Clarology for Conjugated Carbon Nano-Structures: Molecules, Polymers, Graphene, Defected Graphene, Fractal Benzenoids, Fullerenes, Nano-Tubes, Nano-Cones, Nano-Tori, *etc.*

Douglas J. Klein* and Alexandru T. Balaban

Texas A&M University at Galveston, Department of Marine Sciences, 200 Seawolf Parkway, Galveston, TX 77551, USA

Abstract: The 1-, 2-, and 3-dimensional structures obtained from conjugated rings of carbon atoms are reviewed. They include finite small and large molecules (benzenoids, collarenes, beltenes, cyclacenes, cyclophenacenes, Möbius analogs, nanotori) and infinite macromolecules, nets and tilings (graphene, defected graphene, fractal benzenoids, nano-tubes, nano-cones, etc.). A few challenges for future experimental work are also outlined.

I. INTRODUCTION

Benzenoids have a long history as prototypical "aromatic" species, involving delocalized bonding. Indeed there have been different theoretical perspectives to describe aromaticity, including the classically based ideas of E. Clar [1], on which we focus here. But with the great variety of new conjugated-carbon nano-systems in the last few decades some extensions of Clar's ideas are needed, with a natural starting point being the interpretation of Clar's ideas in a quantum theoretic perspective, perhaps most directly by way of Pauling-Wheland resonance theory [2, 3]. Thence such an extension is sought here, mostly in a qualitative format.

I.1. Theoretical Perspective

Pauling and Wheland's theory of benzenoid molecules goes back a few decades before Clar's seminal publication, and has been much more thoroughly investigated in a quantitative mode, though still relatively meager compared to molecular-orbital (MO) theory. Indeed even for resonating valence-bond theory, which is closely related to Clar's ideas, it has only been in the last few decades that quantitative treatments have been made for the case of extended systems. First, about 3 decades ago, there were some resonating VB computations on polyacetylene [4]. Then soon after, there followed a resonating VB treatment [5, 6] of the electronic structure of a general "armchair" class of benzenoid polymers – for which a suggestive 3-periodicity of behavior as a function of the polymer strip width was found. Indeed this periodic behavior was indicated and verified to be reflected [7, 8] in the Hückel model description of this same (infinite) class of polymers. And later in carbon nano-tubes much the same 3-periodicity was observed [9], with 1/3 of the nanotubes being conducting. Yet further the triple periodicity appears also in some form in the leap-frog characterization

of fullerenes, particularly the icosahedral-symmetry ones [10]. Recently, several authors have briefly discussed the Clar-Kekulé structuring in armchair nano-tubes, finding a correlation of properties to a 3-periodicity [11-17], but without an explanation of why the correlation should be of the form it is – indeed often a comment is made that the correlation is backward from what is (by these authors) imagined would be expected from Clar's classical theory [1]. In particular, the nano-tubes with 0-band-gaps are the ones for which they interpret Clar's theory to say that the HOMO-LUMO gap is large. In fact, the above authors make several assumptions beyond Clar, who does not mention HOMO-LUMO gaps, but rather speaks of chemical reactivity. Here a clear (but typically unmentioned) difference appears between Clar's (finite) benzenoids and the bucky-tubes these more recent authors consider: Clar's favored benzenoids are those where the "Clar sextets" tend to be frozen into place by the boundaries, while the bucky-tubes have no such boundaries to freeze in the locations of the Clar sextets. The seeming counter-correlation (involving HOMO-LUMO gap) for extended conjugated-carbon networks is out of step with Clar's wide success for finite benzenoids. Further with Clar's theory being viewable as a special case of resonating VB theory, this counter-correlation would seem out of step with the overall concurrences otherwise found amongst resonating VB theory, MO theory, and experiment, at least in applications to finite benzenoids, to fullerenes, and even to a select few of the extended systems [4-8] such as already noted, as well as some further systems also.

I.2. The Exciting Realm of Conjugated Carbon Nano-Structures

The literature of conjugated carbon nanostructures has grown considerably over the last few decades, starting with the development of polyacetylene [18] and also other conjugated-carbon polymers (such as poly-*para*-phenylene) [19-22]. Upon the discovery and study of polyacetylene, doped versions were prepared and found to behave as "synthetic" metals (H. Shirakawa [23], A. G. MacDiarmid [24], and A. J. Heeger [25]), and many related polymers followed, with

*Address correspondence to this author at the Texas A&M University at Galveston, Department of Marine Sciences, 200 Seawolf Parkway, Galveston, TX 77551, USA; Tel: 409-740-4512; FaX: 409-740-4787; E-mail: kleind@tamug.edu

an extensive growth of the theory as well. This was seen to herald a new possibility of molecular engineering of different sorts of nano-circuits. There was perhaps an even more dramatic nano-structural extension to fullerenes, first with their detection and characterization [26] (R. F. Curl Jr. [27], H. W. Kroto [28], and R. Smalley [29]), soon followed by their preparation (W. Krätschmer, D. R. Huffman, and co-workers [30]). And then further, nano-tubes (S. Ijima [31, 32]) were developed, with a general belief following that these were to be centrally important in the design and construction of nano-devices – as incredibly strong supports, and with the possibility of either conduction or semiconduction. Then additional related nano-structures were prepared: nano-cones (M. Ge and K. Sattler [33]) and nanotori (R. Smalley and coworkers [34]). At the same time, the classical field of molecular benzenoids was extended to ever larger molecules (Müllen and coworkers [35]) and nano-belts (J. F. Stoddart with coworkers [36-40], and other authors [41-50]). But still more developed, with the characterization of different types of edges for graphite, and finally the preparation, manipulation, and study of single graphene sheets (first made by Geim and Novoselov [51, 52]; see also refs. [53, 54]).

All these various discoveries have triggered the publication of numerous reviews, books, and journals (too many to enumerate), concerning fullerenes, nano-tubes, nano-cones, nanotori, cyclacenes, cyclophenacenes, their Möbius counterparts, and graphene. Throughout all of this the theoretical treatments of such extended nano-structures have almost always been completely within an MO-band-theoretic framework. And further there are a number of types of structures which seem not to have yet been realized. Really the whole range of possibilities has somewhat an appearance of different topological mathematical possibilities for (locally Euclidean) surfaces embedded in space – just with hexagon-rich networks embedded on these surfaces.

But even before this fantastic flurry of the last few decades, there is a long history of benzenoids corresponding to small planar polyhex molecules – that is of the benzenoids, which were seen as the prototypical example of delocalized bonding and "aromaticity". Indeed this idea of "aromaticity" seems to be perennially developing, with a special issue of *Chemical Reviews* recently devoted to the subject [55], but not containing all the different viewpoints. One theoretical high point of the theory of benzenoids is found in the books of Pauling [56] and of Wheland [3], and yet another high point of the development of simple ideas for benzenoids is found in Clar's simple ideas [1]. Indeed Clar rather neatly explains (and even predicts) qualitative aspects of several molecular properties – including chemical reactivity, ^{1}H-NMR chemical shifts, conjugated C–C bond lengths, and electronic absorption spectra. And again in the more recent few decades most treatments of benzenoids have devolved to MO-theoretic considerations, the simplest following Hückel's (also now "old") ideas. And again even a much greater proportion of the theoretical work on conjugated-carbon nano-structures has been *via* MO-based approaches. That Clar's ideas have so far been so little successfully considered for these novel nano-structures seems peculiar – and especially there has been practically no reasonable attempt to suitably extend his considerations to the characterization of

properties including HOMO-LUMO gap, electronic conductivity, or magnetic susceptibility of such species.

I.3. Current Overall Aim

Thus it seems appropriate to examine Clar's ideas carefully with a view to their extension to the new conjugated-carbon meso-scale nano-systems, and beyond. Indeed we have recently already made some of this extension to link such ideas [57-59] with Pauling-Wheland resonance theory [2, 3] and also to apply [60] such an extended Clar theory to meso-scale nano-structures. Thus here we review and yet further extend such ideas in the framework of a systematic generalization of Clar's ideas beyond finite benzenoids, to attain a fairly comprehensive perspective of conjugated nano-structures. For instance, we find that there are sextet-resonant species (also frequently called "all-benzenoid" or "fully benzenoid" species) which, in contrast to Clar's finite benzenoids, do not have their Clar sextets localized, and have new "emergent" properties. We show that upon folding graphene sheets into various 3D-carbon nanostructures, the properties of the resulting meso-scale structures depend on the congruence or incongruence of overlap of Clar sextets from a parent graphene sheet. But also in such foldings to 3-dimensional structures (strips cut from graphene, nano-tubes, nano-tori, nano-cones, etc) various sorts of "defects" naturally enter into the picture, so that they need to be appropriately incorporated in the extended theory. If after such operations the overlapping Clar sextets coincide, then special properties of the congruently-folded 3D structures become manifest. In geometrical terms, the result of the operation (*i. e.*, yielding a 3D-structure) and the structure's properties depend on two integer vector-components h and k ($h \geq k$) manifesting a 3-periodicity of the difference $h-k$. The analysis encompasses a very wide range of conjugated-carbon species based upon benzenoids or graphene. In the present review, conditions for electronic conduction and for reactivity in polymers and graphene are noted in the context of this qualitative extended Clar-theoretic picture.

II. FUNDAMENTALS OF CLAROLOGY

Here it is intended to describe first Clar's classical ideas, especially with attention to their relation to the quantum mechanically based resonating VB ideas of Pauling and Wheland [2, 3, 56] though often this connection is not pursued. But such a connection naturally provides an indication of the direction to be taken for a quantum-theoretically consistent extension of Clar's ideas.

II.1. Clar's Ideas

Clar developed classical ideas of "aromaticity" to a simple elegant form which yet made diverse predictions, surprisingly reasonably for the case of conjugated benzenoid molecules for which he illustrated his scheme [1]. Clar's ideas may be viewed as a refinement of the classically based ideas of Armit and Robinson [61, 62] from 1922, such as indeed Clar said was the case. In Clar's approach Kekulé structures are "condensed" so far as possible into "aromatic sextets". More formally, one considers coverings of the π-centers in terms of two types of disjoint subgraph components: 6-cycles (or sextets); and lone pairings (*i.e.*, edges) between adjacent centers. This is done so that amongst the pairings, no triple occurs around a hexagon – if such a so-called *con-*

jugated 6-circuit were to occur it would be recast as an aromatic sextet (*i.e.*, as a Clar-cycle). Thus for naphthalene there are two such *Clar structures*, each with a sextet for one ring and two pairings remaining in the neighboring ring. See Fig. (**1**), where following Clar, the ring associated to a sextet is indicated with a circle inscribed within the hexagonal ring. One benzenoid may have Clar structures with different numbers of sextets, with those Clar structures having a maximum number of sextets being favored. These thus-favored Clar structures are here termed *sextet-maximum*. Thus for triphenylene in Fig. (**2**), there are two Clar structures with the first one in the first formula with the maximum of 3 sextets significantly favored over the second one with but a single sextet.
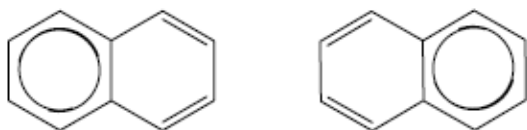

Fig. (1). Two equivalent Clar structures of naphthalene, each containing the three Kekulé structures.
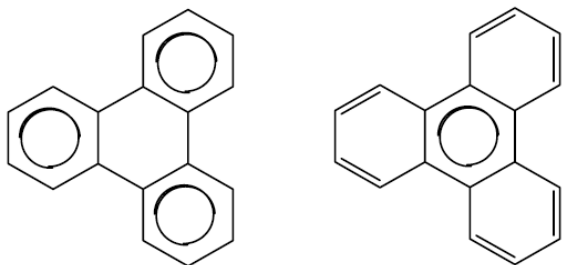

Fig. (2). Two nonequivalent Clar structures for triphenylene; only the first has three Clar sextets.

Clar gave special attention to an exceptional class of benzenoids with a Clar structure consisting entirely of sextets. These were identified by Clar as especially stable, especially aromatic, and we have termed them *sextet resonant*. They have been also called "all-benzenoid", "fully-benzenoid", and "total-resonant sextet", though here and in a recent article [60] we term them *claromatic*. For the class of finite molecules, the sextet covering is unique, and each ring of the benzenoid is either "full" or "empty" in correspondence with this sextet covering. In a recent paper, for such sextet-resonant structures the triangulated sextet-dualist and the anti-sextet dualist have been introduced [63]. The latter is formed by points at the centers of "empty" rings and by lines connecting such points when they correspond to condensed benzenoid rings (*i.e.* rings sharing one edge). As an illustration, Fig. (**3**) shows the anti-sextet dualist for the sextet-resonant hexa-peri-benzocoronene (which was displayed with its sextet-resonant Clar structure on the cover of Clar's book [1]).

For the general case of Kekuléan benzenoids, Clar particularly correlated the (sextet-maximum) Clar structures with molecular properties, primarily chemical reactivity (for electrophilic reactions), thermal stability, bond lengths, ^{1}H-NMR chemical shifts, and UV/optical spectra. The more highly reactive positions were identified as the positions where lone (bond) pairings were located, and these bond

lengths were identified as shorter (more like those of localized double bonds), and any hydrogen atoms attached thereto manifested ^{1}H-NMR chemical shifts like those attached to localized double bonds. More recently the quantum-chemical NICS aromaticity index [64-66] has been found to correlate well in a qualitative sense with full and empty rings in the sextet-maximum Clar structure, and quantitative correlations have been demonstrated [58] when using the whole collection (including sextet-nonmaximum Clar structures). Indeed such work using the full set of Clar structures has also been found [58, 67] to correlate quantitatively with resonance energies, as computed by different suitable methods. Indeed, (especially sextet-maximum) Clar structures show some correlation with a range of different aromaticity indices, both local and global.
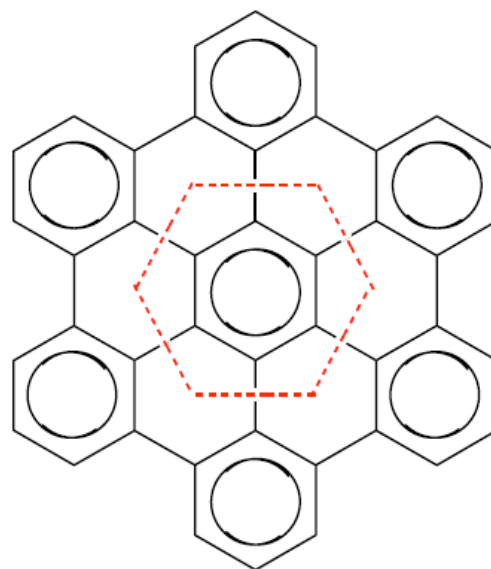

Fig. (3). Anti-sextet dualist graph for hexabenzo-coronene.

But again Clar's ideas (framed in a qualitative manner) were developed in the context of benzenoid molecules, and typically fairly small non-radicaloid ones. For these species the lone double bonds in the sextet-maximum Clar structure are typically on the boundary, *e.g.*, such as where electrophilic reactions would be plausible and where there were H-atoms to chemically shift their ^{1}H-NMR levels. Thence it is plausible that if the sextets and double bonds are not so localized on the boundary, then there may be some modification to Clar's argumentation. And notably it is precisely these altered circumstances which apply not only to radicaloid species but also to many perfectly stable extended nano-structures – to graphene, to nano-tubes, and to nano-cones.

II.2. Clar Sextets in Chemical Graph Theory

In fact a certain amount of attention was paid to Clar's theory, with its incipient novel graph-theoretic definitions and ideas. Clar's ideas presented by way of illustration were thus formalized, with definitions and a few associated consequences. For example, Clar structures were defined [5, 68-71] much as above, but on the other hand several authors defined [72-74] Clar structures to be what we term the "sextet-maximum" Clar structures, in as much as these were clearly illustrated by Clar as the more important. The Clar number C has been defined as the maximum number of sex-

tets, and sometimes related polynomials were introduced. Often schemes were devised to identify families of "sextet-resonant" benzenoids (being those with Clar sextets and no remnant double bonds). But seldom in most of this work were correlations drawn to connections either to other well-founded theoretical pictures or to experiment.

II.3. Relation to Resonance Theory

In fact, some of the motivations of Pauling and Wheland were rather like those of Clar, in that they saw how to formalize previous classical ideas, such as those of Armit and Robinson. The part of their motivation which was different is that they believed that they saw how to connect [2] this classical work to a quantitative quantum mechanical description, in terms of a covalent-space valence-bond model, and particularly to use a resonating VB basis of states (following Rumer [75, 76]). But the then-current difficulty of solution of this model drew them to suggest resonance theoretic solutions in terms of neighbor-bonded Kekulé structures, and ultimately even more simply (especially in Pauling's masterwork [56]) to deal just with enumerations of such Kekulé structures.

Indeed it is natural to view each Clar-sextet to be comprised from two Kekulé sub-structures involving the two possibilities for conjugation around the ring of the Clar sextet. That is, for naphthalene, the Pauling-Wheland resonance theory would consider the three Kekulé structures Ψ_a, Ψ_b, and Ψ_c depicted in Fig. (**4**), and this natural view of Clar structures would take the two respective Clar structures Ψ_I and Ψ_{II} of Fig. (**1**) to correspond to $\Psi_a + \Psi_b$ and $\Psi_b + \Psi_c$. The ground-state so interpreted in terms of Clar structures then would be $\Psi_I + \Psi_{II}$, which of course is just $\Psi_a + 2\Psi_b + \Psi_c$. There are in fact different approaches which indicate this central Ψ_b to be more important than Ψ_a and Ψ_c. This Ψ_b is an example of a *Fries* structure [77] described (for benzenoids) as a favored Kekulé structure manifesting a maximum number of conjugated 6-circuits. Fries described such favored Kekulé structures as the best by which to describe a benzenoid, with bonds tending some towards localization as indicated by his Fries structures. Such a structure with a maximum of conjugated 6-circuits is unique for cata-condensed species [78], but otherwise there generally are more than one. In the Pauling-Wheland VB theory, the weight of Ψ_b for naphthalene is bigger than that for Ψ_a and Ψ_c, but in fact much smaller than 2 (it has a weight of $\cong 1.15$). But for the resonance theoretic model of Simpson [79], one finds a slightly larger relative weight for Ψ_b, around 1.25. Also an improved VB model [80] gives such a slightly higher weight. Yet further the Clar-sextets need not entail equal weights of the pair of Kekulé substructures with different conjugations around the considered ring – say with the Clar structures of naphthalene being non-symmetric as indicated by arrows, which as in Fig. (**5**) indicate the possibility of a Clar sextet to move, while all the others remain fixed. Thus for instance, the Clar sextets of the first structure of triphenylene in Fig. (**2**), would not entail

any such arrows, while the second structure would. That there is some ambiguity of agreement evidently appears to depend on just exactly what one understands by a Kekulé structure, with there being a quite wide range of views, and what it should be for application of Clar-theoretic ideas has not yet been well explored.
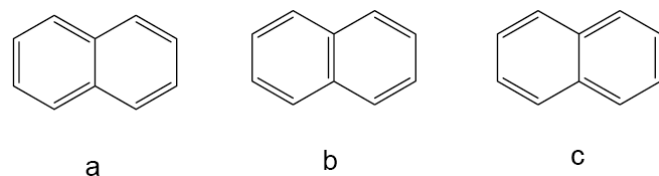

Fig. (4). The three Kekulé structures of naphthalene (the Fries structure is denoted by **b**).
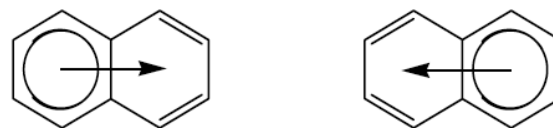

Fig. (5). Modified (arrowed) Clar structures, for naphthalene.

One view [57] of Clar's theory [1] is that it provides a classically based motivation for the structure-resonance theory of Herndon [81, 82] or conjugated-circuits theory of Randić [83-85] for computing resonance energies of benzenoids, and even related molecular species with a few 4- or 5-membered rings. Indeed this theory has been used fairly widely on ordinary molecular species, as well as on fullerenes [86-89] and there are several papers dealing with polymers [90-95] and extended 2-dimensional systems [96, 97].

A general view of Clar's theory is [99] that it operates with a reduced-size space in which to model each conjugated-carbon network. In fact, one may view Clar's theory to provide but one of a sequence of models, with the Herndon-Simpson model (associated with conjugated-circuits theory) to precede it in terms of the size of the structure space, and preceding this in terms of the size of the structure space is the full-covalent space Pauling-Wheland VB model, and yet further preceding this is the covalent-ionic space VB model. The situation is summarized in Fig. (**6**), and the final resultant Clar-theoretic model is anticipated to be similar to that described by Herndon and Hosoya [99]. But here rather than focusing on such a quantitative model Hamiltonian, or related invariants representing expectation values, we try to approach the problem in a manner somewhat like Clar's (and Pauling's less mathematical more chemical presentations) to seek immediate qualitative insight, covering wide classes of materials, especially of the novel nano-structural type.

