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The shape of large single- and multiple-shell fullerenes

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The morphology of multiple-shell fullerenes is investigated by *ab initio* calculations using Yang's $O(N)$ method. It is found that for large single-shell fullerenes with I_h symmetry, the spherical morphology has lower energy than that of polyhedron. The formation energy per atom follows a simple scaling law. Including an estimate of intershell van de Waals interactions leads to the conclusion that spherical multiple-shell fullerenes are likely the most stable structure of large carbon clusters. These results are in good agreement with recent experiments.

The exciting discovery of concentric spherical graphitic shells by Ugarte[1] raises several intriguing questions. Most fundamentally, it suggests that multiple-shell fullerenes are the most stable structures of finite carbon clusters. This and the spherical shape of these fullerenes call for theoretical studies. For cluster size up to $N = 240$ carbon atoms, Adams *et al.*[2] have performed first principle calculations and showed that spherical fullerenes have a lower energy than that of tube-shaped fullerenes. However, based on empirical potentials calculations, geometric consideration, or elastic theory, several groups have concluded that for large fullerenes the morphology is polyhedrally faceted.[3–6] This appears to contradict the experimental observation of spherical shells.

In this paper, we report results of first principle calculations for carbon clusters up to 1000 atoms by the "divide-and-conquer" method of Yang.[7] These are the first *ab initio* calculations for such large molecules. Our results demonstrate that for single-shell fullerenes the spherical morphology has a lower energy than those of polyhedrons. The leading N dependence of the total energy obtained can be understood in term of the Hückel theory. Including the intershell van der Waals interactions leads to the conclusion that the multiple-shell concentric spherical fullerenes is likely the most stable structure of large carbon clusters, as observed in recent experiments.[1]

Most methods of first principle calculations are limited to molecules of small or modest size. Recently one of us has developed an efficient $O(N)$ algorithm,[7] designed specifically for large molecules. The method has been implemented for general molecular computations and tested in small systems against the traditional Kohn-Sham density-functional theory. The tests performed were molecular bonding energetic, molecular internal rotation potential barriers, and total electronic density of states.[7] In our present calculations, a cluster is divided into subsystems with one atom each, and the local basis set for each subsystem used includes the atomic orbitals of the atom as well as those up to third nearest neighbors. We use the local density approximation (LDA) for the exchange and correlation energy and numerical LDA solutions of a spherical carbon atom for atomic orbitals. To reduce the computational effort the non-self-consistent Harris functional[8] is employed as well as the I_h symmetry. Using this new method we are able to carry out *ab initio* calculations for carbon clusters up to 1000 atoms. Selective results are summarized in Table I.

We restrict our investigation to Goldberg type I fullerenes[4,9] with I_h symmetries. The number of atoms in the nth shell is $N(n) = 60n^2$ and the average radius can be approximated by $\bar{R}_n \approx 2.4\bar{b}n$, where $\bar{b}$ is the average bond length. Thus the intershell spacing is close to the interlayer distance in the graphite, giving rise to the maximum intershell van der Waals attraction. For the smallest member C_{60}, all sites are equivalent and the shape can be classified equally well as spherical or polyhedral. The next shell C_{240} has three independent atomic sites (Fig. 1). The I_h symmetry reduces the independent variables to 7. We have investigated four most likely morphologies: (1) sphere (S), in which all three sites are assumed to be on a spherical surface; (2) icosahedrally (I) faceted. Here all three sites are assumed to be on a faceted surface. Extending this morphology to large fullerenes leads to an icosahedron;[5] (3) truncated icosahedron (TI). This is an inflated version of C_{60}, in which sites 1 and 2 (Fig. 1) are assumed to be on the pentag-

TABLE I. Formation energies per atom for various fullerenes with different morphologies: S—spherical, I—icosahedron faceted, TI—truncated icosahedron, YO—the structure given in Ref. 4. $\bar{b}$—average bond length, $\bar{R}$—average radius, SD—standard deviation from a perfect sphere.

