Curvature matching and strain relief in bucky-tori: usage of sp³-hybridization and nonhexagonal rings

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The relief of different types of curvature strain in bucky-tori of elemental carbon is considered in a general formal framework. This theory then is used to aid in the design of several structures, which are treated via molecular mechanics. Novel illustrations of the remnant strain are made, and some modest conclusions as to the nature of the structure of the experimentally observed bucky-tori are suggested. © 2001 by Elsevier Science Inc.

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INTRODUCTION

The consideration of novel carbon species has proliferated after the discovery[1] and preparation[2] of macroscopic quantities of the "uniquely elegant" truncated icosahedral buckminsterfullerene molecule. The preparation of buckytubes,[3,4] and of poly-yne,[5] and now the observation of bucky-tori[6] have only served to further heighten interest. In fact, all of these species had been theoretically surmised earlier. For instance, buckminsterfullerene was foresightfully considered an interesting novel hypothetical possibility first by Osawa[7,8] in 1970, and then independently by Bochvar and Gal'pern[9] in 1973, and by Davidson[10] in 1981. The case of Davidson is interesting in that there evidently was[11] consideration to search experimentally for C_{60} buckminsterfullerene in various hydrocarbon pyrolysis products, while Chapman[12,13a] sought a rational synthesis, and elsewhere Henson[14] thought that there might be some experimental manifestation of C_{60}, perhaps as nucleation centers.[12b]

And also there are the early, brief musings of Jones[15] on the possibility of fullereneic carbon cages. In any event, with fullerenes, bucky-tubes, or bucky-tori, more elaborated theoretical understanding has always followed successful experiments.

Here we further consider the most recently observed[6,16–18] case of bucky-tori. Such tori are potentially of much organic chemical interest because, as emphasized earlier,[19] they can be constructed with face rings entirely of the conventionally "aromatic" benzenoid hexagons—and they can be considered[20] the only plausible "benzenoids" composed entirely of carbon. In fact, there have been several theoretical papers devoted to these species,[20–24] and all possible graphical structures[21–25] have been identified. This is notably distinct from the case of polyhedral fullerenes, where the analogous problem is quite challenging, even to the extent of enumerating the possible graphical structures with a particular number, n, of carbon atoms, such as n = 60. Recently, using some sophisticated mathematics, Brinkmann and Dress[26,27] have developed a computationally efficient scheme to identify all fullerene graphs (with or without the condition of the isolated-pentagon rule) up to a size limited by computer facilities, with current results up to about 200 sites. Notably, however, for tori the graph of a structure is generally only a part of the problem of identifying chemically distinct isomers,[20] there being several topologically distinct embeddings in Euclidean 3-space for each graph. But even this problem can be fully formally solved[28,29] for the case of benzenoid bucky-tori, which have all faces being hexagons. The possibility[30–35] of nonbenzenoid bucky-tori with some 5- and 7-membered rings is not excluded by the current experiments[6,16–18] and, indeed, even the numbers of carbons are undetermined (though the number must be large, $\geq 10,000$).

In general, the benzenoid bucky-tori have "curvature strain," even though as a consequence of the Gauss-Bonnet theorem their net amount of Gaussian curvature must be 0. Basically, for tori[19,30–35] there must be equal contributions of positive and

^aApparently Chapman (at UCLA) worked on routes for a rational synthesis with more than one student, with (incomplete) results appearing in more than one PhD dissertation.
^bEvidently Henson (at Harwell) in approximately 1970 in an X-ray diffraction study of carbon fibers, observed graphene arrangements, which led

him to consider the truncated icosahedron as a possible seed structure, and he wrote up a manuscript, which however was not published

negative Gaussian curvature, the magnitudes of each contribution (in sterradians) being at least 4π, which is the same as the net Gaussian curvature for ordinary fullerenes. Thus there are two (absolute-isotropic curvature) strain contributions, each equaling at least that of an ordinary polyhedral fullerene. That is, bucky-tori have a net absolute isotropic curvature that is double that of ordinary fullerenes; in addition they have some anisotropic curvature, such as "straight" bucky-tubes also have. At the sacrifice of a purely benzenoid structure, some of the curvature strain might be imagined to be relieved with the introduction (of equal numbers) of pentagonal and heptagonal rings. Indeed, several authors[30–35] have proposed this possibility and have reported computations for a number of such representative species. We review general conceptual curvature-strain ideas in the next section to aid in the introduction of bonding patterns that relieve curvature strain. We discuss an approach different than the use of complementary pentagons and heptagons and identufy several example toroidal structures incorporating this idea. We also report molecular-mechanics computations to reveal some relief of curvature strain. The extent of strain is presented pictorially. The final section of this article offers some brief conclusions, e.g., indicating the qualitative type of structure of the experimental tori.[6,16–18]