II.3. Extension of Clar's Theory

For general application to conjugated-carbon nanostructures it is natural to consider some further properties and further circumstances where the sextets (and possibly lone spin-pairings) are not localized, say due to a boundary. As to ^{1}H-NMR chemical shifts, our extended nano-structures without boundaries then have no H atoms to manifest chemical shifts. As to bond lengths, without localization of sextets (and lone spin-pairings) there is no fluctuation in bond lengths. And similarly NICS ring aromaticity indices should
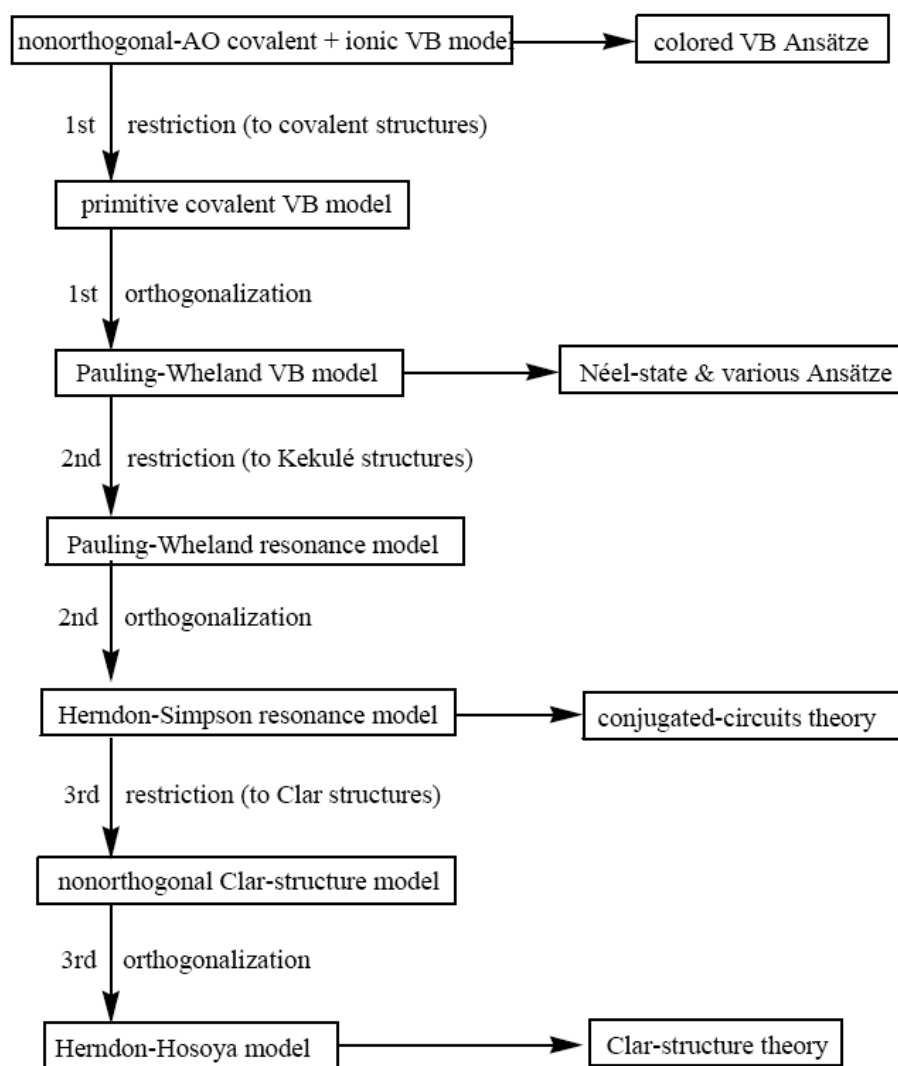
Fig. (6). Hierarchy of models.

have smeared out aromatic values. Finally resonance energies should retain much the same correlation as in benzenoids with localized sextets and lone pairings in their Clar structures – that is, the resonance energy should increase with the number of sextets, and also should be slightly enhanced through their delocalization. This last point indicates that boundary-less sextet-resonant species are of higher resonance energy per site than for the conventional (highly stable) sextet-resonant benzenoids where sextets tend to be frozen in place. Thence the sextet-resonant nano-tubes with zero-band-gap should have the greatest resonance energy, and possibly similar distinctions apply for nano-cones.

Clar's arguments might even be sought to be quantified, as we have done in application to ordinary benzenoids [58], and even benzenoid radicals [59]. In particular, averages over Clar structures including those with non-maximum numbers of Clar sextets were needed to attain good quantitative agreement. This can be notably relevant when the sextet-maximum is unique, while at the same time there are very many Clar structures with but slightly fewer aromatic sextets. That is, though a Clar structure's weight increases with the number of sextets, those with fewer than the maximum number still contribute (even as indicated by Clar) and can

perhaps even dominate if their number is suitably larger. Moreover, this effect can be further exaggerated for extended systems as it turns out that the boundary facilitates the freezing in of aromatic sextets <u>if</u> things are otherwise favorable. This final qualification here is usually irrelevant for ordinary benzenoids, where almost all rings are at or near the boundary. However, for extended species with a large fraction of the rings away from the boundary, the pattern which the boundary would tend to freeze in aromatic sextets might turn out to be inconsistent with the pattern of their delocalization in the (bulk) interior.

It should be emphasized that for Clar's "high-lighted" sextet-resonant benzenoids, the simplified zero-order averages based on the single sextet-resonant Clar structure may be expected to be quite reasonable so long as the system is small enough that a major portion of it is on the boundary. That is, for such a system (as in Fig. **2**), a sextet-non-maximum Clar structure $C_{(b)}$ turns out to have especially fewer sextets than can otherwise occur with systems which are not sextet-resonant. To see this, note that in a sextet-resonant molecular benzenoid such a structure $C_{(b)}$ must have a sextet in a position which is "empty" in the favored

Clar structures $C_{(a)}$ (consisting only of sextets) whence the three adjacent which are full in $C_{(a)}$ must be empty in $C_{(b)}$, so that there is a net cost of two Clar sextets. In contrast for systems which are not sextet-resonant the net cost from a sextet-maximum Clar structure can be just one. See, *e.g.*, phenanthrene in Fig. (**7**), where the approximation neglecting the sextet-non-maximum Clar structures is less severe as involving a cost of just one sextet. This then makes a more severe correction to the bond and ring indices noted in the two preceding paragraphs, *e.g.*, as seen on comparing Fig. (**7**) to the previous triphenylene results of Fig. (**2**). Thence Clar's singling out of the sextet-resonant species as exceptional is further supported.
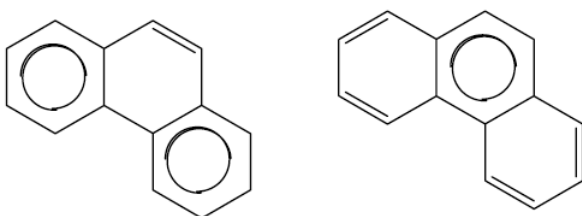
Fig. (7). Two nonequivalent Clar structures for phenanthrene; only the first has two Clar sextets.

The argumentation is a little more subtle for reactivity and especially its oft-assumed correlation to HOMO-LUMO gap. Basically we argue that the direct correlation to HOMO-LUMO gap is naïve – that is, just because there are no localized double bonds in a sextet-maximal Clar structure, there is no immediate rationale for a large HOMO-LUMO gap. Generally even if the HOMO-LUMO gap is small, the reactivity for electrophilic reactions need not be necessarily high – the reactivity being governed by local values of a reactivity index, which can have a large sum over all vertices while being small at all local positions. That is, the reactivity towards electrophilic agents is to be correlated to a high bond order (at the boundary), which does not occur if there is no bond localization, regardless of the HOMO-LUMO gap. *E.g.*, though the HOMO-LUMO gap is zero for graphite, or indeed for any metal, these substances do not always act like a (zero-gap) radical species. Actual reactive radical species, in

addition to having a small HOMO-LUMO gap, also have (thermally accessible) unpaired spin density concentrated on a few sites. Such species should (within an MO framework) have a notable local density of states for energies near the Fermi energy (= 0 for the simple Hückel model) if a species is to be so radicaloid. Or returning to the question of electrophilic reactivity, this is predicated upon localization of localized double bonds, such as may be induced by boundaries, but also perhaps if somehow a degree of localization of unpaired sites occurs. A large band gap occurs with localization of sextets. Further a small band gap occurs either with localized unpaired spins, or possibly with suitably extensively delocalized bonding, such that slight local modifications of the manner of delocalization can lead to an excited state of very nearly the same energy.

The question of electronic conduction within a resonating VB framework (such as is so close to Clar's ideas) can be addressed by either adding or removing an electron, and examining whether there is any subsequent cost of the resonance energy. This idea is elaborated by way of illustration in the benzenoid polymer section.

The consideration of unpaired electrons and associated magnetic properties takes one yet a little farther from Clar's discussion [1]. And this extension is delayed to the radicaloid section.

III. "ZERO-DIMENSIONAL" STRUCTURES: MOLECULES

It seems proper to provide some brief discussion of Clar's ideas in his original realm of work, on the benzenoids of say a dozen rings or less – *i.e.*, on systems with no dimension of great extent. Even in this regime if the species is radicaloid, Clar gave less discussion, so that some discussion of this case needs to be addressed.

III.1. Benzenoid Molecules

These somewhat extended ideas of Clar may now be applied to different classes of nano-structures. As already noted in the Introduction, there are a great variety of these to which Clar's ideas have been little applied, including polymers, semi-infinite graphite, vacancy defected graphite, nanotubes, defected nano-tubes, and more. Most of our ameliora-
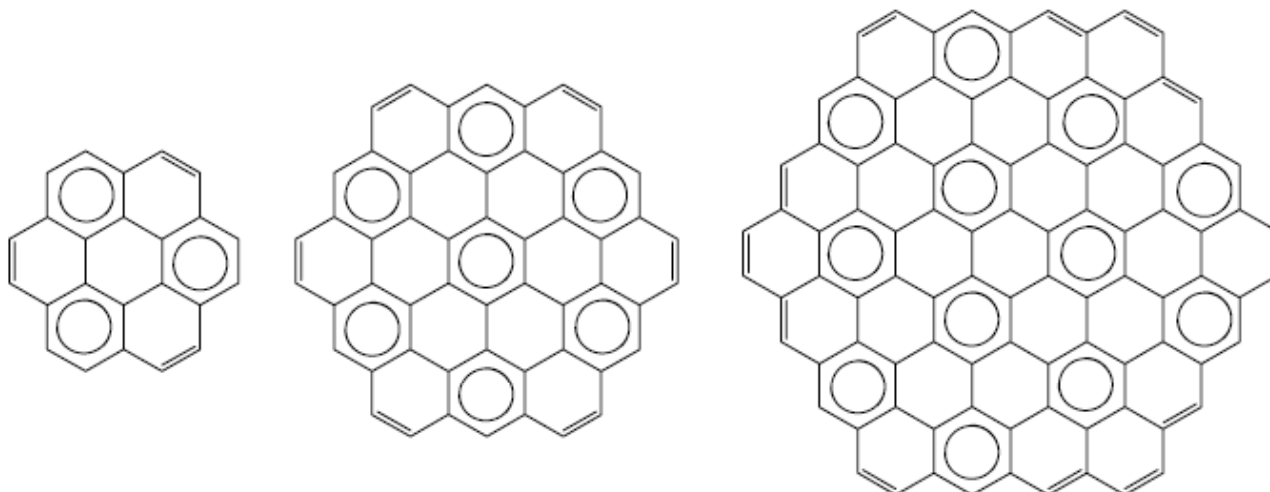

Fig. (8). Peri-fused benzenoids with hexagonal symmetry having 7 rings (coronene), 19 rings, and 37 rings.

tion of Clar's ideas extends consideration to HOMO-LUMO gaps and unpaired spin density, and a main structural elaboration concerns the influence of boundaries. Thus the situation, which notably differs from what Clar considered [1], involves a lot of boundary. In the two preceding sections there are found typical examples for a couple of smaller benzenoids (with relatively fractions of the rings on a boundary). But even if one considers benzenoids which traditionally would be considered rather large, say such as the hexagonal-symmetry 7-, 19-, and 37-ring benzenoids of Fig. (**8**), it turns

out that they still have a considerable fraction of rings on the boundary: namely 6/7, 12/19, and 18/37 for the three benzenoids of Fig. (**8**).

Clar's ideas and related arguments may be more comprehensively tested by considering some other extended nano-structures which differ from those of Clar in being infinite (or even finite if they manifest unpaired electrons). This we do in the following, starting with those which retain a degree of similarity with the systems considered by Clar in having a
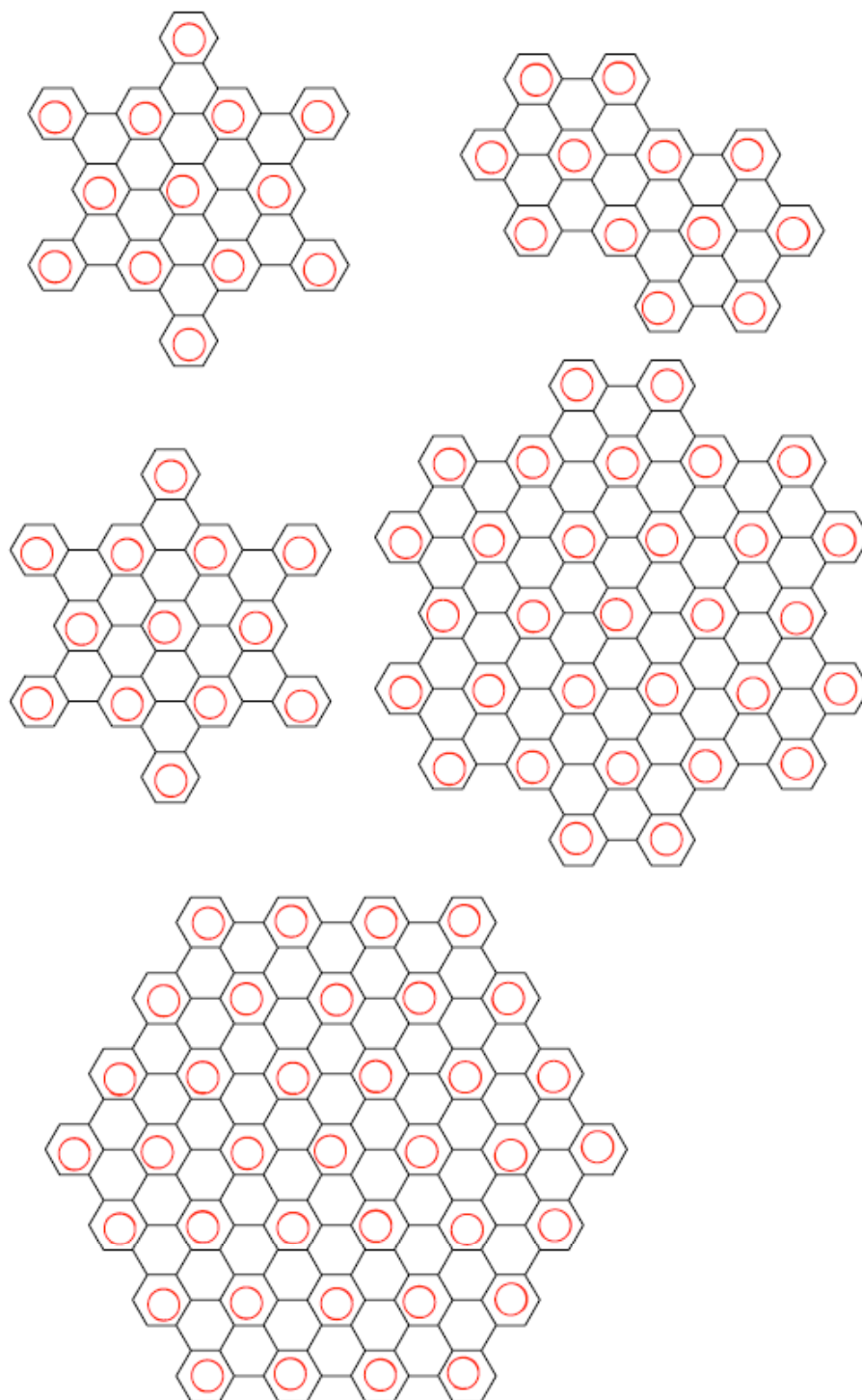

Fig. (9). Some of the large claromatic benzenoids synthesized by Müllen and coworkers.

significant extent of boundary (in comparison to the number of carbons).

II.2. Claromatic Benzenoids

Again these are the (exceptionally stable and aromatic) benzenoids for which there is a Clar structure which consists entirely of Clar sextets. In fact many such exceptionally stable hydrocarbons have been recently synthesized and studied by Klaus Müllen and his coworkers, as illustrated in Fig. (**9**) [35]. Their stability have made possible their formation by Scholl- and Kovacic-type dehydrogenations [20] leading to the formation of dozens of new C–C bonds in a single step, exemplified by eliminating H_2 from *ortho*-terphenyl to form triphenylene.

In principle, long strips of claromatics can be cata-condensed (Fig. **10**) or peri-condensed (Fig. **11**). For peri-fused strips one can imagine a synthetic approach (Fig. **12**) modeled after Mandelbaum's known method for obtaining triphenylene derivatives [100]. On the theoretical side, there has been much work on different chemical graph-theoretic characterizations of Claromatic benzenoids, as referenced in Balaban and Schmalz [63] The nontraditional and extended structures of focus here have rather infrequently been considered from Clar's point of view, though we have recently begun such considerations [58] with some further related elaboration here.
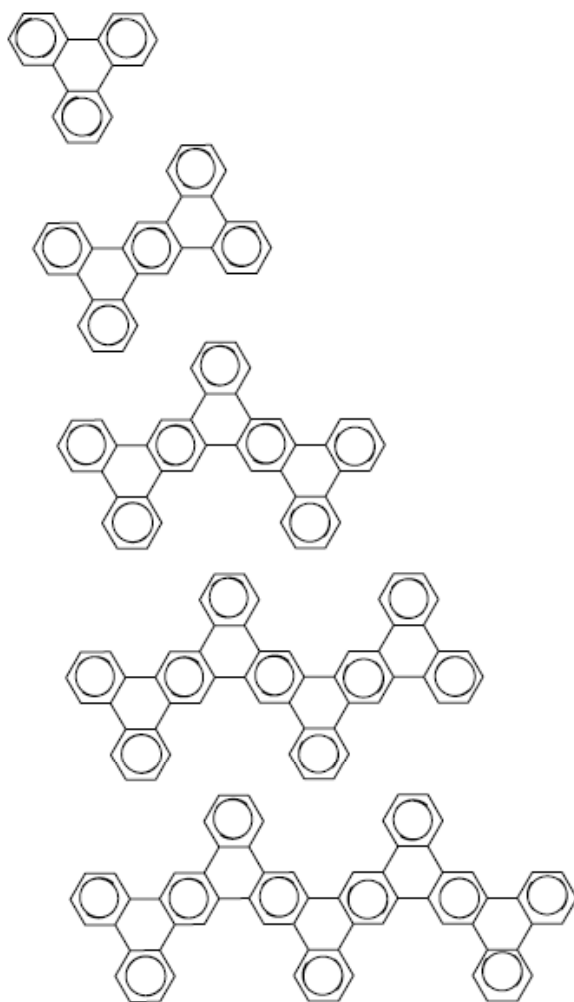

Fig. (10). Cata-condensed claromatic strips.
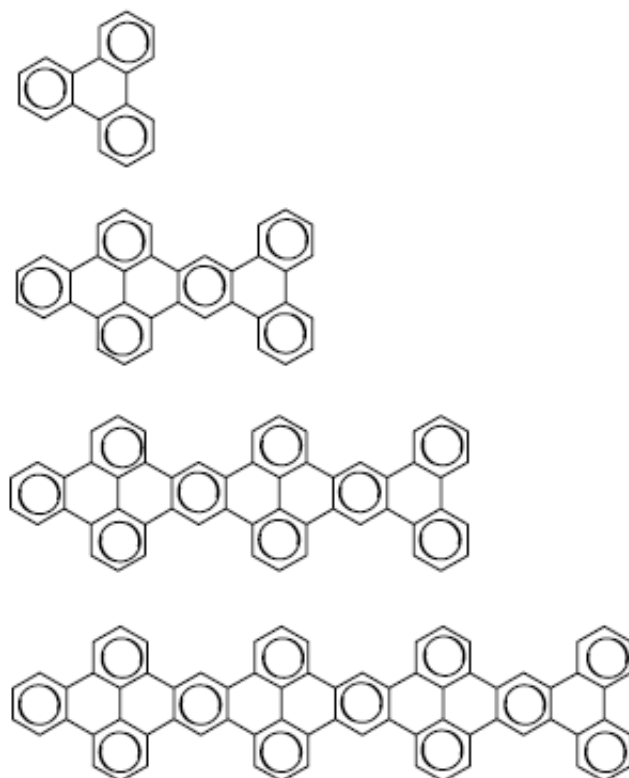
Peri-fused "claromatics"

Fig. (11). Peri-condensed claromatic strips.

