

Density-functional calculations of the structure and stability of  $C_{240}$ 

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Density-functional calculations have been performed to determine optimized geometries and energies of  $C_{240}$  using the divide-and-conquer method. Six initial geometries were considered, resulting in convergence to two optimized configurations. The formation energies of the optimized structures are separated by approximately 0.07 eV/carbon atom. The lower-energy structure is highly spherical in agreement with preliminary studies and experimental observations. The higher-energy structure is polyhedrally faceted. The results support the conclusion that the most stable form of large carbon clusters is that of dense spherical caged structures.

The recent discovery of concentric-shell graphitic structures by Ugarte<sup>1</sup> has generated a great deal of interest and controversy concerning what is the most stable form of carbon in systems of limited size. Ugarte observed that upon irradiating carbon soot particles with an intense electron beam, dense quasispherical "caged" molecules were formed.<sup>1-3</sup> This is in agreement with theoretical predictions that suggest spheroid fullerene structures are energetically preferred over tube-shaped structures.<sup>4,5</sup> In contradiction, other theoretical investigations based on geometric considerations,<sup>6</sup> elastic theory,<sup>7</sup> and empirical models<sup>8-10</sup> suggest large fullerenes are polyhedrally faceted.

In this paper we present evidence from first-principles calculations that the (low-temperature) ground-state structure of  $C_{240}$ , the second Goldberg type-I fullerene, is highly spherical, in agreement with preliminary theoretical investigations<sup>11</sup> and experiment.<sup>1-3</sup> A second faceted form has also been identified that is higher in energy, and qualitatively similar to previously described structures.<sup>8-10</sup>

The present study employs the divide-and-conquer method for density-functional (DF) electronic-structure calculations of large molecules<sup>12,13</sup> to examine the structure and stability of  $C_{240}$ . The method has been shown to be accurate in small systems compared to the conventional Kohn-Sham density-functional theory.<sup>14</sup> The well-established  $I_h$  symmetry of  $C_{240}$  reduces the number of independent degrees of freedom to seven. Several probable morphologies of  $C_{240}$  are considered: a sphere ( $S$ ), icosahedron ( $I$ ), truncated icosahedron (TI), and the low-energy structure reported by Yoshida and Osawa (YO). Preliminary studies examined the relative energies of these structures optimized with respect to two independent bond lengths.<sup>11</sup> The present work extends these studies to consider full geometry optimization of  $C_{240}$  under  $I_h$  symmetry. For convenience, four bond

lengths ( $b_1, b_2, b_3, b_5$ ) and three radii ( $r_1, r_2, r_3$ ) were chosen as the independent variables (Fig. 1).

In the present calculations using the divide-and-conquer method, the  $C_{240}$  molecule is divided into subsystems consisting of a single carbon atom. The local basis set used in the projection of Kohn-Sham Hamiltonian involves atomic orbitals of the central carbon atom and up to third-nearest-neighbor carbon atoms. We employ the Vosko, Wilk, and Nusair<sup>15</sup> local-density approximation (LDA) for the exchange-correlation potential, and numerical LDA solutions for an isolated carbon atom for the atomic orbitals. Calculations were performed using the non-self-consistent Harris functional<sup>16</sup> which has

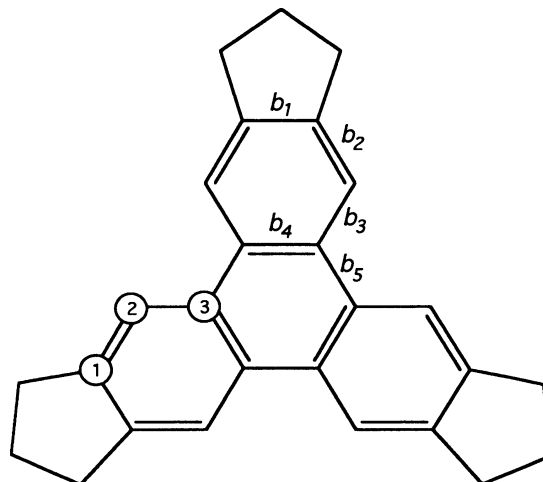


FIG. 1. Region of  $C_{240}$  showing independent atomic sites (1-3) under  $I_h$  symmetry. The independent variables used in the optimization and described in the text are the three radii (magnitudes of the atomic position vectors from the center-of-mass origin)  $r_i = |\mathbf{r}_i - \mathbf{r}_0|$ ,  $i=1,2,3$ , and the four bond lengths ( $b_1, b_2, b_3, b_5$ ).