THEORETICAL VIEW OF CURVATURE STRAINS

Strain is due not only to distortion of bond angles from the ideal, but also to distortion of bond lengths from the ideal. Bond-angle strain is intimately related to geometric curvatures, but especially for cage structures there is a possibility of bond-length strain intimately related to the matching of local graphical structures to the manifested geometry. There is a preference for a "combinatorial curvature" associated to a molecular graph, G, to be matched to geometric Gaussian curvature associated to a smooth surface, S, in which G is embedded.[36–39] To understand this, we begin by identifying a net combinatorial Gaussian curvature to each vertex i of a G, such that when G is embedded, the surface S is partitioned by the edges of G up into faces each homoeomorphic to a disk. This combinatorial curvature Δ_i at vertex i is naturally identified with the Gaussian curvature that would occur if the faces meeting at this vertex were all planar regular polygons. That is, for such a regular face α with n_α sides, the angle at each vertex would be $\pi - 2\pi/n_\alpha$, and the consequent curvature would be given as the Descartes defect,[40] thusly

$$\Delta_i \equiv 2\pi \sum_{\alpha}^{@i} \{\pi - 2\pi/n_\alpha\} \qquad (1)$$

where the sum is over the faces meeting at vertex i. We emphasize that, despite the geometric analogy, this is a purely topo-combinatorially defined quantity for the topological

equivalence class of embeddings of G in S. Rather similarly, one may naturally identify a combinatorial face curvature

$$\Delta_\alpha \equiv 2\pi - \sum_i^{@\alpha} \{\pi - 2\pi/d_i\} \qquad (2)$$

where this time the sum is over vertices i on the face α and d_i is the degree of vertex i. The fundamental nature of these topo-combinatorial quantities is indicated in that the summation of the curvature quantities over vertices (for the Δ_i) or over the faces (for the Δ_α) gives a standard topological invariant (as in [41,42]) which up to proportionality is the *Euler-Poincare characteristic* $\chi(S)$ of the surface S,

$$\sum_i \Delta_i = 2\pi\chi(S) = \sum_\alpha \Delta_\alpha \qquad (3)$$

Indeed, the manipulation of either the right- or left-hand sides of this equation leads (for a graph, G, on a closed surface, S) to a value of $2\pi(V - E + F)$, where V is the number of vertices of G, E is the number of edges of G, and F is the number of faces of the embedding. Thus, Equation 3 really may be viewed as the Euler-Poincare theorem in disguise. But with the Δ_i and Δ_α being identified to curvatures, it is perhaps better to describe Equation 3 as a disguised form of the general Gauss-Bonnet theorem, which says that the geometric Gaussian curvatures sum to this same result ($2\pi\chi(S)$), including the factor of 2π.

A key point of relevance is that[36–39] these combinatorial curvatures seem to need to match the net geometric Gaussian curvatures for the local Dirchlet-cellular region of S in which they are embedded if the bond lengths are to be of near equal length. That is, the greater the mismatch of the combinatorial and geometric curvatures, the greater the distortion of the bond lengths from a uniform length. And since bond-length stretching or compression is typically expensive compared with bond-angle distortion (as accounted for with other absolute isotropic or anisotropic curvatures), the matching is typically quite important. Thus, for the current case of bucky-tori, we desire negative combinatorial curvature around the inside annulus and positive combinatorial curvature around the outside; indeed, this is what has been accomplished earlier[30–35] with the placement of pentagons (giving $\Delta_\alpha = +\pi/6$) and heptagons (giving $\Delta_\alpha = -\pi/6$), for a trigonally hybridized network G. This may also be viewed to be involved in the matching of negative-combinatorial curvature heptagonal rings for extended conjugated fullerene-like structures[43–46] embedded in infinite minimal surfaces, these having constant negative curvature.

Evident now is another way to introduce negative combinatorial curvature: introduce degree-4 sp^3-hybridized sites, while also introducing somewhere else two pentagons (without heptagons) for each such site. Each sp^3-hybridized site may be understood to be arranged with its 4 bonds radiating out in different directions in the surface so that there are 4 bond angles and the resultant negative combinatorial curvature for such a site i surrounded by hexagons is

$$\Delta_i = 2\pi - 4(\pi - 2\pi/6) = -2\pi/3 \qquad (4)$$

(it being assumed that the two counterbalancing pentagons are not adjacent to the sp^3 site). Then, placing tetrahedrally hybridized carbons around the inside of a torus' annulus, one needs to introduce somewhere a counterbalancing positive
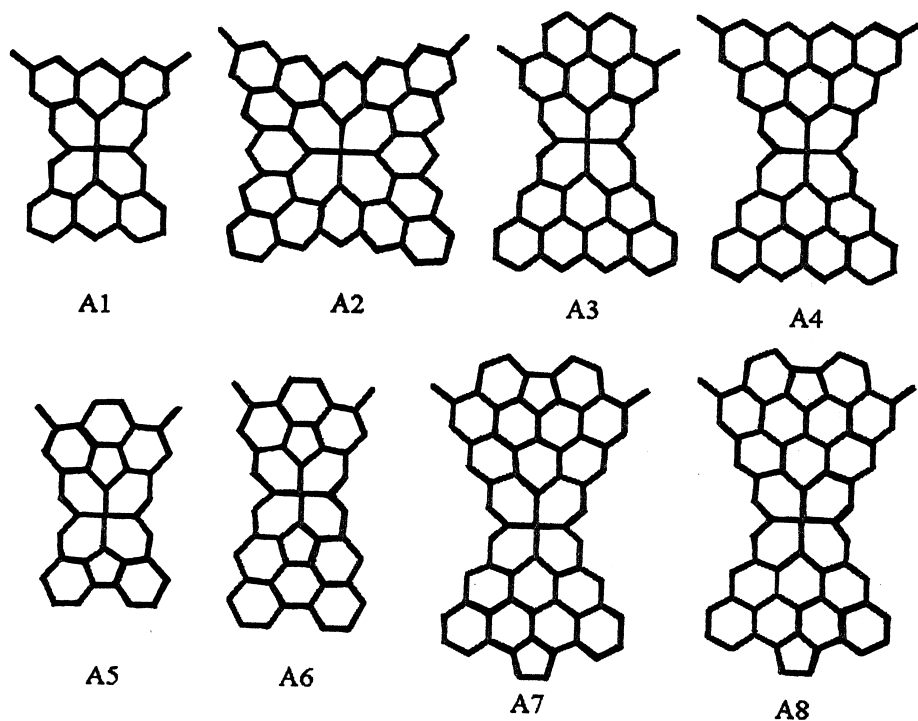
Figure 1. Eight different unit cells for (type A) tori with one sp^3- hybridized site & two pentagonal rings per cell.