II.3. Benzenoid Radicals

Clar [1] was very brief in considering radicaloid species, but really his ideas apply fairly well [59] in this context also. Here structures with unpaired electrons are entertained, such as for perinaphthyl as in Fig. (**13**). Then in addition to bond orders (and ring aromaticity indices), counts for unpaired electrons are appropriate, with the consequent Clar free valence for a site i being

$$\text{CFV}_i = A \cdot \sum_C w_C \cdot u_i(C)$$

with w_C and A as before, and $u_i(C)$ the number (= 0 or 1) of unpaired electrons on site i in Clar structure C. The bond-order and ring-aromaticity indices remain much as before. For the first of the summary structures of Fig. (**13**), the component structures are listed in Fig. (**14**), along with the contributions for the Clar-based bond order, free valence, and ring aromaticity for each one of these contributing component structures. Thence for peri-naphthyl one Clar-based obtains overall free valences, bond orders, and ring aromaticity indices as in Fig. (**15**). The Pauling bond orders in this case come out to be similar (but slightly different when the two Kekulé structures with an unpaired electron in the center site are taken into account).

As another example, note the benzyl radical which has just a single sextet-maximum structure, which if used to
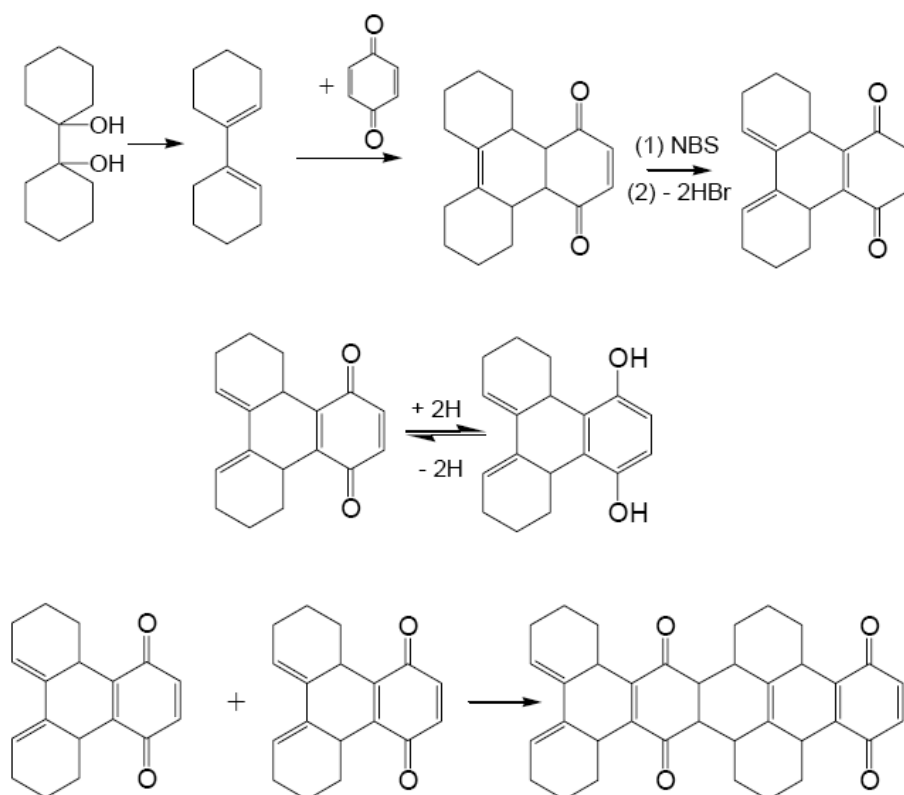
Fig. (12). Putative approach to synthesizing cata-condensed polymer strips *via* Diels-Alder reactions, to be followed by reductions and dehydrogenations.
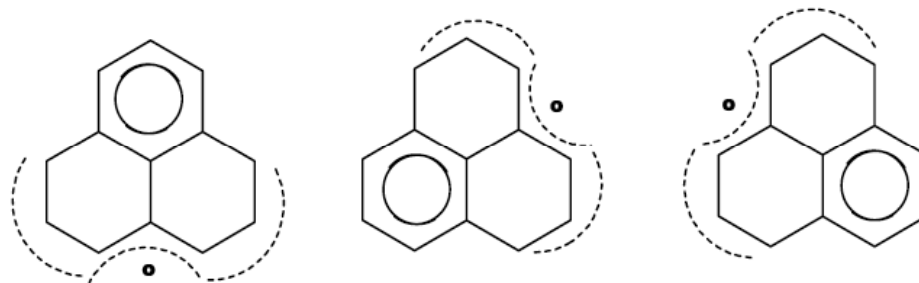

Fig. (13). Representation of radicaloid Clar structures of the perinaphthyl free radical.

compute these various indices give the results in Fig. (**16**). But it is emphasized that if we were to include the three different structures with no Clar sextet rings (involving a double bond directly from the ring to the benzyl radical), a modification to this is obtained, but we are faced with an assignment of relative weights of different structures with different numbers of Clar sextets.

Typically only structures with a minimum of unpairing are considered, as when dealing with Kekulé structures, for ordinary finite polyhex structures. That is, peri-naphthyl structures with triples of unpaired electrons are not considered. This rule though is not firm, especially in dealing with larger systems where the introduction of some small extent of unpairing achieves a much greater freedom in the remaining mode of pair (and sextet) formation. This is addressed later in the next section.

The Clar free valence (CFV) is related [59] to the Clar bond orders (CBO) thusly

$$1 = \mathrm{CFV}_i + \sum_e^{@i} \mathrm{CBO}_e$$

where the sum is over edges incident to site *i*. This is in close analogy for the Pauling free valences and bond orders.

A further point is that in what might be termed "typical" radicals, the unpaired electrons occur solely on sites of one type, starred or unstarred. But this does not always occur, as for the bis-perinaphthyl species of Fig. (**17**), where the maximum-paired Clar structures are indicated – and it is seen that one unpaired electron is on a starred site while the other is on an unstarred site.

IV. "ONE-DIMENSIONAL" CASE: POLYMERS

The case of polymer strips provides a nice beginning to the consideration of nano-structures, where not only unpairing can occur, but also properties such as magnetic susceptibility and electrical conduction become relevant.
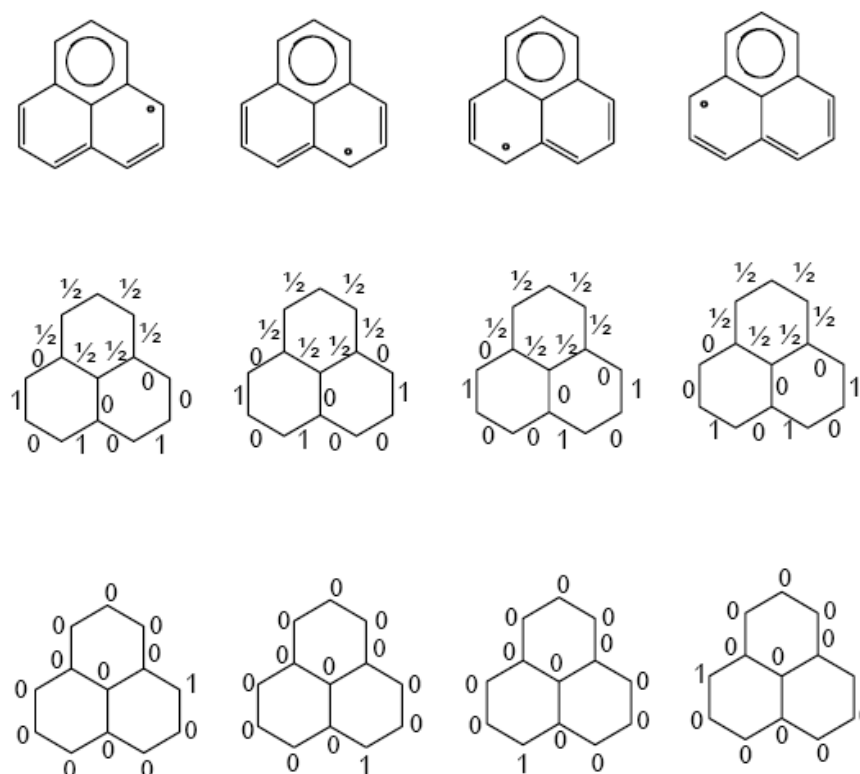
Fig. (14). Resolution of the first radicaloid structure of Fig. **13**. Here the 1st row gives the resolution, the 2nd row gives bond order assignments for each corresponding structure of the 1st row, and the last row gives corresponding free valence assignments.
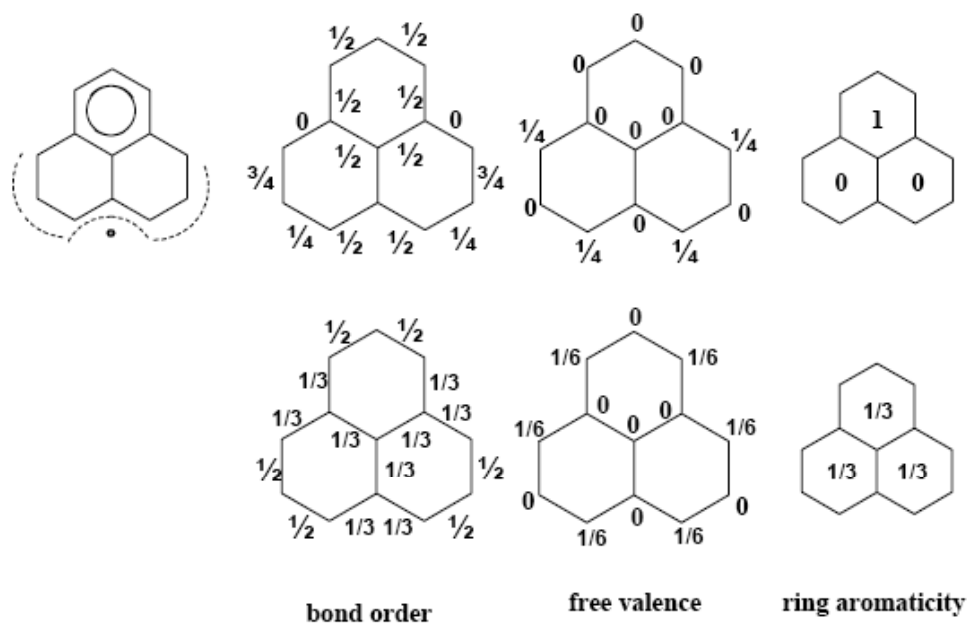

bond order   free valence   ring aromaticity

Fig. (15). Results in the 1st row for the 1st of the summary structures of Fig. 13 (obtained by averaging the results in Fig. **14**). The 2nd row here is for the average over all the three summary structures of Fig. **13**.

IV.1. Benzenoid Polymer Strips

Benzenoid polymers with boundaries on opposite sides of a polymer "chain" or "strip" have comparably as much boundary (per C atom) site as ordinary benzenoid molecules. Thence there is an opportunity for extensive freezing-in of sextets and lone pairings. This may be approached by way of example.

First, consider poly-*para*-phenylene, which is readily seen to be sextet-resonant as seen in Fig. (**18**). Evidently each ring is aromatic while the intervening bonds are near single, which is in agreement with ordinary resonance theory, VB theory, and also with Hückel MO theory. Just as for finite-molecule benzenoids, one can expect the species to be stable with a large band-gap, which indeed is the case at the Hückel and higher levels [98].
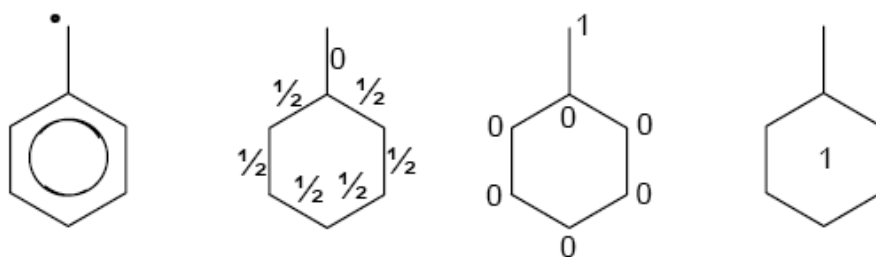
Fig. (16). The sextet-maximum Clar structure of the benzyl free radical. Along with bond order, free valence, and ring aromaticity indices, assuming negligible contribution from the sextet-maximum Clar structures.
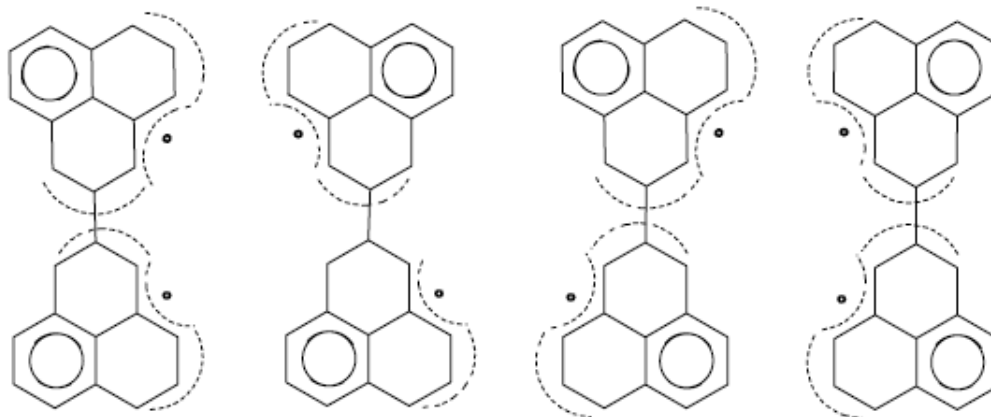

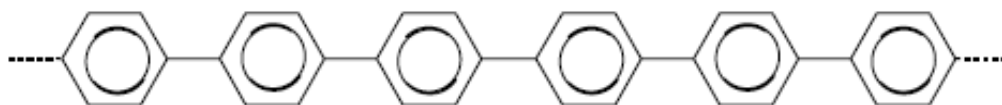**Fig. (17).** The maximum-paired Clar structures for the diradical bis-perinaphthyl.

Fig. (18). Poly-*para*-phenylene.

One "wider" benzenoid polymer has a uniform width of one hexagon, with armchair edges. This is not sextet-resonant as seen from the Clar structure of Fig. (**19**) with alternating rings containing lone pairings. Of course, here there are different Clar structures with many sextets but appearing in different rings, so that there is no overall sextet localization. The overall effect (at least in the interior away from the ends) might be viewed in terms of two sextet-maximum Clar structures: one as in of Fig. (**7**), and a second with the sextet rings displaced one position along the chain. Then Clar bond-orders in terms of these two sextet-maximum Clar structures are as in Fig. (**20**).

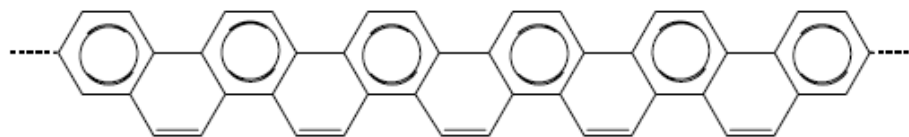Furthermore, from our slight extension of Clar's ideas, still to the case of the long poly-*para*-phenylene polymer,

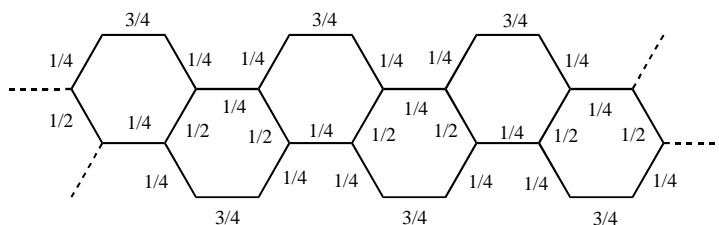**Fig. (19).** A poly-phenacenic benzenoid strip with a uniform width of one hexagon.

Fig. (20). Maximum-sextet Clar bond orders for the polyphenacenic polymer of Fig. (**19**).

one may argue that the band-gap is not zero here, in that if it were, then conduction of electrons would be facile. But even within a Clar-theoretic framework it can be seen that conduction is not favored. That is, if we introduce a site with an extra electron as in Figs. (**21a-21d**), on either a starred or unstarred site, while otherwise drawing in a fully paired Clar structure, something very interesting happens: namely, the pairing pattern on one side from this singular negative site is forced such that there are no sextets (while there are sextets on the other side). That is, with the introduction of such an electron the occurrence of sextets is sacrificed so that much resonance is eliminated, and consequently there is a significant energy cost to the introduction of the extra electron, and there is a notable gap. This too is in agreement with more conventional resonance theory [7, 8] and also with Hückel MO theory [7, 8] and beyond [98], the Hückel band gap being 0.344 $|\beta|$. And it is emphasized that this is not in disagreement with experimental results concerning the conductivity of *doped* poly-*para*-phenylene, in as much as in this case there is a fixing of the number of electrons away from one π-electron per carbon atom – and at present we focus on the electrically neutral (non-ionized) regime.

The next wider species in this sequence is a polymer a uniform width of two hexagons, still with armchair edges. As seen in Fig. (**22a**), this species is sextet resonant, and moreover the sextets are localized, so that again considering just this sextet-maximum Clar structure, one obtains the Clar bond orders of Fig. (**22b**) limited to consideration of the sextet-maximum structure. Again a great similarity is seen. Further as concerns conduction, again consider the introduction

of an extra electron, for which its site is internally paired, and one continues to otherwise draw in a Clar structure with a maximal number of Clar structures, whence one obtains a result like that of Fig. (**23**) depending on whether the new electron is introduced on a starred or unstarred site. Notably, no matter how the electron is introduced, the Clar pattern on one side or the other of the extra electron has half the density of sextets as for the undefected chain, and again there is a resonance energy cost, so that from the point of view of resonance theory the system should not be conductive. Moreover, Hückel theory gives a band gap of 0.494 $|\beta|$ so that also the system is predicted in this MO picture not to be conductive. That the system is sextet resonant indicates a high degree of stability to reactions (*i.e.*, aromaticity in the classical sense) and a high resonance energy, as is consistent with conjugated-circuit computations on this polymer.

