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# DECIPHERING THE INFORMATION CONTENT OF POLYCYCLIC CONJUGATED HYDROCARBON FORMULAS - FROM BENZENOIDS TO FULLERENES*

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*abstract*
While reviewing our contributions directed toward the development of a unified structure theory of polycyclic conjugated hydrocarbons, some formula, structure, and stability relationships of benzenoids to fullerenes are demonstrated. Coupling Clar's sextet rule with Fowler's leapfrog algorithm, one can construct the more stable benzenoid isomers without needing knowledge of the remaining isomers.

## INTRODUCTION

Deciphering the the information content of a chemical formula begins with isomer enumeration. Comparison of known versus unknown isomers provides one with clues to the causal factors and is important to chemical information and molecular modeling studies. The molecular formula of a chemical compound is a universal invariant that vastly delimits the range of structures to isomers. The essence of structural chemistry is the combinatorics of atoms according to definite rules in which stability plays a significant role. The study of isomerism is an important endeavor that not only impacts on the documentation, storage, and retrieval of chemical information per se but also on the fundamentals of energetic/structural chemistry.

Similarity [1], symmetry [2], and elementary substructures [3] are among the more important conceptual tools used to deduce relative chemical information from a molecular structure. Bonds, functional groups, monomeric units, and excised internal structures [4] are examples of elementary substructures. The greater the degree of overlap between two structures, the more they are similar. The closer two molecules are in size and symmetry and the more elementary substructures they have in common, the more they are similar. The

*Dedicated to Professor Carl Djerassi on his 70th birthday.

known dominant properties of the elementary substructures along with their deducible interaction contributions are transferred to the composite molecule. In this way, our visual perception of the identities and spacial relationships of the various molecular components can be translated into a prediction of the properties of the molecule containing them.

From our knowledge of valence and other chemical fundamentals, the formulas $CH_4$, $C_2H_6$, and $C_3H_8$ convey total information on the respective structures. Starting with $C_4H_{10}$, which corresponds to two isomers, increasingly less structural information is contained by molecular formulas of increasing size. Nevertheless, given a particular chemical formula, the range of structure types that can and cannot correspond to it can be deduced [5]. What is usually lacking, though, is a systematic process or set of algorithms by which one can arrive at a corresponding isomer set. This is a combinatoric problem in which chemical reasoning, like relative stability, should be factored-in.

The search and discovery of organizational structures in collections of of facts is one of the essential activities of empirical scientists. Herein, we will present a brief review of our results on deciphering the information content of benzenoid formulas. Structural/formula relationships for benzenoid and related polycyclic conjugated hydrocarbons will be defined. These results have systematized benzenoid compounds into a unified framework for the first time [6]. Our strategy involves the setting up of a periodic table for benzenoids, referred to as Table PAH6, and discovering domains in it where the range of permissible structure types can be identified. The concept of a periodic table set is in-itself an important development [7]. The discovery of constant-isomer series is another important development [8]. Constant-isomer benzenoid series are benzenoid sets of increasing formulas with the same number of isomers. Formulas corresponding to constant-isomer benzenoids have a smaller range of permissible structure types [5]. Several important algorithms have evolved from these developments [8,9]. One example is an algorithm which permits one to identify the more stable subset of benzenoid isomers without requiring one to have knowledge of all the isomers [9]. Overall, the formula periodic table for benzenoids (Table PAH6) establishes a hierarchical ordering of the average properties of benzenoid isomer sets. All benzenoid formulas are found in Table PAH6 and the global properties of benzenoids are determined by it. The classification and enumeration of benzenoid hydrocarbons along with Table PAH6 has helped us define the limits of what we do and can know about this class of compounds.