combinatorial curvature, preferably around the outside, to balance the positive geometric curvature there. This positive curvature may be accomplished with the associated pentagonal faces, as we study here, or, conceivably, hexagonal faces could be retained in a formal sense if one introduces appropriately placed sp-hybridized carbons. But attention needs to be paid to bond-angle strain, too, so that each tetrahedrally hybridized carbon should have two of its bonds oriented around the inside annular equator of the torus, with the other two in a roughly orthogonal plane, and there should be no more than approxi-
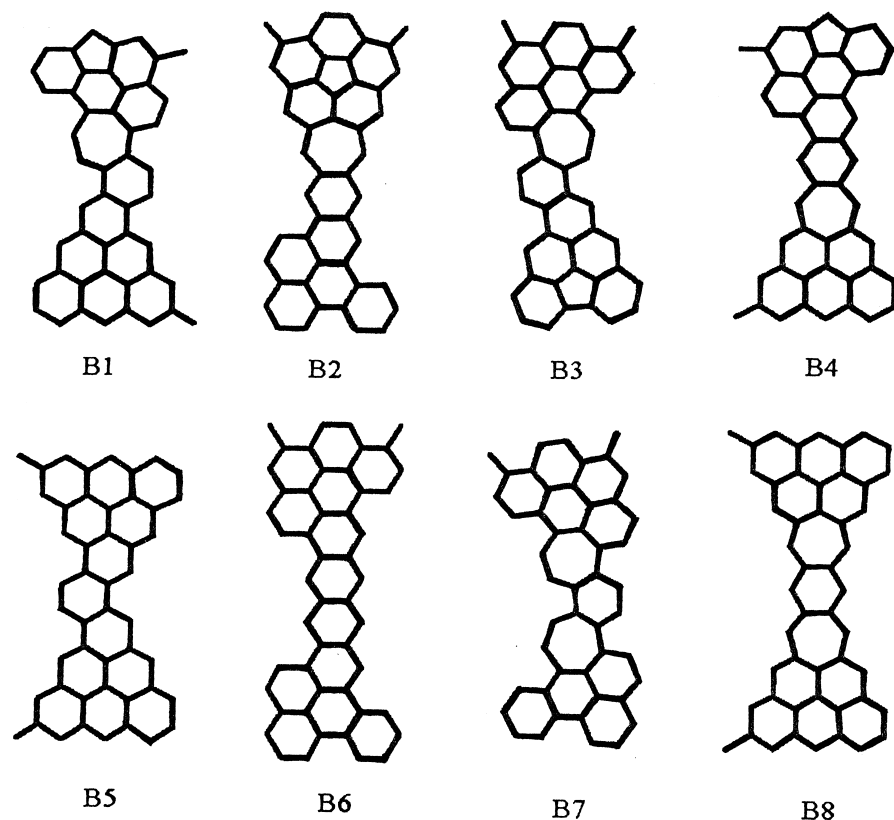

