

# Claromatic Carbon Nanostructures

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Eric Clar's qualitative ideas for benzenoids are described in application to various novel nanostructures: graphene, edges in graphene, carbon nanotubes, carbon nanocones, and carbon nanotori. The specially singled out most highly aromatic species with Clar structures consisting entirely of aromatic sextets are proposed to be termed "claromatic". Several such claromatic nanostructures are identified as manifesting special properties. A molecular structural "(*h,k*)" characterization for benzo/grapheneic nanostructures is shown to link up neatly with Clar's ideas.

## 1. Introduction

Covalent chemical bonding can be localized ( $\sigma$ -bonds) or delocalized (conjugated  $\pi$ -bonds) in organic compounds. A considerable fraction of all known and indexed chemical compounds ( $\sim 5 \times 10^7$  substances) contain "aromatic delocalization" having benzene as the typical representative. Although "aromaticity" may be argued<sup>1</sup> to be a partially ordered concept (with energetic, geometric, magnetic, and electro-optic manifestations), it is useful and essential for understanding and teaching chemistry. Aromatic molecules have distinct chemical, spectral, magnetic, geometric, and energetic properties.<sup>2–5</sup>

Natural selection has resulted in the use of several aromatic networks in various "biochemicals" which enable life processes: (i) building blocks in storing genetic information (DNA and RNA nucleotide bases); (ii) 4 of the 20 natural amino acids, two of which are essential; (iii) porphyrins which first allow the fundamental reaction of photosynthesis to proceed thanks to the chlorophylls, converting carbon dioxide and water into organic compounds and oxygen, and which second allow "reverse" processes with cytochromes involved in electron transport and with hemoglobin carrying oxygen and carbon dioxide in blood; (iv) many coenzymes and vitamins; and (v) many plant and animal hormones such as estrogens. The list of industrially made aromatic compounds includes pharmaceuticals, pesticides, dyestuffs, polymers, etc.

Along with the names traditionally associated with the gradual development of the aromaticity concept, namely Michael Faraday, August Kekulé, Adolf Claus, Emil Erlenmeyer, Eugen Bamberger, Robert Robinson, and Erich Hückel, one should also mention the less recognized names of Josef Loschmidt, Henry Edward Armstrong, Johannes Thiele, and more recently, Ernest C. Crocker.<sup>6</sup> The significance of the "rule of six" by Bamberger and by Thiele in the late 1890s followed by the recognition of the  $\pi$ -electron sextet by Crocker and its symbolization by Armit and Robinson's circle<sup>7</sup> was generalized in Hückel's " $4n + 2$   $\pi$ -electron rule".<sup>8</sup> It was Clar's insight that gave a more profound significance to the sextet circle.

In the present paper, Clar's ideas are reviewed and expressed in a canonical fashion, so as to enable extension to deal with more recently developed conjugated-carbon nanostructures. Thence, we address graphene, nanocones, nanotubes, and

nanotori, with Clar's ideas identifying especially stable "claromatic" subclasses of these different species. A particular molecular structural "(*h,k*)" characteristic is utilized to describe relative locations of selected rings and is shown to link up very neatly with Clar's ideas.

## 2. Clar Sextets

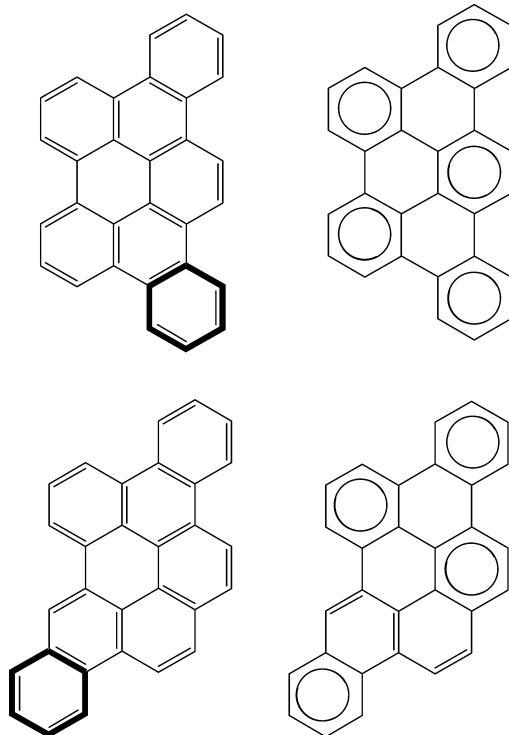
Eric Clar prepared numerous new polycyclic benzenoid hydrocarbons.<sup>9</sup> From their chemical and spectral study, he concluded that some benzenoid rings have "full sextets of  $\pi$ -electrons",<sup>10</sup> leaving adjacent rings depleted of cyclic conjugation, so that when this adjacent ring contains at least one localized double bond, it shows a reactivity resembling that of cyclohexene (as for the middle ring in phenanthrene, prone to addition rather than substitution), or perhaps that of a 1,3-cyclohexadiene (e.g., by Diels–Alder cycloaddition with dienophiles such as maleic anhydride). On comparing the reactions of two newly synthesized tribenzoperylenes (Figure 1), Clar and Zander<sup>11</sup> found that the benzenoid with five sextet rings was unreactive toward maleic anhydride, whereas the isomer that can accommodate only four sextets underwent readily Diels–Alder cycloaddition with maleic anhydride. The difference between the two isomers is in the position of just one ring, indicated by heavy lines in Figure 1. Recently, Gutman and Stanković obtained theoretical confirmation that the former isomer had a higher thermodynamic stability than the latter isomer.<sup>12</sup>

The following rules apply for writing a Clar structure:

1. Each site in a  $\pi$ -network is assigned to either a Clar sextet circle or a double bond.
2. These sextets and double bonds are all disjoint.
3. This covering by rings and double bonds is sextet-maximal in that there is no hexagonal ring with three double bonds.
4. When a ring with a Clar sextet abuts another containing two double bonds, one draws an arrow from the Clar sextet circle to this adjacent ring center or straight through the center ring to a further center of another similar ring.

It is emphasized that rules 1 and 2 imply that adjacent rings do not simultaneously have Clar-sextet circles, following Clar.<sup>10</sup> Rule 3 means that a ring cannot have three double bonds but must have one or two double bonds or possibly be "empty".<sup>13,14</sup> Put another way, rule 3 says that if an (initial) assignment of three double bonds to a ring is made (and is not forbidden by rules 1 and 2), then it is rewritten to replace these three double bonds by a circle. The arrow of rule 4 can be viewed<sup>1</sup> to

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**Figure 1.** Tribenzo[*b,n,pqr*]perylene (upper structures) and tribenzo[*b,k,pqr*]perylene (lower structures) synthesized by Clar and Zander.

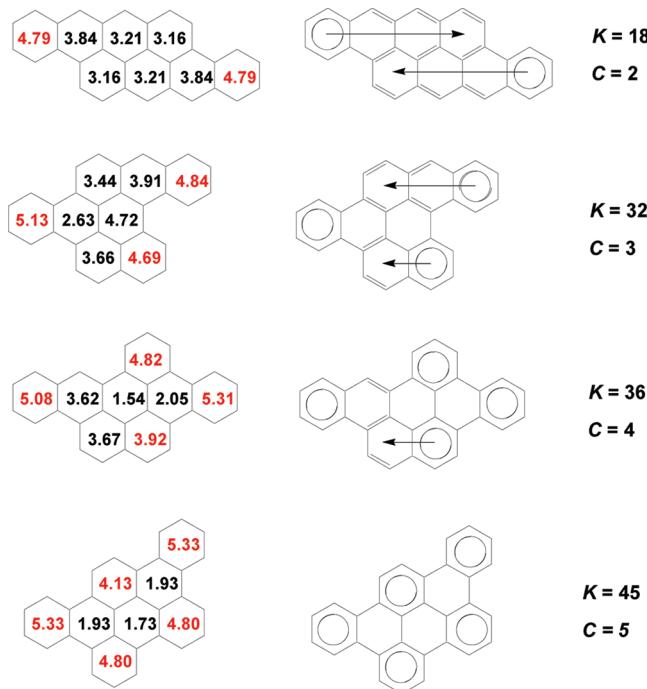
indicate “mobility” of Clar sextets, or in terms of a quantum mechanical resonance-theoretic perspective, an arrow indicates a particularly facile interaction between different Clar structures—it being understood that such interactions enhance stability.

The Clar structures with the maximum number, *C*, of Clar sextet circles are the most energetically favorable and are termed *sextet-maximum*. When there is a significantly greater abundance of the nonmaximum Clar structures, they can become even more important, as can especially happen for very large benzenoids or related nanostructures.