The yet next wider species is a polymer with a uniform width of three hexagons, still with armchair edges. This species is no longer sextet-resonant, and has a sextet-maximum Clar structure as in Fig. (**24a**), and the arrows attached to the sextet circles indicate that they may move about from the ring at the tail of an arrow to the ring at the head of an arrow, whence one perceives that there are many such sextet-maximum Clar structures. In fact there are many more not found from Fig. (**24a**), as indicated in Fig. (**24b**), where the multiplicity of structures is only partially manifested and the sextets are localized. Both types of sextet-maximal Clar structures of (a) and (b) have the same density of sextets, at
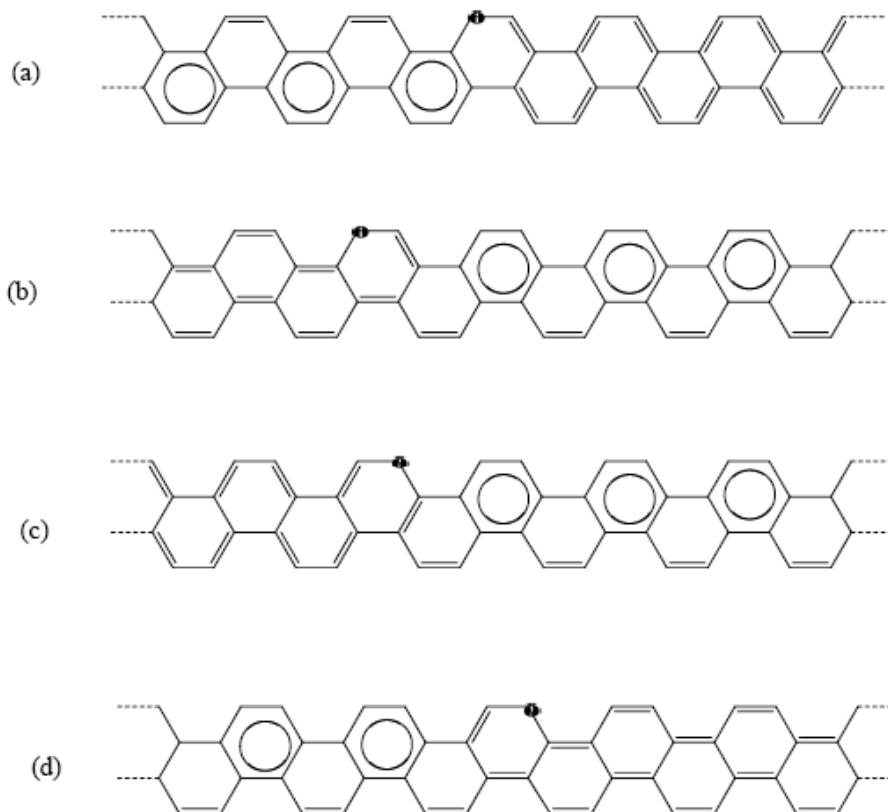

Fig. (21). The poly-phenacenic benzenoid strip having a uniform width of one hexagon as in Fig. **19**, but with one extra p-electron on a "starred site" in (**a**) and (**b**), and on an "unstarred site" in (**c**) and (**d**).
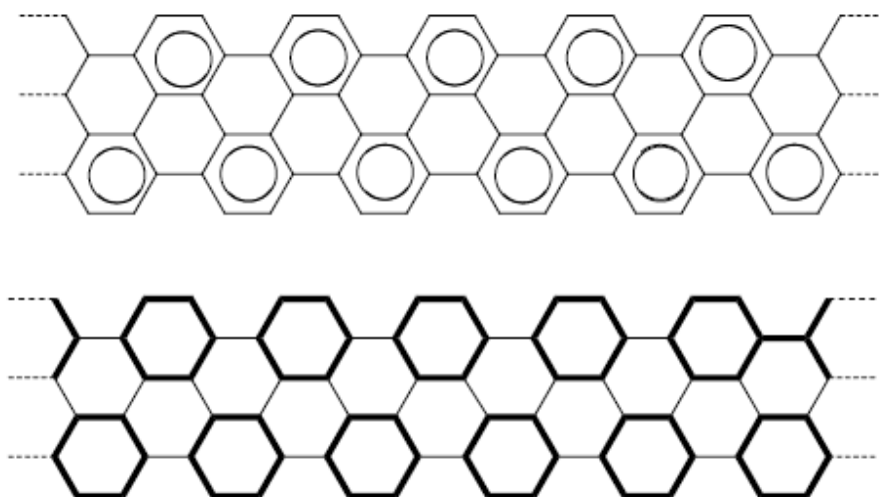
Fig. (22). A benzenoid strip with a uniform width of two hexagons, allowing a sextet resonant Clar structure having only Clar sextet rings and empty rings in (**a**). Then consequent Clar-like bond orders in (**b**) are shown with thick lines for those with value 1/2 and thinner lines for those with value 0.
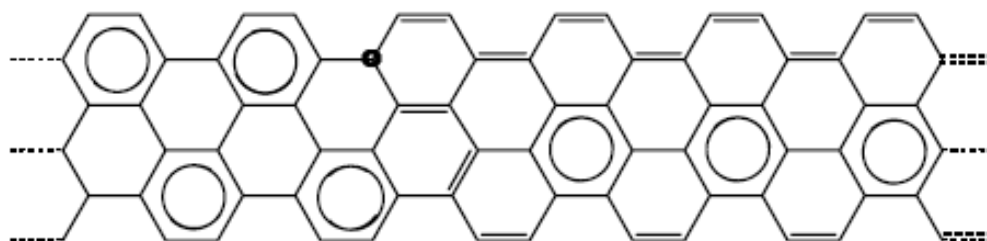

Fig. (23). The benzenoid strip with a uniform width of two hexagons plus one π-electron.

one per column of the polymer. But the two types of Clar structures are very different in another way – namely in terms of the total Clar-bond order for horizontal bonds in any column, it being 1 for the structures of Fig. (**24a**), while for 24(b), it is 2. That is, these two sets of Clar structures in Figs. (**24a**) and (**b**) for a very long polymer are different in every column, and so can not be changed from one class to the other without making changes in every column. That is, these two sets of Clar structures must be (essentially) non-interacting, and the proper averaged bond-orders for the ground state should come from just one of these classes – which class it is depending on a computation of the (resonance) energies associated to each of these classes. Here the two classes should manifest similar (resonance) energies since each has the same density of sextets.

To understand a little more clearly what is going on, note that the structure of 24(b) is of the same class of 25(a) or 25(b) – even though there is a difference in every other column (as to the placement of the sextet rings). The equivalence of 24(b) and 25(a) arises because there are step-by-step "local" changes (from one Clar structure to another) which can be made, each resulting structure being in the same (equivalence) class as the one before, all in such a way that a whole string of such locally changing structures may be identified, starting with 25(a) and ending with 25(e). [Here a "local" change is understood to mean just a shifting of a (small) finite number of bonds and or rings around.] To illustrate this we note: the first step in such a local change in Fig. (**25b**) where the structure of 25(a) has been changed locally

to have one new Clar sextet moved to the new row of 25(a); and a second step in such a local change is found in 25(d); and after a long sequence of such local steps, a next to last step before arriving at 25(a) is shown in 25(e). Notice that these various local motions do not change the number of horizontal π-bonds in each of the columns – all such local changes (which do not introduce unpaired electrons) preserve the number of such horizontal π-bonds per column, so that 24(a) and 24(b) are in different such equivalence classes. Here the two classes [one of 24(a) and the other of 24(b)] should manifest similar (resonance) energies since each has the same density of sextets, and each seems to manifest notable resonance (amongst a number of different locally differing Clar structures). Thence to render a distinction, a more detailed computation is warranted. To distinguish which of the two equivalence classes is more stable one could apply conjugated resonance theory, or quantitative Pauling-Wheland resonance theory, to yield that the class of 24(a) is the more stable.

An average Clar bond-order over even just the sextet-maximum structures is not fully trivial, but one immediately sees that the sum of the horizontal bond orders in each column is 1, while the sum for the diagonal bonds in either of the two directions is 2. For considerations on conduction and band-gap something interesting happens, as illustrated in Fig. (**26**), where one sees that the introduction of a single extra electron in fact leads to a manifestation of what is otherwise a Clar structure such that on one side of the electron it looks like it is associated to that of the class of Fig. (**24a**)
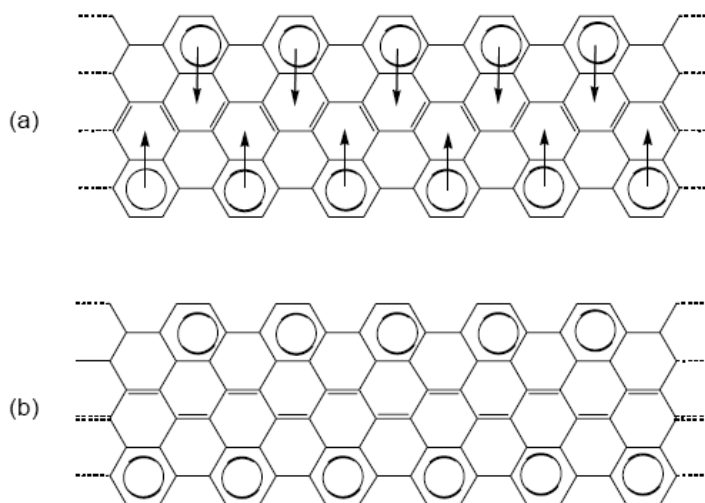
Fig. (24). A benzenoid strip with a uniform width of three hexagons: classes (**a**) and (**b**) have different horizontal bond orders per column, namely 1 and 2, respectively.
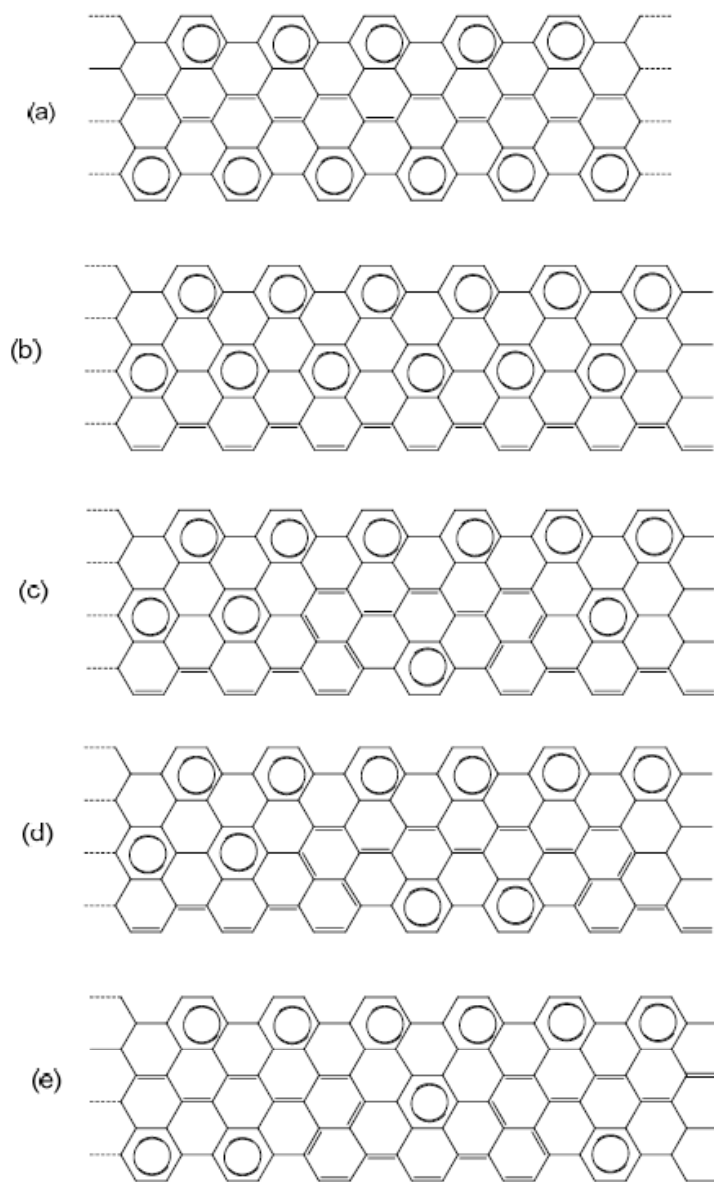

Fig. (25). Strips with width of three hexagons belonging to the same class with bond order per column equal to 2.
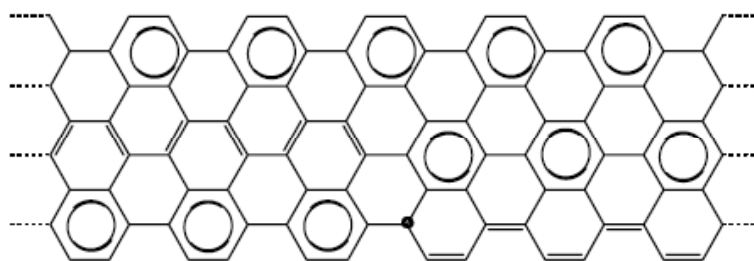
Fig. (26). The benzenoid strip with a uniform width of three hexagons as in Fig. 24 plus one π-electron.

while on the other side it appears like that associated to the class of Fig. (**24b**). And because as we have already decided that these two distinct classes have similar sextet densities and energies, there should not be much cost to the introduction of the extra electron. That is, the gap should be small, notably smaller than for the previous two cases, again in agreement with corresponding resonance theory computations [6], and also with the simple Hückel result [8] of zero for the band gap. [The simple Huckel theory is a 0-order approximation, which in this case should be lifted with better band-theoretic computations – there being many (other) cases where the 0-band gap is not lifted in higher orders because of symmetry – it being understood that the gap can be lifted with a distortion to a lower symmetry which does not preserve the 0-band gap. Indeed this is part of the message of the theory of Peierls distortions, which however we do not pursue here. But for a connection of this theory with VB rationales such as pursued here see ref. [7].

One can proceed on up, to ever wider strips of the sequence begun with Fig. (**18**) (for 1 hexagon width), Fig. (**22**) (for 2 hexagons width), and Fig. (**24**) (for 3 hexagons width). There emerges a pattern of period 3: for hexagon-width $w = 3n - 1$ the polymers are sextet resonant, with localized sextets, and a relatively large band gap; for hexagon width $w = 3n$ there are two sextet-maximum classes with delocalized sextets, and a small band gap; and for hexagon-width $w = 3n + 1$ there is a single class of sextet-maximum Clar structures with delocalized sextets, and a notable band gap. Moreover, both within the simple Hückel MO theory [9] and the simplest resonance theory [7, 8] this pattern of band gaps is reproduced. And yet further the simple Kekulé-structure enumerating resonance theory yields this same pattern of classes (of Kekulé structures rather than Clar structures).

Of course there are many possible benzenoid polymers other than the sequence described in the preceding five paragraphs. But in fact for every single one of the cases we have investigated, the consilience with Kekulé-structure-enumerating resonance theory and simple Hückel theory persists. This includes another infinite class manifesting a similar period-3 oscillation between the three types of behaviors noted in the preceding paragraph – this class is that again with armchair boundaries, but columns alternating in width between two values which differ by 1. Another class is that with polyacenic zigzag edges and deserves consideration under a separate category of benzenoid polymers, with especially low densities of sextets, so that we attend to this in the next section.

The mode of prediction of conductive band gap *via* the use of Clar structures deserves some more general attention,

along with the associated circumstance found for the width-3 polymer of Fig. (**24**) regarding the two equi-energetic but non-interacting classes of Clar structures. This really is a manifestation [7] of a "long-range order (LRO)", such as is of the same sort which distinguishes different thermodynamic phases. But regardless of this, it is very easy to identify (if one knows what to look for). To this end, it can be shown that the considered sum of bond orders for horizontal bonds dividing a polymer identify the different LRO classes to which Clar structures belong (at least for any alternant network such as are all benzenoids). Indeed for any dividing set of parallel bonds in any direction the different bond order sums correspond to different classes.

IV.3. Radicaloid Polymers

There are many radicaloid benzenoid polymers to which Clar's ideas follow much the same pattern of prediction indicated in the examples given here, though one may need to take a some care in listing all the Clar structures, and one looks to see how what occurs in one monomer unit affects what appears in neighboring monomer units. For instance, for poly-(*meta*-phenylene-methylene) that can also be called poly(*meta*-benzylidene), there is the possibility of having an aromatic sextet in a monomer in just one way, with the unpaired electron occurring on the methylene bridge as in the first entry in Fig. (**27**), though there are 7 ways in which the unpaired electron can be moved from the bridge into an adjacent ring, as in the later parts of Fig. (**27**).
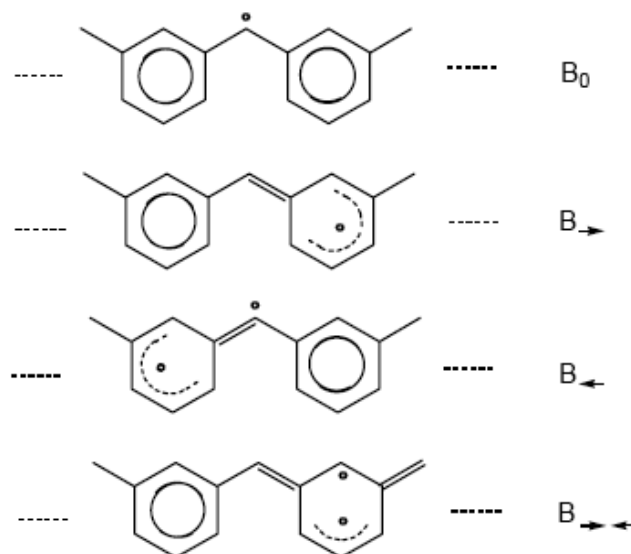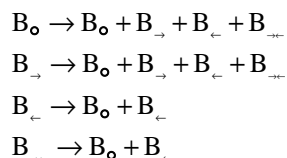

Fig. (27). The different local resonance patterns possible in a long poly(*meta*-benzylidene) chain.

Of these 8 monomer arrangements without an aromatic sextet: 3 (denoted by $B_\circledR$) involve transferring one unpaired bridge electron from the bridge on the left of a ring, 3 (denoted by $B_\neg$) involve transferring one unpaired electron into the ring from the bridge on the right, and 1 (denoted by $B_{\circledR\neg}$) involves transferring unpaired electrons from both adjacent bridges. Thence, further denoting the monomer arrangement with the no unpaired electrons transferred into a ring by $B_\mathbf{o}$, we have 4 types of local Clar structures, and there are only certain possibilities for the type of ring which may follow a given one:

$$B_\mathbf{o} \rightarrow B_\mathbf{o} + B_\rightarrow + B_\leftarrow + B_{\rightarrow\leftarrow}$$
$$B_\rightarrow \rightarrow B_\mathbf{o} + B_\rightarrow + B_\leftarrow + B_{\rightarrow\leftarrow}$$
$$B_\leftarrow \rightarrow B_\mathbf{o} + B_\leftarrow$$
$$B_{\rightarrow\leftarrow} \rightarrow B_\mathbf{o} + B_\leftarrow$$

That is, following an A-type any one of the types of rings may follow, whereas following a $B_{\circledR\neg}$-type there may only follow A and $B_\neg$ types, which do not involve an unpaired electron from the intervening bridge being transferred into the following ring, as it has already been transferred into the preceding ring. Thence the number $\#_{N+1}(\xi)$ of Clar structures in an $N+1$-ring chain such that the last ring is of type ξ is given by

$$\begin{pmatrix} \#_{N+1}(\mathbf{o}) \\ \#_{N+1}(\rightarrow) \\ \#_{N+1}(\leftarrow) \\ \#_{N+1}(\rightarrow\leftarrow) \end{pmatrix} = \begin{pmatrix} x & 3 & 3 & 1 \\ x & 3 & 3 & 1 \\ x & 0 & 3 & 0 \\ x & 0 & 3 & 0 \end{pmatrix} \begin{pmatrix} \#_N(\mathbf{o}) \\ \#_N(\rightarrow) \\ \#_N(\leftarrow) \\ \#_N(\rightarrow\leftarrow) \end{pmatrix}$$

where also we have introduced a weight x when the resulting $N+1$th ring is a Clar sextet. That is, to obtain the literal (unweighted) Clar-structure count, one should take $x = 1$, whereas if one were to seek Kekulé-structure counts, one should take $x = 2$ (corresponding to the two ways to conjugate around a Clar-sextet ring). But other weights might be relevant in a quantitative treatment, and a derivative with respect to x provides an elegant way to average numbers of Clar sextets in the various rings (with of course the weight x favoring different structures differently). Also other averages, say as to the location of the unpaired electrons might be handled similarly. This indeed leads to a transfer-matrix approach to deal with such long polymers, as has been discussed in a fairly general context elsewhere [92].

IV.4. Non-maximum Pairing, Incipient Radicalism, and Defected Polymers.

There are examples of where say for a Kekuléan structure, it may be worthwhile to introduce a few unpaired electrons, so as to obtain many more resonance structures. That is, in suitable circumstances the stabilizing effect of the resonance may overwhelm the destabilizing cost of the unpaired electrons. A prototypical example of this is provided by the case of the polyacenes. For instance, for tetracene there are four Clar structures with a single Clar sextet and no unpaired electrons, while there are six Clar structures with two Clar sextets and two unpaired electrons. In this case there is not very much gain in the number of resonance structures by unpairing electrons to gain an extra Clar sextet, so that these extra structures do not make overly great contributions to the ground-state wave-function. But as one goes to higher N-acenes, the situation changes notably. The number of single-sextet Clar structures in N-acenes is N while the number of double-sextet structures (with 2 unpaired electrons) is $\frac{1}{12}N(N-1)^2(N-2)$, as is illustrated in Fig. (**28**) (for the case of tetracene). Thus the ratio between the double-sextets and the single sextets is $(N-1)^2(N-2)/12$, and eventually, for sufficiently large N, the number of double-sextets becomes overwhelming:

$N = \#_{\text{rings}} = \#_{\text{single-sextets}} =$	1	2	3	4	5	6	7	8	9	10	11	12
$\#_{\text{double-sextets}} =$	0	0	1	6	20	50	105	196	336	540	825	1210

That is, the double-sextet structures with 2 unpaired electrons eventually come to dominate, and the structure appears diradicaloid. This is, in fact consistent with much more elaborate *ab initio* quantum chemical computations – that is, they reveal that the ground-state approaches (say as N increases through 6, 7, 8) having two singly occupied MOs, with a low-lying triplet pairing of these 2 MOs also possible. Moreover, the present argument reveals that for large enough N, it is appropriate to describe the polyacenes as polyradicaloid, with a number of unpairings increasing in proportion to N. Of course, the reactivity of such radicaloid species increases rapidly, so that the experimental situation finds hexacene as the highest well-characterized (but very reactive) species.

