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Toroidal forms of graphitic carbon

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A series of the toroidal cage forms of graphitic carbon is proposed. They have local topological structures of positive Gaussian curvature (for instance C_{60}) and of negative Gaussian curvature. The toroidal forms consist of fivefold, sixfold, and sevenfold carbon rings. The cohesive energies of the tori (C_n, where n ranges from 120 to 1920), which are calculated by molecular dynamics, indicate that these structures are energetically more stable than C_{60}. These structures are also found to be thermodynamically stable by means of a finite-temperature simulation.

I. INTRODUCTION

Recently, much attention has been paid to alternative forms of carbon such as the fullerenes[1] and carbon nanometer-sized tubes,[2] because these appear to be potentially promising in future technology. In a topological sense, these structures are created by mapping the carbon atoms on a graphite sheet onto many types of curvature: a flat plane for graphite, a sphere for fullerenes, and a cylinder for nanometer-sized tubes. It is known that the positive Gaussian curvature in the fullerenes arises from the substitution in the honeycomb network of some of the sixfold rings of carbon atoms by fivefold rings. Quite recently, carbon forms having negative curvature in the periodic minimal surfaces were theoretically proposed by Mackay and Terrones,[3] Vanderbilt and Tersoff,[4] and Lenosky, Gonze, Teter, and Elser.[5] They indicate that replacing sixfold rings by sevenfold or eightfold rings (instead of fivefold) leads to the negative curvature of the D (or so-called F) and P types of schwarzite.[6] Although these are difficult to synthesize at present, theoretical calculations indicate that these structures have lower cohesive energy than fullerene because they are topologically more similar to graphite, whose cohesive energy is lower than that of fullerene. Through the observation by TEM (transmission electron microscopy) of growth of the microtubules, Iijima, Ichihashi, and Ando[7] concluded that the sevenfold rings actually play an important role in the formation of the negatively-curvature surface growth of carbon microtubules. It would be of great interest if one could put forward a quite different covalently bonded form of carbon, having new features of considerable technological interest, by purely geometric considerations.

II. CONSTRUCTION OF TORI

In this paper, we provide a series of constructions of the toroidal forms of graphitic carbon that have a local topology similar to that in a fullerene structure. In the tori, the outermost and innermost circles have positive and negative curvatures, respectively. Therefore the former contains fivefold rings and the latter sevenfold rings. The distortion that is created by the bending nature of the torus is topologically relaxed by the inclusion of fivefold and sevenfold rings. This makes it possible to retain a bond distance almost equal to that in the fullerenes. Thus it is highly likely that the structure will be stable, like other discovered carbon forms.

From the geometrical considerations, we found the toroidal cage forms, which are different from any other carbon forms.[8] The primitive torus form has 120 carbon atoms, and belongs to the point group D_{5d}. The coordinates from the 12 inequivalent sites in the torus are given in Table I. The remaining coordinates of 48 (60 minus 12) atoms on the upper half torus are generated by applying four operations of rotating $2\pi/5$ around the center of the torus (or the fivefold rotation axis). The other remaining coordinates of 60 atoms on the lower half torus are generated by inverting the upper half torus, and rotating by $2\pi/10$ around the center of the torus. Using the prescription of Goldberg, which was also used in deriving the large-scale fullerenes,[9] we can automatically generate large toroidal forms. By performing Goldberg

TABLE I. Relaxed positions of inequivalent atoms in the C_{120} toroidal structure, given in units of Å. Here, the origin is the center of the torus.