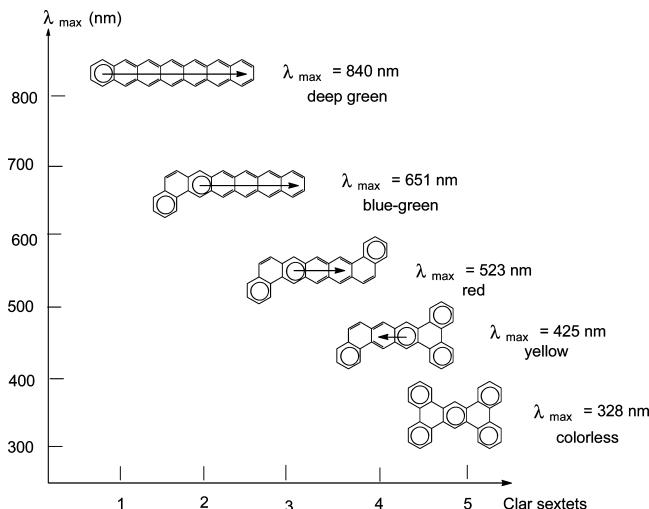
By assuming that all Kekulé structures contribute equally, one can compute a  $\pi$ -electron partition to rings in a polycyclic benzenoid by assigning one electron for a shared double bond, and two electrons for an unshared double bond.<sup>15–17</sup> It was found that there is close similarity between the  $\pi$ -electron content (partition) of rings in benzenoids and sextet-maximum Clar structures. In Figure 2 one can see a few examples of  $\pi$ -electron partitions for peri-condensed benzenoids with eight rings, and the fact that the highest values of the partitions correspond to Clar sextet rings.

A spectacular confirmation of Clar’s ideas is presented in Figure 3, illustrating that the fewer Clar sextets corresponding to longer acenic portions lead to low HOMO–LUMO band gaps and result in light absorption in the visible region so that one may “see” the lower count of Clar sextets by the deeper colors in a series of isomeric benzenoids (bathochromic effect).

Looking back at the last octaperifusene in Figure 2 (which is the also the first tribenzo[*b,n,pqr*]perylene from Figure 1 and the last one from Figure 3), one can see in Figure 4 three different ways of accounting for the 30  $\pi$ -electrons of this benzenoid with 45 resonance structures: one of these is Clar’s “winner-takes-all” mode with five sextets and three “empty rings”, the second is to partition the  $\pi$ -electrons so that a small quota does appear in the “empty rings” of the former Clar structure. There is a third way of keeping track of  $\pi$ -electrons



**Figure 2.** Partitions of  $\pi$ -electrons into rings of peri-condensed benzenoids with eight rings and the correspondence with Clar sextet rings; *K* denotes the numbers of Kekulé structures, and *C* denotes the numbers of Clar sextet rings; the last two benzenoids are those from Figure 1. Clar sextet rings have the highest partitions.



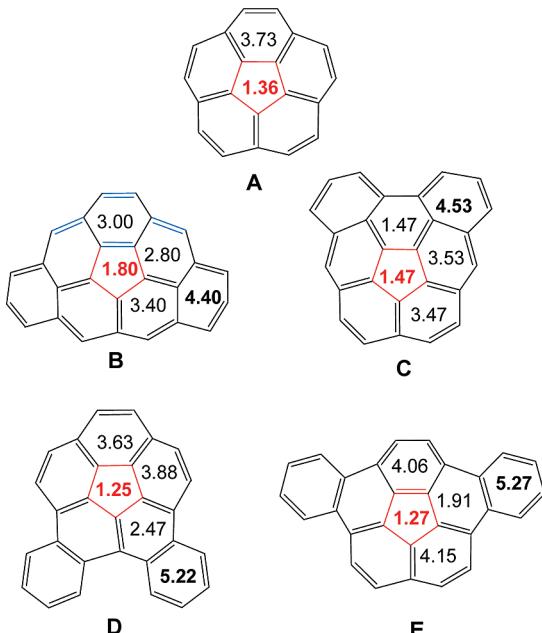
**Figure 3.** “Seeing the colors” of Clar sextets for isomeric heptacatafusenes: the lower *C*, the deeper the color.

in polycyclic benzenoids, namely by the “ $\pi$ -electron-signature”, when one counts in all resonance structures how many times each ring has 6, 5, 4, 3, 2, 1, and 0  $\pi$ -electrons:<sup>15</sup> in all  $8 \times 45 = 360$  rings, there are 40 rings with six  $\pi$ -electrons, ( $s_6 = 40 \times 6/45 = 5.33$ ), 138 rings with five  $\pi$ -electrons, ( $s_5 = 138 \times 5/45 = 15.33$ ), 52 rings with four  $\pi$ -electrons ( $s_4 = 52 \times 4/45 = 4.63$ ), etc. until the 12 rings with zero  $\pi$ -electrons.

Gutman and co-workers observed “the PCP-effect” in benzodervatives of acenaphthylene, fluoranthene, and corannulene,<sup>18,19</sup> manifested in increased values of the  $\pi$ -electron content (and also the “energy effect”) in the five-membered ring when benzo rings are connected by one bond to this ring (“PCP constellation”); by contrast, there is a slight decrease of the values when benzo rings are at topological distance two (“linear constellation”) from the five-membered ring. In Figure 5 these constel-

Clar structure	Partition	Signature
		$s_6 = 5.33$ $s_5 = 15.33$ $s_4 = 4.63$ $s_3 = 1.47$ $s_2 = 2.22$ $s_1 = 1.02$
<hr/>		
30 $\pi$ -electrons		

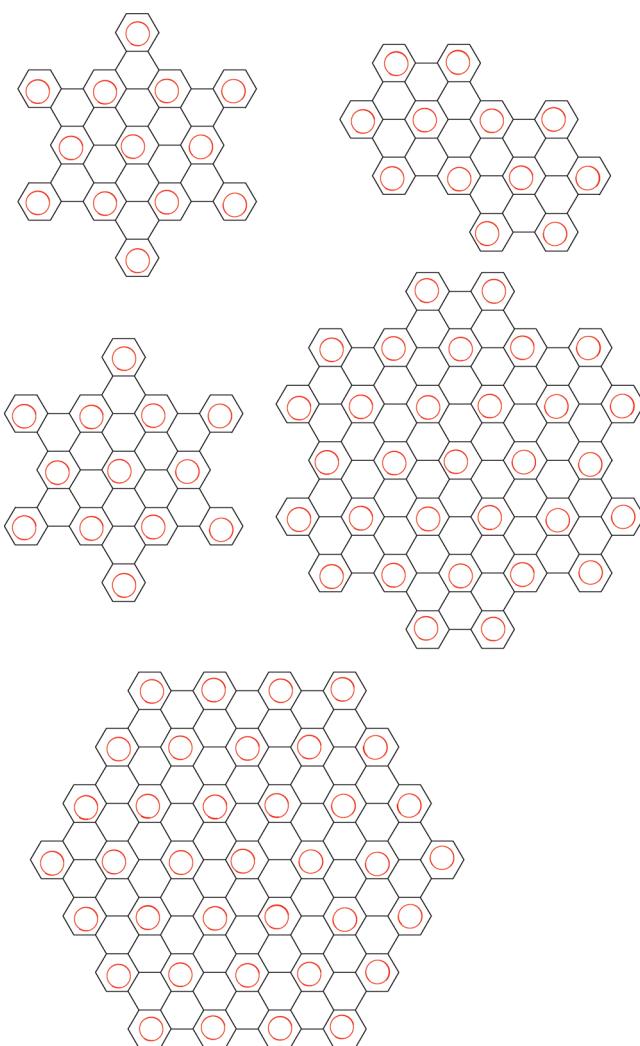
**Figure 4.** Three ways of accounting for the 30  $\pi$ -electrons in the claromatic benzenoid synthesized by Clar and Zander: (i) five sextets (“winner takes all”); (ii)  $\pi$ -electron partitions; and (iii) signatures (see text).



**Figure 5.** Illustration of the PCP (phenyl-cyclopentadienyl) effect with local  $\pi$ -electron content (partition) in rings of dibenzo-derivatives of corannulene (boldface numbers): the  $\pi$ -electron partition of the five-membered ring in corannulene (A) increases when the benzo rings are in linear constellation (B and C), and decreases slightly when they are in linear constellation (D and E); the blue double bonds in B are localized in all resonance structures.

lations are exemplified by dibenzo-corannulenes.<sup>19</sup> actually, in other words, the five-membered ring and the benzo ring in linear constellation are analogous to an acenic system, whereas a five-membered ring and a benzo ring in PCP constellation represents a biphenyl analogue. Then, similarly to what happens in polycyclic benzenoids, one may argue that rings in linear constellation compete for  $\pi$ -electron sextets just as this happens in anthracene which can have only one Clar sextet circle, whereas rings in PCP constellation enhance their aromaticity by conjugation as in phenanthrene, which has two Clar sextet circles.

