PHYSICAL REVIEW B VOLUME 57, NUMBER 7 15 FEBRUARY 1998-I

Fused fullerenes and multiply connected carbon clusters: Proposed new forms of carbon

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(Received 24 September 1996; revised manuscript received 26 August 1997)

We explore forms of carbon obtained from fusing fullerenes and demonstrate that (i) they are energetically more favorable than toroidal forms, and (ii) for small sizes, doubly connected structures resembling gears provide local minima where the strain is reduced via the formation of fourfold coordination. Some of these structures can be treated as a ''superatom'' which, when used as a building block for the solid, yield a crystal with fourfold coordination for all atoms, but with two-thirds the density of diamond. The recent experimental results reported may already point to the existence of fused fullerene structures. [S0163-1829(98)03107-5]

The interest in pure carbon systems was rekindled by the discovery of highly stable caged forms of carbon.[1,2] Among the group-IV elements, carbon is unique in that its special chemistry allows it to form stable clusters with widely differing coordination in the form of chains, rings, and fullerenes. It is now generally accepted that the ground state for carbon clusters for clusters with $N \leqslant 10$ consists of planar geometries with low coordination.[3,4] This can be attributed to the presence of substantial strain energy on account of the small covalent radius of the carbon atom which prevents the formation of close-packed structures ($n_b/N > 2$, where n_b is the number of bonds within a specified cutoff distance) found in clusters of atoms with larger covalent radii, such as silicon for $N \leqslant 10$. For $N \geqslant 20$, formation of fullerenes (closed cages with positive curvature everywhere) becomes possible, with carbon atoms arranged in the form of pentagons and hexagons. All theoretical calculations give an energy minimum even for the smallest fullerene (C_{20}), although the precise geometry is still in dispute.

Further, many other threefold-coordinated structures have been proposed for carbon. They include graphitic tubules,[5–16] capsules (capped tubules),[8] and toroids.[17–20] The tubes and capsules incorporate graphitic features (all hexagons) in their cylindrical part. The capsules also incorporate fullerene features (pentagons and hexagons) in their cap regions. The toroids, on the other hand, are doubly connected carbon molecules with five-, six-, and seven-membered rings (heptagons). They require equal numbers of pentagons and heptagons to provide the necessary curvature to close the torus on itself.[21]

It is generally agreed that introduction of pentagons into graphitic sheets allows folding of these sheets to create three-dimensional structures with threefold coordination. In fullerenes the pentagons bear most of the strain resulting from the curvature. When compared to fullerenes, the toroidal molecules have higher curvature, with the pentagons and heptagons bearing the entire burden of curvature. Strain consideration would suggest them to be less stable than the corresponding fullerene. Furthermore, their complex topology (multiple connectivity) is expected to make their fabrication significantly more difficult than that of fullerenes. Indeed, suggestions have been made to facilitate their fabrication by placing an atom at the center of the structure.[19]

The possibility of the existence of a solid phase of carbon called hyperdiamond, formed by C_{28} fullerenes covalently linked in a diamond lattice, has also been suggested.[22] Recent experiments using low-energy neutral-cluster beam deposition have obtained carbon thin films exhibiting curious structures.[23] These highly metastable films show some characteristic features related to the phonon density of states of diamond, leading to the speculation that they may consist of fused fullerenes in the 20–32-atom size range.

In this paper we explore fused fullerenes,[24] and find a set of multiply connected gearlike carbon clusters [e.g., Figs. 1(c) and 1(e)] with unusual coordination properties. These contain carbon atoms with threefold and fourfold coordination, arranged in the form of four-, five-, six-, seven-, and eight-membered rings. These structures have smaller curvature and higher cohesive energies when compared with the toroidal molecules, making their existence more favorable. Furthermore, their fabrication is made relatively easier by the fact that they are derived from fusing fullerenes that can be abundantly produced in experiments. Also, the presence of incompletely formed fullerenes in the arc might promote the formation of fused cages. It should be noted, however, that in no case is a fused fullerene lower in energy than an isolated fullerene containing the same number of atoms. They have been found to be a local minimum of energy using a quantum molecular dynamics method.

