A Classification Scheme for Toroidal Molecules

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We construct a class of periodic tilings of the plane, which corresponds to toroidal arrangements of trivalent atoms, with pentagonal, hexagonal and heptagonal rings. Each tiling is characterized by a set of four integers and gives rise to an infinite family of toroidal molecules. These may be chosen to fit a desired shape, size or number of atoms in the molecule. The configurational energy and the delocalisation energy of several molecules obtained in this way were computed for Tersoff and Hückel models. The results indicate that many of these molecules would be stable. We studied the influence of size on the Hückel spectrum: it bears both similarities and differences as

compared with the case of tubules.

1 Introduction

The last decade witnessed the discovery of diverse [1] hollow graphitic structures. These may be classified into sphere-like [2] and cylinder-like [3]. A natural question is whether additional topologies, such as tori, also occur. 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. For example, certain quantum and transport phenomena depend on multiconnectivity [4], and it is known that negative curvature has important consequences for the dynamics on the surface [5]. Toroidal molecules may have applications in host-guest chemistry [6], where the "hole" in the torus accomodates the "guest". It has also been suggested that toroidal molecules would have applications as components in nanotechnology [7] and as catalizers [8].

Structures that are actually half tori have been observed [8] when two concentric cylinders inter-connect. In the present study we shall focus on structures in the shape of a doughnut. Miscellaneous proposals for toroidal molecules have been suggested [7, 9, 10].

The purpose of the present study is to present a classification scheme for a wide class of toroidal molecules . We shall consider symmetric (mainly D_{nd}) molecules. Our tool is a set of tiling rules [11], adapted to the description of symmetric noncrumpled toroidal molecules. These tiling rules reflect the energy penalty for stretched bonds and deformed bond angles. Our method is amenable for computarized search (as the “orange-peel” method [12] in the case of spheroids). For simple properties, such as the spectrum in Hückel model, it suffices to give the indices which characterize a molecule as the input to a short program and the results are automatically obtained. The tiling provides also metric information. An announcement of some of the results in the present study is found in [13].

As an application we describe results of a numerical study of several toroidal carbon molecules. The study involved:

1. The relaxation of model carbon atoms represented by tiling to a stable molecular configuration, through minimization of the $\sigma-$bonds geometric potential energy. We have used a phenomenological potential due to Tersoff [14]. From here, average energies and binding energies of the least bound atoms were obtained.

2. Homo-lumo and other properties of the π-electrons in Hückel model.

The results (Table I) support the conjecture that many toroidal carbon molecules would be stable.

2 Tilings

A toroidal carbon molecule can be represented by a bi-periodic planar graph, where atoms sit at vertices and each vertex is trivalent. Since carbon bonds prefer angles near 120°, graphs with pentagonal, hexagonal and heptagonal rings are favored and we allow only these. In hexagons-only tori, as considered in [9], the hexagons must be deformed in order to reproduce the curvature of the toroidal surfaces, leading to prohibitively large energies. We shall represent a molecule by its *dual graph*, i.e. a periodic planar triangular graph with vertices of valences 5, 6 and 7. These triangles are called *tiles*, and the atoms are located at the centers of each tile.

We are interested in smooth tori that approximate the surface of revolution with cartesian representation

$$R\left\{\left(1-\frac{\cos\theta}{\eta}\right)\cos\phi\ ,\left(1-\frac{\cos\theta}{\eta}\right)\sin\phi\ ,\frac{\sin\theta}{\eta}\right\} \tag{1}$$

in the toroidal coordinates $\{\theta,\phi\}$. The parameter $R>0$ determines the size, and the parameter $\eta>1$ determines the shape. (Large η corresponds to thin tori.) Eq. (1) induces the metric and area

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

We shall refer to lines of fixed θ (resp. ϕ) as latitudes (resp. longitudes) and draw them horizontal (resp. vertical). Our set of tiles includes various sizes, reflecting the non uniform metric in the $\{\theta, \phi\}$ plane. (Large tiles are placed where $\cos\theta$ is large and vice versa.) For simplicity, we shall take all our tiles as similar isosceles triangles. In order to accomodate vertices with valence 5, 6 and 7, these triangles have to be right-angled. Due to the privileged role of latitudes and longitudes, we shall (initially) require that each tile have at least one side along one of these directions. More general structures will be discussed in Section 4.