Clar’s ideas may be developed in different ways to quantitatively describe different chemico-physical properties of benzenoids. A couple of decades ago Herndon and Hosoya<sup>20</sup> obtained a successful result for resonance energies. More recently a different quantification<sup>21</sup> gave nice results for bond lengths, resonance energies, and ring-NICS values. Both these quantifications use the Clar structures below the sextet-maximum ones.

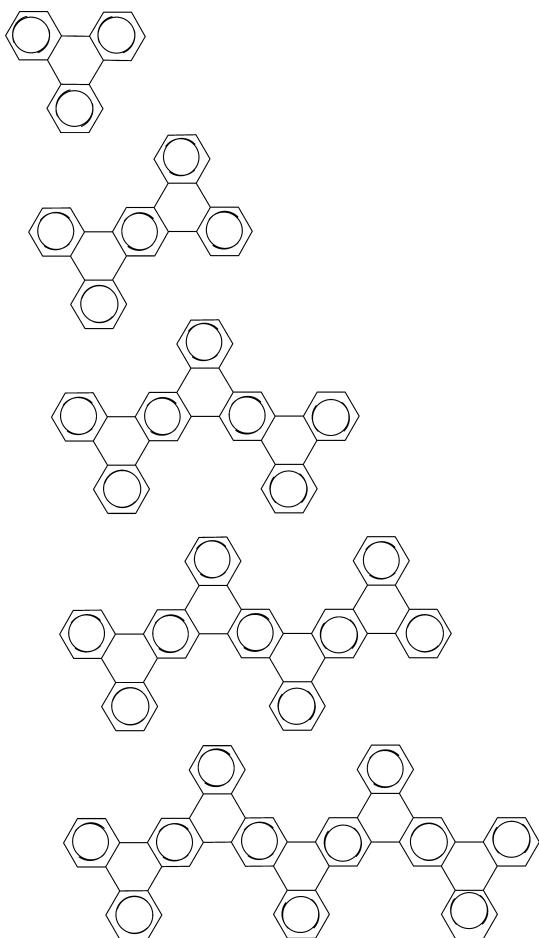


**Figure 6.** Some of the large claromatic benzenoids synthesized by Müllen and co-workers.

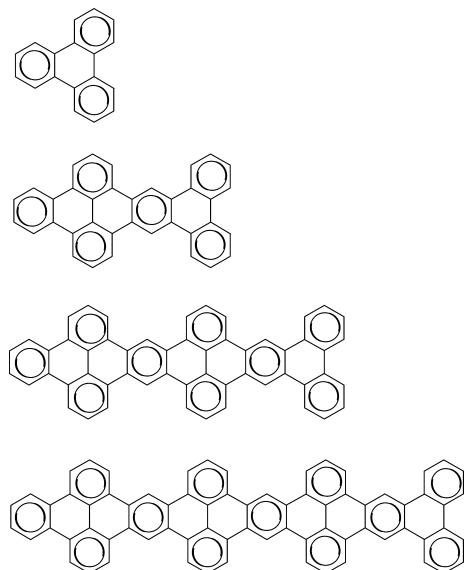
### 3. Two-Dimensional Claromatics

A special place must be reserved for those polycyclic benzenoids which admit a Clar structure without any double bonds. That is, such a Clar structure has sextet rings only, with all other rings “empty”. These special benzenoids have earlier been called “fully-benzenoid” or “all-benzenoid” or “total-benzenoid” polycyclic aromatic hydrocarbons. Because Clar’s ideas are more and more frequently being sought to be employed for selected nonbenzenoids, these names in which “benzenoid” is part of an *adjective* which may be used to describe a nonbenzenoid end up inviting semantic confusion. Therefore, we have simply previously called such compounds “sextet-resonant”, not all of the compounds here being “benzenoid” by common definitions. In the present paper we use the even shorter expression *claromatic* to denote sextet-resonant benzenoids, and in addition, species which are not benzenoids by a common definition, but still allow a Clar structure with no double bonds in the  $\pi$ -network. For finite claromatic benzenoids, there is just a single such Clar structure, and when the benzenoid is suitably small this structure dominates over all others to yield a chemically stable species with a large HOMO–LUMO gap.

Many such exceptionally stable hydrocarbons have been recently synthesized and studied by Klaus Müllen and his co-workers, as illustrated in Figure 6.<sup>22</sup> Their stability made possible their formation by Scholl-type dehydrogenations leading to the



**Figure 7.** Cata-condensed claromatic strips

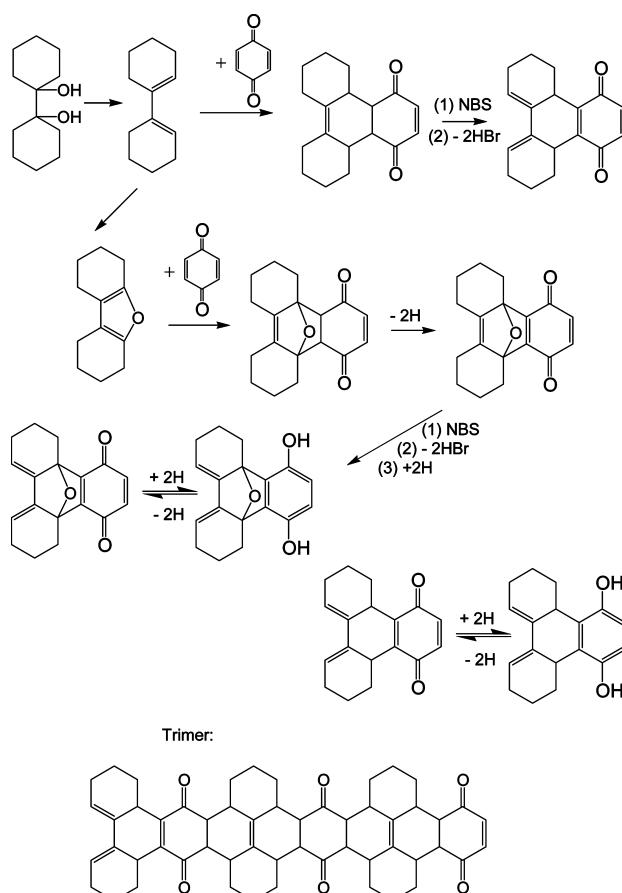


**Figure 8.** Peri-condensed claromatic strips.

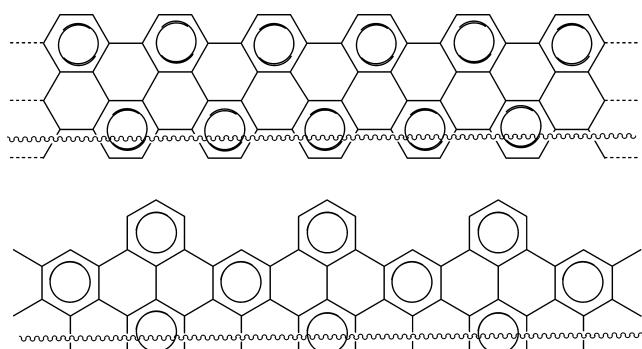
formation of dozens of new C–C bonds in a single step, exemplified by eliminating H<sub>2</sub> from *ortho*-terphenyl to form triphenylene.

In principle, long strips of claromatics can be cata-condensed (Figure 7) or peri-condensed (Figure 8). For peri-fused strips one can imagine a synthetic approach (Figure 9) modeled after the known method for obtaining triphenylene derivatives.<sup>23</sup>

Large portions of graphene (monatomic-thickness graphite flakes) have been first made by mechanical approaches out of

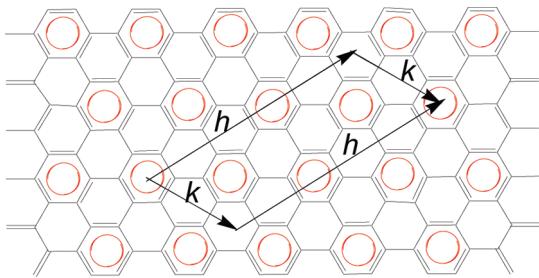


**Figure 9.** Proposed pathway for the synthesis of a benzenoid strip with Clar resonant sextets. The thermal stability should allow the final dehydrogenation to the ladder polymer. The redox process interconverting quinonoid and hydroquinol structures may allow starting the Diels–Alder polymerization electrochemically when passing through metallic spinnerets. The yield may be increased if a furanic ring would be involved.

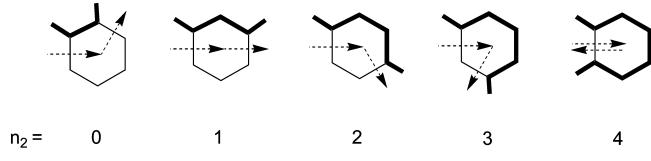


**Figure 10.** Edges of graphene flakes: parallel (above); and orthogonal to C–C bonds (below).

natural graphite by Geim and co-workers,<sup>24</sup> and these flakes have proved to have especially novel electronic conductivity, along with other fascinating properties, giving rise to an intense field of research. Thence, graphene research has become a quite intense field and other ways of making graphene have been devised.<sup>25</sup> By analyzing the influence of flake edges on the properties and stability of graphene, it appears likely that edges admitting claromaticity might be especially stable. In principle, one may have edges whose overall direction runs parallel (“armchair edges”) or orthogonal (“jagged zigzag”) to a subset of the C–C bonds in the graphene flake (Figure 10), each of



**Figure 11.** Vectors  $h$  and  $k$  in graphene. Normally, in claromatics one should have either Clar circles or double bonds but not both.



