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## AN ALTERNATIVE STRUCTURE FOR $C_{576}$

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### Abstract

Carbon nanotubes with rollup vector indices equal, i. e.,  $(n,n)$  nanotubes, are calculated to be metallic electrical conductors. Several years ago, a toroidal fullerene structure,  $C_{576}$ , was proposed and suggested to possess a small bandgap on the basis of its having approximately half of its atoms arranged as in a  $(4,4)$  nanotube. A more recent calculation determined that this structure has a very large anisotropic ring-current diamagnetic susceptibility and is therefore likely to be a good electrical conductor. The present work proposes an alternative structure for  $C_{576}$  which is constructed entirely from six copies of a  $C_{96}$  fragment of a  $(4,4)$  nanotube.

### INTRODUCTION

Carbon nanotubes are conveniently classified by means of a rollup vector  $(n,m)$ , which captures both the circumference and helicity of the tube<sup>1</sup>. The  $(n,n)$  nanotubes are of particular interest because, unlike tubes with other helicities, they are calculated to possess metallic electrical conductivity<sup>2</sup>, even at small diameters<sup>3</sup>. They also seem to be by far the most abundant nanotubes produced synthetically<sup>4</sup>. Toroidal fullerenes that are structurally similar to  $(n,n)$  nanotubes might reasonably be expected to have interesting electrical properties.

In this vein, Dunlap proposed<sup>5</sup> structures derived from cutting an  $(n,n)$  nanotube at  $30^\circ$  to the tube axis and fitting the edge thus exposed against the edge of a  $(2n,0)$  nanotube

cut at  $0^\circ$  to the tube axis. The edges can be fit together to form a  $30^\circ$  joint that is all hexagons except for one pentagon and one heptagon. Twelve such joints bring the structure around  $360^\circ$  to form a torus. Specifically, Dunlap proposed a  $C_{576}$  torus derived from (4,4) and (8,0) nanotubes. The angular cut in the  $(n,n)$  tubes also helps alleviate the mismatch of circumferences, the circumference being  $3n$  for  $(n,n)$  tubes and  $2n/3$  for  $(2n,0)$  tubes (in units of the C-C bond length). The resulting structures have 12 pentagons around the outer circumference of the torus and 12 heptagons around the inner circumference. These non-hexagonal faces also help relieve strain. Pentagons have long been known to relieve positive-curvature strain in spheroidal fullerenes, and heptagons have been proposed for the relief of negative curvature strain in structures that simulate minimal surfaces<sup>6</sup> and "hyperfullerenes".<sup>7</sup> Dunlap conjectured that, because these structures have about half of their atoms in the  $(n,n)$  configuration, their HOMO-LUMO gaps would be small.

Calculations to test this conjecture for the  $C_{576}$  structure were very recently published by Haddon.<sup>8</sup> He found the proposed small bandgap manifested in an exceptionally large anisotropic ring-current diamagnetic susceptibility. Furthermore, in relating magnetic susceptibility to electrical conductivity, Haddon calculated the effective mass (usually considered to be inversely proportional to mobility) for the HOMO electrons  $m^*(C_{576} \text{ HOMO}) = 0.3m_e$  and concluded that high electrical conductivity was to be expected.

In addition to hexagons, the toroidal structures proposed by Dunlap have 12 pentagons and 12 heptagons, while the structure proposed in the present study has 6 rectangles, 6 octagons, and no pentagons or heptagons. A toroid has Euler characteristic  $\chi = 0$ . Because of the Euler closure rule, closed polyhedra must have  $\sum(6 - F_n) = 6\chi$ , where the summation is over all the faces and  $F_n$  is the number of sides of each face. Hexagons do not contribute, since  $6 - 6 = 0$ . Thus, a toroidal polyhedron must have, for example, equal numbers of pentagons and heptagons, or equal numbers of rectangles and octagons, or  $n$  octagons and  $2n$  pentagons. A sphere has  $\chi = 2$ , so spheroidal fullerenes are normally

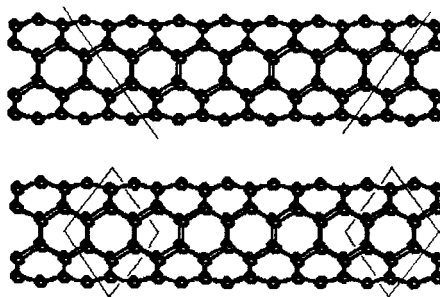
thought of as polyhedra with 12 pentagons and the remaining faces hexagons, although other combinations that satisfy the Euler closure rule have been proposed.<sup>9</sup>

