursors used for the generation of the fullerenes. In fact, we would like to address the fate of the precursors when they are stacked/circumscribed gradually by the ring of carbon belts. When there is a stacking of a precursor through a carbon belt, it may be conceived that the precursor must have undergone substantial changes. On the basis of the qualitative graph theoretical circumscribing algorithm, the seed graphs (precursors) can be selected and stacking the seed graphs with appropriate carbon belts the desired fullerene cages are obtained. It is obvious that these seed graphs are to undergo drastic energy transformations during the circumscribing process. Hence, it is pertinent to visualize the change in the deformation energy and the geometry of the precursors. A quantum chemical AM1 study has been carried out by considering two representative small fullerene cages such as C_{28} and C_{26}. The deformation energies and

* Corresponding author. E-mail: chesll@ccunix.ccu.edu.tw.
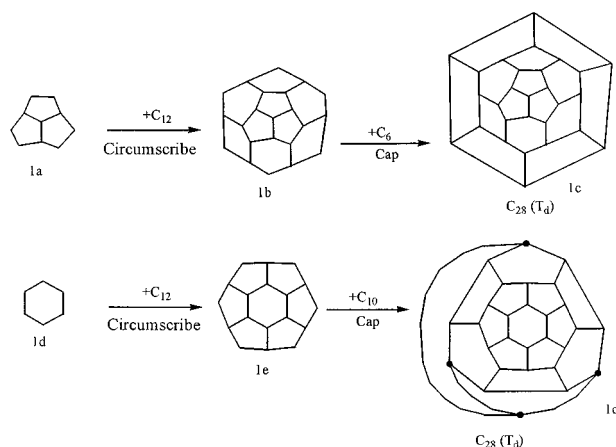† On leave from the Department of Chemistry, Sambalpur University, Jyoti-Vihar 768 019, India.

FULLERENE GROWTH MECHANISM

J. Chem. Inf. Comput. Sci., Vol. 39, No. 6, 1999 **1091**

Figure 1. Formation of C_{28} (T_d) from precursors 1a and 1d.

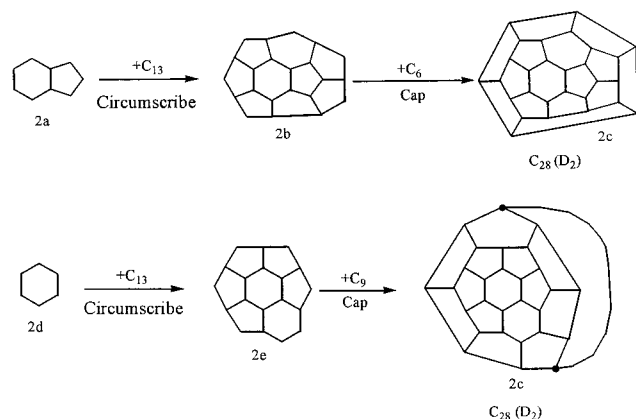**Figure 2.** Formation of C_{28} (D_2) from the precursors 2a and 2d.

Figure 3. Formation of C_{26} (D_{3h}) from the precursors 3a, 3d, and 3f.

the average bond lengths are calculated for the precursors. We believe that the feasible path for the generation of the fullerene should have smaller deformation energy of the precursor during the growth process, ensuring the noncleavage of the precursors.