**Figure 12.** Five different types of edge boundaries at a given ring. The boundary is shown in bold, and the dashed line between ring centers for rings along the boundary gives the overall boundary direction.

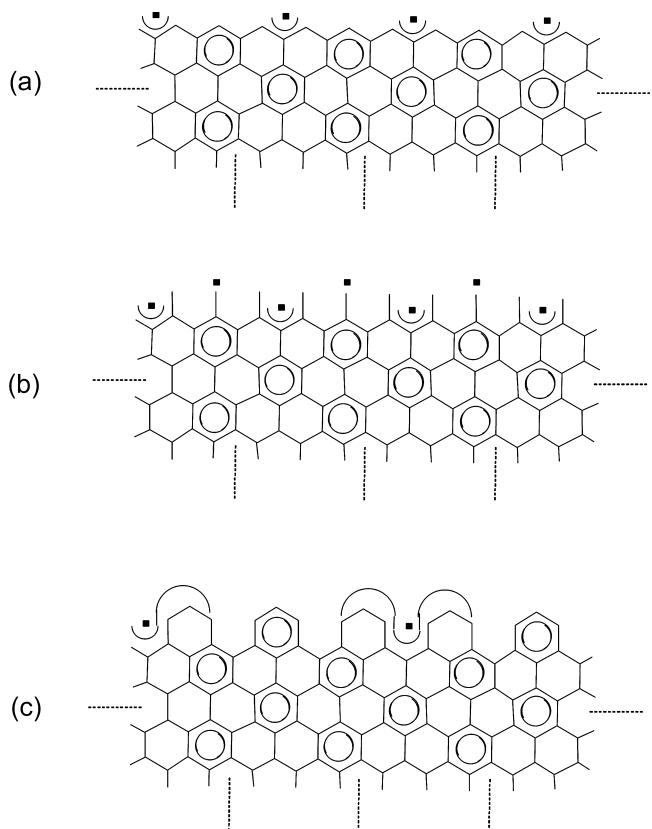
which are seen to allow claromaticity. Also the overall direction of the edge can be skew to each of these directions.

On looking at an armchair graphene sheet with Clar circles it is evident that the Clar circles follow the conjugated poly-*para*-phenylene chains. Indeed they follow every third poly-*para*-phenylene chain which one finds embedded in the graphene network, and there are three choices then for the selected poly-*para*-phenylene chain, so that infinite graphene manifests three equivalent sextet-maximum Clar structures.

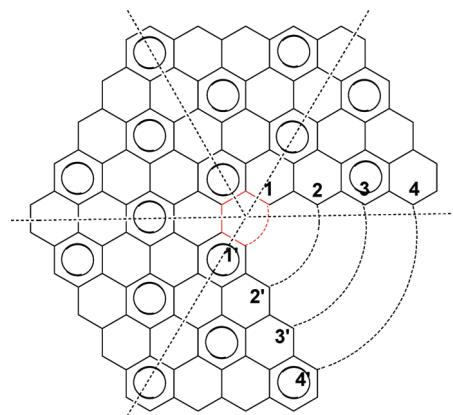
In graphene we define two vectors of length  $h$  and  $k$  (with  $h$  and  $k$  integers,  $h \geq k$ ) along acenic linear directions as in Figure 11. For a claromatic graphene flake, the necessary and sufficient condition for ending on a Clar sextet when starting from one in such a favored sextet-maximum Clar structure is

$$h - k \equiv 0 \pmod{3} \quad (1)$$

Here one Clar-sextet ring and its closest Clar-sextet rings are separated such that  $(h,k) = (1,1)$ , and they cover 1/3 of the rings (i.e., 2/3 are empty). Then for infinite graphene, there are three choices for the location of the Clar-sextets in such a sextet-maximum Clar structure, and since graphene manifests but one bond length in the bulk, the Clar-sextets are not localized. Evidently the sextet-maximum Clar structures admix to such an extent with the nonmaximum ones, so that one should describe bulk graphene in terms of the triple of sextet-maximum ones and implicitly at least, their underlying Clar structures with less than the maximum number of Clar sextets. [The sextet-nonmaximum structures must be admixed since between the sextet-maximum ones, there is essentially no direct interaction, as they are “infinitely” different (i.e., different in an infinite number of locations, when dealing with infinite graphene).] This situation with a multiplicity of sextet-maximum Clar structures contrasts sharply with the finite benzenoids studied by Clar, where the boundaries of the benzenoid often freeze in a particular set of Clar sextets, at least for the usual benzenoids which are claromatic. When there is a single sextet-maximum Clar structure in a finite benzenoid, this freezing in (sextet localization, and if not Claromatic typically also double bond localization) gives localized structures (e.g., with near-single bonds) and a large HOMO–LUMO gap. With graphene there are no localized double bonds, so that the reactivity is like that of a claromatic, but with the delocalization of Clar sextets, there is a great deal of freedom in the electronic structure, so that



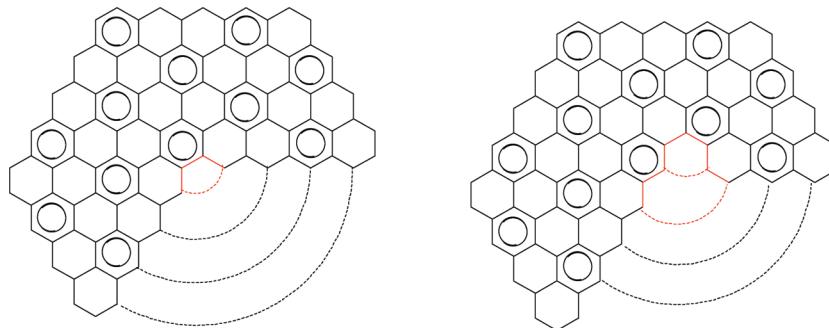
**Figure 13.** Three types of boundaries which give rise to unpaired electrons along the edges. The unpaired electrons occur when there is an odd-length chain of sites along the edge to be accommodated, and since (when this odd length is  $\geq 3$ ) there is more than one way to make pairings, the choice is left open with a curved line next to the sites involved, along with a single unpaired electron dot.



**Figure 14.** Formation of a single-wall blunt nanocone ( $q = 5$ ) with a pentagon at the apex.

slight modifications of this can lead to low-lying excitations. That is, for our nanostructures, the band gap can become quite small—even 0 for bulk graphene.

For real graphene, there are of course boundaries. At such a boundary there are different types of edge rings each characterized by the number  $n_2$  of degree-2 vertices (i.e., CH groups, or the number of appended H atoms the ring needs) encountered as one proceeds along the edge from the preceding ring to the succeeding ring. Then the possible values for  $n_2$  are 0, 1, 2, 3, and 4 (if we deal with benzenoids). An alternative designation for these types of edge rings is in terms of an identifier  $\delta$  taking corresponding values  $-1, 0, +1, +2$ , and  $+3$  such that  $\delta \cdot 60^\circ$



**Figure 15.** Two classes for nanocones with  $q = 4$ : class 1, congruent (left, with a square at the apex) and class 2, incongruent (right, with two condensed pentagons at the apex, see Figure 17). Both are formed by a folded 240°-sector of graphene.

gives the net linear curvature (or change in overall direction)  $\delta$  of the overall edge-direction on passing through the ring, see Figure 12. Thus if overall the edge-direction is straight, then the sum of successive  $\delta$  values should fluctuate around 0—in particular if the edge is translationally symmetric, then the sum of these  $\delta$  values over a unit cell of edge should equal 0. Now each one of these types of rings other than  $n_2 = 0$  has a degree-2 site exposed on the edge, and so to admit claromaticity, must contain a Clar sextet. Thus as we proceed along an edge, successive rings of these types with  $n_2 > 0$  must be displaced from one another in accord with (1), and bracketing each such edge ring (with a Clar sextet), there must be edge rings with  $n_2 = 0$  (since no two adjacent rings can simultaneously have Clar sextets). Thus, in proceeding along an edge, successive rings with Clar sextets must have an  $(h,k) = (1,1)$  separation if full claromaticity is to be achieved. And presuming that not all the rings along an edge have  $n_2 = 0$ , a sextet-maximum Clar structure (of any claromatic edge) is unique. Thus, the edges of Figure 10 are identified as claromatic, in concert with resonance-theoretic results described elsewhere,<sup>26,27</sup> as well as band-theoretic computations on these species.<sup>27–29</sup>