It follows by Pythagoras that the different tiles are related by scaling by powers of $\sqrt{2}$. The largest tiles will be called the *first generation*; the tiles in the *i-th generation* will have an area which is 2^{i-1} times smaller. In the first generation we shall have the two (big) isosceles right-angled tiles of area one in the tiling plane, shown in Fig. 1a. We allow only the two orientations (related by a π rotation) with the hypotenuse along a latitudinal line; this will be required from every odd generation, giving rise to an array of equidistand horizontal lines. (This feature agrees with metric (2), which depends on θ, but not on ϕ. In this way the first generation tiles give the shortest latitudinal lengths.) At the second generation we add the four tiles of area $\frac{1}{2}$ in Fig. 1b. At generation $p+2$, we add the tiles obtained from those in generation p by scaling by a factor of $\frac{1}{2}$. Clearly, tiles that share a common edge differ by at most one generation. Since there is only one way of matching odd generation tiles, the tiling of an odd-generation region is uniquely determined by its border; on the other hand, since a square can be tiled in two ways (see Fig. 2), the tiling of an even-generation region involves a choice of orientation for each square.

Since the linear dimension of the last generation is smaller than that of the first by a factor $2^{(m-1)/2}$, and since the first generation has the hypotenuse along a latitudinal line (what may introduce an additional factor $2^{1/2}$ in the metric along the latitudinal direction), Eq. (2) can be used to relate η to the number of generations m:

$$\frac{\eta+1}{\eta-1} \sim 2^{[m/2]} \ , \tag{3}$$

where $[m/2]$ = integral part of $m/2$. Therefore, the number of generations plays a role analogous to $1/\eta$. A cylinder can be built with one generation, skinny tori are associated with first and second generation tiles and, the fatter the tori, the more generations are needed.

Unlike the sphere, which is unique up to scaling, the tori of Eq. (1) depend on the shape parameter η. *A priori*, it is not clear whether this family has a distinguished member. It turns out that there is such a torus and the case $\eta = \sqrt{2}$ is special. In the theory of surfaces the torus of revolution with $\eta = \sqrt{2}$ is known as the Clifford torus and is distinguished by being the minimizer of the Willmore functional, i. e., it minimizes the square of the mean curvature [15]. The fattest torus we shall study has five generations, inspired by the Clifford torus. As we shall see, it does have a marked stability. For fatter tori, axially symmetric structures are not expected [15].

Valence plays the role of curvature: valence 5 (resp. 6, 7) vertices carry positive (resp. zero, negative) curvature. We want no 5 and 7 valence vertices embedded in single generation regions. The pair of tiles of the odd generations have indeed this behavior built into them: only sixfold vertices can be made with them alone. On the other hand, Fig. 2 shows a tiling by even generation tiles with valences 5 and 7. These pentagon-heptagon pairs do not contribute to the global curvature required by metric (2), but merely produce crumpling, and should be avoided by an additional rule; pentagons or heptagons will be allowed only at the interfaces between different generations.

The connection between the tiling and the Riemanian curvature can be made more stringent. The predominance of pentagons over heptagons should be proportional to the curvature. In our case, it should be a decreasing function of $\cos\theta$ and, also, of the size of the tile. However, since there is an energy penalty for every additional pentagon-heptagon pair, and since we are interested in molecules with numbers of atoms which are not too large, we shall compromise the smoothness of the curvature on behalf of a limited number of pentagons and heptagons. Accordingly, pentagons (resp. heptagons) will be located only where the tiles are smallest (resp. largest). In summary, we impose the following:

5-6-7 Rule: For a torus with m generations, all the heptagons lie at the interfaces between the 1st and the 2nd generation and all the pentagons lie at the interfaces between the m-th and the $(m-1)$-th generation. (If there are only two generations, both the heptagons and the pentagons lie at the interfaces between them.) Furthermore, we require that around every heptagon (resp. pentagon) there be a majority of tiles of generation 1 (resp. m).