Organic chemists know that anthracene and the especially higher N-acenes undergo easily addition of hydrogen and halogens at *meso*-positions, they form moloxides with oxygen from air (i.e., with a peroxide linkage between two C atoms) or *meso*-quinones, and react with dienophiles. The longest stable acene known till now with several specially
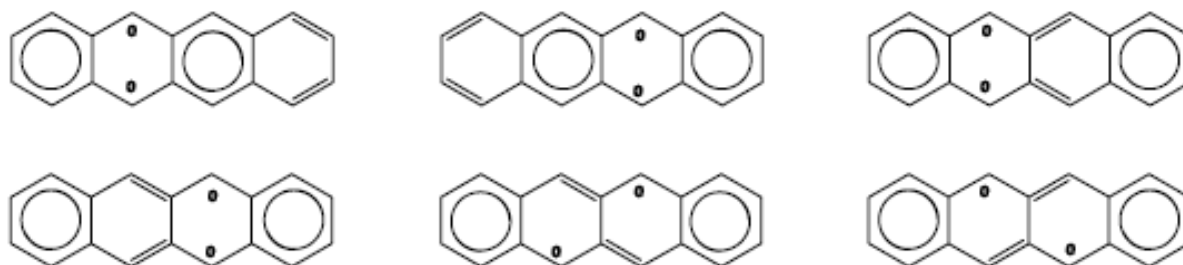

Fig. (28). Radicaloid Clar structures in an acene with an even number $2n$ ($n = 2$) of benzenoid rings.

devised bulky substituents has nine benzenoid rings [101]; the unsubstituted nonacene was obtained by photo-generation in argon matrix at 30 K [102].

This result might be contrasted with a stable species rich in fully paired Clar-structures (and Kekulé-structures), such as the armchair chain of hexagons, for which a Clar structure has already been indicated in Fig. (**29**). Here there is basically no opportunity to introduce more Clar sextets, though one can obtain additional structures with unpaired electrons if one sacrifices one of the Clar sextets. In particular, for a chain of $N = 2n+1$ hexagons, one sees that there is a single sextet-maximum Clar structure with $n + 1$ Clar sextets, and that any one of them might be sacrificed to give structures with unpaired electrons, so that the number of diradicaloid structures one short of the maximum number of Clar sextets is $\sim n \sim N$. Here it is noted that the two unpaired electrons cannot be far separated (for a lone unpaired electron induces a change from one long-range-order class to another, as discussed in conjunction with Fig. (**26**), which costs a number of Clar sextets proportional to the distance), till one switches back to the Clar-structure-rich phase with the second unpaired electron. For the present case, switching between two phases is indicated in Fig. (**30**). That is, not only can one not introduce an additional Clar sextet by adding unpaired electrons, but one in fact one loses one Clar sextet, while one gets back only $\sim N$ resonance structures.
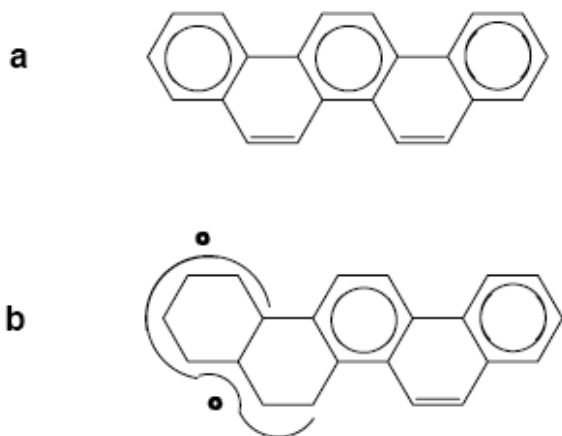

Fig. (29). Diradicaloid Clar structure of a zigzag fibonacene with $2n + 1$ ($n = 2$) benzenoid rings.

Another sort of circumstance occurs when at the end of a long polymer the pattern of termination does not match up correctly with the Clar-sextet-rich phase of the bulk of the polymer chain. This can be simply illustrated by a circumstance, such as indicated in Fig. (**31**), where a (small) poly-*para*-phenylene chain of just $N = 6$ links is imagined to have each end with a lone bond. The result is seen to be
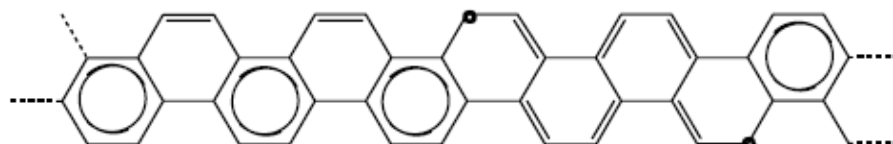
Kekuléan – but with only a single Kekulé structure, as indicated. The point is that there are many more Kekulé structures, and indeed a 6-Clar-sextet Clar structure as also indicated. Thence at least for a sufficiently long chain the Clar-sextet-rich structure will be favored (with much more sextet resonance). Indeed this is supported by MO-band-theoretic computations [103,104].

In fact such occurrences at the ends of benzenoid polymer strips can be anticipated to be typical – because of the long-range order already noted to be present in such strips.

V. "TWO-DIMENSIONAL" STRUCTURES

The two-dimensional structures considered here are those based largely on graphene, and are generally imagined to be confined to a plane, though they need not fill it, and though they need to have two distinct directions of large (*e.g.*, approaching infinite) extent.

IV.1. Graphene

One might seek to see if ideas similar to that of the preceding section apply to localized defects in graphene, but first it is appropriate to address simple extended bulk graphene. Large portions of graphene (monatomic-thickness graphite flakes) have been first made by mechanical approaches out of natural graphite by Geim, Novoselov and coworkers [51,52] and these flakes have proved to have especially novel electronic conductivity, along with other fascinating properties, giving rise to an intense field of research. Numerous applications are likely to appear. Thence graphene research has become a quite intense field, and various other ways of making graphene have been devised. On looking at a piece of a graphene sheet with Clar circles drawn in as densely as possible it is evident that the Clar circles may be viewed to follow poly-*para*-phenylene chains. Indeed they follow every third poly-*para*-phenylene chain in a considered acenic direction – and there are 3 choices then for the selected poly-*para*-phenylene chain, so that infinite graphene manifests 3 equivalent sextet-maximum Clar structures. Now since graphene manifests but a single bond length in the bulk, the Clar-sextets cannot be localized (with shorter aromatic length bonds and longer inter-sextet bonds). Evidently the sextet-maximum Clar structures must admix to such an extent with the non-maximum ones, that one should describe bulk graphene in terms of the triple of sextet-maximum ones, as well as the related underlying Clar structures with less than the maximum number of Clar sextets. [The sextet-non-maximum structures must be admixed since between the sextet-maximum 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 stud-
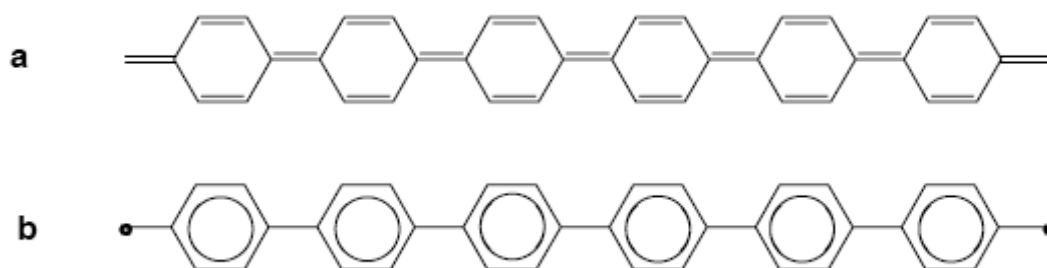

Fig. (30). The poly-phenacenic benzenoid strip having a uniform width of one hexagon as in Fig. **19**, but with two extra π-electrons at a certain distance from one another.

Fig. (31). Diradicaloid character versus loss of aromaticity in poly(*para*-phenylene) chains.

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

IV.2. Vacancy-Defected Graphene

As to the possibilities of defects in graphite, we might consider the example of a defect consisting of a single vacancy in an otherwise perfect graphite net. In this case one has a circumstance as in Fig. (**32**), where also we show a portion of one of the three sextet-maximum Clar structures of graphene, deleting parts of it which would be otherwise incident with the missing site at the vacancy. In this figure one sees that the bulk characteristic of the sextet-maximum Clar structure leaves a net of one site in the neighborhood of
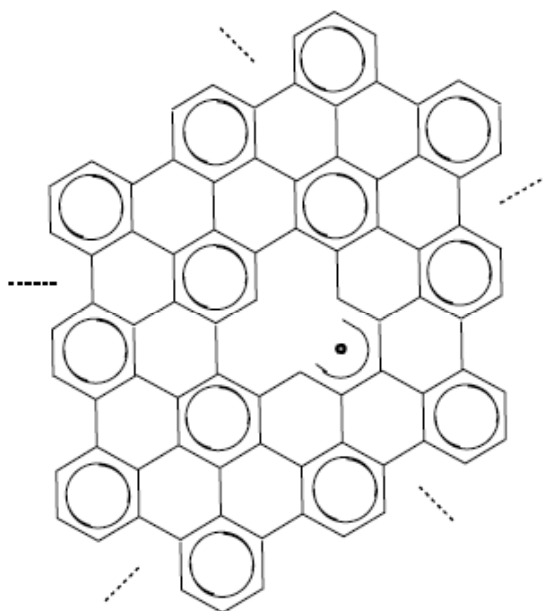
the vacancy unpaired. Each of the other two sextet-maximum Clar structures similarly leave one site unpaired near the vacancy. Thus overall one can expect a single defect-localized unpaired electron in the neighborhood of the vacancy – and indeed one can see that the bulk of the spin density of this unpaired electron should appear on sites of the opposite type (starred *vs.* un-starred) of that the site missing at the vacancy. Indeed this prediction [105,106,] also appears from a resonating VB picture, and is also found [105,106] from numerical evidence for the Hückel model.

The prediction of the preceding paragraph may be contrasted with that for a neighbor-pair double vacancy, such as indicated in Fig. (**33**). There one sees again a similar portion of a grapheneic sextet-maximum Clar structure, and some remnant sites near the defect not included in any Clar-sextet of this structure. In this case there remain no unpaired electrons, which in this case again agrees with a general resonating VB picture, as well as numerical evidence from the Hückel model.
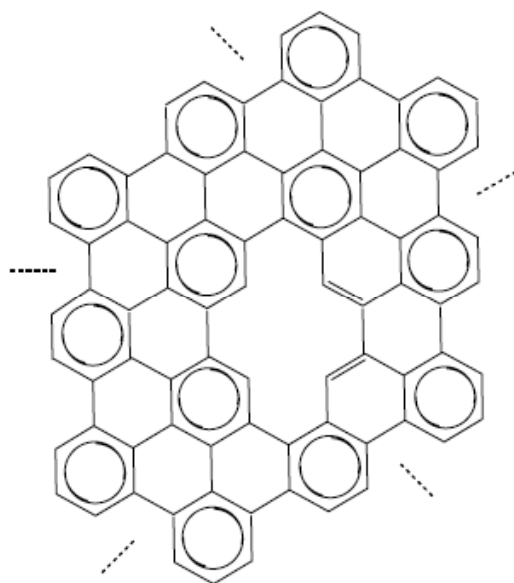

Fig. (33). A graphene portion with a C–C fragment deficiency.

V.3. Semi-Infinite Graphene

A graphene sheet has sextet-maximum Clar structures with a Clar sextet for every third benzenoid ring along each linear acene direction. If the topological (ring-center to ring-center) distances between two "sextet rings" along the acenic portions of an interconnecting path is denoted by h and k (h

Fig. (32). A radicaloid graphene portion with one carbon deficiency.

$\geq k$), then the difference $h - k$ is always a multiple of 3, as has some significance in relations to nano-tori and nano-tubes (in Fig. **34**, h and k are 2 and 5, respectively). Being sextet-resonant, the species should be especially stable, with a notable resonance energy, such as is indeed found from conjugated-circuits computations [96,97], quantitative Pauling-Wheland resonance theory [6], and even Hückel MO theory. Since there are 3 different sextet-maximal Clar structures, and further very many other Clar structures, overall with sextets uniformly spread out over the sheet, there is no sextet (or pairing) localization.
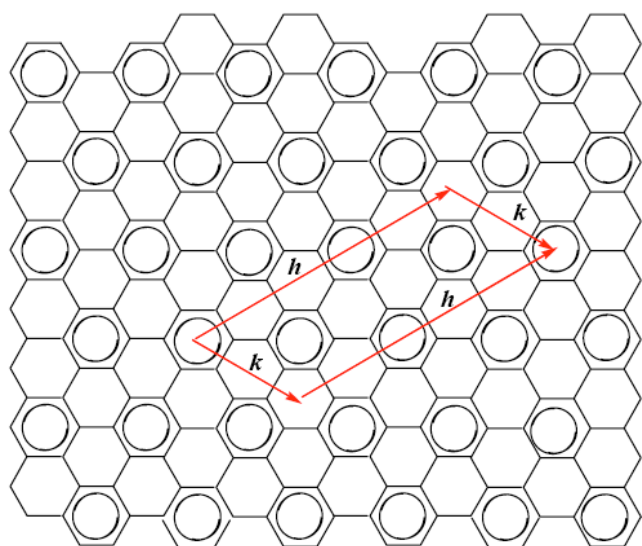

Fig. (34). Part of a graphene sheet with $h = 5$ and $k = 2$ vectors (red arrows) between two "sextet" hexagons.

A further application concerns semi-infinite graphite which is a sheet of graphite from which half the sheet has been cut away, so that a long boundary remains. For these structures one naturally presumes that in the deep interior the relevant Clar structures there look somewhat like that for infinite graphite with a complex of disjoint Clar sextets. Implementation of this idea for the circumstance of an acenic (zigzag) boundary gives a result as indicated in Fig. (**35a**), where one sees that a fully paired structure cannot be propagated all the way up to the edge. Indeed one sees that unpaired electrons necessarily arise somewhere in the region of the edge – with 1 unpaired electron per 3 hexagons of edge. One understands that the Clar sextets are not localized in the interior, so that equally one can imagine a relevant Clar structure with the Clar sextets translated one unit along the direction of the edge. Thence it is better to say that there is 1/3 of an unpaired electron per unit cell of edge. Notably this is in agreement with more conventional resonance-theoretic arguments [105,107] and rather impressively with simple UHF-MO computations. [105,107,108] That is, these computations give a band gap of zero and a boundary localized density of states at the Fermi energy corresponding to 1/3 of an electron per unit cell of boundary – and furthermore this unpaired spin density is localized near the edge on the same class of sites (*i.e.*, starred *vs.* un-starred) as indicated in Fig. (**35a**).

As a second example, one may similarly consider the boundary of Fig. (**35b**), drawing in a sextet-resonant network

in the interior of the network away from the boundary, and extending the sextets and pairings in so as far as possible up to the boundary, as illustrated in this figure. Then one sees that 2/3 of an unpaired electron per unit cell of edge is predicted, as again is in agreement with more conventional resonance theory [109] and with simple UHF-MO computations [108].
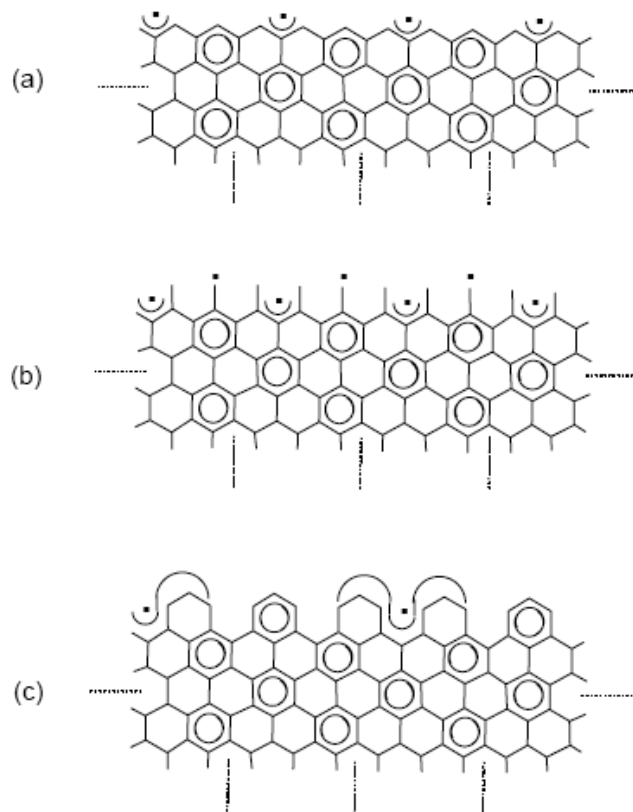

Fig. (35). Part of a graphene sheet with Clar sextet hexagons (black) and with the anti-sextet dualist (red) circumscribing sextet rings.

A third example manifests a different sort of consequence. Consider the armchair edge as of Fig. (**36**) whence one sees that the structure is sextet resonant, with the bonds in the bottoms of the armchairs more nearly single (than aromatic), and hence longer. There are further bonds in the indicated Clar structure which appear as single, and they may be anticipated to be so when near the boundary. But in the interior very far from the boundary the situation should locally appear much as in (boundary-less) graphite, so that there Clar sextets are delocalized to other rings, and in the deep interior all the bonds appear somewhat "aromatic" (Pauling pi-bond order 1/3). Moreover, with this delocalization one anticipates a small band gap, indeed = 0 as for graphene (since the interior looks like graphene). The prediction of no boundary-localized unpaired spins is verified [6, 109] by more conventional resonance-theoretic arguments, and the predictions of zero band gap without edge-localized spin density is verified [109, 110] by simple UHF-MO computations, while the localization of near single bonds near the edge does not seem yet to have been so tested, but it is manifested to a degree in simple Hückel-theoretic computations on large benzenoid fragments [111, 112]. Local aromaticity
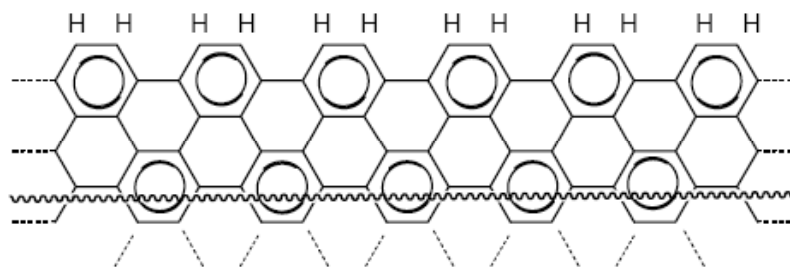
Fig. (36). Armchair border of a semi-infinite graphene sheet.

indices near this boundary should show some localization of aromatic and non-aromatic rings, with the degree of localization falling off toward the interior. Here there seem to be no MO-theoretic tests of this prediction, though one can see such a tendency in NICS values [35] for large benzenoid fragments.

Yet further there is experimental (STM) evidence which is consistent with the predictions for the zig-zag and armchair predictions, as seen in Figs. (**35a** and **36**). In conclusion, the Clar arguments as extended here seem to be quite consistent with chemical reality, at least for the case of semiinfinite graphite. Of course, one should perhaps not be too surprised after the success of resonating VB theory, such as we have argued is intimately related to Clar theory.

V.4. Fractal Benzenoids

One may imagine benzenoids which exceed one dimension yet do not quite get to two dimensions, but are indicated here since they need the Euclidean plane for the proper description. The idea is that there are empty regions at ever larger scales, so that the number of atoms in an area depends on the length scale L of the area $\sim L^2$. That is, the number of atoms at a scale of L would be $\sim L^D$, with D the socalled *fractal dimension* of the structure – following B. Mandelbrot's view [113]. Note here that for a linear polymer (or polymer strip) we have $D = 1$, and for graphene we have $D = 2$. An example of a fractal is typically best built up in stages, and in Fig. (**37**) are the 3 lead stages of one [114]. The first stage structure (as is eminently appropriate for benzenoids) is benzene, and the second stage may be viewed to be obtained by fusing 6 copies of benzene together around a ring – to give coronene. The third stage takes 6 copies of coronene and fuses them together around a (larger) ring. To obtain the $(N+1)$th stage, 6 copies of the Nth stage structure are taken and fused together. Continuation of this process yields structures which approach a fractal benzenoid. Here one may note that the number $\#_n$ of carbon atoms at the nth stage is $\#_n = (3 \cdot 6^n + 2)/3$ and the distance across the structure is $l_n = (3^n + 3)l_0/6$, so that its fractal dimension D should be such that $\#_n$ and l_n^D approach proportionality to one another (as $n \to \infty$), which gives

$$D = \frac{\lim}{n \to \infty} \frac{\log \#_n}{\log l_n} = \frac{\log 6}{\log 3} \cong 1.63093$$

which is a nice intermediate dimension.