## RESULTS AND DISCUSSION

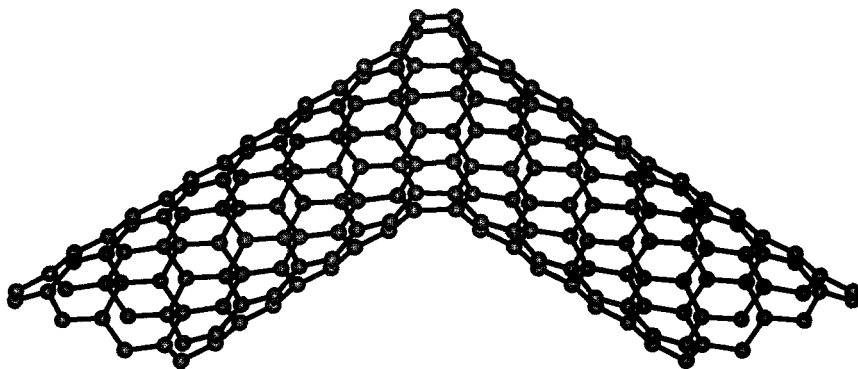
Figure 1 shows a (4,4) nanotube with two views of the planes that cut the tube at  $30^\circ$  angles to the tube axis to excise a 96-atom section. Figure 2 shows two such sections joined together. All new faces formed by the joint are hexagons except for one rectangle at the outer corner and one octagon at the inner corner. By joining six such sections in this manner and further joining the free ends of the first and sixth units, a complete  $C_{576}$  toroid is formed.

It is common practice to visualize all-hexagon toroids as parallelograms cut from the graphite lattice and folded up, and several methods for classifying these parallelograms have been proposed.<sup>10</sup> Following the same pattern, it is convenient to imagine sections of nanotubes cut as in Figure 1 as hexagons cut from the graphite lattice, as in Figure 3. These hexagonal sections may also be classified by several parameters, but that is a tangential subject here and will be published separately. Indeed, such pieces of the graphite lattice seem not to have been considered in the published literature and may represent building blocks for several new classes of fullerenes.

Kekulé structure count,  $K$ , provides an estimate of stability for conjugated hydrocarbons because  $\ln K$  correlates with resonance energy. There are many pitfalls in this approach to estimating stability, however, because  $K$  does not capture strain in the  $\sigma$  skeleton nor distinguish destabilizing  $4n$  cycles from stabilizing  $4n + 2$  cycles. For example, the  $I_h$  isomer of  $C_{60}$  is calculated to be the most stable of all 1812 spheroidal isomers having only pentagonal and hexagonal faces. The isomer with the largest  $K$ , however, is the  $D_{5d}$  structure that is a section of (5,0) nanotube with a cap of six pentagons on each end<sup>11</sup>. Because of the destabilizing effect of pentagon adjacencies, this  $D_{5d}$  structure may be the *least* stable of the 1812 isomers. The foregoing objections notwithstanding,  $K$  is likely to provide



**Fig. 1.** Two views of a section of (4,4) carbon nanotube cut to create the  $C_{96}$  subunit.

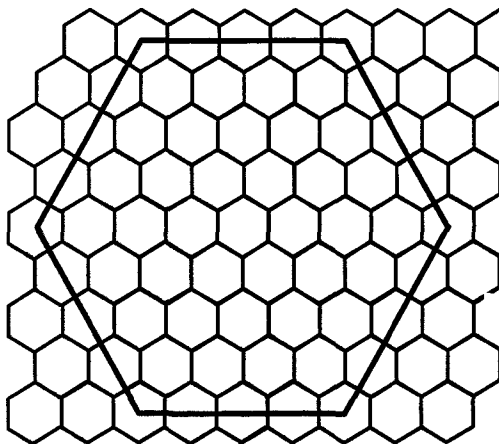


**Fig. 2.** Two  $C_{96}$  subunits joined together. All new polyhedral faces formed at the joint are hexagons except for one octagon on the inner curve and one rectangle on the outer curve.

Six  $C_{96}$  subunits can be so joined to make the complete  $C_{576}$  toroid.

a reasonable estimate of relative stabilities for structures that are not too different from each other.

Calculating an actual value of  $K$  for isomers of  $C_{576}$  would be a formidable undertaking at best. For example, the transfer matrix for either the structure suggested by Dunlap or the one proposed here would have  $(2^8)^2 = 65\,536$  elements, and  $K$  would be equal to the trace of the sixth power of that matrix<sup>12</sup>. The signed adjacency matrix method



**Fig. 3.** A hexagonal  $C_{96}$  piece cut from the graphite lattice. Rolling this piece into a cylinder and joining the four dangling bonds along the top row with the corresponding bonds along the bottom row gives the  $C_{96}$  subunit of the (4,4) nanotube.

described by Klein and Liu,<sup>13</sup> but ultimately due to Kasteleyn,<sup>14</sup> is not generally applicable to toroids<sup>15</sup>. The structure proposed here (but not that of Dunlap) is an alternant, so the permanent of the adjacency matrix would equal  $K^2$ ,<sup>16</sup> but that computation greatly exceeds the capability of currently available algorithms and computers.