Figs. 3-5 are examples of tilings which obey the 5-6-7 rule.

Length: We define the length $L(\theta)$ of a latitudinal line as the number of edges it contains. Clearly, $L(\theta)$ is larger when the line passes through high generation regions. In Fig. 5, $L(\theta)$ varies from 1 to 3. Likewise, we define the length of a longitudinal line as the number of horizontal lines it intersects. Our tiling rules ensure that the total length of longitudinal lines is independent of ϕ, as it should. This length will be dubbed the "girth" and denoted by g. We also define $g_i(\phi)$ as the length within the i-th generation regions.

Note that if a longitudinal line crosses several regions of the same generation i, then $g_i(\phi)$ is defined as the *total* length across all these regions. In Fig. 5, $g_1 = g_3 = 2$ and $g_2 = g_4 = 1$ (independent of ϕ). Clearly, $\sum_{i=1}^{m} g_i(\phi) = g$.

3 Skeletons and Relationships

Given a set of interfaces between generations, the entire tiling is determined uniquely by the 5-6-7 rule (although not for every set of interfaces does a legal tiling exist). The set of interfaces will be called the *skeleton*. The $(2p-1,\ 2p)$ interfaces are zigzag lines (e.g. Fig. 6a) and the $(2p,\ 2p+1)$ interfaces are horizontal lines (e.g. Fig. 6b). Therefore, regions that contain $2p-1$ and $2p$ tiles lie within a horizontal stripe, which will be called a *p-th stripe*. (If there are only 2 generations, there is just one stripe; if the number m of generations is odd, then the last stripe has tiles of the m-th generation only.) Figs. 3 and 4 have one stipe; Fig. 5 has two.

Since according to metric (2) the length of the latitudinal lines has only one minimum and one maximum, we require that the regions of generation i, $1 \leq i \leq m$, be located in monotonic and consecutive order, both when going from region 1 to m by increasing or by decreasing θ. The 5-6-7 rule imposes a very strong constraint on the class of possible skeletons with two or more stripes: with the exception of the vertices at which there is a majority of generation 1, and, if m is even, the vertices with a majority of generation m, all the vertices of the zigzag interfaces lie at the stripe borders and all the zigzag interfaces are parallel to each other (see Fig. 7). This has two consequences: First, the tiling obeys the symmetry D_{nd}, which is the highest symmetry of a torus in three dimensions that could be expected from a discrete construction. The mirrors of the symmetry are at the planes of constant ϕ that contain the pentagons and the heptagons. The centers of inversion lie midway between the heptagons (or pentagons) which are located at different zigzag lines. Second, the g_i's are independent of ϕ, in agreement with the desired metric (2). If the skeleton consists of just one stripe, then the symmetry D_{nd}, the constancy of the g_i's and the zigging between two lines of constant latitude don't follow from the 5-6-7 rule (e. g. Figs. 8-9), but we impose them in order to mimic the metric (2). The independence of the g_i's on ϕ rules out the tori considered in Ref. [10], which are cylindrical tubes connected by elbows.

We are thus left with a class of tilings such that the skeleton (and the entire tiling) is completely determined by four numbers: m (the number of generations), g_1 and g_m (the contributions of the first and last generation to the girth), and z (the number of edges in a zig of the (1,2) interface). If

$i \neq 1, m$, then $g_i = 2^{p-1} z$, where p is the number of the stripe.

The girth of the torus is given by

$$g = g_1 + g_{\text{mid}} + g_{\text{end}} + g_m \ , \tag{4a}$$

with

$$g_{\text{mid}} = \begin{cases} 0 & m \leq 2 \\ z & 2 < m < 5 \\ z + (2^k - 4)z & m \geq 5 \end{cases} \tag{4b}$$

where $k = [(m+1)/2]$ is the number of stripes ([ ] denotes integral part), and

$$g_{\text{end}} = \begin{cases} 2^{k-1} z & m \text{ even and} \geq 4 \\ 0 & \text{otherwise} \end{cases} \tag{4c}$$