The theoretical method used in the present work is the generalized tight-binding molecular dynamics (GTBMD) (Refs. 4 and 25) scheme of Menon and Subbaswamy, that allows for full relaxation of covalent systems with no symmetry constraints. This method has been applied to obtain equilibrium geometries for small silicon and carbon clusters,[4,25–28] in good agreement with *ab initio* results.[3,29] GTBMD has also been found reliable in obtaining good agreement with experimental and local density approximation results for the structural and vibrational properties of fullerenes and nanotubes.[25] The GTBMD scheme gives a graphite-C_{60} energy difference of -0.41 eV/atom, in very good agreement with the experimental estimate of -0.44 eV/atom.[30]

All fused fullerenes and gearlike structures were carefully relaxed to structures that are true local minima of the total energy. The vibrational frequencies were then computed for these relaxed structures within the GTBMD scheme, where

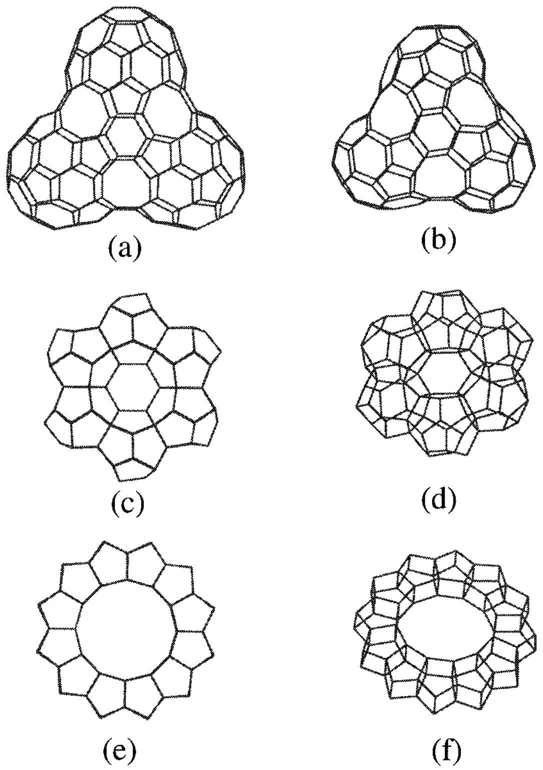

FIG. 1. Relaxed geometries for fused fullerenes containing (a) 150 and (b) 120 atoms. (c) Top view and (d) view at an angle for the 90-atom structure. (e) Top view and (f) view at an angle for the 72-atom structure.

the force constants are obtained by explicitly calculating analytic second derivatives of the electronic structure Hamiltonian matrix elements.[25] This method, while providing better accuracy than numerical derivative schemes, greatly expedites the determination of vibrational modes for large size clusters. None of the structures proposed here had any imaginary frequencies, indicating that they are true local minima of the total energy.

The fused fullerenes may be designated by the notation ${}^{N}({}^{\mu}_{\nu})_{S}$, where N is the number of atoms in the fused cluster, μ is the number of carbon atoms in the starting fullerenes, ν is the number of C_{μ} fullerenes fused, and S is the symmetry designation of the resulting cluster. We begin with the structure ${}^{150}({}^{60}_{3})_{D_{3h}}$ [Fig. 1(a)], namely, one obtained by fusing three C_{60} fullerenes at pentagonal faces, with atoms forming the pentagons at the interfaces between adjacent units being coincident. These ten atoms are then removed and the structure is allowed to relax using the GTBMD scheme to obtain a molecule of D_{3h} symmetry. The resulting structure has threefold coordination for all atoms. The interfullerene connectivity for this molecule is via nine eightfold rings. Additionally, there are 30 fivefold and 38 sixfold rings. Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are doubly degenerate; the gap is 0.76 eV. This cluster is only 0.14 eV/atom less stable than the 150-atom closed tubule. Carbon atoms in this structure are more stable than those in C_{60} molecule by 0.02 eV/atom (Table I).

Fused-fullerene structures involving other fullerene units can similarly be generated. For example, the 120-atom fused fullerene, ${}^{120}({}^{50}_{3})_{D_{3h}}$, is created by fusing three C_{50} fullerenes in the same way as in the case of the ${}^{150}({}^{60}_{3})_{D_{3h}}$ structure. The GTBMD relaxation of this molecule also preserves its D_{3h} symmetry [Fig. 1(b)]. It contains 27 pentagons and 26 hexagons. The interfullerene linkage for this molecule is via three sevenfold and six eightfold rings. The HOMO-LUMO separation for this cluster is 0.41 eV, and the cluster is only 0.23 eV/atom less stable than the 120-atom fullerene. But more importantly, this structure is 1.2 eV more stable than the relaxed 120-atom torus (Table I).

TABLE I. Number of atoms in the molecule, structures, relative energies, and HOMO-LUMO gaps as calculated from the GTBMD scheme. The energies quoted are for fully optimized structures and relative to graphite.