MATERIALS AND METHODS

Hallett et al.[10] have studied the carbon clusters in the range $n = 8-37$, produced by laser vaporization in a supersonic nozzle and investigated with time-of-flight (TOF) mass spectrometry confirming the existence of C_{26}, C_{28}, and other small fullerenes. C_{28} fullerene has been known to be the smallest fullerene molecule and becomes stable as M@C_{28} (M = Ti, Mg, etc.).[11] Recently, Portmann et al.[12] have pointed out that the C_{28} cluster can exist in two different cage structures having T_d and D_2 symmetries with five and one multiplicities on the basis of their B3LYP/6-31G calculations. For the C_{28} (T_d) fullerene two precursors like acepentylenehexyl (three fused pentagons with dangling bonds) and benzenehexyl can be considered for the construction of the required cage structure (Figure 1). Similarly, for the C_{28} (D_2) fullerene, indenylheptyl and benzenehexyl can be chosen to be the precursors (Figure 2). For the formation of the C_{26} fullerene three precursors such as indenylheptyl, pentalenehexyl, and benzenehexyl are considered (Figure 3). All these precursors are gradually circumscribed by the appropriate carbon belts in order to generate the required cage structures. Low-energetic cumulenic carbon belts are considered for the circumscribe purpose. It may be mentioned that the mono-
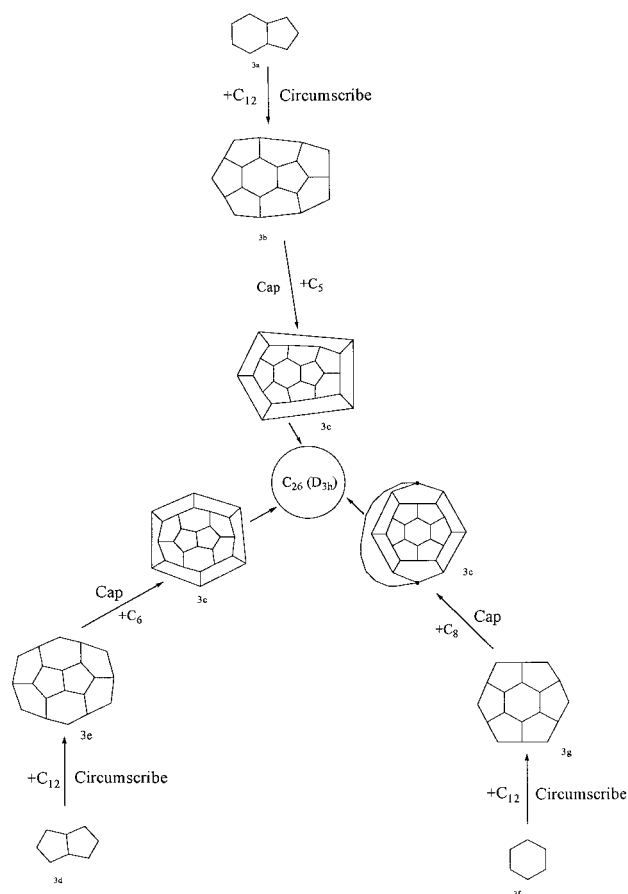
cyclic C_{10}, C_9, and C_8 rings are deformed to give three fused pentagons (acepentylenehexyl), one hexagon and one pentagon (indenylheptyl), and two fused pentagons (pentalenehexyl), respectively, and thereby the dangling bonds are reduced in the precursors. These types of deformations are quite possible as the systems are considered to be in their floppy states.[8] The whole idea of the circumscribing/stacking principle is to reduce the dangling bonds of the precursor which ultimately proceed toward the formation of the cage structure. It may further be noted that the C_6 ring (benzenehexyl) precursor can be chosen as it retains its ring structure after optimization and has been found to be more stable than its corresponding linear form by an amount of 0.6 eV, as evident from the ab-initio calculations.[13]

SEMIEMPIRICAL CALCULATIONS

All of the calculations are performed by using standard AM1 Hamiltonian implemented within the MOPAC93 program.[14] Molecular geometries are completely optimized with the setting of self-consistent field (SCF) convergence criteria to be 10^{-24}. Bakowies et al.[15] have correctly pointed out that closed-shell SCF calculations on large carbon clusters often have problems of nonconvergence or convergence with a reduction in symmetry. The lowering of symmetry does lead to a distortion from the topological symmetry, a deviation in the bond lengths, and the HOMO−LUMO gaps (ΔE_g). But, since the systems considered here are in the floppy state during the fullerene growth process, one can rationalize the deviations in the above-mentioned properties.[16]

1092 *J. Chem. Inf. Comput. Sci., Vol. 39, No. 6, 1999*

MISHRA ET AL.