The number of atoms within a ϕ-range spanned by a zig and a zag is given by

$$A = \begin{cases} 2z \left(g_1 + 2^{[m/2]} g_m \right) & m < 3 \\ 2z \left(g_1 + 2^{[m/2]} g_m + (2^{m-1} - 2) z \right) & m \geq 3 \end{cases} \tag{5}$$

The length of the shortest latitudinal line, within a ϕ-range spanned by a zig and a zag, is given by

$$L_{\text{min}} = 2z - \text{Min}(g_1, z) \ . \tag{6}$$

The length of the longest latitudinal line in the same ϕ-range is

$$L_{\max} = \begin{cases} 2^{k-1}z & m \text{ odd} \\ 2^{k-1}z + \mathrm{Min}(g_m, 2^{k-1}z) & m \text{ even} \end{cases} \tag{7}$$

4 From Tiles to Tori

By associating periodic coordinates $\{\theta, \phi\}$ to the tiling plane, the three-dimensional positions follow by Eq. (1). The line $\theta = 0$ (resp. π) is assigned to the horizontal line through the centers of inversion near the vertices of valence 7 (resp. 5). We then increase (resp. decrease) θ by $2\pi/g$ when going up (resp. down) by one horizontal line. ϕ is assigned by requiring it to span 2π in the periodic tiling and to be linear along the horizontal planar distance in the tiling plane. Finally, we impose periodicity $\{\theta+2\pi, \phi\} \equiv \{\theta, \phi+2\pi\} \equiv \{\theta, \phi\}$.

The ϕ-range spanned by a zig and a zag will be called a *unit cell*, and a torus with n unit cells has symmetry D_{nd}. The number of unit cells in the molecule may be estimated by comparing the difference in the perimeters at $\theta = 0$ and $\theta = \pi$ to that of a geometric torus. This gives

$$n \sim n_0 = 2g/(L_{\max} - L_{\min}) \ , \tag{8}$$

where g, $L_{\max}$ and $L_{\min}$ are given by (4), (6) and (7).

To evaluate the parameters R and η which appear in Eq. (1), R (resp. R/η) is taken proportional to the average latitudinal (resp. longitudinal) length, and the constant of proportionality is a "material parameter". For carbon atoms, appropriate constants are

$$R = 0.2n(L_{\min} + L_{\max})\text{Å} \tag{9}$$

and

$$R/\eta = 0.4g\text{Å} \ . \tag{10}$$

The geometric data in Table I were obtained after refinement through minimization of the interatomic potential.

Given a tiling, several additional structures may be generated from it. This is done by means of Goldberg inclusion, elongation, chirality and torsion.

Inclusion consists of drawing v vertices inside each tile and then connecting both the old and the new vertices to form a new array of triangles in the dual graph. Vertices on the edge between two tiles are counted as $\frac{1}{2}$ in each. This procedure increases the number of atoms by a factor $q = 1 + 2v$. Connections are made so that old vertices retain their valences, new vertices have valence 6, and nearest vertices are connected. We restrict ourselves to the cases in which this rule for the connection of the vertices is unambiguous. If $q = 1 + 2v$ is of the form

$$q = \ell_1^2 + \ell_2^2 + \ell_1\ell_2 \tag{11a}$$

with ℓ_1 and ℓ_2 integers, then a distribution of vertices for which connections are unambiguous is obtained by a variation of the *Goldberg transformation* [16]: using local coordinates for each tile, such that its vertices are at $(x = 0,\ y = 0)$, $(x = 1,\ y = 0)$ and $(x = 0,\ y = 1)$ (with $\hat{\mathbf{x}}$ to the right of $\hat{\mathbf{y}}$), the included vertices are at

$$\begin{aligned} x &= (n_1(\ell_1 + \ell_2) + n_2\ell_2)/q \ , \\ y &= (-n_1\ell_2 + n_2\ell_1)/q \ , \end{aligned} \tag{11b}$$

where (n_1, n_2) are integers such that (x, y) lies inside the tile. Fig. 10 shows the Goldberg transformation $(\ell_1, \ell_2) = (1, 2)$ applied to the tiling $g_1 = 2,\ g_2 = z = 1$.