In this paper, a fusion of Table PAH6 and Table PCH5 (a formula periodic table for fused polypentagonal conjugated hydrocarbons) [10] will be described, and its relationship to fullerenes will be discussed. A comparison of Fowler's leapfrog algorithm for fullerenes [11] and our circumscribing algorithm for constant-isomer series [8] will be detailed. All polycyclic conjugated hydrocarbon structures will be portrayed as $\sigma$-bond molecular graphs consisting of fused rings with perimeter degree-2 vertices that correspond to CH units and degree-3 vertices that correspond to >C= units. Throughout this paper we will disregard the plausibility that a formula might correspond to structures having ring sizes other than pentagonal and hexagonal ones.

## RESULTS AND DISCUSSION

### *A Formula Periodic Table for Polypentagonal/Polyhexagonal Conjugated Hydrocarbons*

*Construction of Table 1.* Table 1 is divided into two parts where the lower part is a continuation of the upper part as one moves from left to right. The formulas $C_nH_s$ ($n=N_c$ and $s=N_H$) change successively by $C_4H_2$ along a row and by $C_6H_2$ along a column. All formulas below and to the right of the staircase dashed line in Table 1 are benzenoid formulas (Table PAH6). Benzenoid formulas in the same row correspond to PAH6 structures with the same number of internal third degree (degree-3) vertices $N_{Ic}$(PAH6); internal third degree vertices are bounded by three fused rings in molecular graphs. The formulas to the left of the double vertical lines (bottom part of Table 1) correspond to fused polypentagonal conjugated hydrocarbons (Table PCH5) with the exception of those formulas with $s<6$ to the left of the $N_{Ic}$(PCH5)=10 column (to the left and above the staircase line). These latter formulas are derived in a formal sense from fullerene formulas by addition of $H_2$ and $2H_2$ and must contain $\leq 12$ pentagonal rings with remaining rings being hexagonal. This is illustrated in the following by addition of hydrogen to dodecahedron in the Schlegel representation:

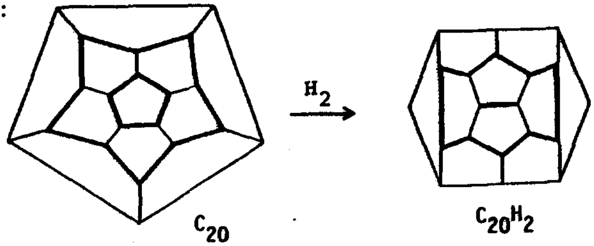


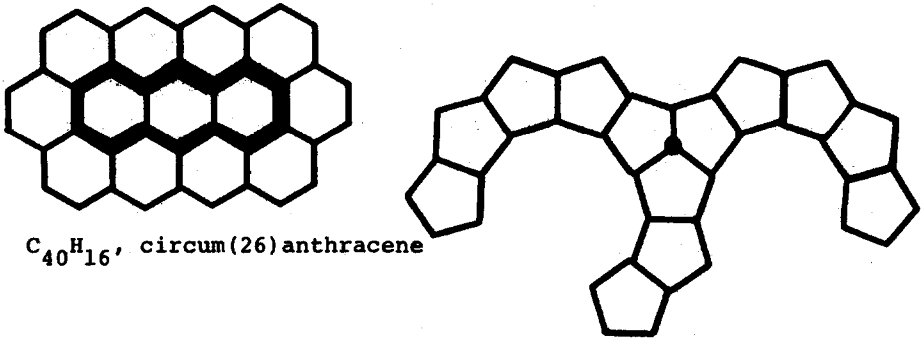
Table 1. Fused Formula Periodic Tables for Even Carbon Polypentagonal (PCH5) and Polyhexagonal (PAH6) Conjugated Systems