	E_c (eV)	$\bar{b}$ (Å) (b_1, b_2)	$\bar{R}$ (Å)	SD (Å)
S-C_{240}	-7.05	1.43 (1.43, 1.43)	7.12	0.00
I-C_{240}	-6.90	1.45 (1.46, 1.42)	7.27	0.39
TI-C_{240}	-6.92	1.46 (1.47, 1.43)	7.09	0.18
YO-C_{240}	-6.97	1.45 (1.45, 1.40)	7.03	0.17
S-C_{540}	-7.09	1.41 (1.42, 1.41)	10.5	0.00
I-C_{540}	-6.86	1.43 (1.44, 1.40)	10.4	0.52
S-C_{960}	-7.15	1.40 (1.40, 1.40)	13.8	0.00

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to be on the pentagonal facet while sites 2 and 3 are on a hexagonal facet; (4) the low energy morphology obtained by Yoshida and Osawa (YO).[4] This morphology is neither spherical nor simply faceted. However, as measured by the deviation from a sphere it is very close to TI.

For the morphologies S, I and TI the total energy was minimized with respect to two independent bond lengths (Fig. 1). For the (YO) shape we take the ratios of various bond lengths to be the same as that given by Ref. 4 and minimize the energy with respect to the average bond length. Table I lists formation energies and corresponding geometric parameters obtained. As one can see, S-C_{240} has a significantly lower energy than that of I-C_{240}, TI-C_{240}, and YO-C_{240}. Therefore, our results demonstrate that for C_{240} the spherical morphology is more stable than that of polyhedrons. This conclusion remains unchanged when the calculations were repeated using the atomic orbitals from up to fourth nearest neighbor atoms.

Included in Table I are also results of similar investigations for C_{540} and C_{960}. Again it is found that the spherical morphology has a significant lower energy. Strong evidence in favor of the spherical shape is the fact that in all cases the formation energy is correlated with the sphericity as measured by the standard deviation (SD) from a perfect sphere (Table I). The more spherical the morphology, the lower the energy. Based on these results we conclude that *for large single-shell fullerenes the spherical shape is the preferred morphology.* Though we believe that our calculations provide a strong support of this conclusion, we do caution that it is based on limited calculations. We hope our results will stimulate other groups to pursue similar first principle calculations. The complete relaxation for C_{240} within the LDA should be possible in the near future (see the paragraph after our conclusion).

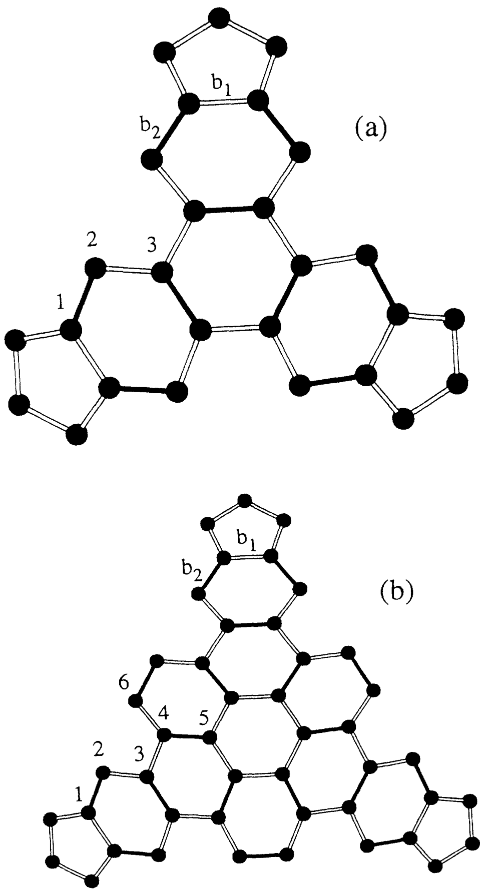

FIG. 1. The asymmetric part of large fullerene structures. (a) C_{240}; shown are three independent sites and two bond labeling (see text). (b) Similar drawing for C_{540}.

To understand the N dependence of the formation energy several more clusters are examined. Plotted in Fig. 2 are the formation energy per atom E_c versus $1/N$. E_c decreases monotonically with increasing fullerene size N. A straight line fitting to the four largest fullerenes calculated leads to

$$E_c(N) = -7.178\left(1.0 - \frac{4.69}{N}\right)\ \text{eV}\,. \qquad (1)$$

Thus $E_c(\infty) = -7.178$ eV is the extrapolated cohesive energy per atom for single graphitic layer. This number is close to that found by other LDA calculations (7.7 eV) and by experiments (7.37 eV).[10] The absolute value of $E_c(\infty)$ is less reliable as it is an extrapolation. The following results do not depend sensitively on this value.

