PHYSICAL REVIEW A VOLUME 51, NUMBER 2 FEBRUARY 1995

Tiling rules for toroidal molecules

J. E. Avron and J. Berger
Department of Physics, Technion-Israel Institute of Technology, 32000 Haifa, Israel

(Received 11 April 1994)

We describe a class of periodic tiling that corresponds to toroidal arrangements of trivalent atoms with pentagonal, hexagonal, and heptagonal rings. The relaxation of model carbon atoms in molecules represented by these tilings is used to yield estimates of the energy per bond, the energy of the least bound atoms, and the highest occupied and lowest unoccupied molecular-orbital energies. The results support the point of view that stable toroidal carbon molecules can exist.

PACS number(s): 36.10.−k, 36.20.Fz

Fullerenes are carbon molecules that approximate spheres [1]. It is natural to ask whether carbon also forms stable molecules that approximate other surfaces. Since closed two-dimensional surfaces are either spheres or (in general, multihandle) tori, this is the same as asking whether carbon makes molecules that approximate tori with one handle or more. All such molecules, if they were to exist, would have an even number of carbon atoms. Fullerenes are simply connected and have positive Gaussian curvature. It is reasonable to expect that molecules that are multiply connected and have negative curvature (i.e., have regions that approximate a saddle) would have distinct physical and chemical properties [2]. For example, certain quantum and transport phenomena depend on multiconnectivity [3] and it is known that negative curvature has important consequences for dynamics [4]. Finally, the "holes" in the tori may be tailored for the purposes of host-guest chemistry [5]. In this paper we address the question of stability of toroidal carbon molecules (with one handle). Proposals that carbon might make toroidal molecules have been made in [6].

Our main tool is a set of tiling rules [7] for constructing molecules that approximate the family of tori with Cartesian representation

$$R\,\{(\eta-\cos\theta)\cos\phi\ ,(\eta-\cos\theta)\sin\phi\ ,\sin\theta\}\,, \qquad -\pi\le\theta,\phi<\pi, \quad (1)$$

with $R>0$ and $\eta>1$ fixed. $R\eta$ determines the size ($2R$ is the "height") and η the shape. Large η corresponds to thin tori and $\eta=\infty$ are tubules [8]. We focus on tori with η near 2.

Using a phenomenological potential due to Tersoff [9], we let the model carbon atoms represented by tiling relax to a stable molecular configuration, for which the average energies per atom, the bindings of the least bound atoms, and the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) [10] are computed. The results (see Table I below) support the point of view that many toroidal carbon molecules are stable.

A toroidal carbon molecule can be represented by a periodic planar triangular tiling with vertices of valences 5, 6, and 7. The atoms are associated with the centers of the (triangular) tiles and the valence condition says that the molecule has pentagonal, hexagonal, and heptagonal rings [11]. Thinking of the tiling plane as (universal cover of) the toroidal coordinates (θ,ϕ), Eq. (1) induces the metric and area

$$\begin{aligned} R^{-2}ds^2 &= (d\theta)^2+(d\phi)^2\ \ (\eta-\cos\theta)^2\ , \\ R^{-2}dA &= d\theta\, d\phi\,(\eta-\cos\theta). \end{aligned} \qquad (2)$$

The metric suggests stratified patterns and tiles of different sizes: bigger tiles near $\theta=0$ and smaller tiles near $\theta=\pi$. A family of tilings that mimic these metric properties and thus carry combinatorial and topological information is the following.

(i) All tiles are similar, right, isosceles triangles. See, e.g., Fig. 1, which shows the unit cell of a tiling pattern.

(ii) The tiles come in generations: the largest tiles are those of the first generation, those in the second generation are scaled by $1/\sqrt{2}$, etc.

(iii) There are two tiles in the first and third generations, related by a rotation by π, and four tiles in the second and fourth generations, related by $\pi/2$ rotations.

Remark 1. The number of generations m plays a role analogous to $1/\eta$: a cylinder can be built with one generation [8]. Fatter tori involve more generations.