TABLE I. Starting configurations and final states for C<sub>240</sub> optimization.

Morphology	Bonds ( $b_1, b_2, b_3, b_4, b_5$ ) (Å)	Radii ( $r_1, r_2, r_3$ ) (Å)	$E_c^a$ (eV)	Final <sup>b</sup>
sph1 <sup>c</sup>	(1.44,1.43,1.44,1.43,1.44)	(7.12,7.12,7.12)	-7.05	<i>S</i>
sph2 <sup>c</sup>	(1.43,1.44,1.43,1.43,1.44)	(7.12,7.12,7.12)	-7.05	<i>S</i>
fac1 <sup>d</sup>	(1.48,1.44,1.48,1.44,1.48)	(7.03,7.42,6.97)	-6.93	<i>S</i>
fac2 <sup>e</sup>	(1.47,1.43,1.47,1.43,1.47)	(7.63,7.21,6.75)	-6.90	<i>P</i>
fac4 <sup>f</sup>	(1.45,1.40,1.47,1.45,1.46)	(7.49,7.19,7.05)	-6.97	<i>P</i>
YO <sup>g</sup>	(1.43,1.38,1.45,1.42,1.43)	(7.36,7.06,6.92)		<i>P</i>

<sup>a</sup>Binding energy per atom of starting geometry:  $E_c = E_{\text{total}} - E_{\text{carbon}}$  where  $E_{\text{total}}$  is the total energy/atom in the molecule and  $E_{\text{carbon}}$  is the energy calculated for an isolated carbon atom (-1019.556 eV).

<sup>b</sup>Final converged state (*S*, highly spherical; *P*, polyhedral; see text and Table II).

<sup>c</sup>Spherical geometries resulting from two-parameter optimization starting from a spherical (*S*) morphology.

<sup>d</sup>Faceted geometry resulting from two-parameter optimization starting from a truncated icosahedron (TI).

<sup>e</sup>Faceted geometry resulting from two-parameter optimization starting from an icosahedron (*I*).

<sup>f</sup>Faceted geometry resulting from two-parameter optimization starting from the structure reported by Yoshida and Osawa (YO) (Ref. 9).

<sup>g</sup>Faceted structure reported by Yoshida and Osawa obtained from an empirical potential (Ref. 9).

been demonstrated to be reliable in the prediction of the structure and normal modes of C<sub>60</sub> (Ref. 17) and the geometries and relative energies of a variety of carbon clusters.<sup>4</sup>

The divide-and-conquer code has been modified to perform nongradient geometry optimizations for limited degrees of freedom using a simplex algorithm. To circumvent the local minima problem in multidimensional optimization, several initial configurations were considered (Table I), including four faceted geometries. Optimizations were terminated when adjustment of the independent variables (Fig. 1) by  $\pm\delta$  [ $\delta = 1.0(10^{-5})$  Å] produced no further reduction in the total energy. Optimization of the six starting structures converged to two local energy minima (Table II), designated *S* (spherical) and *P* (polyhedral). The difference in binding energy per atom ( $E_c$ ) was 0.07 eV/carbon atom.<sup>18</sup> The binding energy per atom of the optimized C<sub>240</sub> structures (-7.00 and -7.07 eV/carbon) was considerably larger in magnitude than for the optimized C<sub>60</sub> molecule (-6.81 eV/carbon). The lower-energy *S* structure is close to spherical (Table II), as indicated by the small standard deviation (SD) of the radii (the magnitudes of the atomic position vectors from the center-of-mass origin; a perfect sphere has 0 SD). The higher-energy *P* structure is polyhedrally faceted. The *S* and *P* structures are shown in Fig. 2. The *S* structure is quite similar to the optimized spherical morpholo-

gy previously reported.<sup>11</sup> The *P* structure is qualitatively similar to structures obtained from realistic empirical potentials reported by Yoshida and Osawa<sup>9</sup> and Dunlap and co-workers,<sup>10</sup> and described by Maiti and co-workers.<sup>8</sup> The *P* structure appears spherical if viewed along the fivefold symmetry axis, but appears polyhedral when viewed from a different perspective [compare Figs. 2(b) and 2(c)], in agreement with observations of Maiti and co-workers.<sup>8</sup>