N	Structure	Symmetry	Energy (eV/atom)	HOMO-LUMO gap (eV)
60	Fullerene	I_h	0.41	1.34
72	Fullerene	D_{6d}	0.38	1.13
	Gearlike structure	D_{12h}	2.12	1.08
84	Fullerene	D_{6h}	0.33	1.10
	Gearlike structure	D_{6h}	1.34	1.12
90	Fullerene	T_d	0.32	0.44
	Gearlike structure	D_{6h}	0.85	1.41
120	Fullerene	T_d	0.26	1.14
	Tubule[a]	D_{5h}	0.28	0.47
	Torus	D_{5d}	0.50	1.00
	Gearlike structure	D_{2h}	0.70	0.74
	${}^{120}({}^{30}_{3})_{D_{3h}}$	D_{3h}	0.49	0.41
150	Tubule[b]	D_{3h}	0.25	0.70
	${}^{150}({}^{60}_{3})_{D_{3h}}$	D_{3h}	0.39	0.76
180	${}^{180}({}^{70}_{3})_{D_{3h}}$	D_{3h}	0.36	0.50

[a] Capped$^{[5,5]}$ tubule in the notation of Ref. 11.

[b] Capped$^{[6,6]}$ tubule in the notation of Ref. 11.

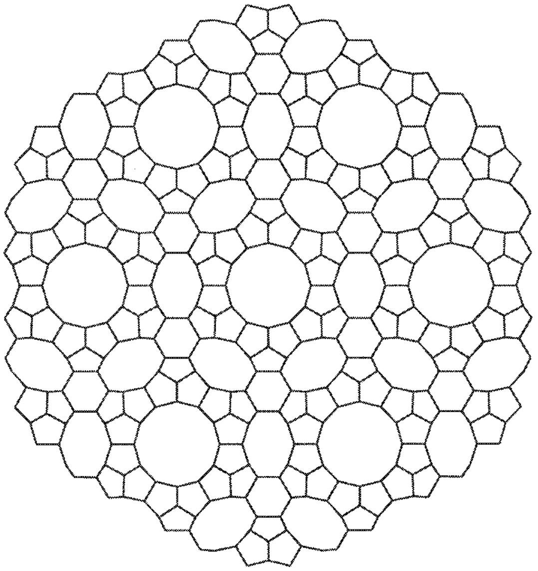

FIG. 2. Two-dimensional Bravais lattice formed by the 84-atom structures.

The C_{70} fullerene can be used in the creation of the fused structure ${}^{180}\binom{70}{3}_{D_{3h}}$. The HOMO and LUMO levels for the relaxed cluster are doubly degenerate with a gap of 0.50 eV. In addition to nine eightfold rings, it contains 30 pentagons and 53 hexagons. This structure is also found to be more stable than the C_{60} molecule (Table I). It may be readily shown that the fused-fullerene structures in this class obey the Euler formula $N(5)-N(7)-2N(8)=12$, where $N(5)$, $N(7)$, and $N(8)$ are the number of pentagons, heptagons, and octagons, respectively.

The sequence ${}^{N}\binom{\mu}{\nu}_S$ no longer yields simply connected cages with fullerene units containing smaller number of atoms than C_{50}. This is because an overall increase in the curvature, with a corresponding decrease in μ causes an increase in the C-C bond distances between carbon atoms belonging to adjacent units, eventually exceeding a critical value, preventing the fusing of multiple fullerenes. In such cases linkage is possible only when not all the ten atoms forming the pentagons at the interfaces between adjacent units are removed. Then a class of structures with multiple connectivity can be generated by fusing smaller fullerenes at pentagonal faces but removing only five atoms from each unit. These molecules have higher curvature than fused fullerenes, and contain a large fraction of atoms with fourfold coordination. They are local-energy minima of the energy surface and preserve their high symmetry under GTBMD relaxation.

We illustrate their construction by choosing the fullerene with the highest curvature, namely, C_{20}. The structure containing 90 carbon atoms, is generated by fusing six C_{20} fullerenes after removing five carbon atoms forming a pentagon from each fullerene [Figs. 1(c) and 1(d)]. The GTBMD relaxation yields a cluster with D_{6h} symmetry containing 30 atoms with fourfold coordination, and a remaining 60 atoms with threefold coordination. With the exception of a single hexagon in the middle, this structure is made up entirely of pentagons. The HOMO-LUMO gap for this cluster is 1.41 eV, and the structure is 0.53 eV/atom less stable than the 90-atom fullerene.