Remark 2. The two tiles in the first and the third generation serve to distinguish the θ direction from the ϕ direction: any tiling pattern has well defined horizontal lines—latitudes—which can be labeled by counting, and the border between the second and third generation is a straight horizontal line.

In a periodic tiling, the number of latitudes in a unit cell will be dubbed the "girth" and denoted by g. The (horizontal) length of the unit cell is measured by counting edges along a given latitude and is denoted by $L(j)$, $j=1,\ldots,g$. The length is larger in high generation regions and is made to mimic the behavior of the latitudes by approximating $(\eta-\cos\theta)$. The tiling patterns we consider give a piecewise linear approximation to this function with slopes $0,\pm1$ (and we do not know how to do better). We denote $\Delta L=\max\{L(j)\}-\min\{L(j)\}$.

Valence plays the role of curvature: vertices with valence 5 (7) are associated with positive (negative) curvature. Since metric and curvature are related, we are led to a rule that dictates where pentagons and heptagons should be placed.

5-6-7 rule. Heptagonal vertices are at the interfaces between the first and the second generation with a majority of generation 1 and pentagonal vertices are at the interfaces between the last and the next to last generation with a majority of the last generation. All other vertices are hexagonal.

An example of a unit cell for a periodic tiling with four generations of tiles is shown in Fig. 1. The boundaries between the 1-2 and 3-4 generations are diagonal line segments and between 2-3 horizontal. All the zigs and zags are parallel and those between the 1-2 and 3-4 generations touch the horizontal 2-3 boundary. (This is a consequence of the 5-6-7 rule.) The tiling is determined by three integers (g_1, g_m, z) (g_1 even). g_1 and g_m are the respective widths of the first and the last generation, measured in latitudes along any vertical line; z is the length of a 1-2 zig, measured in edges. Except for the restriction that g_i is even for i odd, any quadruple of integers m, g_1, g_m, and z is allowed.

The following general properties apply.

(i) There are two heptagons and two pentagons per unit cell.

(ii) A tiling is determined by the interfaces between generations.

(iii) The tilings have mirrors of symmetry at the (vertical) planes that contain the pentagons and the heptagons, and centers of inversion midway between the heptagons (or pentagons) that are located at different zigzag lines.

(iv) The girth g, the number of tiles in a period, and ΔL are functions of (g_1, g_m, z).

Starting from any given tiling, one can, by simple geometric operations, construct an infinite tower of other tilings. Leapfrogging [12] enlarges the class of admissible tilings and generates a molecule with three times as many carbon atoms, which is guaranteed to be a closed shell [13]. Similarly, inflation, which is the discrete analog of scaling, gives an infinite tower of tilings from an initial parent. Inflation by a factor ℓ replaces *all* the tiles by "supertiles" where each new tile is made of ℓ^2 scaled copies of the old tile (and its π rotated image). It takes (g_1, g_m, z) to $(\ell g_1, \ell g_m, \ell z)$ and generates a family of molecules for which the number of pentagons and heptagons and their relative positions remain fixed. Inflation by 3 is the square of a leapfrog.

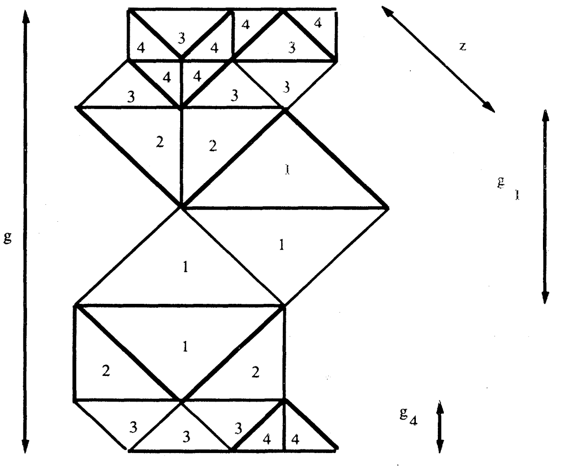

FIG. 1. A unit cell of a tiling with four generations. The tiles are numbered by generation. In this example the girth is 6 and the tiling has labeling (2, 1, 1). g_1, g_4, and z are shown. The border between generations is drawn thick.