Inclusion generates a family of molecules for which the number of pentagons and heptagons and their relative positions (and therefore the overall shape) remain fixed. Except for the cases $\ell_1 = \ell_2$ and ℓ_1 or $\ell_2 = 0$, which are considered below, the Goldberg inclusion gives rise to chiral molecules.

A Goldberg inclusion with indices $(\ell_1, \ell_2) = (\ell, 0)$ (or $(0, \ell)$) will be called *inflation.* Inflation is the discrete analog of scaling. Inflation by a factor ℓ replaces all the tiles by "super-tiles" where each new tile is made of ℓ^2 scaled copies of the old tile (or its π rotated image). Inflation preserves the distinction among generations, increasing by the factor ℓ^2 the number of atoms in each. Inflation by a factor ℓ gives a tiling within the class we have considered, leaving m and n unchanged, while leading to multiplication of z and all the g_i's by ℓ. Therefore, for classification purposes it is convenient to consider primitive tiling, i.e. sets of numbers (g_1, g_m, z) which have no common divisor. (Note that for odd generations g_i must be even.)

A Goldberg inclusion with indices $\ell_1 = \ell_2 = 1$ is a *leapfrog* [17]. In three dimensional space, the leapfrog operation is a vertex truncation through the mid-points of the edges, so that every old vertex turns into a hexagon and the number of atoms is multiplied by 3. Leapfrogged structures are guaranteed to have closed shells in the Hückel spectrum [18]. The effect of leapfrogging twice is the same as that of inflation by a factor 3.

The tori of Ref. [10] may be obtained by *elongation*. Elongation is defined for tilings with two generations. It consists of cutting the tiling along an approximately longitudinal line (following the edges of the tiles), separating the two pieces by an integer latitudinal distance, and filling in with tiles of generation 2, in such a way that all additional vertices are hexagonal. Fig. 8 shows an elongation of the tiling $g_1 = 2,\ g_2 = z = 1$.

For many tilings there exist latitudinal lines $\theta = \theta^*$ which are embedded in a single odd generation (first or last, with $L(\theta^*) \equiv L^*$ equal to either $nL_{\min}$ or $nL_{\max}$). If this is the case, manifest *chirality* [19] may be introduced by using θ in the range $\theta^* \leq \theta < \theta^* + 2\pi$ and associating to the coordinates

$\{\theta, \phi\}$ in the tiling the coordinates $\{\theta, \phi + j\theta/L^*\}$ in three dimensional space, with j integer. (This is the analog of Dehn twist in the theory of Riemann surfaces.) This amounts to identification of the edge at $\theta = \theta^*$ with the edge at $\theta = \theta^* + 2\pi$ shifted by j. The 5-6-7 rule will still be fulfilled. Unless $|j| << L^*$ and $|j| << g$, this shift produces considerable strain.

Shifts in the longitudinal boundaries of the tiling would lead in general to a misfit in the skeleton. However, if there are only two generations, *torsion* can be introduced by drawing zigs (z_1) longer than the zags (z_2), as in Fig. 9. The sinus of the pitch angle may be estimated as $2(z_1 - z_2)/(L_{\text{max}} - L_{\text{min}})$. Helical structures have been studied in [20].

Let us mention that better approximations to metric (2) can be achieved by two-generation tilings in which the skeleton consists of two parallel jagged lines, so that the number of heptagons minus the number of pentagons in the range $[0, \theta]$ is proportional to $|\sin\theta|$. Tilings like this would have a very large number of atoms per unit cell and, also, a very large n_0 in Eq. (8).

5 Implementation

For each molecule, we calculate two complementary phenomenological contributions to the energy. The geometric contribution is calculated by means of an interatomic potential, and the contribution of delocalized electrons by means of Hückel model.

Interatomic Potential: We use Tersoff's potential [14].

The tiling rules of the previous sections not only describe the connectivity of the molecule, but also suggest values for n, R and η through Eqs. (8)-(10). The carbon atoms (located at the centers of each triangle), are assigned initial positions in space which correspond to their toroidal coordinates. The positions of all the atoms are then allowed to vary in three-dimensional space to minimize the total potential energy of the bonds. Good tilings flow to a nearby local minimum. Uncontrolled guesses for the initial coordinates result in atoms being lost to infinity.