The *S* and *P* structures differ significantly in the planarity of the  $\sigma$  bonds of the  $sp^2$  carbons. Since each carbon atom is covalently bound to three neighbor carbons, three angles ( $\theta_i, i=1,2,3$ ) are easily identified with each atom. If the central carbon lies in the plane of its three neighbors, then  $\phi \equiv 360^\circ - (\theta_1 + \theta_2 + \theta_3)$  is  $0^\circ$ . If the carbon is out of the plane,  $\phi$  is correspondingly greater than zero. Hence,  $\phi$  is a simple measure of the planarity of the  $sp^2$  carbons. The  $\phi$  values of the three independent atomic sites 1-3 (Fig. 1) of the *S* structure (1.5°, 4.2°, 3.2°) are more evenly distributed than those of the *P* structure (13.4°, 0.4°, 1.8°). Presumably, the strain energy of curved graphitic surfaces is primarily due to the planarity of the carbons.<sup>4</sup> Hence, it is apparent that the *S* structure more evenly distributes the nonplanar strain (with less overall deformation), whereas the *P* structure focuses the strain at the pentagon carbons (atom 1 in Fig. 1).

The results reported here provide insight into the ap-

TABLE II. Binding energy and geometric parameters for optimized C<sub>240</sub> structures.

State <sup>a</sup>	Bonds ( $b_1, b_2, b_3, b_4, b_5$ ) (Å)	Radii ( $r_1, r_2, r_3$ ) (Å)	$\bar{r}^b$ (Å)	$E_{\text{total}}^c$ (eV)	$E_c^d$ (eV)
<i>S</i>	(1.428,1.434,1.446,1.421,1.438)	(7.009,7.128,7.143)	7.106 (0.056)	-1026.625	-7.07
<i>P</i>	(1.434,1.417,1.508,1.470,1.464)	(7.660,7.191,7.068)	7.247 (0.244)	-1026.552	-7.00

<sup>a</sup>*S*, (highly) spherical; *P*, polyhedral (see text).

<sup>b</sup>Average radius; standard deviation is given in parentheses.

<sup>c</sup>Total energy per atom in the molecule.

<sup>d</sup>Binding energy per atom  $E_c = E_{\text{total}} - E_{\text{carbon}}$  where  $E_{\text{carbon}}$  is the energy calculated for an isolated carbon atom (-1019.556 eV).

parent controversy about the ground-state structure of giant fullerenes. Our theoretical model predicts the most stable (low temperature) structure of  $C_{240}$  is highly spherical, and is consistent with observations by high-resolution electron microscopy.<sup>1-3</sup> These studies show that carbon particles obtained from an arc discharge [in the form of graphitic tubes and faceted (hollow) caged particles] transform into dense multiple-layered spheroidal particles when subjected to an intense electron beam.<sup>1,2</sup> This has led to the conclusion that the dense spherical caged structure is the canonical form of large carbon clusters.<sup>2</sup> Interestingly, however, structures obtained from high-temperature annealing of carbon soot<sup>19</sup> appear fundamentally different than those from electron bombardment.<sup>1-3</sup> Unlike the dense spherical caged structures of the latter, the structures of the former can be hollow and polyhedral shelled (the structures were observed to depend on the maximum temperature used in the annealing process). Hence, existence of a low-energy polyhedral structure of  $C_{240}$  is of interest. The relative importance of these structures in the formation of multiple layered carbon clusters under different conditions has yet to be determined. Nonetheless, the overall results of our study support the suggestions of Ugarte<sup>1-3</sup> that the most stable form of large (finite) carbon clusters is that of a dense spherical caged structure. Intense effort in the development and exploitation of pure forms of molecular carbon provides optimism that further interplay of theory and experiment will be fruitful in unraveling the formation mechanism and ground-state properties of a host of fullerene compounds.