Table 1. $\Delta H_f/n$ (kcal/mol), ΔE_g (eV), D (D), and ν(max, min) (cm^{-1})

cluster	point group[a]	$\Delta H_f/n$	ΔE_g	D	ν_{max}	ν_{min}
1a	C_{3v}/C_s	46.37	7.8607	0.928	2362.42	128.61
1b	C_1/C_1	44.95	5.7804	2.727	2033.13	89.20
1c	T_d/T_d	33.53	5.3696	1.037	1734.78	404.10
1d	D_{6h}/D_{6h}	67.86	7.0868	0.000	1881.94	351.50
1e	C_{6v}/C_{3v}	51.31	5.6561	0.873	1705.77	176.60
2a	C_{2v}/C_{2v}	47.93	7.0382	1.706	2321.09	188.41
2b	C_1/C_1	46.76	5.4751	2.728	1917.67	139.90
2c	D_2/D_2	33.80	5.9400	0.017	1765.20	421.40
2d	D_{6h}/D_{6h}	67.86	7.0868	0.000	1881.94	351.50
2e	C_s/C_s	47.11	5.8885	0.917	1999.15	165.00
3a	C_{2v}/C_{2v}	47.93	7.0353	1.707	2320.33	186.56
3b	C_1/C_1	48.18	6.2105	1.994	1760.20	161.70
3c	D_{3h}/D_{3h}	35.76	5.8025	0.402	1734.99	428.10
3d	D_{2h}/C_{2v}	54.18	7.4520	1.790	2278.50	172.60
3e	C_{2v}/C_{2v}	48.76	5.4800	4.584	1771.55	40.90
3f	D_{6h}/D_{6h}	67.11	7.0868	0.000	1881.94	351.50
3g	C_{6v}/C_{3v}	51.31	5.6561	0.873	1705.77	176.60

[a] The first entry refers to the topological point group, and the other one is found in the geometry optimization.

Table 2. DE/Atom (kcal/mol) and $\langle R \rangle$ (Å) of the Precursors

fullerene	precursor	route	DE/atom	$\langle R \rangle$
C_{28} (T_d)	1a	1−1	0.0	1.9018
			29.25	1.6852
			28.99	1.4629
	1d	1−2	0.0	1.3170
			9.94	1.4133
			11.70	1.4400
C_{28} (D_2)	2a	2−1	0.0	1.5452
			25.55	1.4357
			23.70	1.4469
	2d	2−2	0.0	1.3170
			10.52	1.4123
			12.32	1.4325
C_{26} (D_{3h})	3a	3−1	0.0	1.5548
			24.17	1.4365
			26.71	1.4560
	3d	3−2	0.0	1.5432
			26.53	1.4514
			26.48	1.4560
	3f	3−3	0.0	1.3170
			9.94	1.4133
			12.98	1.4560

Slanina et al.[17] have also performed the semiempirical AM1 study of some small and large carbon clusters in order to find the stability of the clusters. The Hessian Matrix, constructed from the second derivative of the energy with respect to geometry, has been created; diagonalization of this matrix gives the force constants for the relevant clusters.[14] The force matrix, weighted for isotropic masses, has been used for the calculations of the vibrational frequencies. Before the construction of the force matrix, the gradients are evaluated to ensure that the geometry has the minimum energy at a stationary point. The gradient norms are fixed at the default value, i.e., 1.0. To compute the deformation energy of a precursor, the equilibrium geometry is first obtained with the force calculation. In the subsequent steps (i.e., the intermediate and the final steps) the precursor is isolated from their optimized structures obtained through the force calculations. The single point geometry calculation is carried out for this fragment (precursor), and the difference in the energy between the single point geometry of the precursor and its equilibrium geometry is called the deformation energy of the precursor at different situations. After that the average bond length $\langle R \rangle$ of the precursor at different environments are calculated to provide a clear visualization of the fate of the precursor when it undergoes the circumscribing process.

RESULTS AND DISCUSSIONS

Making use of semiempirical AM1 method, we have calculated the heat of formation (ΔH_f), the HOMO−LUMO gap (ΔE_g), the dipole moment (D), and the vibrational frequencies (ν) of all the clusters in various routes (Figures 1−3). Further, ($\Delta H_f/n$), where n = the number of carbon centers, has been calculated in order to judge the stability of the clusters, and the change in the point group during the geometry optimization has also been noticed. All these data are presented in Table 1. Again, the deformation energy (DE) and the average bond lengths $\langle R \rangle$ of all the precursors at different situations are given in Table 2.