| | | | | ... | 16 | 15 | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 | $N_{Ic}$(PAH5) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | $C_{18}H_4$ | $C_{22}H_6$ | |
| | | | | | | | | | | | | $C_{20}H_4$ | $C_{24}H_6$ | $C_{28}H_8$ | |
| | | | | | | | | | | | $C_{22}H_4$ | $C_{26}H_6$ | $C_{30}H_8$ | $C_{34}H_{10}$ | |
| | | | | | | | | | $C_{20}H_2$ | $C_{24}H_4$ | $C_{28}H_6$ | $C_{32}H_8$ | $C_{36}H_{10}$ | $C_{40}H_{12}$ | |
| | | | | | | | | | $C_{26}H_4$ | $C_{30}H_6$ | $C_{34}H_8$ | $C_{38}H_{10}$ | $C_{42}H_{12}$ | $C_{46}H_{14}$ | |
| | | | | | | $C_{20}$ | $C_{24}H_2$ | $C_{28}H_4$ | $C_{32}H_6$ | $C_{36}H_8$ | $C_{40}H_{10}$ | $C_{44}H_{12}$ | $C_{48}H_{14}$ | $C_{52}H_{16}$ | |
| | | | | | | $C_{26}H_2$ | $C_{30}H_4$ | $C_{34}H_6$ | $C_{38}H_8$ | $C_{42}H_{10}$ | $C_{46}H_{12}$ | $C_{50}H_{14}$ | $C_{54}H_{16}$ | $C_{58}H_{18}$ | |
| | | | | $C_{24}$ | $C_{28}H_2$ | $C_{32}H_4$ | $C_{36}H_6$ | $C_{40}H_8$ | $C_{44}H_{10}$ | $C_{48}H_{12}$ | $C_{52}H_{14}$ | $C_{56}H_{16}$ | $C_{60}H_{18}$ | $C_{64}H_{20}$ | |
| | | | $C_{26}$ | $C_{30}H_2$ | $C_{34}H_4$ | $C_{38}H_6$ | $C_{42}H_8$ | $C_{46}H_{10}$ | $C_{50}H_{12}$ | $C_{54}H_{14}$ | $C_{58}H_{16}$ | $C_{62}H_{18}$ | $C_{66}H_{20}$ | ... | |
| | | | $C_{32}H_2$ | $C_{36}H_4$ | $C_{40}H_6$ | $C_{44}H_8$ | $C_{48}H_{10}$ | $C_{52}H_{12}$ | $C_{56}H_{14}$ | $C_{60}H_{16}$ | $C_{64}H_{18}$ | $C_{68}H_{20}$ | ... | | |
| | | | $C_{38}H_4$ | $C_{42}H_6$ | $C_{46}H_8$ | $C_{50}H_{10}$ | $C_{54}H_{12}$ | $C_{58}H_{14}$ | $C_{62}H_{16}$ | $C_{66}H_{18}$ | $C_{70}H_{20}$ | $C_{74}H_{22}$ | | | |
| | | | $C_{44}H_6$ | $C_{48}H_8$ | $C_{52}H_{10}$ | $C_{56}H_{12}$ | $C_{60}H_{14}$ | $C_{64}H_{16}$ | $C_{68}H_{18}$ | $C_{72}H_{20}$ | $C_{76}H_{22}$ | ... | | | |
| | | | $C_{50}H_8$ | $C_{54}H_{10}$ | $C_{58}H_{12}$ | $C_{62}H_{14}$ | $C_{66}H_{16}$ | $C_{70}H_{18}$ | $C_{74}H_{20}$ | $C_{78}H_{22}$ | ... | | | | |
| | | ... | $C_{56}H_{10}$ | $C_{60}H_{12}$ | $C_{64}H_{14}$ | $C_{68}H_{16}$ | $C_{72}H_{18}$ | $C_{76}H_{20}$ | $C_{80}H_{22}$ | ... | | | | | |
| ... | $C_{60}$ | ... | $C_{62}H_{12}$ | $C_{66}H_{14}$ | $C_{70}H_{16}$ | $C_{74}H_{18}$ | $C_{78}H_{20}$ | $C_{82}H_{22}$ | ... | | | | | | |
| | ... | | $C_{68}H_{14}$ | $C_{72}H_{16}$ | $C_{76}H_{18}$ | $C_{80}H_{20}$ | $C_{84}H_{22}$ | $C_{88}H_{24}$ | | | | | | | |
| | | | $C_{74}H_{16}$ | $C_{78}H_{18}$ | $C_{82}H_{20}$ | $C_{86}H_{22}$ | $C_{90}H_{24}$ | ... | | | | | | | |
| | $C_{78}H_6$ | | $C_{80}H_{18}$ | $C_{84}H_{20}$ | $C_{88}H_{22}$ | $C_{92}H_{24}$ | ... | | | | | | | | |
| | ... | | $C_{86}H_{20}$ | $C_{90}H_{22}$ | $C_{94}H_{24}$ | ... | | | | | | | | | |
| | | | $C_{92}H_{22}$ | $C_{96}H_{24}$ | ... | | | | | | | | | | |
| | $C_{150}H_{30}$ | | $C_{98}H_{24}$ | ... | | | | | | | | | | | |
| | ... | | ... | | | | | | | | | | | | |