Given a periodic tiling, one can construct from it many different tori. For example, in [14] a large family of (chiral, in general) tubules is constructed by identifying the edges of strips in the plane of graphitic tiling. (The various tubules depend on the width and orientation of the strip.) Here we consider only tori constructed by identifying (opposite edges on) the boundaries of a region obtained by n horizontal shifts of a unit cell. The corresponding tori have symmetry D_{nd} and are labeled by five integers (m, g_1, g_m, z, n).

Because of the way the tilings were constructed, the period n is not a free parameter: in Riemanian geometry the big and small perimeter of a torus and the height are related. This leads to the relation $n = 2g/\Delta L$. (For the tiling pattern of Fig. 1, $g = 6$, $\Delta L = 2$, and $2g/\Delta L = 6$.) Indeed, the largest binding energies were found for molecules with n close to $2g/\Delta L$. However, the optimal value of n depended on the criteria used: for example, for the tiling in Fig. 1, the largest binding energy of the entire molecule was obtained for $n = 6$, while the largest binding energy of the most strained atoms for $n = 5$.

The tilings determine the coordinates of all the atoms through Eq. (1), where for R and η we take

$$\eta = 1 + 2z/\Delta L, \quad R = 2.5\ \text{Å}\ \frac{g}{2\pi}. \tag{3}$$

The positions of the atoms, as determined by the tiling, are allowed to vary in three-dimensional space to minimize the total potential energy of the bonds. Good tilings flow to a nearby local minimum. Bad tilings and, in general, uncontrolled guesses for the initial coordinates of the atoms result in atoms being lost to infinity.

Tersoff's interatomic potential [9] associates with the atom i the energy

$$E_i = \frac{1}{2} \sum_j [A \exp(-\lambda_1 r_{ij}) - B b_{ij} \exp(-\lambda_2 r_{ij})] \ , \tag{4}$$

where the sum is over the three atoms j adjacent to i, r_{ij} is the distance between these atoms,

$$b_{ij} = (1 + \beta^\gamma \zeta_{ij}^\gamma)^{-1/2\gamma},$$

$$\zeta_{ij} = \sum_k \{1 + c^2/d^2 - c^2/[d^2 + (h - \cos\theta_{ijk})^2]\} \ , \tag{5}$$

θ_{ijk} is the angle between bonds ij and ik, k runs over the two neighbors of i other than j, $A = 1393.6$ eV, $B = 346.74$ eV, $\lambda_1 = 3.4879$ Å^{-1}, $\lambda_2 = 2.2119$ Å^{-1}, $\beta = 1.5724 \times 10^{-7}$, $\gamma = 0.727\,51$, $c = 38\,049$, $d = 4.3484$, and $h = -0.570\,58$.

TABLE I. Energetic and geometric values for several toroidal molecules, according to Hückel's theory and Tersoff's potential. The last column gives the corresponding data for C_{60}. All the molecules have five unit cells and symmetry group D_{5d}. The second to fourth columns are inflations of the first. $\epsilon_{h,\ell}$ is the energy of the highest occupied or lowest unoccupied molecular orbital, $\bar{\epsilon}$ is the average energy of delocalized electrons, $\bar{E}$ is the average geometric energy per atom, $E_G = -7.40$ eV is the geometric energy per atom of an ideal graphitic plane, and E_{worst} is the geometric energy associated with the least bound atom.

m	2	2	2	2	2	4	C_{60}
g_1	2	4	6	8	2	2	
g_m	2	4	6	8	4	1	
z	2	4	6	8	4	1	
Number of atoms	120	480	1080	1920	400	120	60
$\epsilon_h(\beta)$	0.43	0.16	0.08	0.10	0.24	0.04	0.62
$\epsilon_\ell(\beta)$	-0.27	-0.22	-0.02	-0.11	-0.21	0.04	-0.14
$\bar{\epsilon}(\beta)$	1.56	1.57	1.57	1.57	1.57	1.55	1.55
$\bar{E} - E_G$(eV)	0.91	0.24	0.12	0.10	0.42	0.56	0.67
$E_{\text{worst}} - E_G$ (eV)	1.34	0.84	0.80	0.84	1.03	0.90	0.67
Inner radius (Å)	4.05	8.33	12.57	16.22	10.09	2.02	
Outer radius (Å)	7.29	14.21	21.17	28.22	14.43	6.02	
Height (Å)	2.93	5.68	8.00	11.41	4.66	4.57	7.38

We have used Powell's method [15] to flow to a local minimum of the molecular energy. Even for large molecules, tiling provided initial guesses for the atomic positions within the basin of convergence of the minimization algorithm.