The $\Delta H_f/n$ and the ΔE_g values (Table 1) clearly reflect the gradual increase in the stability of the clusters when a

particular precursor is circumscribed with appropriate carbon belts. While trying to make an analysis of the two possible routes for the formation of C_{28} (T_d), we noticed in the 1−1 route, 1a → 1b → 1c (Figure 1) the change in the energy per carbon center is 12.8422 kcal/mol, whereas, in the 1−2 route, 1d → 1e → 1c, it is 34.3303 kcal/mol. Hence, one can easily say that the first route seems to be a more feasible one than the second route. But, when we tried to calculate the deformation energy (DE) of the precursors in both routes, we observed that the DE per atom is 28.9949 kcal/mol in the first route and only 11.6992 kcal/mol in the second route. This clearly indicates that though the total energy change in the first route is less than the second route, the DE per atom is more than the second route. Hence, we feel that the three-pentagons-fused precursor undergoes a drastic deformation than the monocyclic six-membered ring. During the process of deformation there is a chance of bond cleavage and might not lead to the target cage compound. Moreover, we observed that the average bond lengths $\langle R \rangle$ (Table 2) gradually decrease in the 1−1 route, but increase in 1−2 route. On the basis of these $\langle R \rangle$ values, one can argue that there is a shrinkage in the precursor in the first case, whereas the precursor swells in the monocyclic case. It is quite logical to think that as the cluster grows, the precursor should also show a tendency to swell in order to corroborate the growing nature of the cluster. Hence, we can say that the monocyclic precursor is preferred over the polycyclic one. For the formation of C_{28} (D_2) an identical situation is observed. The DE per atom for the 2−2 route (Figure 2) is small though the total energy change in this route is larger than in the 2−1 route. Here also the monocyclic precursor is preferred over the bicyclic one. Considering the $\langle R \rangle$ values again, we can say that C_6 swells up and indenylheptyl precursor shrinks. Hence, a possible cleavage of the latter might be expected during the growth process. When we considered the formation of C_{26} (D_{3h}) fullerene with three different precursors (Figure 3), like indenylheptyl, pentalenehexyl, and benzenehexyl, we observed that the total energy changes in routes 3−1, 3−2, and 3−3 are 12.1654, 18.42, and 32.0926 kcal/mol per atom, respectively. On the other hand, the DE per atom are found to be in the reverse trend suggesting a

possible cleavage of the bicyclic precursors. Further, the $\langle R \rangle$ values of the precursors are also observed to decrease in the 3−1 and 3−2 routes but gradually increasing in the case of the 3−3 route. Hence, we can conclude that the bicyclic precursors (first and second routes) shrink and the monocyclic precursor swells up, favoring the cluster formation.

From this study it is clear that the natural starting point for the formation of fullerene should be from a monocyclic precursor rather than bicyclic/polycyclic precursor, when the growth process is to proceed through a circumscribe/stacking procedure. Further, we can conclude that the monocyclic benzenehexyl could be a better precursor than other bicyclic/polycyclic precursors for generating C_{28} (T_d), C_{28} (D_2), and C_{26} (D_{3h}) fullerene clusters. It has been pointed out in the ring-stacking technique that the monocyclic C_{10} ring is to be considered as a precursor for the fullerene formation. But, since the C_{10} ring contains as many as 10 dangling bonds, it has to undergo deformation in order to reduce the number of dangling bonds. On the other hand, the C_6 ring cluster, which is found to be more stable[13] than its linear form, is having only six dangling bonds and might serve as a better precursor than the monocyclic C_{10}, C_9, and C_8 ring clusters as proposed in this work.