No.	x	y	z
1	2.294	0.000	0.353
2	2.510	0.000	1.933
3	2.209	2.583	2.554
4	3.139	1.303	2.554
5	4.709	1.401	2.357
6	2.787	4.045	2.357
7	5.437	0.000	1.973
8	4.258	4.099	1.727
9	5.214	2.783	1.727
10	6.392	0.000	0.689
11	5.884	2.693	0.277
12	4.379	4.764	0.277

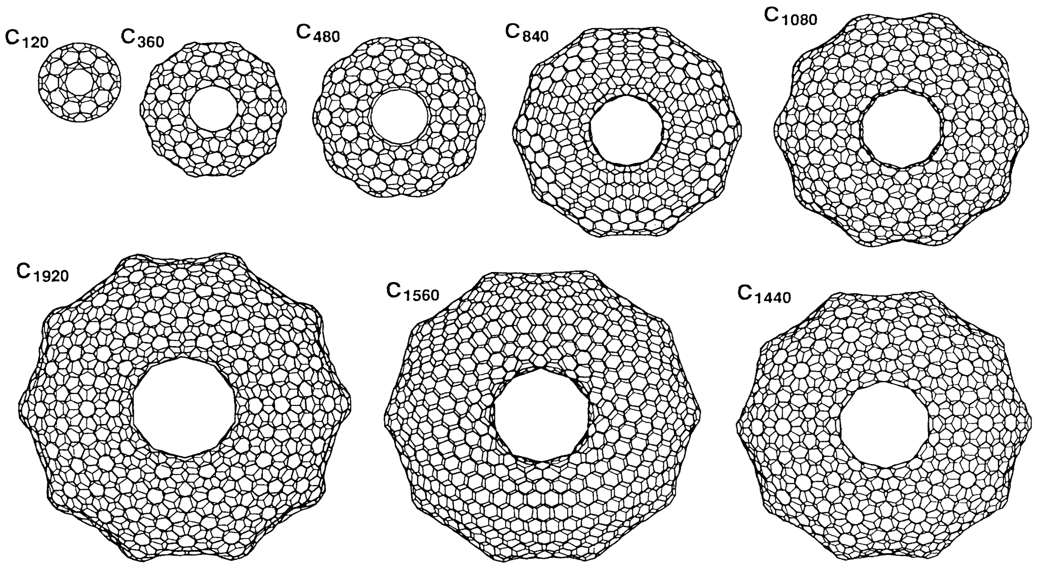

FIG. 1. Top view of the toroidal cage forms of carbon. The subscript of C represents the number of atoms in the toroidal structure. The depicted net represents the nearest-neighbor bonding between the carbon atoms.

transformations,[10] sixfold rings are inserted into the original C^{120} toroidal structure, and the directions of the fivefold and sevenfold rings are turned appropriately as the toroidal cage increases in size. Each structure thus obtained has N carbon atoms, where $N = Nb(n^2+nm+m^2)$ ($Nb = 120$, n and m are non-negative integers).[11] Here we provide the results of the toroidal forms containing N atoms, where $N = 120$, 360, 480, 840, 1080, 1440, 1560, and 1920 (see Fig. 1). The structures provided here might be referred to as "toroidal cage forms of carbon." In the tori, the number of the sevenfold rings is ten, and is set equal to that of fivefold rings to eliminate the excess dangling bonds on the surfaces. (Furthermore, in our construction procedure for C_{120}, the number of fivefold rings in the outermost circles is set equal to the number of fivefold rings in the meridian of the C_{60} sphere.)

III. METHOD OF CALCULATION

Molecular dynamics is a powerful method for studying both structural and dynamical properties without requiring adequate initial geometrical information. Thus molecular-dynamics methods were used to confirm the stability of the toroidal structures proposed here. The empirical interatomic potential of the carbon atoms is as follows. Stillinger-Weber-type three-body potentials[12] were used to take account of the covalency.[13] Parameters used in these forms were taken from those for graphite proposed by Abraham and Batra:[14] $A = 5.373\,203\,7$, $B = 0.508\,245\,71$, $a = 1.894\,361\,9$, $\lambda = 18.707\,929$, and $\gamma = 1.2$. Note that the constant in the three-body term of one-third is replaced by a half to represent a graphite sheet (the two-dimensional honeycomb structure).