But more than this, if claromaticity is not achieved at an edge, one may consider what happens when the bulk of the sheet is assigned a sextet-maximum Clar structure. One then further considers what pairing patterns are implicated along the edge, even allowing for the possibility of unpaired electrons. Thus for the zigzag edge, one sees from Figure 13a that there remains at the edge one unpaired electron for every three rings along the edge. Also in Figure 13b there is another edge for which this construction leaves two unpaired electrons for every three rings along the edge, and in Figure 13c there is a case where there is left one electron for every nine rings along the edge. [In this figure, it is understood that the localization of the unpaired electrons need not be so severe as displayed, but may propagate into the interior some slight distance, still otherwise maintaining the same amount of pairing, so that the net amount of unpairing remains fixed]. Indeed there appears to be full agreement between our present Clar-theoretic ideas and both earlier resonance-theoretic results,<sup>26–28,30</sup> and band-theoretic computations.<sup>26,27,30</sup>

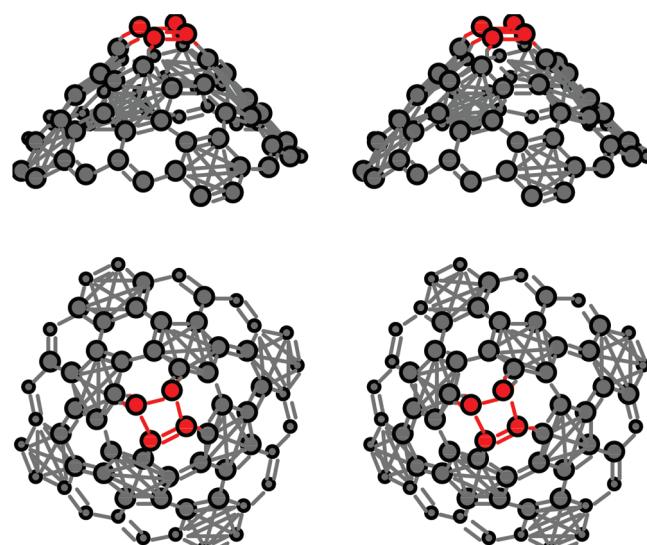
#### 4. Three-Dimensional Claromatics

The unexpected mass spectral detection of buckminsterfullerene<sup>31</sup> was honored with the 1996 Nobel Prize for Chemistry awarded to Curl,<sup>32</sup> Kroto,<sup>33</sup> and Smalley.<sup>34</sup> Soon after the detection work in 1985, it was shown that one may obtain bulk amounts of  $C_{60}$  and  $C_{70}$ .<sup>35</sup> Methods for producing nanotubes were discovered by Iijima.<sup>36</sup> Nanocones and nanohorns came next,<sup>37</sup> followed by nanotori.<sup>38</sup> Numerous related forms of

carbon, and analogous structures of some other elements, were discovered, and many reviews or books followed, a few of which are cited here.<sup>39,40</sup>

**4.1. Clar Structures and Nanocones.** On cutting out six sectors of 60° each out of a honeycomb lattice (graphene sheet) and folding the remaining dangling edges to obtain nanocones, several possibilities must be taken into account, according to the number,  $q$ , of folded sectors (Table 1). In this table, the planar angle subtended by all  $q$  sectors is indicated in the second column, and the apical angle of the cone is presented in the third column.

For an extended cone, these apical angles should be very close to exactly correct, as the result is simply predicated upon the assumption that the local network geometry of the cone approaches closely to that of graphene when very far from the apex of the cone. However, to realize the different types of cones, one needs to place in the apex region some sort of defect in an otherwise graphenic network. This is conveniently given in terms of the net Gaussian curvature of the cone, when one assigns<sup>41</sup> a formal *combinatorial curvature* to each ring  $\alpha$ , which for the present case with an ambient condition of degree-3 vertices and six-membered faces gives combinatorial curvatures of  $\pi(6 - |\alpha|)/3$  for each ring  $\alpha$  of  $|\alpha|$  sites, or  $2\pi(3 - |i|)/6$  for each site of degree  $|i|$ , where  $|\alpha|$  and  $|i|$  denote the respective numbers of edges around  $\alpha$  and  $i$ . This combinatorial curvature comes in multiples of  $\pi/3$ , and is exactly equal to this for either a pentagon or a degree-2 vertex, e.g., 12 pentagons yields  $4\pi$ .



**Figure 16.** Stereoview of the congruent class 1 nanocone ( $q = 4$ ) with a square at the apex formed by a folded 240°-sector of graphene. Clar sextet rings are denoted by diagonal lines.

**TABLE 1: Eight Cases of Single-Wall Nanocones (SWNC)**

60° sectors folded $q$	angle degrees	apex degrees	class	single wall nanostructure
0	0	0		nanotube (SWNT)
1	60	19.2	congruent	first (sharp) nanocone (SWNC)
2	120	38.9	congruent (1)	second nanocone (SWNC)
			incongruent (2)	second nanocone (SWNC)
3	180	60	congruent (1)	third nanocone (SWNC)
			incongruent (2)	third nanocone (SWNC)
4	240	83.6	congruent (1)	fourth nanocone (SWNC)
			incongruent (2)	fourth nanocone (SWNC)
5	300	112.9	congruent	fifth (blunt) nanocone (SWNC)
6	360	180		graphene

of curvature which matches to that for a polyhedron (a fullerene), and 6 pentagons give a fullereneic cap to a nanotube. Leaving out this common factor of  $\pi/3$ , we obtain a succession of equivalences of combinatorial curvatures for different “defects”:

### 1 pentagon (see Figure 14)

4-gon (or square)  $\approx$  2 pentagons  $\approx$  degree-2-vertex.  
 3-gon (or triangle)  $\approx$  3 pentagons  $\approx$  1 square + 1 pentagon  $\approx$  deg.-2-vertex + 1 pentagon  
 2-gon (or lune)  $\approx$  4 pentagons  $\approx$  2 squares  $\approx$  1 square + 2 pentagons, etc.

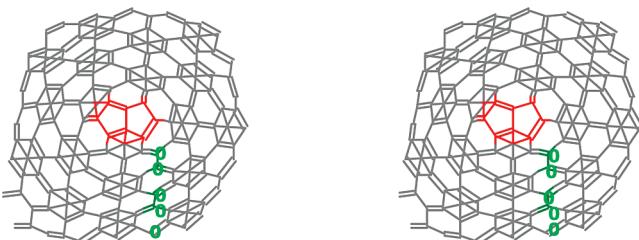
5 pentagons  $\approx$  2 squares + 1 pentagon  $\approx$  4-gon + 3-gon, etc. respectively, for  $q = 5, 4, 3, 2$ , or 1 sectors. Here constructions solely with curvature from pentagons are the bucky-structures, with only up to five allowed for cones. If the total curvature is to match that of a closed compact surface,  $S$ , with Euler–Poincaré characteristic,  $\chi_S$ , then this leads to

$$\sum_d v_d(6 - d) + 2 \sum_k f_k(3 - k) = 6\chi_S \quad (2)$$

where  $f_k$  is the number of  $k$ -membered faces and  $v_d$  is the number of vertices of degree  $d$ . Indeed, for such a case for closed compact surfaces, this is a rigorous theorem following from the Euler formula (as extended to general genus  $g = 1 - \chi_S/2$ , from the case of a polyhedron with  $\chi_S = 2$ ).

On going from two to three dimensions by folding graphene sheets, the Clar sextet rings where sheets are joined may or may not coincide in the overlap. One is reminded of de Broglie’s interpretation of Bohr’s hydrogen-atom quantization condition that an electron wave fit a whole number of wavelengths along the circumference of the electron’s orbit. Congruent overlap according to eq 1 reinforces the Clar sextets, leading to enhanced stability of the 3D architecture.

There are eight classes of positive-curvature nanocones.<sup>42,43</sup> These appear in Table 1 for  $q = 1, 2, 3, 4$ , or 5 sectors, and also indicated there are the  $q = 0$  case of the different nanotubes, and the  $q = 6$  case of the different graphenic structures, with different “dislocations”. If after folding, the Clar sextets appear

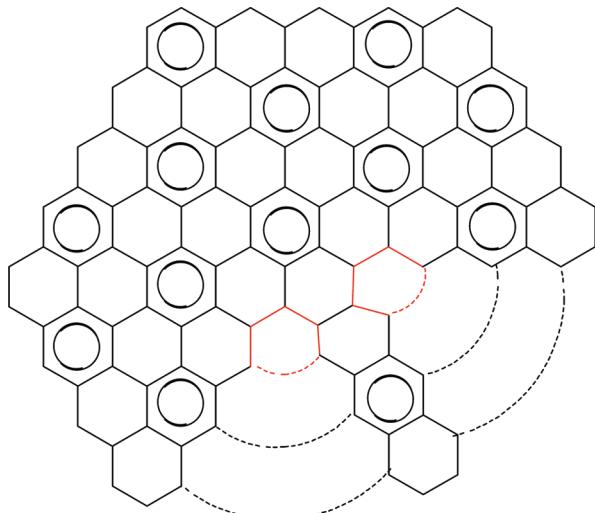


**Figure 17.** Stereoview of the incongruent class 2 nanocone ( $q = 4$ ) with two condensed pentagons at the apex. The green-colored carbon atoms break the Clar structure of the folded 240°-sector of graphene. Clar sextet rings are denoted by diagonal lines.