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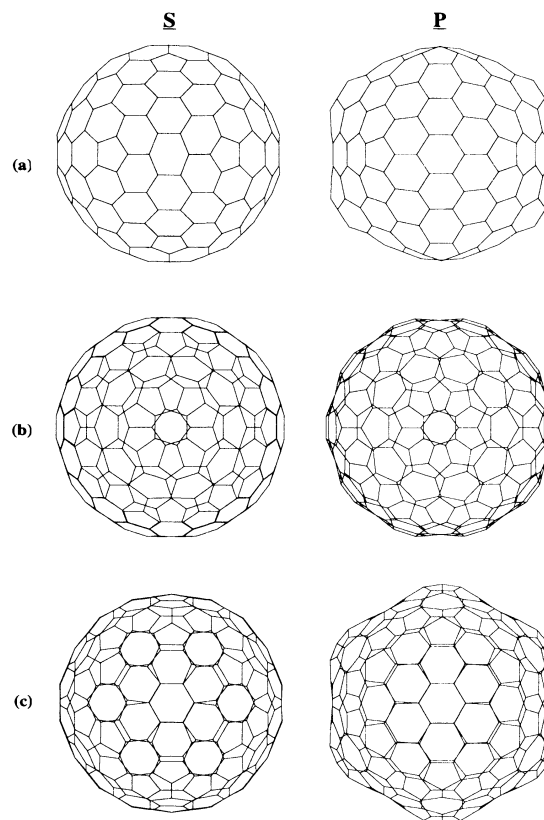


FIG. 2. Nonperspective views of the *S* and *P* optimized  $C_{240}$  structures. (a) View is along a twofold rotation axis (atoms are eclipsed). (b) View is along a fivefold rotation axis. (c) View is along a threefold rotation axis to illustrate the nonsphericity of the *P* structure.

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<sup>1</sup>D. Ugarte, *Nature* **359**, 707 (1992).

<sup>2</sup>D. Ugarte, *Europhys. Lett.* **22**, 45 (1993).

<sup>3</sup>D. Ugarte, *Chem. Phys. Lett.* **207**, 473 (1993).

<sup>4</sup>G. B. Adams, O. F. Sankey, J. B. Page, M. O'Keeffe, and D. A. Drabold, *Science* **256**, 1792 (1992).

<sup>5</sup>G. E. Scuseria, in *Buckminsterfullerenes*, edited by W. E. Billups and M. A. Ciufolini (VCH, New York, 1992).

<sup>6</sup>K. G. McKay, H. W. Kroto, and D. J. Wales, *J. Chem. Soc. Faraday Trans.* **88**, 2815 (1992).

<sup>7</sup>J. Tersoff, *Phys. Rev. B* **46**, 15 546 (1992).

<sup>8</sup>A. Maiti, C. J. Brabec, and J. Bernholc, *Phys. Rev. Lett.* **70**, 3023 (1993).

<sup>9</sup>M. Yoshida and E. Osawa, *Fullerene Sci. Tech.* **1**, 55 (1993).

<sup>10</sup>B. I. Dunlap, D. W. Brenner, J. W. Mintmire, R. C. Mowrey,

and C. T. White, *J. Phys. Chem.* **95**, 8737 (1991).

<sup>11</sup>J. P. Lu and W. Yang, *Phys. Rev. B* (to be published).

<sup>12</sup>W. Yang, *Phys. Rev. Lett.* **66**, 1438 (1991).

<sup>13</sup>W. Yang, *Phys. Rev. A* **44**, 7823 (1991).

<sup>14</sup>C. Lee and W. Yang, *J. Chem. Phys.* **96**, 2408 (1992).

<sup>15</sup>S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).

<sup>16</sup>J. Harris, *Phys. Rev. B* **31**, 1770 (1985).

<sup>17</sup>G. B. Adams, J. B. Page, O. F. Sankey, K. Sinha, and J. Menendez, *Phys. Rev. B* **44**, 4052 (1991).

<sup>18</sup>Inclusion of atomic orbitals up to fourth- and fifth-nearest-neighbor atoms does not alter the relative energy (0.07 eV) of the optimized *S* and *P* structures.

<sup>19</sup>W. A. de Heer and D. Ugarte, *Chem. Phys. Lett.* **207**, 480 (1993).