RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 3 15 JANUARY 1993-I

Toroidal form of carbon C_{360}

Satoshi Itoh and Sigeo Ihara
Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo 185, Japan

Jun-ichi Kitakami
Hitachi VLSI Engineering Corp., Kodaira, Tokyo 187, Japan

(Received 24 August 1992)

This paper proposes a new carbon form in the shape of a cage torus. This toroidal form of carbon contains 360 carbon atoms, formed in fivefold, sixfold, and sevenfold rings. Using a Stillinger-Weber-type potential, molecular-dynamics simulations show that the cohesive energy of the C_{360} torus is lower than that of C_{60} fullerenes and that the proposed structure is thermodynamically stable.

In 1985 (Ref. 1) a new carbon form, fullerene (C_{60}), was added to two existing structures, diamond and graphite. This structure has the highest symmetry discovered in the mass spectra of laser-vaporized graphite.[1,2] Subsequently, lower-symmetry fullerenes ($C_{32}, C_{70}, C_{76}, \ldots$) were synthesized and various larger cage clusters ($C_{240}, C_{540}, C_{960}, \ldots$) were also proposed. In addition, sevenfold and eightfold rings forming a negatively curved carbon network of minimal surface had been theoretically predicted,[3–5] and recently carbon tubes with sevenfold rings were produced by an arc-discharge evaporation of carbon.[6,7] By combining these sevenfold and eightfold rings with sixfold and fivefold rings, it is possible to construct complicated carbon networks.

In this paper, we wish to propose a toroidal form of carbon,[8] which is completely different from previous carbon forms. The concept of this form was obtained from consideration of the dangling bonds in the carbon tube. The edges of the carbon tubes may be closed by carbon network caps to eliminate dangling bonds. The dangling bonds can also be eliminated by bending the carbon tube such that the two edges are connected. Topologically a torus can thus be obtained. Although the distortions that arise by forming the toroidal form may raise the potential energy, eliminating the dangling bonds will decrease the potential energy. If the latter is more dominant than the former, by relaxing the arrangement of fivefold and sevenfold rings in sixfold rings the toroidal form of carbon will become stable.

The torus proposed here was constructed based on the C_{60} fullerene. The inner surface of the torus was obtained by removing the two parallel fivefold rings and replacing ten remaining fivefold rings with sevenfold rings. The inner surface thus obtained forms arcs when cut by a vertical cross section, and the outer surface of the torus was constructed by extending this arc until the arc became closed. Since the great circle of C_{60} consists of ten polygons, the arc of the torus was also closed by connecting ten polygons (which consist of a sevenfold and a fivefold ring and eight sixfold rings). Ten of these arcs can be created if they are formed along each of the ten sevenfold rings. Finally, gaps are filled by sixfold rings. This structure consists of 360 carbon atoms and belongs to the point group D_{5d}. Fivefold and sevenfold rings provide positive and negative Gaussian curvature along the outside and inside portions of the torus, respectively. Three bonds are connected to each atom and there are no dangling bonds on the surface. The distortion formed by bending the tube is relaxed by the fivefold and sevenfold rings. It is expected that the carbon torus is as stable as other discovered carbon forms. This structure might be referred to as toroidal carbon.

Molecular dynamics using empirical potentials was used to find the minimum energy structure and to confirm the thermal stability of the toroidal form of carbon proposed above. Periodic boundary conditions were applied in all directions of the computational box. The size of the computational box is at least three times larger than the size of the cluster. The equation of motion is solved by the leapfrog algorithm using a time step of 0.36×10^{-15} s. Quenching from the initial structure to the stable structure (relaxation at 50 K and cooling to 0 K) was performed. The velocities of the carbon atoms were normalized at every time step for the first 1000 steps (0.36 ps). After the relaxation of 800 time steps, the system was eventually cooled down to 0 K in 2200 steps by

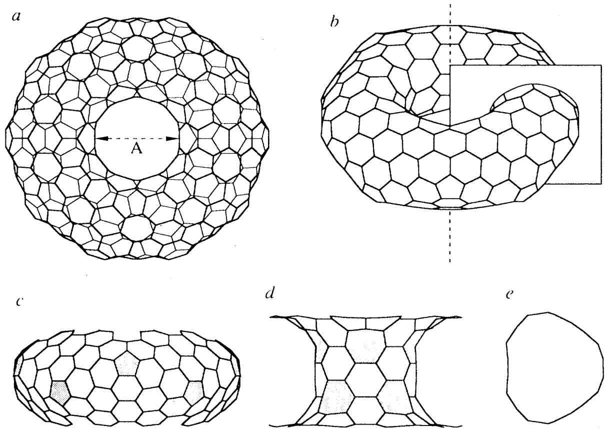

FIG. 1. A top view (a) and a side view (b) of the toroidal carbon C_{360} structure. The outside (c) and the inside portions (d) of the toroidal carbon C_{360} are shown. The cross section through the fivefold rotational axis [dashed line in (b)] forms the distorted ellipse (e).

TABLE I. Structural properties and cohesive energy for C_{60} fullerene and the toroidal form of carbon C_{360}. d, θ, and E are the bond length (Å), bond angle (deg), and cohesive energy (eV/atom), respectively. θ_5, θ_6, and θ_7 are the bond angles for fivefold, sixfold, and sevenfold rings, respectively. d (expt.) for C_{60} was measured in a fcc solid. E (*ab initio*) for C_{60} was calculated by *ab initio* methods (Refs. 11 and 12).