Table I collects the results for a few of the molecules we have studied and, for the sake of comparison, also the corresponding values for C_{60}. All the data in the table are for molecules with $n = 5$, i.e., molecules with ten pentagons and ten heptagons. (The corresponding values for molecules with $n = 6$ are close to those in the table.) Tersoff's energies are given relative to that of an ideal graphitic plane, which is -7.40 eV per atom and is denoted by E_G. The table also contains the results for the HOMO-LUMO energies obtained from Hückel theory [10]. In some cases, the HOMO-LUMO gap turns out to be independent of the period n. The average energy per delocalized electron is insensitive to the period n.

Figures 2 and 3 show three-dimensional views of two (relaxed) molecules corresponding to tiling with two generations $(g_1, g_m, z) = (4,4,4)$ and with four generations $(2,1,1)$, and periods $n = 5$ for both. The molecule shown in Fig. 3 was studied also in [6].

Inflating $m = g_1 = g_2 = z = 2$ shows that the configurational energy per atom rapidly approaches that of graphite and large tori have larger binding energies than C_{60}. However, the energy of the least bound atoms saturates. This effect is probably due to the fact that the number of pentagons is fixed and they bear the entire burden of curvature. (For all the cases considered, the most strained atoms belong to the pentagons.) Figure 2 clearly shows pentagons sticking out.

The geometric method described here can be used to

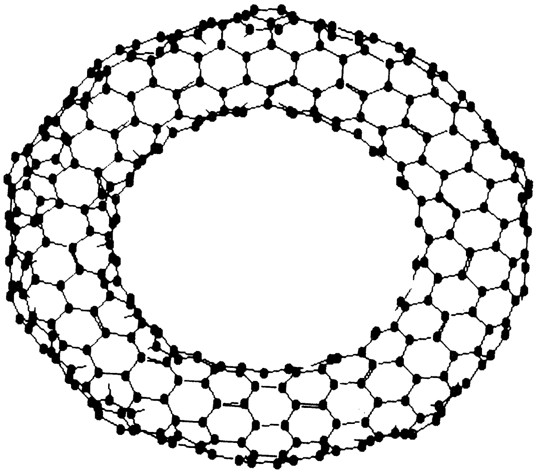

FIG. 2. Three-dimensional view of the molecule ($m = 2, g_1 = 4, g_2 = 4, z = 4, n = 5$), according to Tersoff's potential. The molecule is seen from "above" ($0 \leq \theta \leq \pi$). For clarity, only atoms in the foreground are shown.

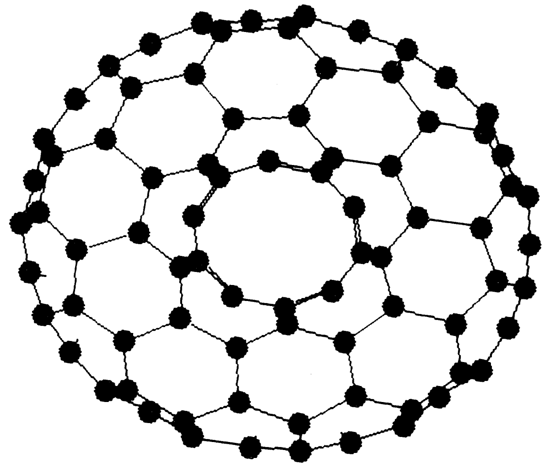

FIG. 3. Three-dimensional view of the molecule ($m = 4, g_1 = 2, g_4 = 1, z = 1, n = 5$), seen from above.