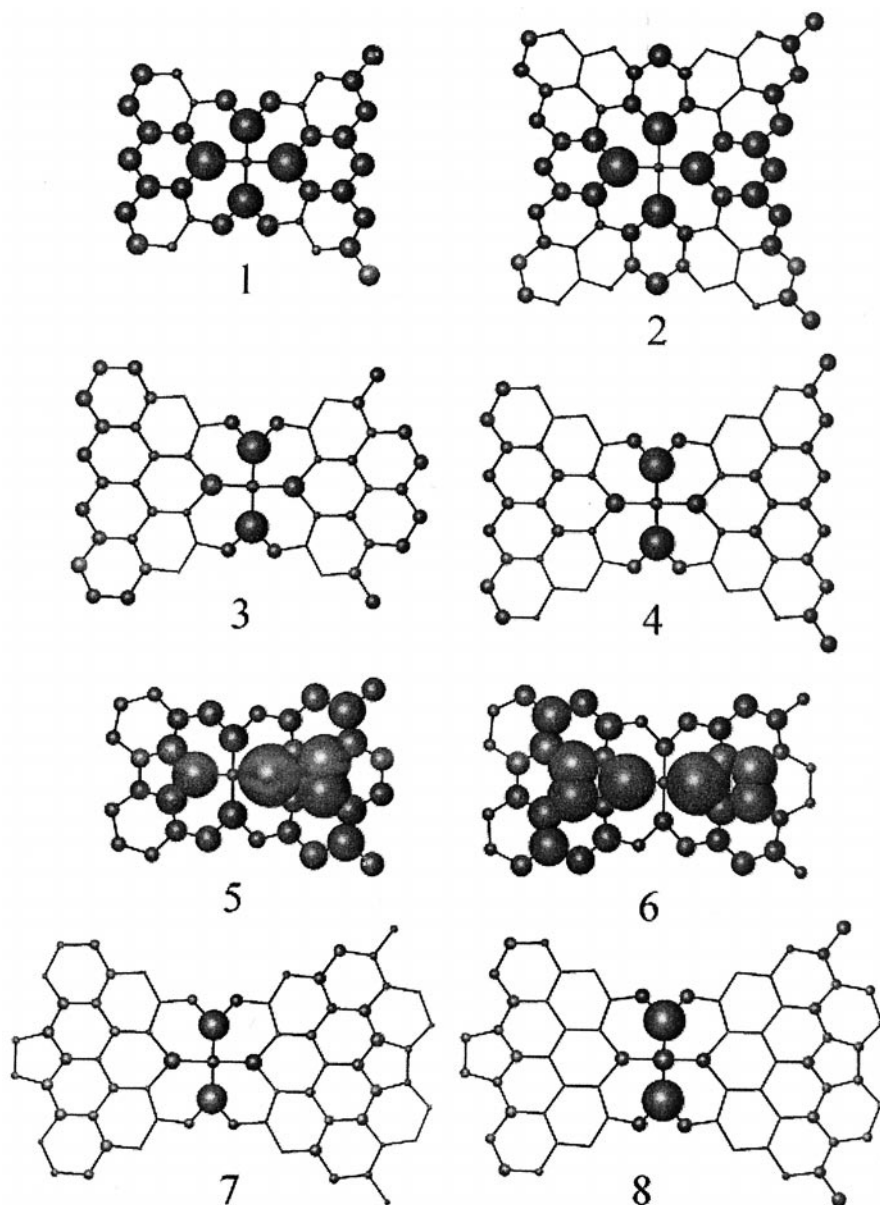*Figure 2. Eight different unit cells for (type B) tori with one pair of matched 5- & 7-membered rings per cell.*

Figure 3. Strain-indicating depictions for the unit cells of the tori resulting from the sp^3-containing cells of Figure 1. Note that the unit cells here are rotated 90° from those in Figure 1.

mately 6 such sp^3-hybridized carbons along this equator, if the total combinatorial curvature is not to exceed in magnitude the geometric curvature of -4π associated to the inside annular region of typical tori. This value[19,37–39] of -4π may be established by imagining a torus wrapped in cellophane, which then forms a surface homeomorphic to a sphere having a total curvature of $+4\pi$, but since the Gauss-Bonnet theorem indicates that the total Gaussian curvature for a torus is 0, one sees that the annular region where the cellophane does not match the torus must contribute -4π.

We might consider that there could be a few more sp^3 carbons than the suggested 6, because if the angles were unstrained with ideal tetrahedrally hybridized bond angles, the Gaussian geometric curvature at each such site would, via Descartes formula, be $2\pi - 4 \cdot \cos^{-1}(-1/3) \approx -1.36$ (sterradians). That is, ideal tetrahedral bond angles would need about 9 sp^3 sites to obtain -4π of Gaussian curvature, whereas only 6 such sites give -4π of combinatorial curvature, so that

matching geometric and combinatorial curvatures evidently entails some degree of strain from the hybridization-ideal bond angles. On the other hand, we can check to see how much net *linear* curvature results from n ideal sp^3 bond angles, all imagined to be coplanar around the inside equator. The result is $n \cdot \{\pi - \cos^{-1}(-1/3)\}$, which for n = 5 is $\approx 1.96\pi$ (radians) and matches very nearly to the needed value of 2π (radians).

Support for our general idea for relieving strain is found in the argument and computations of Hiura et al.,[47] where sp^3 carbons are used to introduce negative-curvature kinks in bucky-tubes, where again some counterbalancing positive curvature defect, such as pentagons, needs also to be introduced on the opposite side of the tube. But that the combinatorial curvature of the sp^3 sites does not match perfectly to the Gaussian curvature for ideal sp^3 bond angles indicates that this approach may not relieve quite as much strain as the introduction of heptagonal-pentagonal ring pairs.