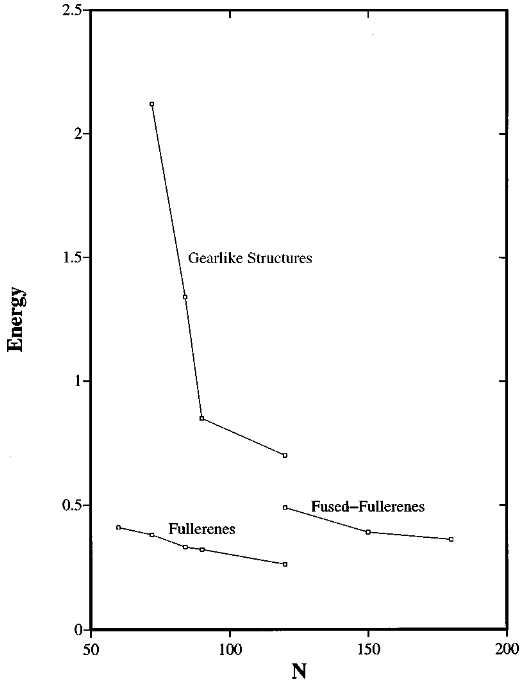

FIG. 3. Energy vs number of atoms for fullerenes, fused fullerenes and gearlike structures. Energies are in eV/atom, and relative to graphite.

Smaller gearlike-structures can be formed by strategic eliminations of certain symmetrically placed atoms from larger structures. For example, the 84-atom structure (D_{6h} symmetry) can be obtained by removing the six central atoms and relaxing the resulting structure. The relaxation produces several new bond formations, changing the overall coordination. This structure can be visualized as consisting of six circularly connected 14-atom closed units with faces composed of eight pentagons and four rectangles, with eight of these atoms having threefold coordination and the rest fourfold coordination. This structure contains no hexagons. Bond lengths range from 1.451 to 1.621 Å. There are 12 C-C bonds exactly parallel to the symmetry axis, making the structure highly incompressible in that direction. The vibrational analysis shows most of the soft modes to be associated with vibrations in directions perpendicular to the symmetry axis, and stiff modes associated with vibrations in directions along to the symmetry axis. The HOMO-LUMO separation is 1.12 eV, with both levels nondegenerate. This is 1.01 eV/atom less stable than the 84-atom fullerene.

Further, the 72-atom structure, [Figs. 1(e) and 1(f)] can be obtained by removing the 12 farthest atoms from the center of the 84-atom one and relaxing the structure. This structure has D_{12h} symmetry. Both the negative and positive curvatures are provided by fourfold rings. Additionally, there are 24 pentagons, 12 of them at the top and 12 at the bottom. The cluster contains no hexagons. The presence of so many pentagons in such a relatively small cluster makes this structure highly strained. However, 48 of the atoms have fourfold coordination, relieving some of the strain. This structure has a (HOMO)-(LUMO) gap of 1.08 eV, and is 1.74 eV/atom less stable than the 72-atom fullerene.

The D_{6h} symmetry of the 84-atom structure allows it to form a hexagonal Bravais lattice in two dimensions with large ‘‘holes’’ (Fig. 2). This property may have an important application in host-guest chemistry, where the hole can accommodate a ‘‘guest.’’[20] Interestingly, the host atoms surrounding the hole are all fourfold coordinated and, therefore, unreactive. This makes any strong chemical reaction between the host and the guest atoms unlikely. Further, by stacking these layers directly on top of each other along the symmetry axis, one can create a bulk solid with fourfold coordination for all carbon atoms. The resulting solid has two-thirds the density of diamond, and a predominant number of C-C bonds parallel to the symmetry axis.

In Fig. 3, we show a plot of relative energies of various structures with respect to graphite. Carbon atoms in the ${}^{150}\binom{60}{3}_{D_{3h}}$ and ${}^{180}\binom{70}{3}_{D_{3h}}$ structures are more stable per atom than those in C_{60}. The higher fused fullerenes are expected to be similarly more stable with decreasing energies. Although this is not a strict criterion for measuring relative stabilities with respect to C_{60}, nevertheless, formation of these metastable structures is plausible under favorable experimental conditions. While the fabrication of toroidal molecules requires host atoms, generation of gearlike structures involves fusing of abundantly producible fullerenes. The experimental results reported in Ref. 23 may already point to the existence of such structures.

We are indebted to J. Berger for supplying us with the initial coordinates for the 120-atom torus. This research was supported in part by USDOE Contract No. DE-FC22-93PC93053, by NSF Grant No. OSR 94-52895, and by the University of Kentucky Center for Computational Sciences.

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