In our simulation, periodic boundary conditions were applied in all directions. The toroidal forms were placed on the center of the large computational box, whose side length is at least three time larger than the maximum diameter of the torus. The integration of equations of motion for atomic coordinates was performed by the leapfrog algorithm with a time step of 0.36 fs. Simulation runs, of 2000 steps (0.72 ps), were initialized with the atoms' positions mentioned previously. The initial temperature was 50 K. The excess energy, which stems from relaxation of the atoms, was removed by rescaling the velocities at every step for the first 1000 steps (0.36 ps, and thereafter removed more gradually, with total energy being conserved after 800 steps. For the calculation of the ground state of the cohesive energy, the system was eventually cooled down to 0 K in 2200 steps by using the first-order equations of motion (dynamical steepest descent method). Less than 10^{-12} J/m of force acting on an atom was used as the convergence criterion. While usual second-order equations of motion were employed for the high-temperature simulations, having 20 000 steps, the temperature was gradually raised up to 2000 K using 15 000 steps with total energy being conserved after 16 000 steps.

IV. RESULTS AND DISCUSSIONS

Before discussing our results, we must mention the efficiency of the potential used in the simulations. In order to evaluate this, molecular-dynamics simulations of the fullerene C_{60} were also performed. The cohesive energy (-7.29 eV/atom) of the fullerene C_{60} calculated by this potential was close to the results (-7.4 eV/atom) of *ab initio* calculation.[15,16] The bond length (1.60 Å) of the fullerene C_{60} optimized by this potential was only 10% larger than the experimental values (1.43 Å). The cohesive energy of a graphite sheet obtained by our simulations was -7.44 eV/atom with a bond length of 1.59

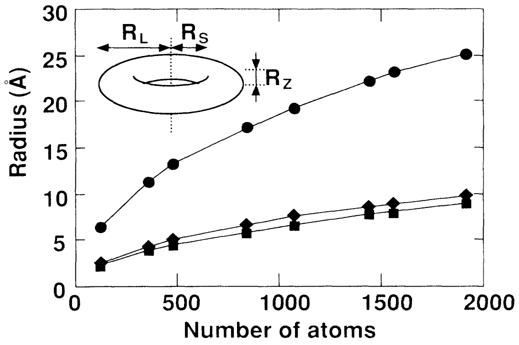

FIG. 2. The radii of the toroidal structures vs the number of atoms in the toroidal structure. R_L (●), R_S (■), and R_Z (♦) are the lengths of the radii shown in the inset.

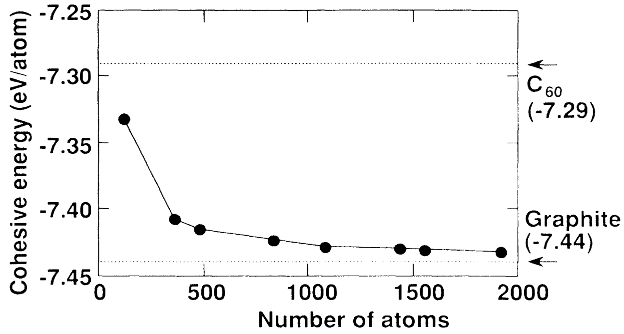

FIG. 4. The dependence of the average bond length on the number of atoms in the torus.

Å. The values are also consistent with the experimental values: −7.41 eV/atom (Ref. 17) and 1.42 Å.[18] Therefore the empirical potential used here is suitable in evaluating the stability and the cohesive energy in the fullerenelike structures as well as in a graphite sheet.

We now discuss the results of the toroidal carbon forms. Figure 1 shows the top view of the relaxed structures of the toroidal carbon forms obtained by steepest-descent molecular-dynamics simulations. Since in our series of toroidal structures the numbers of fivefold and sevenfold rings are kept constant, the local curvatures near the fivefold and sevenfold rings become more and more different from the global ideal curvature of the torus, with increasing number of carbon atoms, N. Thus the toroidal structures become ragged with increasing N, as one can see from Fig. 1. The various radii (see inset of Fig. 2) versus N are given in Fig. 2. As expected from the topological considerations, the radii of the tori increase with $\sqrt{N}$.