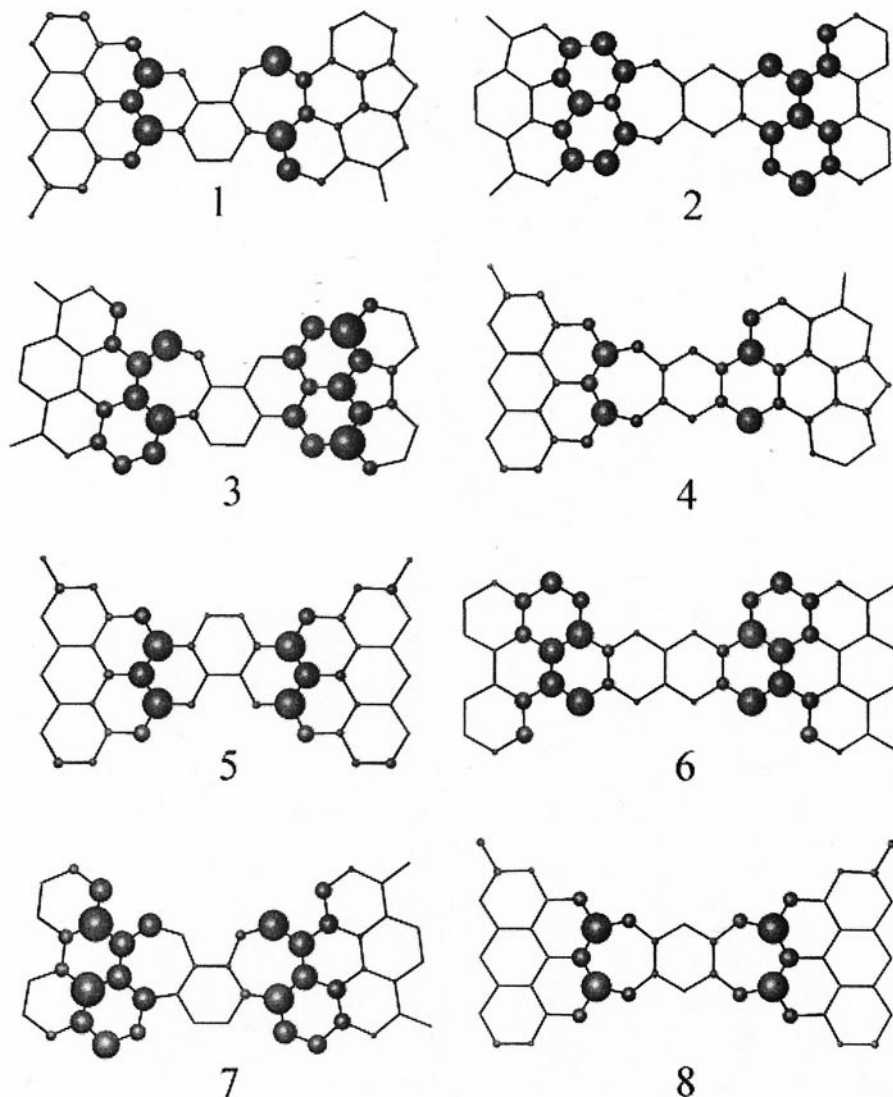The considerations so far have neglected strain due to[19,36–39]

Figure 4. Strain-indicating depictions for the unit cells of the tori resulting from the 5- and 7-membered-ring-matched cells of Figure 2. Note that the unit cells here are rotated 90° from those in Figure 2.

absolute anisotropic curvature, which occurs when the magnitudes of the two principal linear curvatures are different. For example, for a "straight" bucky-tube a first principal linear curvature k_{Max} is the inverse of the radius of the tube while the second linear curvature k_{min} is 0, and there evidently is some angle strain. It seems clear that bucky-tori, being bent finite bucky- tubes with cyclic boundary conditions, must always have some net anisotropic curvature, and indeed there is[48,49] the "Willmore" conjecture that there is a bound

$$\int (k_{Max} - k_{min})^2 dA \geq 8\pi(\pi - 2) \qquad (5)$$

with the minimum value achieved only for rather "plump" tori. For the rather "skinny" tori experimentally observed[6,16-18] this bound is undoubtedly significantly exceeded. In any event, anisotropic curvature provides an additional substantial source of strain not rationally accommodated with either of the schemes so far considered involving nonhexagonal rings or sp^3 hybridization.

Another way to aid in the accommodation of curvature strain is to hydrogenate relevant carbon sites connected to 3 other carbons. The resulting carbons, rather than preferring 120° bond angles, then prefer tetrahedral bond angles ≈109.5°, so that ideally each such site with 3 such angles assigned to the surface considered allows ≈0.184 (ster-radians) of Gaussian curvature in the carbon network. Then the requisite positive Gaussian curvature in a torus could ideally be approximately accommodated by 34 H atoms at 34 carbons around the outer periphery of a torus. To accommodate negative Gaussian curvature carbons around the inner annulus could be imagined to be hydrogenated with the H atoms on the interior of the torus, i.e., with the H atoms in the "dough" of a doughnut. Presumably, hydrogens could be placed to accommodate even the anisotropic curvature strain, but all hydrogenated structures are no longer elemental carbon species, and are not further considered here.

EXAMPLE STRUCTURES AND COMPUTATIONAL RESULTS

Here we examine several particular toroidal structures, some with combinatorial and geometric Gaussian curvature mutually

matched to some degree either using sp³ sites (around the inner negatively curved annulus) or instead using heptagon–pentagon pairs (with the heptagons around the inside of the annulus and the pentagons around the outer periphery of the torus). Again, these degree-4 sites are to be suitably located to turn up on the inner part of the annulus and also to have bonds appropriately directed. The considered structures then are treated in a standard molecular mechanics computation with geometry optimization. Thereafter the net angle strain is obtained from the computed geometries in terms of deviations of bond angles away from ideal sp² and sp³ angles as well as of deviations of bond lengths away from an aromatic ideal.