We have used Powell's method [21] to flow to a local minimum of the molecular energy. In all cases, our tilings provided initial guesses for the atomic positions within the basin of convergence of the minimization algorithm. When the number of coordinates is large, analytic expressions for the derivatives of the energy must be supplied in order to obtain reliable minima.

For every tiling, we tried several values for the number n of unit cells. For the tilings considered, the largest binding energies of the entire molecule were usually obtained for $n = 6$ and the largest binding energy of the most strained atom, for $n = 5$. The results are shown in Table I. Since the differences between $n = 5$ and $n = 6$ are small, we present the results for $n = 5$

only. To facilitate comparison, Tersoff's energies are given relative to that of an ideal graphitic plane, which is -7.40 eV per atom. It is instructive to compare these energies with those of a torus with girth 4 and 160 atoms, but with hexagonal rings only: in this case $N(\bar{E} - E_G)/|E_G| = 29$ and $10^3(E_{\text{worst}} - E_G)/|E_G| = 411$ (and strain increases for larger girth).

Hückel Model: Hückel model [22] associates an $N \times N$ incidence matrix to a graph of N carbon atoms, whose eigenvalues, $E_j,\ j \in \{1, \ldots, N\}$ correspond to the discrete energies of independent delocalized π electrons. A closed shell, where half the eigenvalues are negative and half positive (N is even) implies stability (protecting e.g. against Jahn-Teller instability). The largest negative eigenvalue, $E_{N/2-1}$, is known as *homo*-energy and the smallest positive one, $E_{N/2}$, as *lumo*. A large gap is a criterion for stability. Taking $\frac{1}{N}\sum E_j$ as the reference, $|E_j| \leq 3|\beta|$, where β is the nearest-neighbor overlap integral.

A computer program which calculates the Hückel spectrum for arbitrary g_1, g_2, z and n is available upon request. Illustrative values are summarized in Tables I and II. The average energy per atom is almost insensitive to the number n of unit cells.

The Hückel model also provides an estimate for the electronic charge distribution in the torus. The general trend is that five (resp. seven)-atoms rings capture (resp. release) electrons from/to their adjacent atoms. The total capture/release is of the order of a quarter of an electron per ring.

Choice of Examples: The method described above allows to design and analyze infinitely many toroidal molecules. One can for instance require the inner radius of the torus (which is proportional to $nL_{\min}$) to fit the size of a given "guest"; given the mass of a molecule, one could fix $N/n = A$ in Eq. (5); in order to design an elbow that fits a given tubule or cap, one would require a given girth.

The case of two connected concentric cylinders [8] may be reproduced by a two-generation torus with $g_1 \approx g_2 >> z$. Since experimentally found "turn around" edges have a small difference between the external and internal radius (relative to the radii themselves), elongation as in Fig. 8 is necessary. The outer cylinder contains tiles of generation 2, connections contain the zigzagging boundaries, and the inner cylinder contains tiles of generation 1 and separating fringes of generation 2. From geometric arguments and comparison with Eqs. (9) and (10), we estimate g_1 and g_2 as $0.4 \times$ (length of the cylinders), nz as $2.5 \times$ (difference in radii of cylinders) and the total horizontal witdth of the separating fringes as $5 \times$ (the internal radius) minus $2.5 \times$ (the external radius), with all lengths in Å. Note that in this case Eq. (1) is not a good approximation and that interlayer interaction has not been taken into account.

The primitive tori C_{120} and C_{240} in [7] may be traced to be $g_1 = 2,\ g_4 = z = 1$ and the leapfrogged of $g_1 = g_3 = 2,\ z = 1$, respectively.

For the purpose of illustration, we have focused on small values for g_1, g_m and z. Molecules with longitudinal perimeters of the order of that of C_{60} imply $g \sim 10$. For tori with roughly circular cross section, we may also expect that the difference in the latitudes of the pentagon and the heptagon lying at the same longitude be at least about $2\pi/3$.