"design" toroidal molecules with prescribed dimensions. We did not find a privileged molecule that stands out in the way that C_{60} does. From the energetic point of view, several toroidal molecules are comparable to C_{60}.

We benefited from discussions and correspondence with N. Alon, I Appeloig, E. Berger, M. Burt, M. Dresselhaus, E. Kolodny, D. Levine, R. Meshulam and P. Zograf. We are grateful to M. Kaftory for his help with Figs. 2 and 3. The research is supported by GIF and DFG, through Grant No. SFB288, and the Fund for the Promotion of Research at the Technion.

---

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature **318**, 162 (1985); H.W. Kroto, *ibid.* **329**, 529 (1987); W. Krätschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, *ibid.* **347**, 354 (1990); H.W. Kroto, A.W. Allaf, and S.P. Balm, Chem. Rev. **91** 1213 (1991); R.F. Curl and R.E. Smalley, Sci. Am. **265** (10), 54 (1991).

[2] In D. Vanderbilt and J. Tersoff, Phys. Rev. Lett. **68**, 511 (1992) an intriguing proposal for a negatively curved periodic surface with hexagonal and heptagonal carbon rings was studied.

[3] A. Shapere and F. Wilczek, *Geometric Phases in Physics* (World Scientific, Singapore, 1989); J. E. Avron, M. Klein, A. Pnueli, and L. Sadun, Phys. Rev. Lett. **69**, 128, (1992).

[4] N. Balasz and A. Voros, Phys. Rep. **143**, 103 (1986); see also in *Chaos and Quantum Physics*, Proceedings of the Les Houches Summer School of Theoretical Physics, Course LII, 1989, edited by M.-J. Giannoni, A. Voros, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).

[5] See, e.g., in *Host-Guest Molecular Interactions: From Chemistry to Biology*, Ciba Foundation Symposia (Wiley, Chichester, 1991).

[6] L.A. Chernozatonskii, Phys. Lett. A **170**, 37 (1992); B.I. Dunlap, Phys. Rev. B **46**, 1933 (1992); S. Itoh, S. Ihara, and J. Kitakami, *ibid.* **47**, 1703 (1993); S. Ihara, S. Itoh, and J. Kitakami, *ibid.* **47**, 12 908 (1993); S. Itoh and S. Ihara, *ibid.* **48**, 8323 (1993); E.G. Gal'pern, I.V. Stankevich, A.L. Chistyakov, and L.A. Chernozatonskii, Fullerene Sci. Technol. **2**, 1 (1994).

[7] B. Grünbaum and G.C. Shepard, *Tiling and Patterns* (Freeman, New York, 1987).

[8] P.W. Fowler, J. Chem. Soc. Faraday Trans. **86**, 2073 (1990); S. Ijima, Nature **354**, 56 (1991); T.W. Ebbesen and P.M. Ajayan, *ibid.* **358**, 220 (1992); Z.Ya. Kosakovskaya *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 26 (1992) [JETP Lett. **56**, 26 (1992)]; N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992); A.A. Lucas, P.H. Lambin, and R.E. Smalley, J. Phys. Chem. Solids **54**, 587 (1993).

[9] J. Tersoff, Phys. Rev. B **37**, 6991 (1988); Phys. Rev. Lett. **61**, 2879 (1988).

[10] *Chemical Applications of Graph Theory*, edited by A.T. Balaban (Academic, New York, 1976); D.M. Cvetkovic, M. Doob, and H. Sachs, *Spectra of Graph Theory and Applications* (Academic, New York, 1979).

[11] There is evidence that the necks in certain microtubules have heptagonal rings.

[12] P.W. Fowler, Chem. Phys. Lett. **131**, 444 (1986); P.W. Fowler and J.I. Steer, J. Chem. Soc. Chem. Commun. 1403 (1987).

[13] D.E. Manolopoulos, D.R. Woodwall, and P.W. Fowler, J. Chem. Soc. Faraday Trans. **88**, 2427 (1992).

[14] R. Saito, M. Fujita, G. Dresselhaus, and M.S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).

[15] W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986).