ACKNOWLEDGMENT

REFERENCES AND NOTES

(1) Piskoti, C.; Yarger, J. C_{36}, a New Carbon Soild. *Science* **1998**, *393*, 771−774.
(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C_{60}: Buckminsterfullerene. *Nature* **1985**, *318*, 162−163.
(3) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Solid C_{60}: A New Form of Carbon. *Nature* **1990**, *347*, 354−358.
(4) Ebbesen, T. W.; Tabuchi, J.; Tanigaki, K. The Mechanism of Fullerene Formation. *Chem. Phys. Lett.* **1992**, *191*, 336−338.
(5) Helden von, G.; Hsu, M.-T.; Gotts, N.; Bowers, M. T. Carbon Cluster Cations with up to 840 Atoms: Structures, Formation Mechanism, and Reactivity. *J. Phys. Chem.* **1993**, *87*, 8182−8192.
(6) Hunter, J. M.; Fye, J. L.; Roskamp, E. J.; Jarrold, M. F. Annealing Carbon Cluster Ions: A Mechanism for Fullerene Synthesis. *J. Phys. Chem.* **1994**, *98*, 1810−1818.
(7) Straut, D. L.; Scuseria, G. E. Cycloaddition Model for Fullerene Formation. *J. Phys. Chem.* **1996**, *100*, 6492−6498.
(8) Wakabayashi, T.; Achiba, Y. A Model for the C_{60} and C_{70} Growth Mechanism. *Chem. Phys. Lett.* **1992**, *190*, 465−468. Wakabayashi, T.; Shiromaru, H.; Kikuchi, K.; Achba, Y. A Selective Isomer Growth of Fullerenes. *Chem. Phys. Lett.* **1993**, *201*, 470−474.
(9) Dias, J. R. Isomer Enumeration of Polycyclic Conjugated Hydrocarbons. *J. Chem. Inf. Comput. Sci.* **1984**, *24*, 124−135. Dias, J. R. Constant-Isomer Benzenoid Series and Their Topological Characteristic. *Theor. Chim. Acta* **1990**, *77*, 143−162. Cyvin, S. J. Enumeration and Classification of Benzenoid Hydrocarbons. Further Development for Constant-Isomer Series. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 413−418. Dias, J. R. Fullerenes to Benzenoids and Leapfrog Algorithm. *Chem. Phys. Lett.* **1993**, *204*, 486−490. Dias, J. R. Bendenoids to Fullerenes and Circumscribing Algorithm. *Chem. Phys. Lett.* **1993**, *209*, 439−444. Dias, J. R. Algorithm for Generating Fullerenes by Circumscribing. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 248−251.
(10) Hallett, R. P.; McKay, K. G.; Balm, S. P.; Allaf, A. W.; Kroto, H. W.; Stace, A. J. Reaction Studies of Carbon Clusters. *Z. Phys.* **1995**, *D34*, 65−70.
(11) Guo, T.; Smalley, R. E.; Scuseria, G. E. Ab-Initio Theoretical Predictions of C_{28}, $C_{28}H_4$, $C_{28}F4$, $(Ti@C_{28})H_4$, and $M@C_{28}$ (M = Mg, Al, Si, S, Ca, Sc, Ti, Zr, and Sn). *J. Chem. Phys.* **1993**, *99*, 352−359.
(12) Portmann, S.; Galbraith, J. M.; Schaefer, H. F.; Scuseria, G. E.; Luthi, H. P. Some New Structures of C_{28}. *Chem. Phys. Lett.* **1999**, *301*, 98−104.
(13) Raghavachari, K.; Binkley, J. S. Structure, Stability, and Fragmentation of Small Carbon Clusters. *J. Chem. Phys.* **1987**, *87*, 2191−2197.
(14) Stewart, J. J. P. *MOPAC93 Manual*; Fujitsu Ltd.: Japan, 1993.
(15) Bakowies, D.; Thiel, W. MNDO Study of Large Carbon Clusters. *J. Am. Chem. Soc.* **1991**, *113*, 3704−3714.
(16) Lin, Y.-T.; Mishra, R. K.; Lee, S.-L. Quantum Chemical AM1 Study of Growth Mechanisms of Fullerenes: A Facile C_2 Insertion Technique. *J. Phys. Chem.* **1999**, *103*, 3151−3155.
(17) Slanina, Z.; Lee, S.-L.; Yu, C.-h. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, pp 1−62.

CI9903105