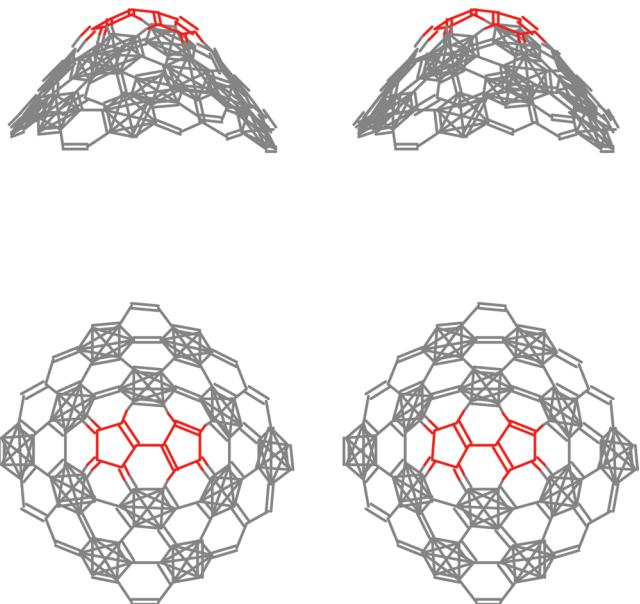
congruent fulfilling eq 1, then the nanocones belong to class 1, which has been often characterized as “standard” (and also as “quasi-spin 0”<sup>42</sup>). If the Clar sextets are incongruent, they belong to class 2 (also described as “quasi-spin 1”<sup>42</sup>). In Figure 15 one can see for the case when  $q = 4$  (240° sector) the two classes, one with congruent Clar sextets having a square at the apex, and the other with incongruent Clar sextets having two condensed pentagons at the apex. Both these nanocones are shown as stereoviews in Figures 16 and 17, respectively. It turns out that when the two pentagons are connected by one C–C bond, the folding becomes congruent, as seen in Figure 18, and then in stereoview in Figure 19. Generally speaking then one anticipates that the claromatic “standard” nanocones should be more chemically stable, i.e., less chemically reactive.

**4.2. Clar Structures and Nanotubes.** The case when the folding of the graphene sheet proceeds without any full sector ( $q = 0$ ) leads to a nanotube, which can be considered as a nanocone with apical angle 0°. Multiwalled collections of such nanotubes were first obtained by Iijima,<sup>36</sup> with their ends capped by hemispherical half-fullerenes. Because the five-membered rings are more reactive, the caps may be removed chemically, and also one may obtain single-wall nanotubes (SWNTs) of various lengths. Their study revealed interesting features which has led to an intense research activity and various applications.

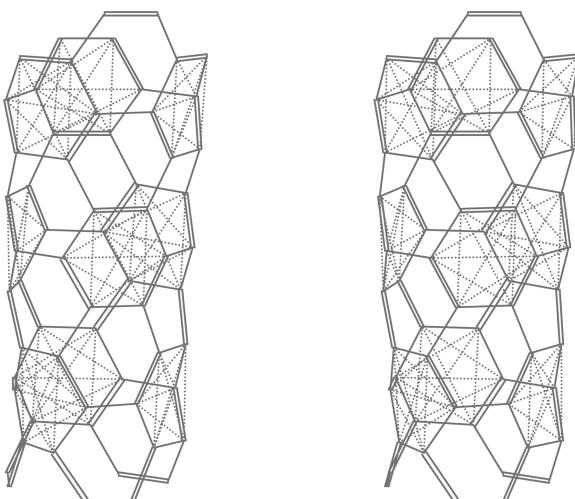
For a nanotube one may select<sup>44</sup> the earlier mentioned vector displacements  $h$  and  $k$  to be such that they lead back to the initial ring, and so characterize the tube. When  $k = 0$ , one obtains a so-called “zigzag” SWNT, and when  $h = k$ , one obtains an “armchair” SWNT. When  $0 \neq k \neq h$ , one obtains



**Figure 18.** Class 1 congruent nanocone with  $q = 4$ , with two pentagons connected by a C–C bond at the apex formed by a folded 240°-sector of graphene.



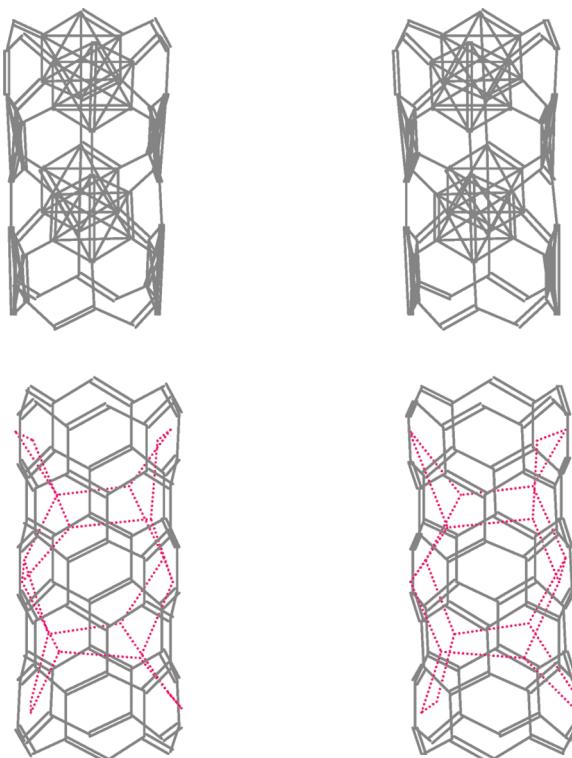
**Figure 19.** Stereoview of the class 1 congruent nanocone with  $q = 4$ , with two pentagons connected by a C–C bond at the apex formed by a folded 240°-sector of graphene.



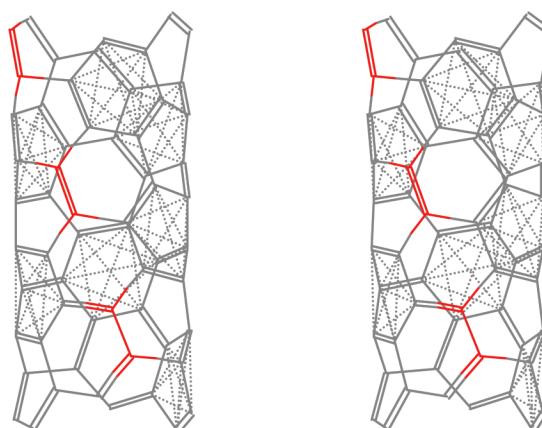
**Figure 20.** Stereoview of an armchair SWNT with congruent Clar sextets denoted by dotted lines.

an (intrinsically) chiral nanotube, often described as “helical”. Most interestingly, the electrical conductivity and the HOMO–LUMO gap depend on whether the folding makes Clar-sextets (in a sextet-maximum Clar structure) congruent or incongruent. When  $h - k = 0 \pmod{3}$  the overlap is congruent, whence the material is like graphene, and like graphene has<sup>44</sup> a bandgap = 0 (neglecting curvature variations of the Hückel parameters), so that such claromatic nanotubes should be readily *conductive*. Otherwise (with incongruent overlap) there is<sup>44</sup> a nonzero band gap, and the nanotube is *semiconductive*. As a result, all armchair SWNTs and  $\sim 1/3$  of zigzag and chiral SWNTs are readily conductive, whereas  $\sim 2/3$  of zigzag SWNTs are semiconductive. Moreover, following Clar’s ideas, the nonclaromatic nanotubes should manifest greater chemical reactivity.

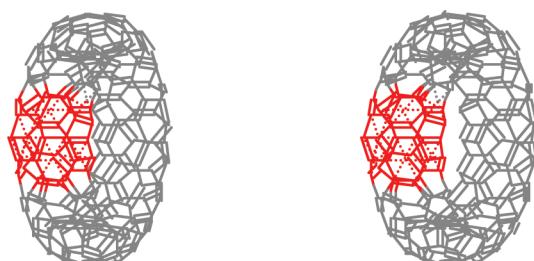
Three stereoviews illustrate the above statements: a congruent armchair SWNT is presented in Figure 20, a congruent zigzag SWNT in Figure 21, and an incongruent chiral SWNT in Figure 22. In these cases, congruent means “claromatic” with only full



**Figure 21.** Stereoview of a zigzag SWNT with congruent Clar sextets denoted by dotted lines (upper views, black) and with the anti-sextet sextet dualist (red dotted lines, lower views).