We have treated 8 tori for each manner of strain relief, involving some degree of accommodation of the curvature mismatch intrinsic to purely polyhex tori. Unit-cell graphs and corresponding whole geometry-optimized tori for the several examples of type A tori with sp³ carbons (and counterbalancing pentagons) are indicated in Figure 1. Similarly, unit cells and whole tori for examples of type B with matched heptagon–pentagon pairs are indicated in Figure 2. Here each unit-cell graph G corresponds to an ordinary unit-cell structure by rolling G into a bracelet so that the corresponding sites at the top and bottom come near, at about one bond length, and then connect these corresponding sites by a bond. Several (5 or 6) such unit-cell structures may then be connected to one another in a cyclic manner and the geometries optimized. These structures with up to about 400 sites for type A are in rough correspondence with the sizes of the pentagon–heptagon strain-relieved bucky-tori previously treated by Itoh et al.,[30,31] although they are smaller by perhaps a factor of 1,000 than the experimentally realized tori.[6,16–18]

Structures of even 200 atoms are too large to be easily treated by reliable quantum chemical methods beyond Hückel theory, but are easily handled by molecular mechanics. We have used the updated MM2 version sometimes termed MM+ as implemented in Hyperchem 4.5. One of our team (D.B.) has previously made MM+ and PM3- MO calculations for all isolated-pentagon-rule fullerenes up to 100 sites, with separate geometry optimization for each method, and has found overall reasonable comparison between the molecular-mechanics strain and the PM3 heat of formation. Thus there appears to be some degree of agreement with this more advanced quantum-chemical theory.

It is evident from the discussions of the preceding section that a bucky-torus and a fullerene have comparable mean absolute-isotropic curvature strain per site only when the torus has somewhat more than twice the number of atoms as for the corresponding fullerene. The numerical energetic results of our molecular-mechanics computations for each torus as a whole are summarized in Table 1. Three of the type A tori (A2, A5, and A6) are somewhat more strained than the others. The type B (heptagonal–pentagonal) tori seem to be somewhat less strained than the type A (sp³-hybridized-pentagonal) tori, which is not unexpected from our theoretical considerations. Molecular-mechanics computations on a suite of pure poly-hex tori of comparable sizes reveal strain energies per site that are always a few times greater than for our strain-relieved tori. But the difference might be more modest for significantly larger bucky-tori, because there is more "ring crinkling" around the inside annulus for smaller bucky-tori. In fact, one may rather generally understand the origin of the nonplanarity or "crinkling" of rings on the inside annulus: for degree-3 sites with only three planar rings meeting at each site the Descartes defect (being 2π minus the sum of the 3 incident face angles) can only be positive, whereas to make a torus we must have negative curvature on the inside of the annulus. The assumption that the rings on the inside annulus are planar must evidently be violated, so that in a mathematical sense each nonplanar chemical ring may be viewed as a union of smaller planar polygonal sections, with new implicit edges not corresponding to covalent chemical bonds. These new edges then give rise to a piecewise planar toroidal surface with more than 3 edges (counting these new edges) occurring at now negatively curved sites on the inside annulus, and Descartes version of the Gauss-Bonnet theorem for the torus is satisfied.

Local angle-strain results are neatly encoded by placing at

Table 1. MM Results (in kcal/mole) for various strain-relieved Bucky-Tori

Torus	# atoms	Bond	Angle	Dihedral	VdW	Stretch-bend	Total
A1	185	46.24	214.02	1293.59	232.34	−25.16	1761.02
A2	315	66.00	276.01	1765.35	358.86	−30.21	2436.00
A3	265	35.00	231.83	1095.69	218.30	−16.09	1564.75
A4	295	38.23	227.31	1037.55	236.65	−14.05	1525.70
A5	222	229.28	747.98	1409.17	351.96	−8.68	2729.71
A6	270	357.76	1085.97	1305.74	467.53	10.68	3227.70
A7	335	57.89	285.23	947.15	263.20	−9.24	1544.24
A8	402	107.02	307.43	1068.16	304.53	−14.30	1772.84
B1	240	29.16	193.62	723.12	204.69	−9.12	1141.47
B2	240	50.30	249.58	839.03	221.55	−12.16	1348.30
B3	240	64.00	294.74	831.65	249.86	−10.12	1430.13
B4	240	26.01	196.52	709.45	177.00	−5.40	1103.59
B5	240	31.17	192.56	734.73	210.47	−8.88	1160.05
B6	250	40.64	225.45	799.93	204.03	−8.90	'1261.16
B7	240	64.87	297.17	832.60	248.36	−9.61	1433.39
B8	250	29.51	199.07	676.29	192.50	−7.63	1089.74