The simple $1/N$ dependence can be understood in terms of the Hückel theory. In the nearest neighbor tight binding calculation there are two contributions to the energy difference between fullerenes and that of a graphitic layer. The first is due to the finite size of fullerenes. This can be regarded also as the defect energy associated with the twelve pentagons. Straightforward calculations show that the tight binding energy per atom increases linearly with $1/N$, $E_t(N) = -1.574t(1 - \frac{0.835}{N})$, where t is the nearest neighbor hopping integral.[12] This relation should reflect the approximate N dependence of the σ

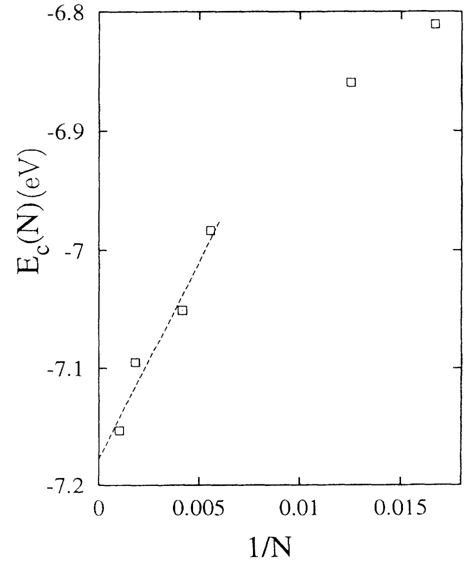

FIG. 2. The formation energy vs $1/N$ for N =60,80,180,240,540,960. The straight line [Eq. (1)] is the least squares fit for the four largest fullerenes. $E_c(N)$ is measured in eV.

bonding energy. The second, and more important contribution comes from the fact that the nearest neighbor π orbital overlap depends on the molecular size.[2] For the spherical morphology t_π is approximately proportional to $\cos(\phi)$, where ϕ is the radial angle spanned by the nearest neighbor CC bond, $t_\pi = t_0 \cos\phi = t_0 \cos[2\arcsin(\frac{b}{2R_N})]$, where R_N is the radius of the sphere and t_0 is the limiting value for the graphitic plane. Taking $R_N \approx 2.4b\sqrt{N/60}$ and expanding in $1/N$ to the leading order one gets

$$t_\pi \approx t_0 \left(1.0 - \frac{5.21}{N}\right). \tag{2}$$

Compared with Eq. (1) one sees that the dominant contribution to the N dependence is due to the change in p_π orbital overlaps.

We now discuss the energetics of multiple-shell fullerenes and their morphology. Here one needs to include the intershell interactions. In Goldberg type I fullerenes the spacing between successive shells, ~ 3.4 Å, is almost the same as that of the interlayer spacing in graphite. Therefore one expects that interactions are dominated by the van der Waals force. In solid C_{60}, intermolecular interactions have been successfully modeled using the van der Waals interactions.[11] There it was found that 90% of the cohesion energy can be calculated by simply summing over all interfullerenes CC interactions using the Lennard-Jones potential. For multiple-shell fullerenes, this method should be an even better approximation as the intershell spacing is uniform. Therefore, we use the same Lennard-Jones potential ($\epsilon = 2.964$ meV, $\sigma = 3.407$ Å) to evaluate intershell interactions.

The fact that $R_{n+1} - R_n \sim \sigma$ suggests that the intershell attraction is the largest when both shells have the spherical shape. Indeed our calculations show that the attractive interactions in the sphere morphology are significantly larger than that of polyhedrons. For example, the attraction between S-C_{240} and S-C_{540} (-17.7 eV; see Table II) is significantly larger than that between I-C_{240} and I-C_{540} (-12.3 eV). Thus the intershell van der Waals interaction also favors the spherical shape. Therefore, we conclude that *the shape of a multiple-shell fullerene is spherical.* In Fig. 3 a nonperspective view of a five-shell fullerene is shown.[13]