Fig. 11 shows three dimensional views of the molecule $m = 2,\ g_1 = g_2 = z = 4$ after relaxation to the minimal energy, and Fig. 12 shows $m = 5,\ g_1 = g_5 = 2,\ z = 1$. This is the five-generations molecule with the smallest possible tiling. The difference in η is apparent, with Fig. 12 being close to a Clifford torus [15].

Comparison of different levels of inflation of $m = g_1 = g_2 = z = 2$ shows that the configurational energy per atom relative to graphite decreases roughly as $1/N$. The same result was obtained in [7]. However, the energy of the least bound atoms saturates. This effect is probably due to the fact that the number of pentagons and heptagons is kept unchanged, and they have to bear the entire burden of curvature. In Fig. 11a it is clearly seen that pentagons stick out as protuberances. It is also interesting to note in Fig. 11b how the pentagons deviate from the latitude $\theta = 0$ which they have in the tiling.

Fig. 13 shows a chiral molecule, as obtained by shifting by $j = 1$ the tiling of the molecule in Fig. 12 at $\theta^* = \pi$.

The influence of inflation on the Hückel spectrum was studied for $g_1 = g_2 = 2$ and $1 \leq z \leq 3$. The results are summarized in Figs. 14 and 15. Fig. 14 describes the homo-lumo gap. Since there are N energy levels, and since they are bound in the interval $[3\beta, -3\beta]$, the gap might naively be expected to be inversely proportional to N, and thus to ℓ^2. The trend is, however, that the gap is inversely proportional to ℓ. This result resembles the case of tubules, where the gap is inversely proportional to the diameter [23]. There are some inflation values for which the regular trend is not obeyed. These are a reminiscent of gap closure for tubules whose width is divisible by 3.

Fig. 15 shows how the delocalisation energy per atom approaches that of graphite. The difference from graphite is inversely proportional to ℓ^2.

6 Conclusion

Tori are closed surfaces, like spheres,but unlike spheres are not simply connected. They may provide an arena for a variety of physical and chemical properties.

Table I shows that, from the energetic point of view, there are toroidal molecules which are roughly as stable as C_{60}. One could say that the fact that toroidal carbon molecules have not been observed is as significant as the fact that C_{60} molecules were not observed until recently. The energies and geometries we have found are similar to those in [7], in spite of having used a different potential and minimization technique.

We have developed a classification scheme which can be used to "design" toroidal molecules with prescribed dimensions. As long as these molecules are not found, it may help to suggest candidates; if they are found, it may help to analyze them.

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Table I

m	2	2	2	2	3	4	5	5[1]
g_1	2	4	6	2	4	2	2	2
g_m	2	4	6	2	2	1	2	2
z	2	4	6	3	6	1	1	1
N	120	480	1080	180	1200	120	240	240
$\epsilon_h(\beta)$	0.43	0.16	0.08	0.45	0.07	0.04	0.19	0.20
$\epsilon_\ell(\beta)$	-0.27	-0.22	-0.02	-0.18	-0.02	0.04	0.01	-0.04
$10^3(\bar{\epsilon} - \bar{\epsilon}_G)(\lvert\beta\rvert)$	16	4	2	11	2	25	11	9
$10^3(\bar{E} - E_G)/\lvert E_G\rvert$	123	32	16	118	16	76	39	43
$10^3(E_{\text{worst}} - E_G)/\lvert E_G\rvert$	181	114	108	170	115	122	101	100
$N(\bar{E} - E_G)/\lvert E_G\rvert$	14.8	15.6	17.5	21.2	19.5	9.1	9.4	10.4
inner radius (Å)	4.05	8.33	12.57	6.87	14.15	2.02	2.09	2.12
outer radius (Å)	7.29	14.21	21.17	10.14	23.42	6.02	8.49	8.61
height (Å)	2.93	5.68	8.00	3.37	8.13	4.57	6.89	6.96

Table II

$\backslash$ g_2	1	2	3	1	2	3
z $\backslash$		$g_1 = 2$			$g_1 = 4$	
1	35	17	22	36	0	1
2	61	70	8	11	51	13
3	71	62	22	44	27	21