A trend may be observed, however, in comparing  $K$  values for some  $C_{120}$  isomers. (The values below were obtained from the signed adjacency matrices.<sup>13</sup>) The spheroidal  $C_{120}$  fullerene with the largest HOMO-LUMO gap<sup>17</sup> has  $K = 134\,824\,212$ , while the isomer that is analogous to the highest- $K$   $C_{60}$  isomer above, i. e., a section of (5,0) nanotube capped with sextets of pentagons, has  $K = 246\,062\,501$ . Both of these structures ideally have  $D_{5d}$  symmetry. By analogy with  $C_{60}$ , the latter isomer may have the largest  $K$  of all the  $C_{120}$  spheroids. If, however, a  $C_{120}$  section of (4,4) nanotube is closed by bonding the divalent atoms to make a tetracyclobuta[*a,c,e,g*]cyclooctatetraene system at each end, the resulting

$C_{120}$  structure has two octagons, eight rectangles, 52 hexagons, and  $K = 1\,625\,161\,444$ , a value approximately 6.6 times larger than that for the large- $K$  spheroid. This difference might be attributed to the presence of a metallic (4,4) vs. semiconducting (5,0) nanotube, but the "carbon cylinder" isolated-pentagon isomer of  $C_{120}$  (ref. 17, p. 62) which is a capped section of (6,6) nanotube, has only  $K = 145\,851\,948$ . Therefore, a more likely cause of the much larger  $K$  in the capped (4,4) structure is the absence of odd-numbered cycles. By the same line of reasoning, the  $C_{576}$  isomer proposed here would have much larger  $K$  than the one containing 12 pentagons and 12 heptagons. This difference may indicate greater stability, but its effects on electronic properties such as diamagnetic ring current susceptibility are unknown.

The presence of "antiaromatic"  $4n$  rings is usually considered to decrease stability, and that of "aromatic"  $4n + 2$  rings to increase stability. Indeed, this notion is the basis of conjugated circuit theory.<sup>18</sup> Conjugated circuit theory, however, assumes that the ring is planar, or nearly so, so that the circuit is conjugated. An example where conjugated circuit theory does not apply is 1,3,5,7-cyclooctatetraene, which would be predicted to be antiaromatic and highly reactive, but in fact can be purchased commercially and stored at room temperature. This discrepancy occurs because 1,3,5,7-cyclooctatetraene exists in a highly non-planar conformation, so that the double bonds are effectively isolated. In the structure proposed here, all six of the 8-cycles are frozen into the same sort of non-planar conformation.

It seems that the 4-cycles, as analogues of cyclobutadiene, would compromise stability. Gao and Herndon calculated,<sup>9a</sup> however, that relative  $\Delta H_f^\circ$  clearly favors structures with 4-membered rings over the standard 12-pentagon isomers as the size of the polyhedra becomes smaller, and that UHF MNDO HOMO-LUMO separations favor 4-membered rings even for structures as large as  $C_{60}$ . These workers concluded that the putative antiaromatic character of the 4-cycle does not contribute in these situations and should not be used as a

criterion in selecting plausible structures. More recently, Babić and Trinajstić<sup>10c</sup> performed conjugated circuit computations on all 141 325 possible isomers of  $C_{\leq 60}$  made up of only rectangular, pentagonal, and hexagonal faces. According to these calculations, the most stable isomer for each of the each of the 21 possible carbon numbers had at least four rectangular faces. This is a very important and relevant result, since conjugated circuit theory explicitly includes a destabilizing term for 4-cycles. The foregoing evidence suggests that, in the  $C_{576}$  structure proposed here, the 4-cycles and 8-cycles will not adversely affect electronic stability.

Finally, examination of Figure 2 shows considerably greater nonplanarity around the four-membered rings than elsewhere in the structure. In the unoptimized structure, the pyramidalization angle of the four relevant atoms averages  $25^\circ$ , but molecular mechanics optimization (MMX force field) reduces this to less than  $20^\circ$ . (The pyramidalization angle is found by constructing a vector that makes the same obtuse angle with all three  $\sigma$  bonds, then subtracting  $90^\circ$  from that angle<sup>19</sup>.) Several years ago, Haddon persuasively argued that the maximum pyramidalization angle for molecules isolable under normal conditions is about  $13^\circ$ <sup>20</sup>. By comparison, a typical atom in the (4,4) tube itself has a pyramidalization angle of only  $7.6^\circ$ , somewhat less than the  $11.64^\circ$  value<sup>20</sup> for buckminsterfullerene. A larger tube, say (6,6), would decrease the pyramidalization angles around the rectangular faces. Also, the very recent isolation and characterization of a  $C_{36}$  fullerene<sup>21</sup> indicates that, under circumstances yet to be characterized, pyramidalization angles can exceed  $13^\circ$ .

## CONCLUSIONS

A  $C_{576}$  toroidal fullerene has been proposed in the literature and postulated to have interesting electrical properties, specifically, high electron mobility around the toroid. The present paper suggests an alternative but similar structure, also  $C_{576}$ , and argues that it may be expected to possess greater electronic stability. This structure is composed entirely of



sections of (4,4) carbon nanotubes and might be expected to support a large ring current around the toroid and provide a nanoscale current loop if it could ever be fabricated. Kinetic stability against dimerization and attack by other chemical species may depend on unknown factors relating to the large pyramidalization angles around the rectangular faces.

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