From Table II the van der Waals interaction between the nth and $(n+1)$th shell is well described by $V_{n,n+1} = -3.0n(n+1)$ eV. Using Eq. (1) for the single-shell fullerene energy, one can estimate that when $n \geq 3$ a two-shell fullerene with $N(n) + N(n+1)$ atoms is more stable than a single-shell fullerene with the same total number of atoms. For example, the two-shell fullerene $C_{(540,960)}$ is more stable than single shell C_{1500}. This result is rather different from an earlier calculation where the crossover was found to occur at $N \sim 6000$.[5] Finally, it is clear that for large clusters the dense multiple-shell fullerenes are most stable. This is because for a l-shell fullerene the van der Waals attraction is $\sim l^3$, while the cost compared with a single-shell fullerene with the same number of atoms is $\sim l$.

TABLE II. The van der Waals interactions between the first five shells of a dense spherical multiple-shell fullerene.

V_{ij} (eV)	C_{240}	C_{540}	C_{960}	C_{1500}
C_{60}	-5.57	-0.81	-0.20	-0.07
C_{240}		-17.7	-2.34	-0.55
C_{540}			-35.9	-4.28
C_{960}				-59.9

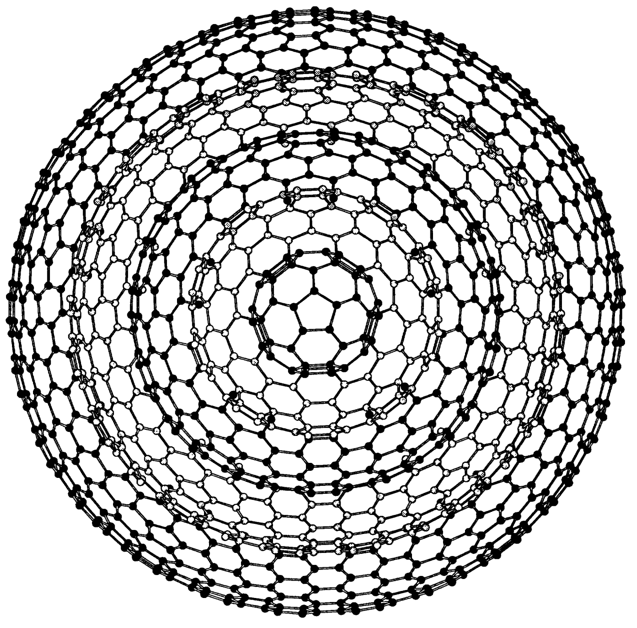

FIG. 3. A nonperspective view of the five-shell dense fullerenes $C_{(60,240,540,960,1500)}$. For clarity, only a portion of each shell is shown.

Experimentally, both spherical and polyhedral multiple-shell fullerenes are found. However, polyhedral fullerenes transform into spherical shape after annealing.[1] This suggests that the spherical shape has the lowest energy and the polyhedral shape is metastable. Our calculations fully support this picture as the difference in energies is small.

In conclusion, we have shown that the shape of a large fullerene is spherical regardless of whether it is single or multiple shell.[14] By including van der Waals interactions between shells it is demonstrated that spherical dense multiple-shell fullerenes are likely the most stable structures for large carbon clusters. This is in good agreement with recent experimental observations of these concentric spherical shells. The possibility of forming a lattice of multiple-shell fullerenes should open up a new area of fullerene research and many interesting physical properties can be expected.

Recently, we have found that in a complete geometry optimization for C_{240} the same spherical morphology is found to be the lowest energy structure.[15]

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[12] If all nearest neighbor hoppings are identical, calculations show that all type I Goldberg series are close shelled. This is generally not true for type II in which $N(n) = 20n^2$.

[13] For spherical morphology, the rotational barrier of inner shell vs outer shell is very small; free rotation is expected. In contrast, for polyhedron morphologies the barriers are very high, which leads to very different intershell vibrational modes. This and related issues will be examined elsewhere.

[14] After our paper was written we were informed about the paper by B. I. Dunlap *et al.*, J. Phys. Chem. **95**, 8737 (1992), in which they use the Brenner empirical potentials (Ref. 9) to obtain the optimal structure of C_{240}. Their results are almost identical to that of Yoshida and Osawa (Ref. 4). For example, the standard deviation from sphere is 0.17 Å (which was mistakenly stated as 0.085 Å).

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