There is a question of what novel properties such structures might manifest. The Kekulé structures and conjugatedcircuits resonance energies appear [114] much like that of other stable benzenoids, and one imagines qualitatively the same from drawing in Clar sextets to make Clar structures (of which there are many). Of course, the mass density is anomalous, but also there presumably should be a variety of "self-similarity" characteristics, suspected from the mode of construction. For instance, it has been argued [114] that the C−H stretching spectrum, the proton-NMR spectrum, and the ^{13}C-NMR spectrum should show fractal characteristics. We also imagine that the Hückel eigenvalue spectrum should be fractal for this molecule, which should have a notable HOMO-LUMO gap even in the limit of large structures. If one constructs a fractal species which manifests fractality in the eigen-spectrum near the Fermi level, then this should manifest notable behavior in terms of the temperature dependence of electrical conductivity. The heat capacities should also have "anomalous" (*i.e.*, non-Debye) behavior. Relatively few theoretical studies have been made (from any theoretical perspective). But such species have not yet been prepared – at least in any remotely well characterized form. One might plausibly imagine that coal can be viewed as fractal, but of a random sort, with regions where there are unpaired electrons, and various impurity hetero-atoms attached.

There are of course, many other possible structures conceivable for fractal benzenoids. One other based on the socalled "Sierpinski gasket" has been considered in some detail [115]. Yet another possibility, based on a different iteration of a coronene (and then later of a different "supercoronenic") unit, is illustrated in Fig. (**38**). One may speculate that coal may be well viewed as a random fractal of conjugated benzenoid network, with holes at ever larger scales (as well as occasional substitutional side groups, involving other types of atoms).

VI. "3-DIMENSIONAL" CONJUGATED-CARBONS CURVED IN 1 DIRECTION

Here we have in mind structures which globally bend the conjugated π-network away from the local molecular plane. The bending away from a plane generally introduces some degree of stress and strain, so that some general consideration of the relation of this to curvature of the molecular "plane" is appropriately first discussed. Yet further because now we use "dimensionality" somewhat differently than in the preceding sections, and because there is a great diversity of such 3-dimensional structures, just the finite ones are discussed in this chapter while the extended ones are considered in the next chapter.
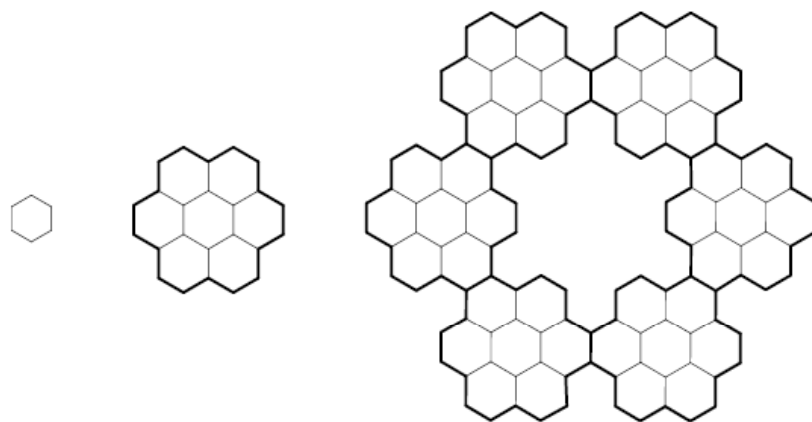
Fig. (37). Fractal benzenoid composed of coronene fragments (thick lines) examined in ref. [114].
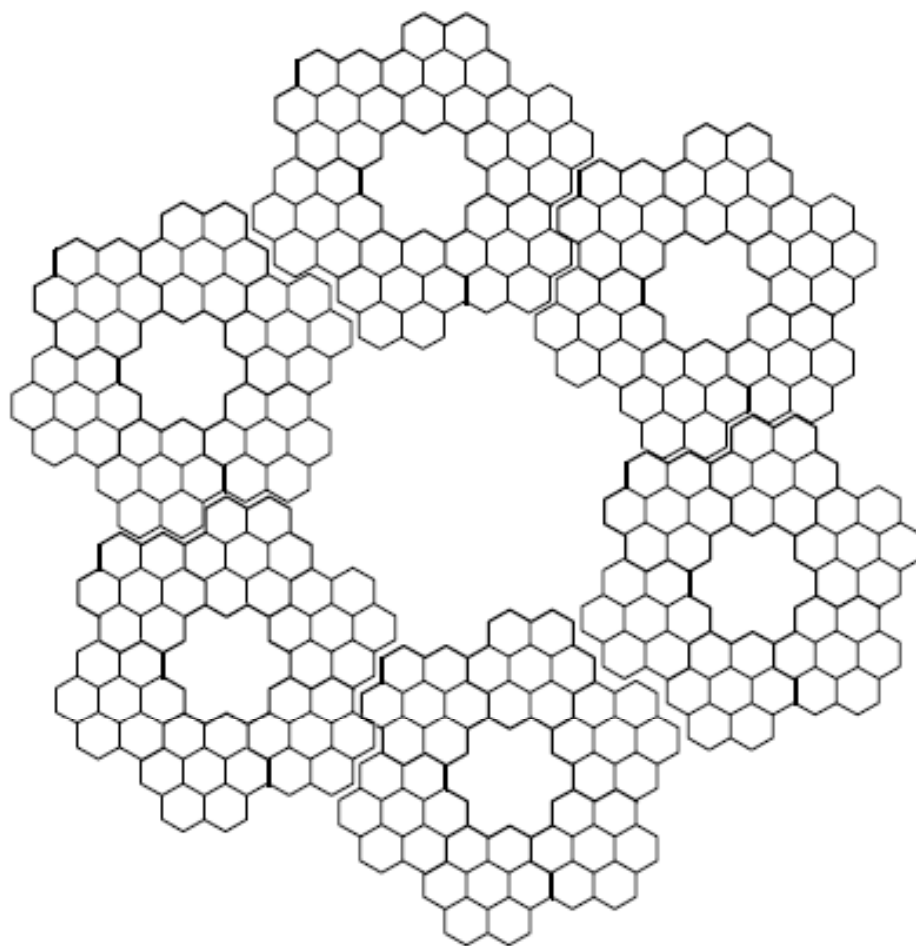

Fig. (38). A fractal benzenoid, indicating how 6 coronene units combine into a unit U that surrounds a "coronenic hole" by merging 6×3 C–C bonds, and how 6 such resultant units U combine into a larger unit surrounding the larger hole modeled after U, by merging 6×9 C–C bonds. In the latter case the merging of these 6×9 C–C bonds has not yet been quite completed.

VI. 1. Single-Direction Curving into Three Dimensions

Given a conjugated network defining a locally Euclidean surface, a curving into three-dimensions may take place with the curving occurring either in one or two directions in the surface. But the simpler curving occurs in only one direction identified with a straight line in the parent surface. Then the *linear curvature* γ measures the rate of change of direction with distance, so that

$$\gamma \equiv 1 / r$$

with r the radius of the circle which "kisses" as closely as possible the curve (this circle occurring in a plane normal to the network surface at the point of contact). If this curvature remains constant the surface circles back on itself, to give either a circular polymer (if the extent in the transverse direction is limited) or else a nano-tube (if the structure is ex-

tended in the transverse direction). If the curvature is not constant, the surface can still join back to itself, after an integrated curvature change say of a full cycle (2π radians) is achieved. Of course, something else could happen, with the structure wrapping into a layered or scroll-like structure, which however in many cases would tend to unwrap unless there were something to keep it in this curved state. The net curvature γ_{net} along a piecewise straight path is the sum of the curvatures integrated along each straight segment.

Even without curvature reaching the full cycle value a benzenoid structure may turn about within its molecular plane and return to itself, most simply to form a so-called coronoid. But also the structure can turn about to return to the same region without bonding to its original self, if steric hindrance keeps the curving from relaxing. Indeed this is what happens with helicenes [116], where the conjugated-network surface then overlays itself – the structure in the common helicenes just being a cata-condensed chain of hexagons just a single hexagon wide. If such a benzenoid chain continues on after passing over its original beginning, it can still ultimately rejoin to its beginning. Though the curvature needs to deviate from 0, the net integrated curvature can still be 0. In such cases, cycles can be imagined to form knots, or two or more cycles can form links [117]. A simple graphical measure of the amount of turning of such a benzenoid cycle in the surface is in general relevant, and may be given in terms of a path traced out from ring-center to adjacent ring center, with the path being straight at a given ring if it passes through opposite sides of the hexagon, and being $\pm 60^{\circ} = \pm \pi / 3 \ \text{rad}$ for a turn with the path entering and exiting through next-neighbor sides of a ring to the left or right. Thus the turn at the central ring of anthracene is 0, and at the central ring of phenanthrene, it is $\pm 60^{\circ}$. The *net turn* τ of such a path then is the sum of the local turn values in each hexagon along the path. Thus usual coronoids, one of which appears in Fig. (**39a**), exhibit $\tau = 2\pi$, whereas Fig. (**39b**) exhibits a cyclic chain with $\tau = \pi$, and Fig. (**39c**) shows a cyclic chain with $\tau = 0$. Note however that the net curvature is $\gamma_{net} = 0$ in the first combinatorially "flat" case, $\gamma_{net} \cong \pi$ in the second case, and $\gamma_{net} = 2\pi$ for the third case "bracelet". That is, for such cyclic chains one expects a complementarity

$$\tau + \gamma_{net} \cong 2\pi$$

where we have defined τ in a combinatorial graphical way, and γ_{net} in a geometrical way. This mixing of graphical and geometric invariants makes the result approximate, though we anticipate that for the equilibrium structures it should be close to correct.

VI.2. Molecular Belts: Cyclo-acenes, Cyclo-phenacenes, Möbius Analogs, Etc.

Molecular belts may be viewed as polymers without ends, but rather with cyclic boundary conditions. If it is a strip of single hexagons, we term it a cyclo-phenacene, and if every ring in such a strip is conbinatorially straight (with the ring-center to adjacent ring-center passing through opposite

sides of a ring), then it is termed a cyclo-acene, or cyclo-polyacene. Granted non-Mobius connection, the cyclacenes have net curvature $\gamma_{net} = 0$ (as in Fig. (**39c**)), while the general poly-phenacenes can have other nonzero values of net curvature, though often the literature considers just the case of $\gamma_{net} = 0$.
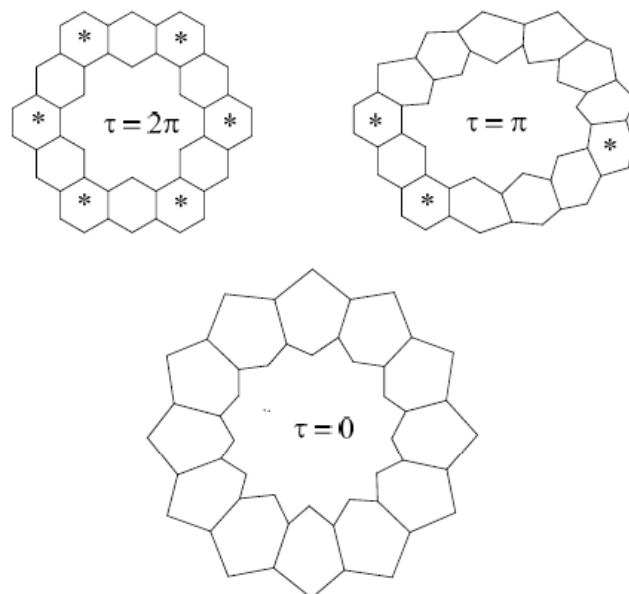

Fig. (39). Three coronenes or cyclophenacenes with different net turn angles. The rings which make $\pi/3$ contributions are marked with an asterisk. The first coronene is kekulene, and the last is [12]cyclacene.

Unlike non-conjugated molecular belts such as collarenes (Fig. (**40a**)) or beltenes (Fig. (**40b**)), cyclo-polyacenes (Fig. **41**) do possess conjugation and the reduction of *p*-orbital overlap decreases with increasing number of benzenoid rings; however, as argued earlier, the stability of acenes decreases markedly under this circumstance.
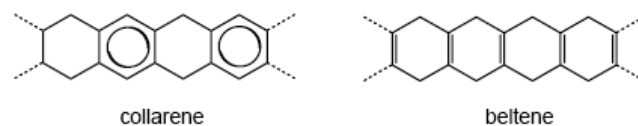

Fig. (40). Collarenes (benzenoid rings separated by pairs of CH_2 groups) and non-conjugated beltenes.

So far, no such simple polyacenic molecular belts are known [117-119]. But as a first estimate they should be not too unlike the poly-acene strips considered earlier, though these belts differ in not being geometrically flat, and further the cyclic ones do not admit even a single Clar sextet without unpaired electrons. To obtain a single Clar sextet in a cyclo-*N*-acene, one needs to introduce 2 unpaired electrons – there are *N* possible positions for the Clar sextet, and $(N-1)^2$ positions for the unpaired electron, so that again the structures with 2 unpaired electrons become more numerous by a factor now of $\frac{1}{4}N(N-1)^2$, and are expected to dominate for sufficiently high *N*. That is, much as for the flat poly-acenes, our extension of Clar's ideas predicts that the

cyclo-polyacenes should manifest incipient diradicalism (and for larger cycles, polyradicalism). However, one can imagine that adding benzenoid rings for obtaining claromatic conjugated molecular belts, one could obtain stable 3D-systems; one example is shown in Fig. (**42**).
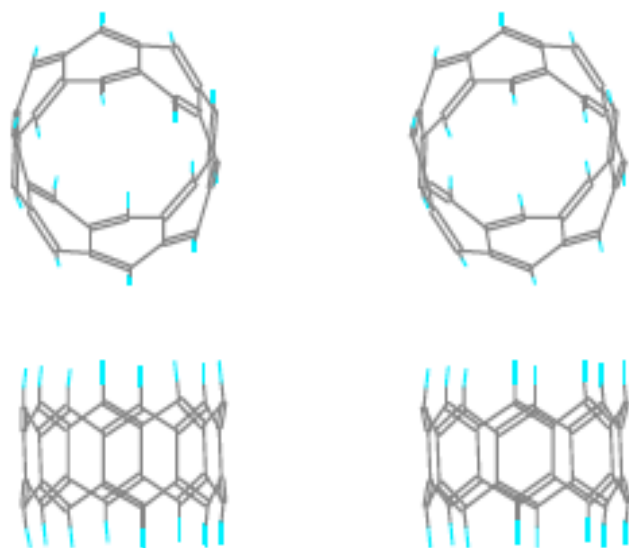

Fig. (41). Stereo-view of [8]cyclacene with hydrogens (blue).
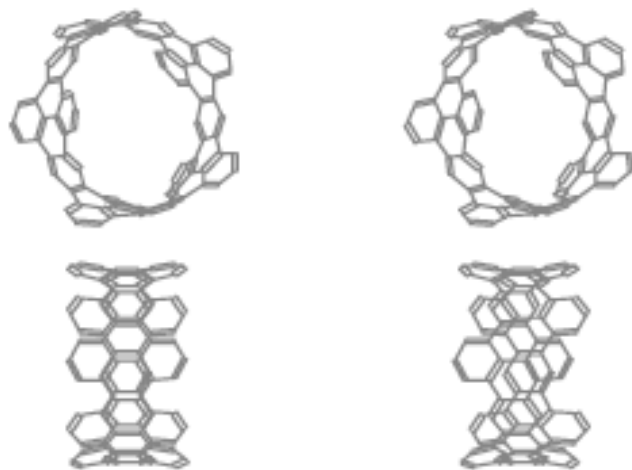

Fig. (42). Stereo-view of a conjugated belt with sextet-resonant (claromatic) structure.

Gleiter and coworkers [120] synthesized a non-benzenoid conjugated system: [6.8]$_3$-cyclacene with three benzenoid rings condensed with three crown-shaped cyclo-octatetraene rings, shown in Fig. (**43**). Whereas all bonds of the 6-membered rings are practically planar, the 8-membered rings are in crown (tub) form, as in cyclo-octatetraene – where the stress due to the linear curvature is presumably relieved, in as much as such an anti-Hückel eight-membered ring, even on its own, prefers to so distort. Such systems are actually related to collarenes, in which the pairs of −CH$_2$− groups have been replaced by pairs of vinylene groups −CH=CH−.

If an armchair construction is taken, the situation is much different, as these structures (cyclophenacenes) are rich in Clar structures with many Clar sextets (up to every other
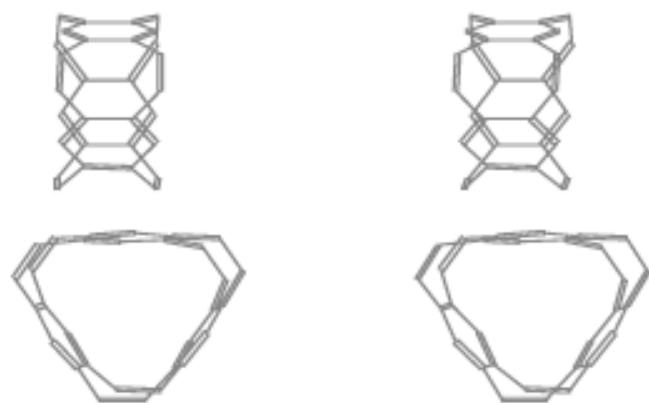

Fig. (43). Stereo-view of the [6.8]$_3$-cyclacene with three benzenoid rings condensed with three crown-shaped cyclooctatetraene rings, a pseudo-conjugated belt synthesized by Gleiter and coworkers [120].

ring) without the introduction of any unpaired electrons. Again these structures are much like their open-chain analogues, and both are predicted to be stable species, with a notable HOMO-LUMO gap. The [10]-cyclo-phenacene is illustrated in Fig. (**44**). It can be considered to be a short nano-tube. An ingenious approach for the synthesis of [10]-cyclo-phenacene (as part of a fullerene skeleton) was devised by Nakamura and coworkers [11-13]: (i) buckminsterfullerene was converted by a methyl-copper reagent into its penta-methyl derivative; (ii) the acidic proton of the cyclo-pentadienic "north pole" was protected by replacement with a cyano group; (iii) the "south pole" was similarly phenylated with a phenyl-copper reagent; (iv) the cyano-pentamethyl-pentaphenyl-C$_{60}$-fullerene on treatment with molecular oxygen afforded C$_{60}$Me$_5$Ph$_5$O$_3$(OH)$_2$, with an "equatorial [10]-cyclo-phenacene" belt containing 40 sp^2-hybridized carbon atoms that showed less bond alternation (by X-ray analysis) than C$_{60}$-fullerene, which presents marked bond alternation (1.36 vs. 1.47 Å). Only the rings in this belt have high negative NICS values indicative of aromaticity, whereas the remaining rings have negligible NICS values.
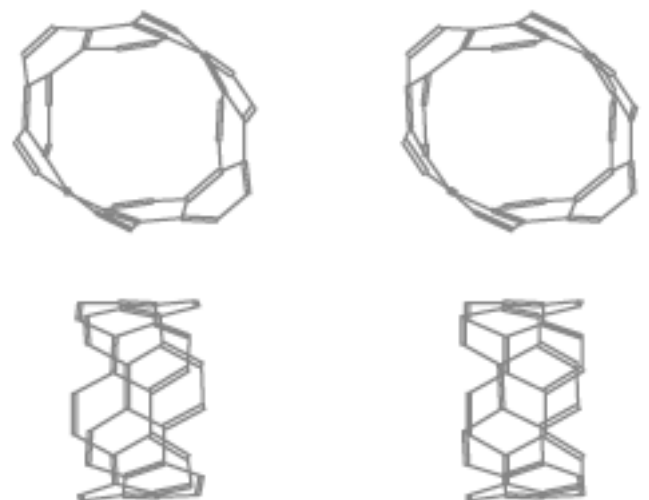

Fig. (44). Stereo-view of [10]cyclophenacene (hydrogens are not shown).

One can also imagine claromatic conjugated molecular belts derived from various other Fibonacci-like benzenoid strips other than zigzag ones. In the case presented in Fig. (**45**), however, steric hindrance between hydrogen atoms may destabilize the molecule; the molecular mechanics model shows the slight helicity due to this steric interaction.
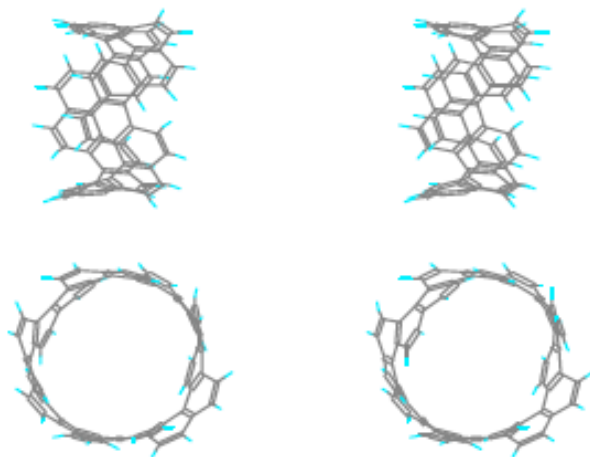

Fig. (45). Stereo-view of a congruent (claromatic) cyclo-crown ($C_{60}H_{32}$) related to fibonacenes; hydrogens are shown in blue.