The N dependences of the cohesive energy of the toroidal carbon forms are given in Fig. 3. The cohesive energies per atom of tori C_{120}–C_{1920} decrease from −7.33 to −7.43 eV/atom with increasing N. Note that the cohesive energy of the fullerene C_{60} is −7.29 eV/atom and that of the graphite sheet is −7.44 eV/atom. The cohesive energies of the toroidal carbon forms are lower than that of the stable C_{60}. Thus the toroidal carbon forms are predicted to be energetically stable. The increase in N, which means an increase in the number of sixfold rings, leads to cohesive energies of the toroidal forms much closer to that of graphite. This may arise from the stress relaxation by introducing sixfold rings.

In Fig. 3, the cohesive energy of C_{120} is higher than that of others. This also arises from the stress: in C_{120}, the sevenfold rings are directly connected to each other, while in other structures, the sevenfold rings are connected through neighboring sixfold ring(s). Thus, in the inner wall of C_{120}, there is no stress relaxation by sixfold rings. As can be seen from Figs. 4 and 5, the N dependences of the bond length and bond angle of fivefold rings are smaller than that of the sevenfold rings. In the inner wall of the torus, local topology changes are stronger, as mentioned previously, than in the outer wall. This indicates that in order to relax the stress of the inside of the torus, the sevenfold rings must change their shape. This is in contrast to the relaxation in the outer wall of the torus, where local topology around the fivefold rings changes, retaining the original shape of the fivefold rings.

We found that the toroidal forms of carbon (C_{120}–C_{1920}) are energetically stable. To confirm the thermodynamical stability, simulations at higher temperature were also performed. As we heated them up to 2000 K,

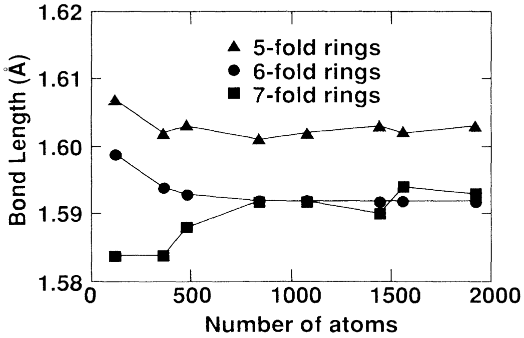

FIG. 3. The cohesive energy per atom of the toroidal structure vs the number of atoms in the torus.

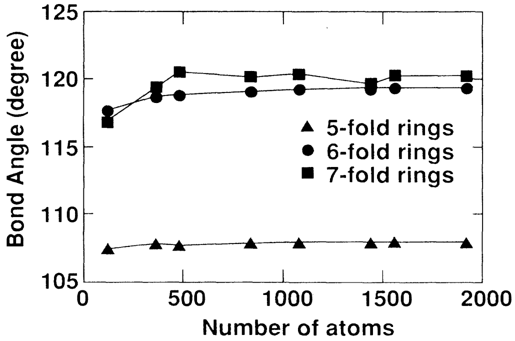

FIG. 5. The dependence of the average bond angle on the number of atoms in the torus.

the geometrical structures retained their stability, though their vibrational amplitude increased with increasing temperature. Thus we can conclude that toroidal forms of carbon are thermodynamically stable.

Because we used an empirical interatomic potential for the carbon atoms, electronic, optical, and chemical properties of toroidal carbon forms remain unexplored. Thus *ab initio* total energy calculations should be performed to confirm our results, however, the number of atoms and electrons in the toroidal structures considered here seems to be too large to be handled by the present computational resources. As far as the thermodynamics is concerned here, the essential part of our study obtained by the Stillinger-Weber potential may not change if one is going to study by more elegant quantum-mechanical calculations or by more complicated empirical potential forms. It is quite interesting to study the properties of the combined forms of the toroidal microclusters such as one-, two-, three-dimensional crystals or the macromolecules and the toroidal nesting, and those studies are currently under way. We suggest that the structures proposed here are candidates for further theoretical investigations and attempts at synthesis.

V. SUMMARY

We have proposed toroidal forms of the carbon structure, having similar geometrical characteristics to fullerene C_{60} or schwartzite, where fivefold and sevenfold rings are introduced in the sixfold rings. The toroidal carbon forms are predicted to be energetically and thermodynamically stable. We believe that the structures will someday be discovered or synthesized.

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