Table Captions

Table I Energetic and geometric values for several toroidal molecules, according to Hückel's theory and to Tersoff's potential. All the molecules have 5 unit cells. The second and third columns are inflations of the first. N is the number of atoms in the molecule, $\epsilon_{h,\ell}$ is the energy of the highest occupied/lowest unoccupied molecular orbital, $\bar{\epsilon}$ is the average energy of delocalized electrons, $\bar{E}$ is the average geometric energy per atom, $E_{\rm worst}$ is the geometric energy associated with the least bound atom, and $\bar{\epsilon}_G = 1.575\beta$ and $E_G = -7.40$eV are the delocalisation and the geometric energy per atom of an ideal graphitic plane. The molecule in the last column (denoted by $m = 5^1$) is obtained by a chiral shift $j = 1$ of $(m, g_1, g_m, z, n) = (5, 2, 2, 1, 5)$

Table II $10^2 \times (\epsilon_\ell - \epsilon_h)/|\beta|$ for molecules with 2 generations and 5 unit cells, for various values of $g_1,\ g_2$ and z.

Figure Captions

Fig. 1 (a) Odd generation tiles. (b) Even generation tiles.

Fig. 2 Even generation tiling with unnecessary crumpling.

Fig. 3 The tiling $m = g_1 = g_2 = z = 2$.

Fig. 4 The tiling $m = g_1 = g_2 = 2,\ z = 3$.

Fig. 5 The tiling $m = 4,\ g_1 = 2,\ g_4 = z = 1$.

Fig. 6 (a) Interface between even generation higher than the odd generation. (b) Interface between odd generation higher than the even generation.

Fig. 7 Skeleton of tiling that obeys the 5-6-7 rule and has more than one stripe. (In the figure $m = 6$ and there are 3 stripes.) The numbers denote the generation of the tiles in the region. g_1, g_m and z determine completely the unit cell of the tiling.

Fig. 8 The tiling $g_1 = 2,\ g_2 = z = 1$, after elongation by 1.

Fig. 9 Three unit cells of the tiling $g_1 = g_2 = z_1 = 2,\ z_2 = 1$.

Fig. 10 Unit cell of the tiling $g_1 = 2,\ g_2 = z = 1$, after a Goldberg inclusion with indices $\ell_1 = 1,\ \ell_2 = 2$. The circles signal the original vertices before the inclusion.

Fig. 11 Three-dimensional view of the molecule $(m, g_1, g_2, z, n) = (2, 4, 4, 4, 5)$, which minimizes Tersoff's potential. For clarity, only atoms in the foreground are shown. (a) View from "above". (b) Side view.

Fig. 12 Same as Fig. 11, for $(m, g_1, g_2, z, n) = (5, 2, 1, 1, 5)$.

Fig. 13 Same as Fig. 12, with a chiral shift $j = 1$.

Fig. 14 Gap in the Hückel spectrum for molecules $(m, g_1, g_2, z, n) = (2, 2\ell, 2\ell, \ell, 5)$, $(2, 2\ell, 2\ell, \ell, 6)$, $(2, 2\ell, 2\ell, 2\ell, 5)$, $(2, 2\ell, 2\ell, 2\ell, 6)$, $(2, 2\ell, 2\ell, 3\ell, 5)$, $(2, 2\ell, 2\ell, 3\ell, 6)$. For $z/\ell = 1$ (resp. 2, 3), calculations were carried up to $\ell = 9$ (resp. 8, 5). The numbers in the graph stand for z/ℓ. Calculations for $n = 6$ were carried up to $\ell = 5$; for the values of ℓ for which a number appears only once, the values of the gap for $n = 5$ and $n = 6$ are either identical or indistinguishable within the resolution of the graph. For every z/ℓ, $\ell(\epsilon_\ell - \epsilon_h)$ exhibits approximate periodicity as a function of ℓ, with period 3.

Fig. 15 Delocalisation energy for the same molecules studied in Fig. 14. $\bar{\epsilon}_G = 1.575\beta$ is the delocalisation energy per atom of an ideal graphitic plane.