A further consideration concerns what happens for a rather general chain with a mixture of aceneic zig-zag (aceneic) and armchair sections is considered. In such a case one could continue with the Clar-theoretic considerations, and something like this has already been done [48] – in terms of Kekulé structures, though because of the closeness of these ideas to Clar's, one can anticipate similar successful results. Dobrowolski [47] has reported *ab-initio* computations for each of the 52 (non-Möbius twisted) [6]cyclophenacenes with all various degrees of curvature, and it has been found [48] that the net turning angle τ correlates well with the stress involved in these species.

There is also the possibility of other sorts of benzenoid cyclic strips of more than hexagon width, even with the possibility of some being claromatic. Fig. (**46**) presents such a claromatic hydrocarbon, which is actually a short nano-tube.
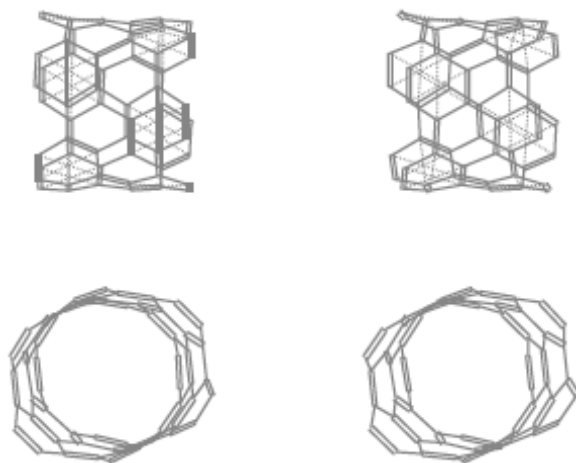

Fig. (46). Stereo-view of congruent sextet-resonant cyclo-bis-polyphenacene (cyclic strip 2,2) with 20 benzenoid rings. In the upper view, dotted lines denote 10 Clar sextet rings.

We end this section by mentioning that belt *para*-polyphenylenes are conjugated claromatic molecules, and could be considered to be the shortest possible nano-tubes. One must also mention cyclic 3D-systems derived from higher benzenoids, such as the belt formed from four anthracenic fragments attached by 9,10-bonds synthesized by Herges and coworkers [121a] and shown in Fig. **47**). With substituted anthracene fragments, chiral molecules resulted, and they could be separated into enantiomers [121b]. Interestingly, pyrolysis converted the compound of Fig. (**48**) into a system with a 7-membered ring [121c] as seen in Fig. (**48**).
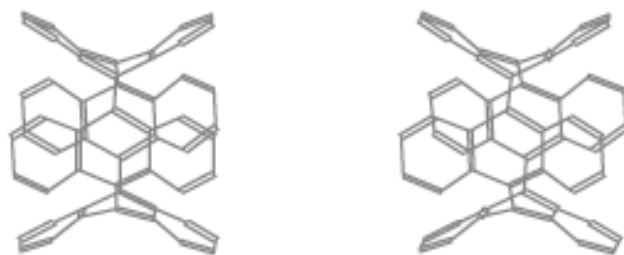

Fig. (47). Stereo-view of a belt formed from four anthracenic fragments attached by 9,10-bonds.
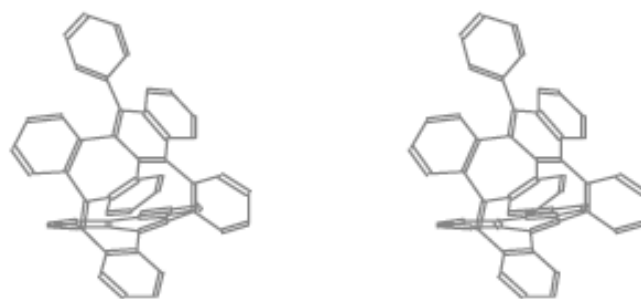

Fig. (48). Stereo-view of the hydrocarbon formed by thermal rearrangement of the tetra-anthracenic belt shown in the previous figure.

A modified situation is encountered with Möbius analogs of conjugated belts. Herges and coworkers [121d] have recently reviewed a number of theoretical and experimental facts connected with Möbius molecules, starting with the theoretical and experimental contributions of Heilbronner [41,42], Zimmerman [122a,b], Rzepa [122c,d] and Türker [122e], but evidently restricted to the circumstance of combinatorial "flatness" $\gamma_{net} = 0$. A survey of recent theoretical work including non-zero net curvature along with Möbius-twisting is found in [48]. Indeed with the stress introduced by such twisting, there seems to us to be no special reason to imagine that the combinatorially "flat" case is preferred. The coupling between linear (geometric) curvature, combinatorial turning, and twisting seems not to have yet been systematically explored. In so far as claromaticity is involved, one may expect that the Möbius analog (Fig. **49**) of the molecule presented in Fig. (**42**) would not benefit from aromaticity since it distorts the system more severely from planarity. More than a single twist of the plane could be considered also, whence the full treatment of such systems would include a twist number (which would be an indicator of geometric "torsion").
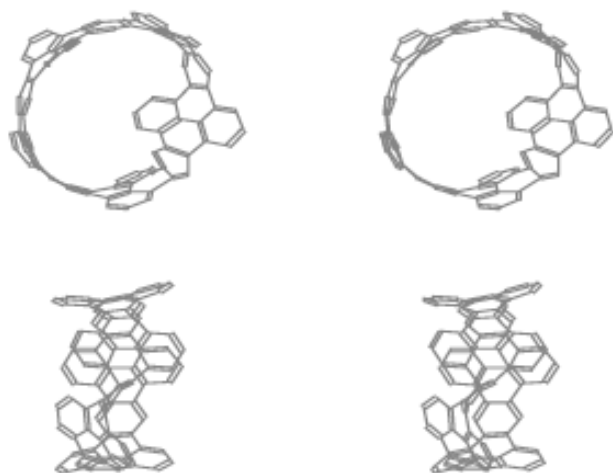
Fig. (49). A Möbius analog of the conjugated belt with decorated structure from Fig. **42**.

VI.3. Nano-Tubes and Clar-Sextets

As shown above, Geim, Novoselov and coworkers could isolate graphene flakes one-atom thick. On rolling such a flake into a cylinder, one obtains a single-wall nano-tube (SWNT). Ijima discovered in 1991 [31] that in the presence of transition metal atoms, carbon atoms at high temperatures and under controlled inert-gas conditions are able to generate multiple-wall nano-tubes (MWNTs). From them under oxidizing conditions one can obtain SWNTs.

The case when the folding of the graphene sheet proceeds without any full sector ($q = 0$) leads to a nano-tube, which can be considered as a nano-cone with apical angle 0°. Multi-walled collections of such nano-tubes were first obtained by Ijima, with their ends capped by hemispherical half-fullerenes [15]. Because the 5-membered rings are more reactive, the caps may be removed chemically by oxidation, and also one may obtain single-wall nano-tubes (SWNTs) of various lengths. Their study revealed interesting features which has led to an intense research activity and various applications.

For a nano-tube one may select [44] 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 "zig-zag" SWNT, and when $h = k$, one obtains an "armchair" SWNT. When $0 \neq k \neq h$, one obtains an (intrinsically) chiral nano-tube, 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 [9] a band-gap = 0 (neglecting curvature variations of the Hückel parameters), so that such claromatic nano-tubes should be readily conductive. Otherwise (with incongruent overlap) there is [9] a non-zero band gap, and the nano-tube is semi-conductive. As a result, all armchair SWNTs and ~1/3 of zigzag and chiral SWNTs are readily conductive, whereas ~2/3 of zigzag SWNTs are semi-conductive. Moreover, following Clar's ideas, the non-claromatic nano-tubes should manifest greater chemical reactivity.

Three stereo-views of claromatic (sextet-resonant) nano-tubes illustrate the above statements: a congruent armchair SWNT is presented in Fig. (**50**), a congruent zigzag SWNT in Fig. (**51**), and a congruent chiral SWNT in Fig. (**52**). An example of incongruent folding is shown in Fig. (**53**). In these cases, congruent means "claromatic" with only full and empty sextets, whereas incongruent means that the 3D architecture must contain double bonds associated with higher reactivity.

Fig. (50). Stereo-view of a sextet-resonant congruently-folded armchair SWNT with Clar sextet rings denoted by black dotted lines.

Fig. (51). Stereo-view of a sextet-resonant congruently-folded zigzag SWNT with Clar sextet rings denoted by dotted lines (upper views, black) and with the anti-sextet sextet dualist (red dotted lines, lower views).
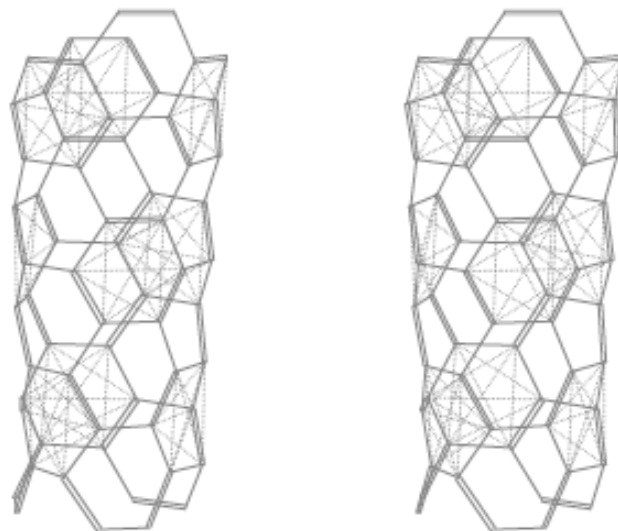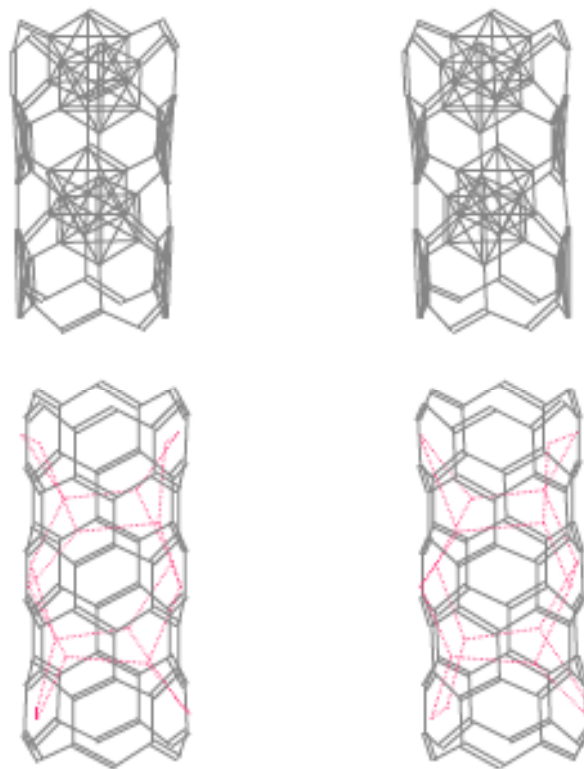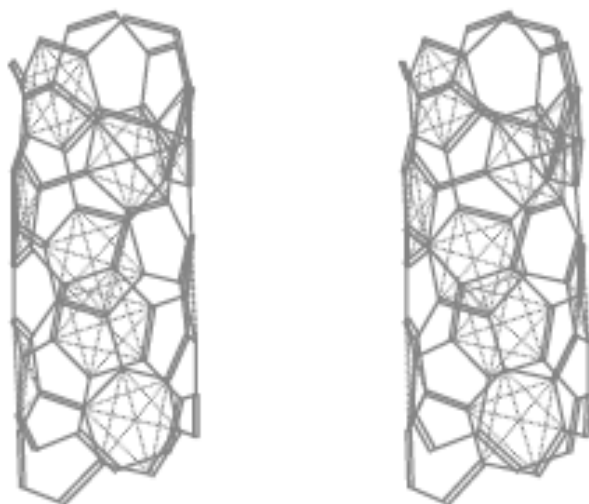
Fig. (52). Stereo-view of a sextet-resonant congruently-folded chiral SWNT with Clar sextet rings denoted by black dotted lines.
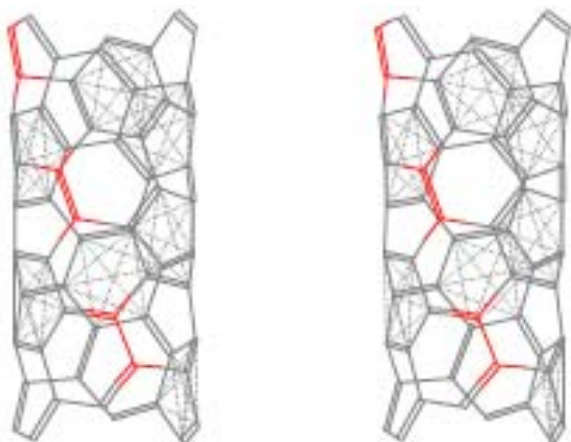

Fig. (53). Stereo-view of a chiral incongruently-folded SWNT: the red-colored carbon atoms break the Clar sextet-resonant structure of the folded graphene sheet.

The folding obeys [60] the same vector rules (h, k) as indicated in Fig. (**34**) and eq. (1). When $k = 0$, the folding occurs along an acenic portion and leads to an achiral SWNT with a zigzag edge. In this case a congruent folding of Clar sextet rings occurs if h is a multiple of 3. When $h = k$, the folding occurs along a poly-*para*-phenylenic direction and affords also an achiral SWNT but now with an armchair edge. In this case a congruent folding occurs if $h - k$ is a multiple of 3. Otherwise ($h \neq k \neq 0$) chiral SWNTs result, and congruent folding occurs whenever eq. 1 is fulfilled, which covers also the previous situations with achiral SWNTs.

$$h - k \equiv 0 \pmod 3 \qquad (1)$$

The resulting band-gap is zero when curvature variations of the Hückel parameters are neglected, so that the nano-tube will have a metallic conductivity, and otherwise it will behave as a semiconductor. As a result, all armchair SWNTs and one-third of zigzag and chiral SWNTs are metallic, whereas two-thirds are semiconducting.

Interestingly, the same purely graph-theoretic condition (1) holds if the positions of sextet rings overlap after rolling the Clar structured graphene sheet to a tubular structure. In this case the resulting structure is sextet-resonant (except perhaps at the tube ends) and so may be expected to have enhanced stabilization.

Some fullerenes which are doubly-capped nano-tubes and some fullerenes that obey the isolated-pentagon rule have Clar structures which are also sextet-resonant. Such Clar structures which are sextet-resonant (except possibly at the ends) are reasonably termed *bulk resonant* (as this identifies a bulk property of the tubes, rather than some global feature which would involve attention to the ends of the tube).

By contrast, on rolling up a Clar-structured graphene sheet into a nano-tube so that Clar sextet rings do not overlap, there result Clar structures with residual C=C double bonds that do not belong to Clar-sextet rings, and the resulting SWNT does not have a bulk resonant Clar structure .

Thence the occasional assertions of a contradiction with Clar's ideas that the 0-band-gap nano-tubes are sextet resonant is premature (or even incorrect) – rather the failure comes with a presumed correspondence of zero HOMO-LUMO-gap with reactivity. What Clar's ideas predict for these sextet-resonant nano-tubes then is that they are "aromatic" in terms of reactivity, and further that there is no bond localization. Indeed, both these things are also true for the nano-tubes which are not sextet resonant. The differences in behavior between small benzenoids and extended nano-structures is that the boundaries of small benzenoids play a significant role – *e.g.*, for the sextet-resonant case, the boundaries tend to "freeze in" the Clar sextets and thereby lead to bond localization – while extended sextet-resonant nano-tubes (or also graphene) do not have frozen in Clar sextets, or localized bonds.

VII. "3-DIMENSIONAL" CONJUGATED-CARBONS CURVED IN TWO DIRECTIONS

When there is curving of the conjugated-network surface the relevant geometric curvature has different features. And this we briefly review in the first section here, where-after various possible nano-structures involving such curvature ideas are considered.

VII.1. Double-Direction Curving into Three Dimensions

For curving in two directions in the network surface, the appropriate measure is conveniently given in terms of the net Gaussian curvature of the cone, when one assigns [123,124] a formal *combinatorial curvature* to each ring α, which for the present case with an ambient condition of degree-3 vertices and 6-membered faces gives combinatorial curvatures of

$$\kappa_\alpha \equiv \pi(6 - |\alpha|)/3$$

where $|\alpha|$ is the number of sites in α (or also the number of edges around α). Alternatively one can consider combinatorial curvatures

$$\kappa_i \equiv 2\pi(3 - |i|)/6$$

for each site of degree $|i|$ (also the number of edges around i). These combinatorial curvatures come in multiples of $\pi / 3$ (for these cases), and is exactly equal to this for either

a pentagon or a degree-2 vertex. *E.g.*, 12 pentagons yields 4π of curvature which matches to that for a polyhedron (a fullerene), and 6 pentagons give a fullereneic cap to a nano-tube. Leaving out this common factor of $\pi/3$, we obtain a succession of equivalences of combinatorial curvatures for different "defects":

5-gon (or $\bigcirc$)

4-gon (or $\square$) $\approx 2\,\bigcirc$ $\approx$ degree-2-vertex.

3-gon (or $\triangle$) $\approx 3\,\bigcirc$ $\approx 1\,\square + 1\,\bigcirc$ $\approx$ deg.-2-vertex $+ 1\,\bigcirc$

2-gon (or $\diamondsuit$) $\approx 4\,\bigcirc$ $\approx 2\,\square \approx 1\,\square + 2\,\bigcirc$, *etc.*

$5\,\bigcirc \approx 2\,\square + 1\,\bigcirc$ $\approx \square + \triangle$, *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 5 allowed for cones. If the total curvature is to match that of a closed compact surface S with Euler-Poincaré characteristic χ_S, then this leads to:

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

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 $\chi_S = 2$). Also this is equivalent to the statement, that

$$\sum_i \kappa_i = 2\pi \cdot \chi_S \text{ or } \sum_\alpha \kappa_\alpha = 2\pi \cdot \chi_S$$

which are natural (and rigorous) analogues of the Gauss-Bonnett theorem (involving geometric curvatures).

VII.2. Nano-Tori

Nano-tori, just like graphene, have no boundary and no defects, *i.e.*, no rings of any sizes other than 6, so that such nano-tori can be [125,126] viewed as elemental benzenoids (in having no H atoms). Indeed they can be viewed as graphene with cyclic boundary conditions (in two dimensions). It has been found [127] that SWNTs with a diameter ≈ 1.4 nm can be induced to coil and form tori (nano-tube 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 nano-tube to form a torus (that is, when a claromatic nano-tube forms a claromatic nano-torus). In Fig. (**23**) such a nano-torus is presented in stereo-view with a colored portion indicating Clar sextets. There are different ways [125,126,128] to describe nano-tori, 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 nano-tube. Thus to start, we characterize nano-tori in terms of the (h,k) pair for the nano-tube out of which it is constructed (h and k again indicating lengths of acenic portions of a circumscribing annular path around the generator nano-tube). Next there

is a *length* of the nano-tube, and this might be attempted to be specified by the number L of these complete (h,k) sections in the nano-tube used to construct the nano-torus. 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 nano-torus to fuse ends together is perhaps simplest when the nano-tube has $(h,k) = (h,0)$, for then the two ends of the nano-tube can each be viewed as zig-zag 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° give rise to distinct graphs. [Though two twists different by 360° give graphs which are the same, they are [126] embedded into Euclidean 3-space in topologically distinct ways, but this problem we do not address here. There is [126] also another embedding possibility interchanging the order of introduction of the two cyclicizing boundary conditions on a grapheneic 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 nano-tube.] Thus even when the nano-tube 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 3 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 nano-tube in the case when $k > 0$ is a little different. Then the two ends of the nano-tube are still conveniently chosen to have two aceneic 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 nano-tube, one can add short k-length acenes to one end such that the end remains of type (h,k); 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 aceneic 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°, which again leads to the same graph. Again even when $h - k = 0, \text{mod } 3$ the nano-torus may end up not having Clar-sextets at the two ends of the nano-cylinder whose ends are to be matched coincidently together to form a nano-torus, and thereby miss claromaticity. Again claromaticity is (disregarding curvature effects) necessary and sufficient for a zero HOMO-LUMO gap.

Overall for nano-tori 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 nano-tube (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 nano-tori 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 $h - k = 0, \mathrm{mod}\, 3$ and $H - K \neq 0, \mathrm{mod}\, 3$, one can anticipate an exceptionally small HOMO-LUMO splitting as the ratio $H + K$ becomes very large. Indeed this is somewhat as for the nano-tube case where one anticipates the band gap to approach 0 as $h + k$ approaches the grapheneic limit (of ∞). Indeed the bucky-tori may be seen as just being grapheneic 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.