each site a sphere with a radius proportional to the strain at that site. Angle strain is assigned to the central site; bond strain is divided evenly between the two sites at the ends of the bond; and dihedral strain is divided evenly between the two central atoms. The consequent results for the type *A* and *B* examples are shown in the unit-cell depictions of Figure 3 and Figure 4. Corresponding strain-attendant figures for the full tori embedded in Euclidean 3-space are shown in Figure 5 and Figure 6. We see that strain is only partially relieved and what remains is not uniformly spread out. One main reason for this is that although we have focused on Gaussian curvature, anisotropic-curvature strain remains. Another reason is that the matching of combinatorial and Gaussian curvatures is not perfect or complete either for nonhexagonal rings or for sp^3-hybridization. An aspect not foreseen from our general considerations of the preceding section is that for the (type *A*) case of sp^3- hybridized

sites, there is often a great deal of strain at two of the immediately adjacent sp^2 sites. Still, it seems that the strains on the inside of the annuli and around the outer periphery are modestly reduced from the sites at intervening positions. Overall, although strain is at least modestly relieved by either of these schemes, they sacrifice the purely benzenoid character of the all-polyhex bucky-tori structures.

CONCLUSIONS

It may be argued via our theoretical discussion and our numerical results, that experimentally observed[6,16–18] bucky-tori do not involve a systematic use of either of the varieties of strain relief considered here, even though only global descriptions (without atomic-level detail) of the experimental bucky-tori are at present available. With either strain-relief scheme consid-
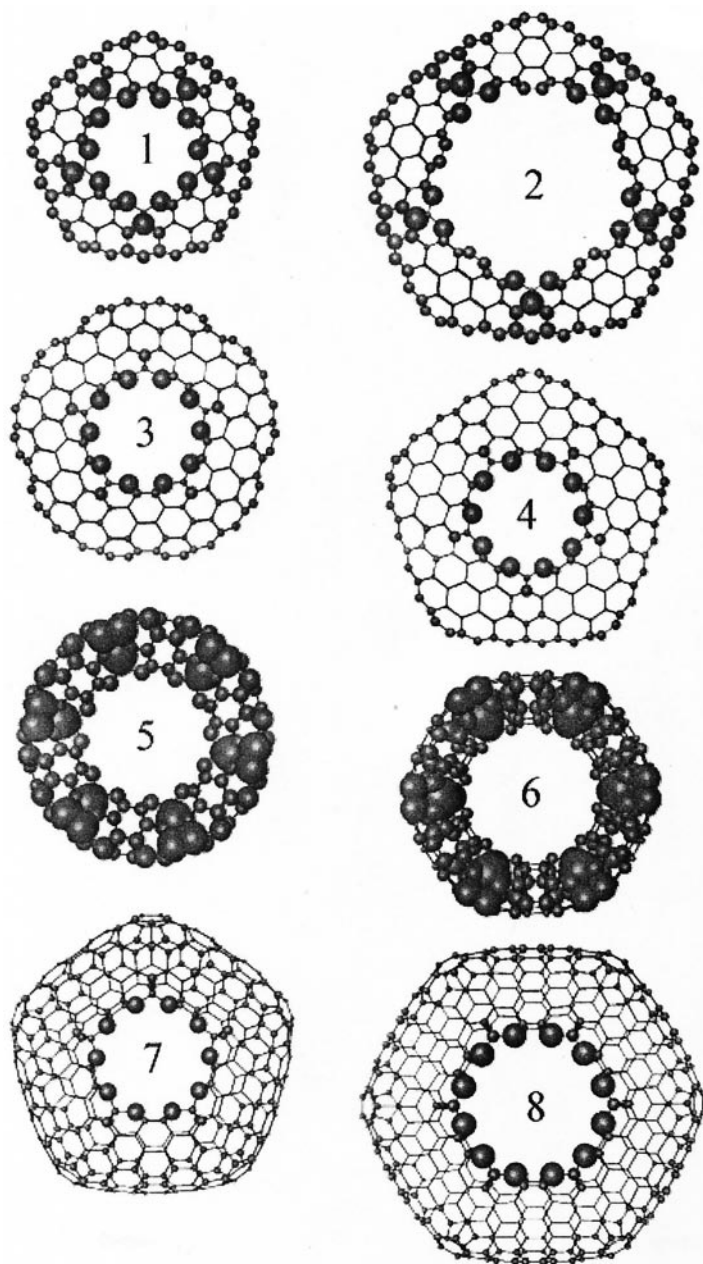