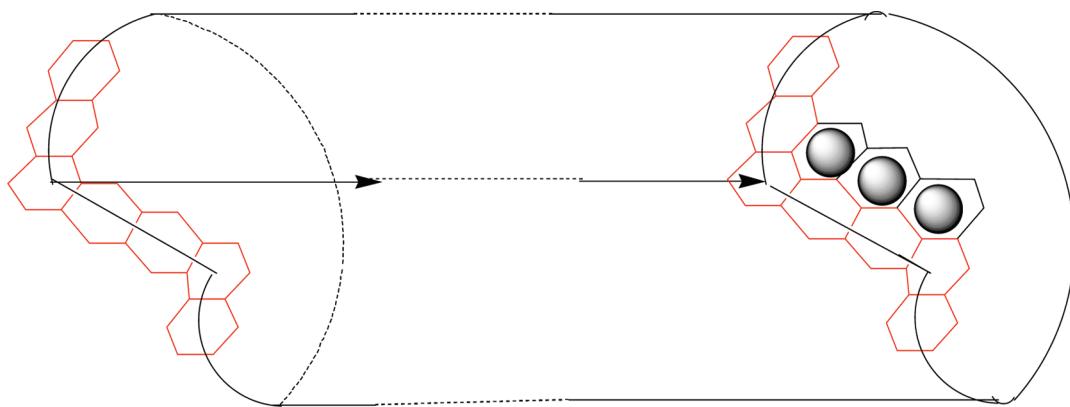
**Figure 22.** Stereoview of a chiral SWNT with incongruent Clar sextets denoted by dotted lines; the red-colored carbon atoms break the Clar structure of graphene.



**Figure 23.** Stereoview of a sextet-resonant nanotorus whose colored portion has Clar sextet rings denoted by dotted lines.

and empty sextets, whereas incongruent means that the 3D architecture must contain double bonds associated with higher reactivity.

**4.3. Clar Structures and Nanotori.** Nanotori, just like graphene, have no boundary and no defects, i.e., no rings of



**Figure 24.** Long section of an  $(h,k)$ -nanotube with  $k = 3$ , showing left and right ends related by translation, and an extra 3-aceneic strip with gray discs inside being added to yield left and right ends of the same  $(h,k)$ -form but not related by a pure translation along the tube length.

any sizes other than six, so that such nanotori can be viewed as elemental benzenoids (in having no H atoms).<sup>45,46</sup> Indeed they can be viewed as graphene with cyclic boundary conditions (in two dimensions). It has been found<sup>38</sup> that SWNTs with a diameter  $\approx 1.4$  nm can be induced to coil and form tori (nanotube rings or “crop circles”) with much larger overall diameters of 600–800 nm on treatment with acids plus hydrogen peroxide under sonication. Again, one expects enhanced stabilization when “sextet-resonant rings” denoted by circles in the Clar structure overlap on connecting the ends of the nanotube to form a torus (that is, when a claromatic nanotube forms a claromatic nanotorus). In Figure 23 such a nanotorus is presented in stereoview with a colored portion indicating Clar sextets. There are different ways<sup>45,46</sup> to describe nanotori, but especially for the experimentally realized ones (with a very large ratio of the overall torus radius to the tube radius), it seems desirable as a first step to characterize it in terms of the underlying nanotube. Thus, to start, we characterize nanotori in terms of the  $(h,k)$  pair for the nanotube out of which it is constructed ( $h$  and  $k$  again indicating lengths of acenic portions of a circumscribing annular path around the generator nanotube). Next there is a *length* of the nanotube, and this might be attempted to be specified by the number,  $L$ , of these complete  $(h,k)$  sections in the nanotube used to construct the nanotorus. And finally there is a *twist*,  $t$ , indicating the extent to which the first and last annular paths are twisted with respect to one another.

The wrapping of a finite nanotorus to fuse ends together is perhaps simplest when the nanotube has  $(h,k) = (h,0)$ , for then the two ends of the nanotube can each be viewed as zigzag ends, and it is seen that there are  $h$  different ways to fuse them together, depending on how much each end is twisted. Actually there are more than  $h$  different twistings, though only those twistings within less than a range of  $360^\circ$  give rise to distinct graphs. [Though two twists different by  $360^\circ$  give graphs which are the same, they are<sup>45</sup> embedded into Euclidean 3-space in topologically distinct ways, but this problem we do not address here. There is<sup>45</sup> also another embedding possibility interchanging the order of introduction of the two cyclizing boundary conditions on a graphenic fragment from which the torus is to be made—but this is more-or-less avoided in our present considerations when we presume that the boundary conditions first introduced are those which make the smaller diameter nanotube.] Thus, even when the nanotube is provisionally claromatic with  $h = 0, \text{mod } 3$ , the adjoining of the two ends succeeds in preserving claromaticity only in 1/3 of the cases—only for 1/3 of the twists do Clar-sextet rings lie over one another. Again, as for graphene, and these claromatic species manifest three sextet-maximum Clar structures, and should (disregarding

effects of curvature) have a HOMO–LUMO gap = 0, whereas if the twist condition is not met (or if  $h \neq 0, \text{mod } 3$ ) then the gap should be  $>0$ . This is in fact the case.

The fusing of the ends of a finite nanotube in the case when  $k > 0$  is a little different. Then the two ends of the nanotube are still conveniently chosen to have two acenic sections of lengths  $h$  and  $k$ , but these two end sections (to be fused) need not be related by a translation down the length of the tube. That is, given two translationally equivalent ends of a nanotube, one can add short  $k$ -length acenes to one end such that the end remains of type  $(h,k)$ , as in Figure 24, and after adding  $h$  such strips, one will have again an end that is translationally equivalent to the other end and have increased  $L$  by  $k$ . We take the number of these  $k$ -length acenic strips added to be a twist  $t < h$  (and  $t \geq 0$ ), whence the number of rings is  $(h+k)L + kt$ . Of course, now once the two ends are chosen (regardless of whether the two  $(h,k)$  ends are translationally equivalent) there is no possibility for connection other than by a multiple of a full rotation of  $360^\circ$ , which again leads to the same graph. Again even when  $h - k = 0, \text{mod } 3$  the nanotorus may end up not having Clar-sextets at the two ends of the nanocylinder whose ends are to be matched coincidentally together to form a nanotorus, and thereby miss claromaticity. Again claromaticity is (disregarding curvature effects) necessary and sufficient for a zero HOMO–LUMO gap.

Overall for nanotori we see that 1/3 of them have  $(h,k)$  values consonant with claromaticity, though of these only 1/3 of them achieve claromaticity when the two ends are joined together. One might expect similar difficulties with retention of claromaticity when one puts bucky-caps on the ends of a nanotube (whence there could occur the possibility of unpaired electrons in the bucky-caps, somewhat as we have already noted for edges of graphene). For the nanotori the claromaticity problem can be viewed to arise since the condition (1) on a cyclic path becomes for tori twice as complicated, as there are  $(h,k)$ -cycles both around the tube-like direction, as well as circumscribing all the way around the whole torus. If around this long way the requisite cycle is described as having values  $(H,K)$ , while around the short way, we use the notation  $(h,k)$ , then if  $h - k = 0, \text{mod } 3$  and  $H - K \neq 0, \text{mod } 3$ , one can anticipate an exceptionally small HOMO–LUMO splitting as the ratio  $H + K$  becomes very large. Indeed, this is somewhat as for the nanotube case where one anticipates the band gap to approach 0 as  $h + k$  approaches the graphenic limit (of  $\infty$ ). Indeed the bucky-tori may be seen as just being graphenic fragments with cyclic boundary conditions, and the conditions on  $h,k$  and  $H,K$  for claromaticity to just be conditions that one selects from the

Brillouin zone the (isolated) points where the grapheneic band gap falls to 0.

## 5. Conclusion

It is seen that Clar's ideas, originally empirically developed exclusively in the context of finite benzenoids, also apply to provide interesting insight for several of the more modern closely related nanostructures: graphene, edges in graphene, nanocones, nanotubes, and nanotori. The idea and nomenclature of claromaticity is advocated. This overall Clar-theoretic picture supports the interpretation of these nanostructures in terms of the  $h,k$  vector-displacement cycles/relations, and the fundamental distinctions associated with the difference  $h - k \pmod{3}$ . In addition to Clar's ideas having their traditional empirical justification for finite benzenoids, we also have noted for our nanostructures a degree of consonance with ordinary tight-binding band-theoretic results, as well as Pauling-like resonance-theoretic ideas. In some cases, particularly those of nanocones, the predictions have not yet been well checked from a band-theoretic perspective.

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## References and Notes

- (1) Klein, D. J. *J. Chem. Educ.* **1992**, *69*, 691–694. Klein, D. J.; Babic, D. *J. Chem. Inf. Comput. Sci.* **1997**, *37*, 656–671.