Nano-tori, just like graphene, have no boundary and no defects (in the sense of no rings of any sizes other than 6, on the toroidal surface). It has been found that SWNTs with an average diameter of 1.4 nm can be induced to coil and form tori (nano-tube rings or "crop circles") with 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 nano-tube when forming a torus (that is, when a bulk resonant bucky-tube forms a globally sextet-resonant bucky-torus). In Fig. (**54**) such a nano-torus is presented with a colored portion indicating Clar sextets. In general, nanotori are characterized by a sequence *of* numbers: *h and k*, indicating lengths of aceneic portions of a circumscribing annular path around the narrow part of the torus, *L* indicating the number of paths which are repeated around the torus, and a further number *t* indicating the extent to which the first and last annular paths are twisted with respect to one another. (A further specification is needed if topological aspects beyond graph-theoretic aspects are to be encoded, but its value does not change the molecular graph, and is not considered here.) Here if $h - k$ is a multiple of 3, then the nano-torus is potentially sextet-resonant, depending on the values of *L* and *t*, it needing that $L - t$ also be a multiple of 3. If $h - k$ is a multiple of 3 while $L - t$ is not, then there are relatively few lone pairings, and in particular no more than $h - k$ as we can locate in the region where the two ends of a long tube of length L are joined to form the torus – that is such a species (for the stress-favored case when $L \gg h + k$), the nano-torus is nearly sextet-resonant. In all these cases, the sextets and any lone pairings are delocalized, so that no bond localization is predicted.

VII.3. Nano-Cones

These species may be theoretically constructed on cutting away from a graphene sheet $q = 1$ through 5 wedge-shaped sectors with planar angle 60° and then folding the remaining
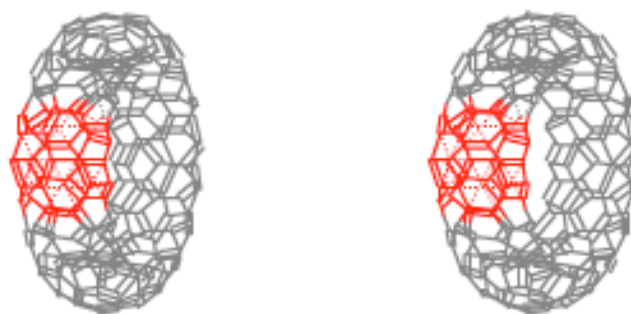

Fig. (54). Stereo-view of a sextet-resonant nano-torus whose red-colored portion has Clar sextet rings denoted by dotted lines.

sheet so as to connect the dangling bonds in some fashion. The so obtained single-wall nano-cones (SWNCs) are formed such as to fall into classes according to whether the Clar sextets can be arranged to be separated by cross-cut paths complying (or not complying) with condition (1).

Earlier we discussed [129] the classification of nano-cones with a part of the basic description being the number *q* of constituent 60°-sectors: with *q* = 6 sectors we have a flat graphene sheet with apical angle α = 180°; when *q* = 0, the nano-cone has an apical angle α = 0°, and is actually a nano-tube. In each of these one may view there to *p* = 6 − *q* "disclinations" – a type of defect. It was also shown that for *q* = 2, 3, and 4, in each case two classes of cones resulted, so that a total of eight classes of positive-curvature nano-cones exist. We show now that the pairs of classes for *q* = 2, 3, and 4 correspond to congruent ("class-1") versus incongruent folding of the corresponding sector ("class-2"). These classes are fundamental since a cone in one of these classes cannot be changed [129,130] into one from any other class with only a finite number of permutations/additions/deletions (in the apex region of the hypothetically infinitely extended cone). However, no such set of finite inter-conversions can transform a class 1-into a class-2 nano-cone, or *vice versa*. Data on the eight classes of nano-cones are presented in Table **1**. The solid angle is denoted by σ (in steradians). The following relationships hold:

$Q = \pi q / 3$ in radians

$\alpha = 2 \arcsin(Q/2\pi)$

$\sigma = 2\pi[1 - \cos(\alpha/2)] = 2\pi - (4\pi^2 - Q^2)^{1/2}$ in steradians

Thus, Fig. (**55**) shows a front stereo-view of a class-2, *i. e.* an incongruent, nano-cone formed by cutting off a 120°-sector from a graphene sheet and reconnecting the dangling bonds of the remaining the 240°-sector of the graphene sheet so as to have two adjacent pentagons at the apex of the resulting nano-cone. In this case (*q* = 4), one pentagon replaces a "sextet" hexagon, and the other pentagon replaces a "non-sextet" hexagon from the 240°-sector of the graphene sheet.

By contrast, a class-1, i. e. a congruent, nano-cone results when a 240°-sector of the graphene sheet is folded and reconnected so as to form a nano-cone such that both pentagons at the apex replace "sextet" hexagons (Fig. **56**). In consonance with the Euler theorem, two pentagons are equivalent to one 4-membered ring at the apex, and Fig. (**57**) presents such a nano-cone.

Table 1. **The Eight Cases of Single-Wall Nano-Cones**

60° sectors folded q	Angle Q (degrees)	Apex α (degrees)	Class	Solid angle σ (steradians)	Single Wall Nanostructure (SWNT or SWNC)
0	0	0	many	0	nano-tube (SWNT)
1	60	19.2	congruent	0.087	first (sharp) nano-cone (SWNC)
2	120	38.9	congruent	0.36	second nano-cone (SWNC)
	120	38.9	incongruent	0.36	second nano-cone (SWNC)
3	180	60	congruent	0.84	third nano-cone (SWNC)
	180	60	incongruent	0.84	third nano-cone (SWNC)
4	240	83.6	congruent	1.60	fourth nano-cone (SWNC)
	240	83.6	incongruent	1.60	fourth nano-cone (SWNC)
5	300	112.9	congruent	2.81	fifth (blunt) nano-cone (SWNC)
6	360	180	pure or defect	$6.28 = 2\pi$	graphene
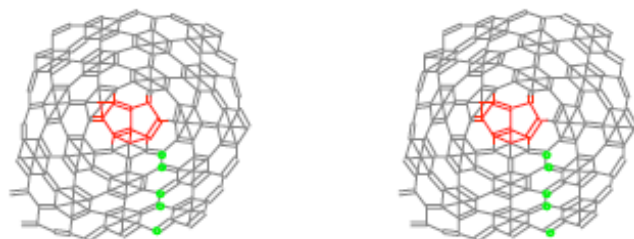
Fig. (55). Stereo-view from top of an incongruently-folded class 2 nano-cone with two adjacent pentagons (red) at the apex. The green-colored carbon atoms break the Clar structure of the folded 240°-sector of the graphene sheet.
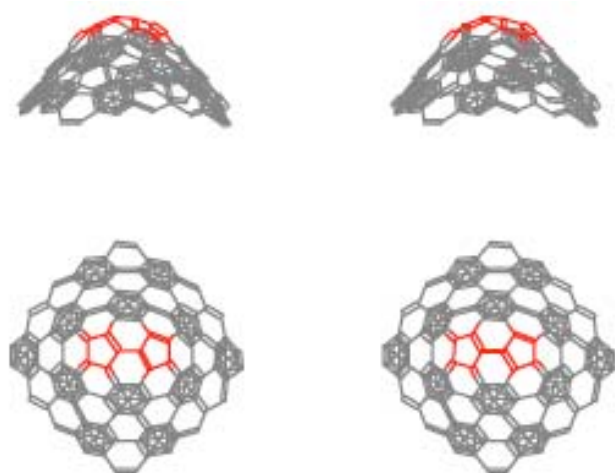
Fig. (56). Stereo-views (side and top views) of a class 1 sextet-resonant congruently-folded nano-cone with two pentagons at distance 1 at the apex (red color), and with Clar sextet rings denoted by dotted lines in the folded 240°-sector of the graphene sheet.

VII.4. Fullerenes

The leap-frog transformation of fullerenes [10,131-133] converts one fullerene into another special one which has three times as many vertices, preserving its symmetry and achieving a "Fries electronic structure" with a closed-shell electronic configuration. Such Fries electronic structures have a maximal number of benzenoid rings with three double bonds, for example the first resonance structures of phenanthrene and triphenylene in Figs. (**2** and **3**) where the sextet rings are converted into Kekulé structures such that two rings share a double bond. These ideas may be extended back to the benzenoids, whence a large number of leap-frogs of smaller benzenoids turn out to be benzenoids which are sextet-resonant, particularly for the circumstance [78] where the benzenoids are cata-condensed. The leap-frog idea may be even extended [134] to other structures.
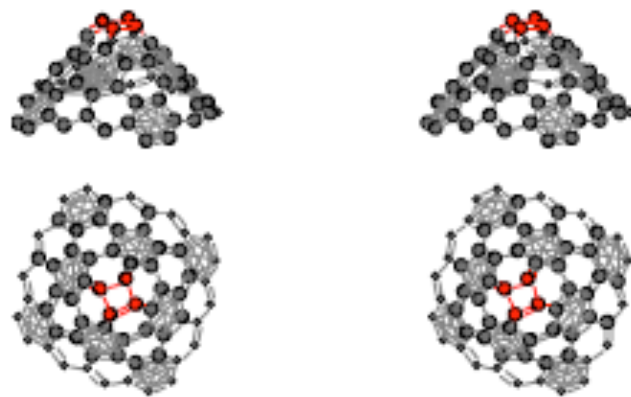
Fig. (57). Top stereo-view of a class 1 sextet-resonant congruently-folded nano-cone having a 4-membered ring at the apex (red) and with Clar sextet rings denoted by dotted lines in the folded 240°-sector of the graphene sheet.

Icosahedral-symmetry fullerene cages with N carbon atoms can also be characterized [60,87,131,135] by a pair of integer non-negative numbers h and k such that:

$$N = 20(h^2 + hk + k^2)$$

It was also shown that such cases with $h - k \neq 3m$ (with m an integer) have a HOMO-LUMO gap of 0.Taking into

account that $h^2 + hk + k^2 = 49$ when the pair (h,k) is either $(7,0)$ or $(5,3)$, one may conclude that nano-tubes with both these parameter pairs have the same diameter. However, they are not Clar-sextet-resonant nano-tubes, and neither are the same diameters as $(14,0)$- and $(10,6)$-nano-tubes because they do fulfill relationship (1). However, the same-diameter nano-tubes with (h,k) being $(21,0)$ and $(15,9)$ have sextet-resonant Clar structures.

The Clar-theoretic ideas may also be sought to be applied to general fullerenes, with special attention to those manifesting a high maximum number C of Clar sextets. Again we anticipate the Clar number C at a given number of hexagonal rings to be an indicator of higher stability C. For buckminsterfullerene, the structure is that of a truncated icosahedron, without any abutting 5-membered rings, which is to say that it satisfies the "isolated pentagon rule" (IPR), such as has been suggested [87,136,137] (and indeed found) to be a reasonable indicator of higher stability. In fact this C_{60} structure is [87] the smallest fullerene to satisfy the IPR, and the next smallest fullerene satisfying the IPR is [138] the experimentally observed C_{70}. As to Clar-theoretic ideas, some of these are found [139] to be in correspondence with leap-frog theoretic ideas for stability, and the leap-frog cages satisfy the IPR. The Clar number is $C = 8$ for buckminsterfullerene, as is [140] reasonably high, probably a maximum at $N = 60$ atoms, and the Clar sextet polynomial has been generated [141]. For C_{70} one has [142] $C = 9$, which is also high.

VII.5. Negatively Curved Species

There have been a number of extended species proposed with negative Gaussian curvature everywhere, or at least almost everywhere [142-144]. That is, the surface on which the carbon network is to be embedded is to have one or more saddle shaped regions (where the Gaussian curvature is negative), and in consilience with our earlier discussion, the combinatorial curvature should be negative in the same regions. Clearly combinatorial curvature is relevant, as also are the idea of matching the combinatorial curvature and its matching to geometric Gaussian curvature (as earlier mentioned) are certainly relevant. Indeed the idea of combinatorial curvature is implicit in different considerations made in physics or chemistry, e.g., as indicated by Sadoc and Moseri [145], but the more explicit recognition of the ideas, as in [123,124,146] should be relevant. In any event the usually considered simple translationally symmetric structures embedded on negatively curved surfaces do not seem to have been experimentally observed – and here we do not further discuss these (interesting) structures.

VIII. COMPOSITE CONJUGATED-SATURATED SYSTEMS

Besides the various purely conjugated systems indicated in the previous sections, there are a number of systems which though extended allow a limited range to the conjugation. That it, there are just many fragments of planar pi-networks, separated either by sp^3-hybridized (or saturated) carbons, or else by near orthogonal orientations for neighboring planes of conjugation. There of course is a vast number of small mixed-sp^2, sp^3 molecules, say based on ordinary benzenoids, but these we generally avoid here, mentioning only a few novel possibilities of extended nano-structures.

VIII.1. Buckminsterfullerene Super-Atoms, Super-Molecules, Super-Polymers, *Etc.*

Granted the (arguably "uniquely elegant") buckminsterfullerene structure, there is the possibility of joining them together *via* bonds between the different C_{60} units. Such a dimeric $(C_{60})_2$ structure has been experimentally found [147-150] with two adjacent C atoms in each C_{60} unit becoming sp^3 hybridized to bond to a corresponding atom in the second C_{60} unit. Also even longer oligomeric chains are known [151-153].

Indeed such chains (with two -bonds between each pair of C_{60}s) may be continued to give a linear chain of C_{60} "pearls", for which there is experimental evidence, that the chains arise from either high-pressure [154] or photo-induced [155] polymerization. In fact one may make other more complicated structures, such as an infinite triangular net of C_{60}s, as studied by Xu and Scuseria [156], and as such seemingly occurs [154]. These generally are believed to manifest bonding between two C_{60}s by way of a pair of sp^3-bonds from neighboring C atoms on one C_{60} to similar neighboring C atoms on the adjacent C_{60}. In fact, C_{60} manifests a variety of possible arrangements [157] for bonding patterns, with there being several possible super-polyhedra which one can make, as well as different extended networks. *E.g.*, one can place the C_{60} units at the corners of a simple cubic lattice and interlink them in this fashion or simply form a cube from eight C_{60} units.

Another rather amusing case involves taking 60 units of C_{60} to be placed at the corners of giant truncated icosahedron, and institute the same sort of bonding pattern (without any angle strain beyond that already present in the dimer connection) to obtain [157] a bucky-ball bucky-ball $(C_{60})_{60}$. But a distinction for all these mentioned constructions is that this sacrifices some of the conjugated-carbon network, for the introduction of sp^3 carbons to make the interconnections. Indeed there are enormous numbers of possibilities, with the C_{60} units playing the parts of complicated "super-atoms" which might be connected up in any of the sorts of patterns considered for our element C atoms to make different conjugated-carbon networks – and indeed many more ways can be imagined since the C_{60} "super-atoms" allow rather high effective "valences" – and yet further one could entertain the possibility of other fullerenes as such basic "super-atom" building blocks. Though some of these other fullerenes are in fact realized, and though one can imagine that the Clar-theoretic ideas are still applicable to the remnant π-network portions, these species are not our current subject of focus, so that we go on to different possibilities.

In passing it may be noted that one can imagine ways in which to interconnect C_{60} fullerenes, possibly without the use of sp^3 hybrids. Thus Fig. (**58a**) shows the result of joining two pentagonal rings in C_{60} units: the bonds within each ring are deleted and two new bonds from each atom are made to two atoms in the other ring. Then in Fig. (**58b**), the possibility of fusing two rings in the two fullerenes is indicated. It is understood that the faces at which the adjoining is made, instead of being pentagons, could be hexagons – with there being two possible orientations of the two hexagons relative to one another (as pentagons alternate with hexagons around each hexagon). For the fusion joining, this then leads to C_{114} from two C_{60} units, with each C_{60} unit having $60 - 6 =$

54 π-centers, whilst for the displayed C_{115} case each C_{60} unit has a radicaloid number $60 - 5 = 55$ π-centers. This ends up with regions of negative curvature (both combinatorial and Gaussian, so that we are led back to consideration of our structures which are extensively negatively curved.
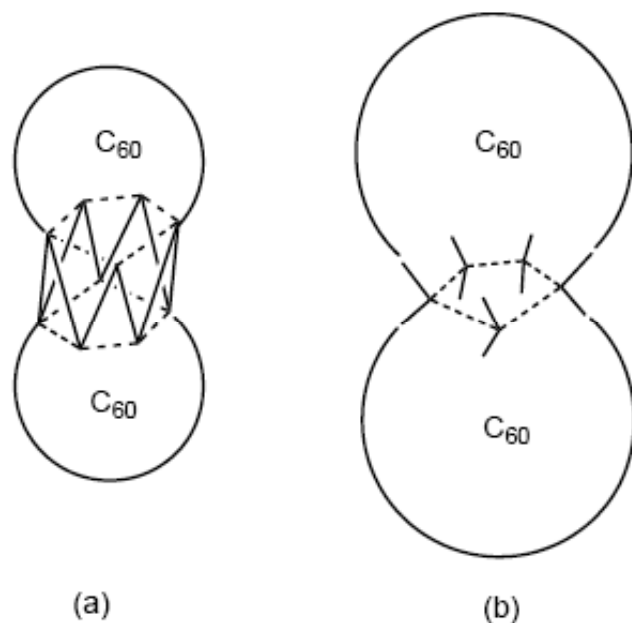

Fig. (58). Strategies for interconnecting two C_{60} fullerenes at two neighboring faces, here chosen to be pentagons. In (**a**) the ith atom in one ring is disconnected from the $(i - 1)^{th}$ and $(i + 1)^{th}$ bonds in that ring and joined to the corresponding atoms in the other ring. In (**b**) the two rings are fused together (thereby giving sp^3 atoms and a net C_{115} structure for just two C_{60}-units).

VIII.2 Three-Dimensional Nets

Besides diamond and graphene one may imagine other extended networks not C_{60}-based, with perhaps even all the C atoms equivalent, but at least very few different equivalence classes of C atoms. In fact there is a tremendous range of such possibilities for carbon networks. Some of these correspond to the everywhere negatively curved surfaces already previously mentioned, though sometimes one may imagine to contain some sp^3-hybridized carbons. With the restriction to all sp^2 one might imagine that there should be rather few possibilities susceptible to comprehensive characterization. But even for purely sp^2-conjugated networks allowing twisted orientations between different sets of sp^2 sites, there are many possibilities – though it may be that that there is no infinite network communicating through comparably oriented π-bonding. Several such networks were early on [158] identified, and then later numerous computations were performed [159,160] on such. Additional classes of such species sometimes with mixes of sp^2 and sp^3 hybrids have been identified [161]. But again none of these species seem yet to be realized as translationally symmetric structures, and we do not here try to treat these in any detailed way. It should perhaps be mentioned that mixed sp^2-sp^3 species of an amorphous nature do occur [162]. For either the translationally symmetric or amorphous materials, Clar-theoretic ideas generally have not yet been explored.

IX. CONCLUSIONS

In the previous pages, we could not do justice to a series of important contributions to developments of Clar's theory (and we try to compensate by adding a few bibliographic references) due to several authors, such as Ivan Gutman and Sven Cyvin [163,164], Oskar E. Polansky [165], Yuansheng Jiang [166], and Milan Randić [167].

We find that there is a surprising richness to the possibilities for conjugated-carbon nano-structures, and that Clar's ideas seem to be quite generally applicable across the range here considered – at least when these are properly extended as outlined in a qualitative format indicated here. In particular, it is noted that for small benzenoids (with < 10 hexagonal rings) such as Clar considered, the boundary tends to "freeze in" the Clar sextets, especially when there are few double bonds (remaining after introduction of the sextet circles). It is emphasized that for larger systems with a smaller fraction being on the boundary, such sextet localization does not (typically) occur, thereby leading to "novel" properties, e. g. there are naturally smaller excitation energies (which translate to small HOMO-LUMO gaps) even for Clar's favored "sextet resonant" species. And then the species can be electrically conducting, as for graphene. But there are numerous other predictions, concerning unpaired electrons, and their localization.

There is an immensely rich array of possibilities for embedding hexagon-rich networks on surfaces in turn embedded in Euclidean space, and there are great many of these structures which have been experimentally realized, mostly in the last 3 decades – so that one wonders what the next 3 decades may bring. There still are enormous numbers of speculated structures of various types which have not yet been experimentally observed, though seemingly well founded not only in terms of classical chemical ideas, but also often in terms of modern quantum chemical computational methodology. It would seem that Clar's ideas, rather than being archaic classical ideas deserving to be left behind, still actually provide much qualitative insight to characteristics of these various novel structures. It is surmised that more quantitative versions of Clar's ideas should yield further insight, and therefore should be pursued.

ACKNOWLEDGEMENT

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