Figure 5. Complete-torus strain-indicating depictions for type A bucky-tori of Figure 1 and Figure 3.
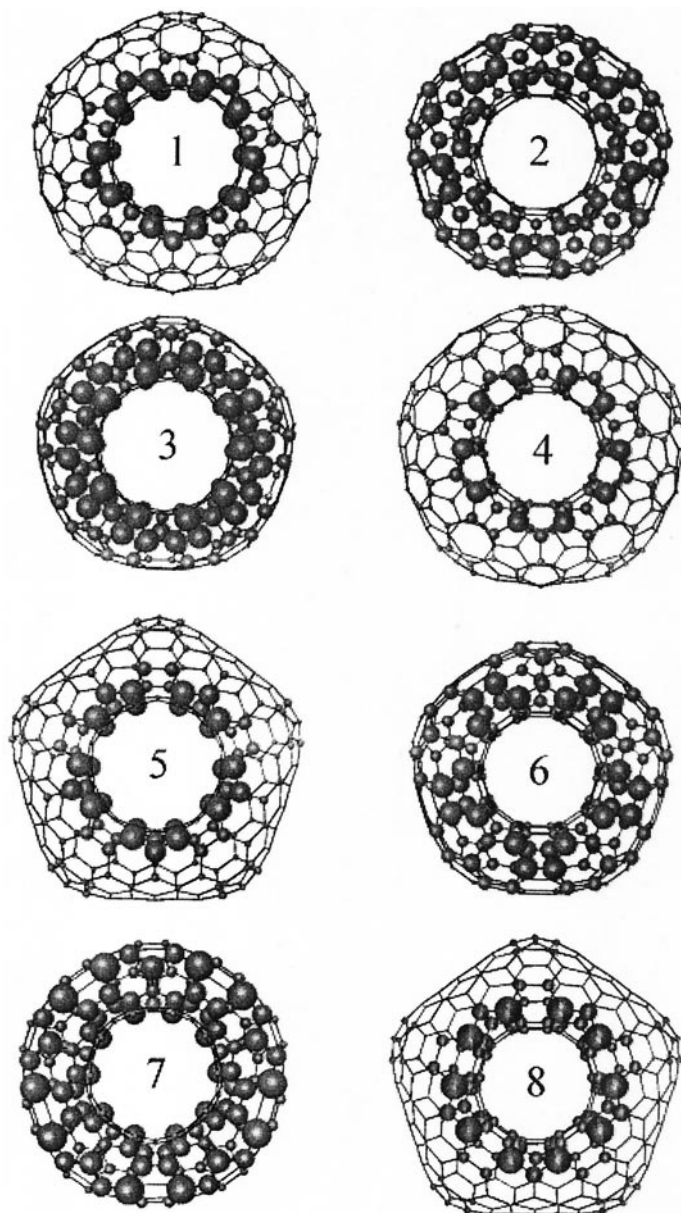
Figure 6. Complete-torus strain-indicating depictions for type B bucky-tori of Figure 2 and Figure 4.

ered here, the Gaussian curvature comes in discrete localized "lumps," of which no more than 12 "lumps" correspond to one sign of curvature. With the positively and negatively curved centers on nearby opposite sides of the toroidal tube, the geometric curvatures should accumulate in the same regions as the "defect" structures (to achieve matching of combinatorial and geometric curvatures), and "polygonized" tori with sections appearing like straight cylinders should result. In viewing a skinny tube as a line, the tori appear somewhat like polygons. Although our example bucky-tori are somewhat small, this polygonization effect may be observed in the type-*A* cases of *A*1, *A*2, *A*4, *A*7, and *A*8 of Figure 5 as well as the type-*B* cases *B*4 and *B*8 of Figure 6. That is, one perceives rounded-off "corners" on these tori. The other cases appear circular, with curvatures uniformly distributed around the tori, but this is presumably because the tori are so small that there is not yet room for the curvatures to become localized between otherwise straighter tube-like portions. Two such cases are displayed with

the *B*1 and *B*2 tori of Figure 6. On the other hand, the observed (SEM and SFM) images evidently represent tori that have more than 1,000 times as many atoms and have very skinny tubes compared with the overall torus diameter, so that with any strain-relieving centers, of, say, no more than 12 in number, the associated polygonized curvature strain (manifested as "corners") should become only more pronounced. But in fact the experimental images appear to display fairly uniform curvature around the tori so that they appear more similar in form to bicycle tires, or perhaps even skinnier. Thus these should be pure polyhex and all-sp^2-hybridized, or at least any positive and negative curvature defect structures should not be correlated with one another on nearby opposite sides of the tube. That is, granted that these experimental bucky-tori consist solely of carbon, they seem in essence to be "elemental benzenoids." In any event, the schemes of strain relief examined in this article do not seem to be operative in the experimentally observed structures.

Overall, the general theoretical formalism[37–39] that interrelates strain and curvature is seen to be insightful and useful and should have much further utility. To our knowledge, the condition of better local matching of combinatorial and geometric curvatures to diminish bond-length strain has not yet been cast as a mathematical theorem, but it is consistent with the global Gauss-Bonnet theorem, as well as some heuristic arguments and a sizeable number of examples. Previous discussions[36–39] have mentioned some of this rationale, and have focused on applications to polyhedral fullerenes, and e.g., the manner in which curvature matching leads one to anticipate "icosahedrization," instead of "sphericalization," of larger icosahedral-symmetry fullerenes. But there are many other possible types of structures where the same ideas should be relevant. Generally, the approach might be made more quantitative.

It seems that both the considered structural schemes, *A* and *B*, for Gaussian-curvature strain relief, should yield stable toroidal species. But for very skinny tori the anisotropic curvature strain is much greater than the absolute isotropic curvature strain. Comparable very large purely benzenoid systems, which would not have curvature matching, should have nearly the same stability as our strain-relieved structures. Which type of species is formed may be a matter of the manner of formation. There evidently are a number of feasible possibilities for bucky-tori, with the current usage of degree-4 (sp^3) sites in the region of the inner annulus, and thereby the possibilities are notably increased.

We hope that Professor Osawa will be pleased with our general theoretical framework, the pictorial presentation of strain, the further characterization of a novel type of aromatic species, and our results.

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