(2) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley: New York, 1994.

(3) Pozharskii, A. F.; Soldatenkov, A. T.; Katritzky, A. R., *Heterocycles in Life and Society: An Introduction to Heterocyclic Chemistry and Biochemistry and the Role of Heterocycles in Science, Technology, Medicine and Agriculture*; Wiley: New York, 1997.

(4) Krygowski, T. M.; Cyrański, M. K.; Czarnocki, Z.; Häfleinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783–1796.

(5) Balaban, A. T.; Oniciu, D. C.; Katritzky, A. R. *Chem. Rev.* **2004**, *104*, 2777–2812.

(6) Balaban, A. T.; Schleyer, P. v. R.; Rzepa, H. R. *Chem. Rev.* **2005**, *105*, 3436–3447.

(7) Armit, J. W.; Robinson, R. *J. Chem. Soc.* **1925**, 1604–1630.

(8) Hückel, E. *Ztschr. Elektrochem.* **1937**, *43*, 752–788, 827–849.

(9) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London; Springer Verlag: Berlin, 1964.

(10) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.

(11) Clar, E.; Zander, M. *J. Chem. Soc.* **1958**, *186*, 1–1865.

(12) Gutman, I.; Stanković, S. *Monatsh. Chem.* **2008**, *139*, 1179–1184.

(13) Balaban, A. T. *Polycycl. Arom. Comp.* **2004**, *24*, 83–89.

(14) Gutman, I.; Turković, N.; Jovović, J. *Monatsh. Chem.* **2004**, *135*, 1389–1394.

(15) Randić, M. *Chem. Rev.* **2003**, *103*, 3449–3636. Randić, M. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 365–372. Randić, M.; Balaban, A. T. *Polycyclic Arom. Comp.* **2004**, *24*, 173–193. Balaban, A. T.; Randić, M. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 50–59. Balaban, A. T.; Randić, M. *New J. Chem.* **2004**, *28*, 800–806. Vukicević, D.; Randić, M.; Balaban, A. T. *J. Math. Chem.* **2004**, *36*, 271–279. Balaban, A. T.; Randić, M. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 1701–1707. Balaban, A. T.; Randić, M. *J. Math. Chem.* **2005**, *37*, 443–453. Gutman, I.; Randić, M.; Balaban, A. T.; Furtula, B.; Vuković, B. *Polycycl. Arom. Comp.* **2005**, *25*, 215–226. Balaban, A. T.; Randić, M.; Vukicević, D. *J. Math. Chem.* **2008**, *43*, 773–779. Balaban, A. T.; Furtula, B.; Gutman, I.; Kovacević, R. *Polycycl. Arom. Comp.* **2007**, *27*, 51–63. Balaban, A. T.; Gutman, I.; Stanković, S. *Polycycl. Arom. Comp.* **2008**, *28*, 85–97. Balaban, A. T.; Randić, M. *J. Universal Comput. Sci.* **2007**, *13*, 1514–1539. Balaban, A. T.; Randić, M.; New, J. *J. Chem.* **2008**, *32*, 1071–1078. Balaban, A. T.; Pompe, M.; Randić, M.; Balaban, A. T. *J. Phys. Chem. A* **2008**, *112*, 11769–11776.

(16) Randić, M.; Balaban, A. T. *Int. J. Quantum Chem.* **2008**, *108*, 865–897. Balaban, A. T.; Randić, M. *Int. J. Quantum Chem.* **2008**, *108*, 898–926.

S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2007**, *448*, 457–460.

(26) Klein, D. J.; Bytautas, L. *J. Phys. Chem. A* **1999**, *103*, 5196–5210.

(27) Ivanciu, O.; Klein, D. J.; Bytautas, L. *J. Chem. Phys.* **2002**, *116*, 4735–4748. Ivanciu, O.; Klein, D. J.; Bytautas, L. *Carbon* **2002**, *40*, 2063–2083.

(28) Nakada, K.; Fujita, M.; Wakabayashi, K.; Kusakabe, K. *Czech. J. Phys.* **1996**, *46*–*55*, 2429–2430. Fujita, M.; Wakabayashi, K.; Nakada, K. *J. Phys. Soc. Jpn.* **1996**, *65*, 1920–1924.

(29) Klein, D. J. *Rep. Molec. Theory* **1990**, *1*, 91–95.

(30) Klein, D. J. *Chem. Phys. Lett.* **1994**, *217*, 261–265.

(31) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163.

(32) Curl, R. F., Jr. *Angew. Chem., Int. Ed.* **1997**, *36*, 1566–1576.

(33) Kroto, H. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1578–1593.

(34) Smalley, R. E. *Angew. Chem., Int. Ed.* **1997**, *36*, 1594–1601.

(35) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354–358.

(36) Iijima, S. *Nature* **1991**, *354*, 56–58. Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603–605.

(37) Ge, M.; Sattler, K. *Chem. Phys. Lett.* **1994**, *220*, 192–196. Klein, D. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2099–2110. Klein, D. J. *Int. J. Quantum Chem.* **2003**, *95*, 600–616. Balaban, A. T.; Klein, D. J.; Liu, X. *Carbon* **1994**, *32*, 357–359. Klein, D. J.; Balaban, A. T. *J. Chem. Inf. Model.* **2006**, *46*, 307–320. Balaban, A. T. *Nanostructures: Novel Architecture*; Diudea, M. V., Ed.; Nova Publishers: New York, 2005; pp 113–142.

(38) J. Liu, J.; Dai, H.; Hafner, J. H.; Colbert, D. T.; Smalley, R. E.; Tans, S. J.; Dekker, C. *Nature* **1997**, *385*, 780–781. Han, J. *Chem. Phys. Lett.* **1998**, *282*, 187–191. Shea, H. R.; Martel, R.; Avouris, Ph *Phys. Rev. Lett.* **2000**, *84*, 4441–4444. Martel, R.; Shea, H. R.; Avouris, Ph *Nature* **1999**, *398*, 299.

(39) Kirby, E. C. *From Chemical Topology to Three-Dimensional Geometry*; Balaban, A. T., Ed.; Plenum Press: New York, 1997; pp 263–296. Klein, D. J. *Mathematical Chemistry*, Vol. 4: *Chemical Topology*; Bonchev, D.; Rouvray, D. H., Eds.; Gordon and Breach Publishers: New York, 1999; pp 39–83. Kirby, E. C.; Mallion, R. B.; Pollack, P. J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1945–1953. M. Diudea, M. *Fullerenes, Nanotubes, Carbon Nanoclusters* **2002**, *10*, 273–292.

(40) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. *The Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996. Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; World Scientific: Singapore, 1998. Dresselhaus, M. S.; Dressel-

haus, G.; Avouris, P., Eds. *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Vol. 80, In *Topics in Applied Physics*; Springer-Verlag: Berlin, 2000. Ebbesen, T. W., Ed. *Carbon Nanotubes, Preparation and Properties*; CRC Press: Boca Raton, 1997. Harris, P. J. F. *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century*; Cambridge University Press: Cambridge, 1999. Tanaka, K.; Yamabe, T.; Fukui, K. *The Science and Technology of Carbon Nanotubes*; Elsevier: Amsterdam, 1999. Reich, S.; Thomsen, C.; Maultzsch, J. *Carbon Nanotubes. Basic Concepts and Physical Properties*; Wiley-VCH: Weinheim, 2004. Yasuda, E.; Inagaki, M.; Kaneko, K.; Endo, M.; Oya, A.; Tanabe, Y., Eds. *Carbon Alloys. Novel Concepts to Develop Carbon Science and Technology*; Elsevier: Amsterdam, 2003. Biró, L. P.; Bernardo, C. A.; Tibbets, G. G.; Lambin, P., Eds. *Carbon Filaments and Nanotubes: Common Origin Different Applications*, Vol. 372 of *NATO Science Series E: Applied Sciences*; Kluwer Academic Publishers: Dordrecht, 2001.

(41) Klein, D. J.; Liu, X. *Internat. J. Quantum Chem.* **1994**, 28 S, 501–523. Klein, D. J.; Zhu, H. In *From Chemical Topology to Three-Dimensional Geometry*; Balaban, A. T., Ed.; Plenum Press: New York, 1997; pp 297–341.

(42) Klein, D. J. *Phys. Chem. Chem. Phys.* **2002**, 4, 2099–2110.

(43) Klein, D. J.; Balaban, A. T. *J. Chem. Inf. Model.* **2006**, 46, 307–320.

(44) Klein, D. J.; Seitz, W. A.; Schmalz, T. G. *J. Phys. Chem.* **1993**, 97, 1231–1236.

(45) Klein, D. J. *J. Chem. Inf. Comput. Sci.* **1994**, 34, 453–459.

(46) Kirby, E. C. *Croatica Chem. Acta* **1993**, 66, 13–26.

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