Structure	d (calc.)	d (expt.)	θ_5	θ_6	θ_7	E (calc.)	E (*ab initio*)
	(Å)			(deg)		(eV/atom)	
Torus C_{360}	1.59		107.9	118.8	119.4	−7.41	
Fullerene C_{60}	1.60	1.43	108.0	120.0		−7.29	−7.4

using first-order equations of motion. The convergence criterion used in the cooling is that the maximum value among forces acting on atoms is less than 10^{-12} J/m.

The Stillinger-Weber-type potential[9] was used in our simulations. Parameters for the carbon atoms, which were optimized for a graphitic carbon sheet,[10] are as follows: $A = 5.373\,203\,7$, $B = 0.508\,245\,71$, $a = 1.894\,361\,9$, $\lambda = 18.707\,929$, and $\gamma = 1.2$. Length unit $\sigma = 1.418$ Å and energy unit $\varepsilon = 7.946\,416 \times 10^{-12}$. (Here the meanings of the parameters are the same as in Ref. 10.) The potential is truncated at 2.7 Å. In the three-body term the constant of one-third is replaced by one-half to represent the graphite form. To evaluate the efficiency of this potential in fullerenes, we calculated the cohesive energy and the minimum energy structure of C_{60}. The cohesive energy (−7.29 eV/atom) of C_{60} calculated by this potential is nearly equal to the result from *ab initio* calculations (−7.4 eV/atom).[11,12] The bond length (1.60 Å) of C_{60} fullerene optimized by this potential is only 10% larger than the experimental value of 1.43 Å, which is the average value of the double bonds (1.40 Å) and single bonds (1.45 Å).[13] In our simulations, the single and double bonds in the carbon were not clearly distinguished by the empirical potential form. Nevertheless, it may work in evaluating the tendency of the cohesive energies and the stability, because more accurate calculations would not change these properties.

The minimum structure of the torus C_{360} was calculated by the previously described procedure. The optimized structure is shown in Fig. 1. The geometrical properties and the cohesive energies are summarized in Table I. Diameters of the inside and outside circles of the torus are 7.8 and 22.6 Å, respectively. The section through the fivefold rotational axis forms a distorted ellipse [see Fig. 1(e)]. The major axis (8.8 Å) of the distorted ellipse of the torus is in the same direction as the fivefold rotational axis. Since the diameter of C_{60} is 7.1 Å,[2] the diameter of the hole [Fig. 1(a), dotted line A] and the diameter of the cross section [Fig. 1(e)] of the torus are approximately equal to the diameter of C_{60}. The bond length of the torus C_{360} is 1.59 Å, which is in good agreement with that of C_{60} (1.60 Å) calculated by the same potential. Bond angles of the fivefold and sixfold rings in the torus C_{360} are almost equal to those of C_{60}. Sevenfold rings have the same bond angles as sixfold rings, because they are buckled out of the plane. If a sevenfold ring is placed on a flat plane, at least one of the bond pairs will have a larger angle than $5\pi/7$ (~128.6°). Therefore, sevenfold rings are buckled out of the plane and raise negative curvature to keep angles of sixfold rings to $2\pi/3$ (=120°).

The most important result is that the cohesive energy per atom of the C_{360} (−7.41 eV/atom) is slightly lower than that of C_{60} (−7.29 eV/atom). Therefore it is expected that the toroidal carbon C_{360} is more stable than C_{60}. The thermodynamical stability of the C_{360} was also confirmed by higher-temperature simulations. The temperature of the C_{360} was raised up to 2000 K in 16 000 time steps, and thereafter the total energy was conserved for 4000 time steps. The topology of the geometrical structure at the high temperature was the same as that of the cooled structure. It was thus concluded that C_{360} is stable as C_{60}.

In summary, we have proposed a carbon torus structure which is predicted to have lower cohesive energy per atom than C_{60} fullerene. The toroidal carbon C_{360} kept its geometrical structure at higher temperature. Thus we believe that this structure could be discovered or synthesized.

We would like to thank Dr. S. Nagashima and S. Miyamoto for their encouragement. We also thank Dr. P. M. Lee for a careful reading of the manuscript.

---

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] W. Krätschmer, L. D. Lamb, K. Fostriropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[3] A. L. Mackay and H. Terrones, Nature (London) **352**, 762 (1991).

[4] T. Lenosky, X. Gonze, M. P. Teter, and V. Elser, Nature (London) **355**, 333 (1992).

[5] D. Vanderbilt and J. Tersoff, Phys. Rev. Lett. **68**, 511 (1992).

[6] S. Iijima, Nature (London) **354**, 56 (1991).

[7] S. Iijima, T. Ichihashi, and Y. Ando, Nature (London) **356**, 776 (1992).

[8] After completing this paper, we became aware of a similar study: B. I. Dunlap, Phys. Rev. B **46**, 1933 (1992). His construction of the tori was connecting carbon tubules $(2L,0)$ and (L,L) of integer L, while ours is constructed by use of symmetry of C_{60}, which turns out to be derived from tubules (8,2).

[9] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985); **33**, 1451(E) (1986).

[10] F. F. Abraham and I. P. Batra, Surf. Sci. **209**, L125 (1989).

[11] Q.-M. Zhangm, Jae-Yel Yi, and J. Bernholc, Phys. Rev. Lett. **66**, 2633 (1991).

[12] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).

[13] C. S. Yannoni, P. P. Bernier, D. S. Bethune, G. Meijer, and J. R. Salem, J. Am. Chem. Soc. **113**, 3190 (1991).