| 6 | 5 | 4 | 3 | 2 | 1 | 0 | | | | | | $N_{Ic}$(PAH6) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $C_{10}H_8$ | $C_{14}H_{10}$ | $C_{18}H_{12}$ | ... | 0 |
| | | | | | | $C_6H_6$ | $C_{12}H_8$ | $C_{16}H_{10}$ | $C_{20}H_{12}$ | $C_{24}H_{14}$ | | 2 |
| | | | | | $C_{10}H_6$ | $C_{14}H_8$ | $C_{18}H_{10}$ | $C_{22}H_{12}$ | $C_{26}H_{14}$ | $C_{30}H_{16}$ | | 4 |
| | | | | $C_{12}H_6$ | $C_{16}H_8$ | $C_{20}H_{10}$ | $C_{24}H_{12}$ | $C_{28}H_{14}$ | $C_{32}H_{16}$ | $C_{36}H_{18}$ | | 6 |
| | | | $C_{14}H_6$ | $C_{18}H_8$ | $C_{22}H_{10}$ | $C_{26}H_{12}$ | $C_{30}H_{14}$ | $C_{34}H_{16}$ | $C_{38}H_{18}$ | $C_{42}H_{20}$ | | 8 |
| | | $C_{16}H_6$ | $C_{20}H_8$ | $C_{24}H_{10}$ | $C_{28}H_{12}$ | $C_{32}H_{14}$ | $C_{36}H_{16}$ | $C_{40}H_{18}$ | $C_{44}H_{20}$ | $C_{48}H_{22}$ | | 10 |
| | $C_{18}H_6$ | $C_{22}H_8$ | $C_{26}H_{10}$ | $C_{30}H_{12}$ | $C_{34}H_{14}$ | $C_{38}H_{16}$ | $C_{42}H_{18}$ | $C_{46}H_{20}$ | $C_{50}H_{22}$ | $C_{54}H_{24}$ | ... | 12 |
| $C_{20}H_6$ | $C_{24}H_8$ | $C_{28}H_{10}$ | $C_{32}H_{12}$ | $C_{36}H_{14}$ | $C_{40}H_{16}$ | $C_{44}H_{18}$ | $C_{48}H_{20}$ | $C_{52}H_{22}$ | $C_{56}H_{24}$ | ... | | 14 |
| $C_{26}H_8$ | $C_{30}H_{10}$ | $C_{34}H_{12}$ | $C_{38}H_{14}$ | $C_{42}H_{16}$ | $C_{46}H_{18}$ | ... | ... | ... | ... | ... | | ... |
| $C_{32}H_{10}$ | $C_{36}H_{12}$ | $C_{40}H_{14}$ | $C_{44}H_{16}$ | $C_{48}H_{18}$ | $C_{52}H_{20}$ | ... | ... | ... | ... | ... | | |
| $C_{38}H_{12}$ | $C_{42}H_{14}$ | $C_{46}H_{16}$ | $C_{50}H_{18}$ | $C_{54}H_{20}$ | $C_{58}H_{22}$ | ... | ... | ... | ... | | | |
| $C_{44}H_{14}$ | $C_{48}H_{16}$ | $C_{52}H_{18}$ | $C_{56}H_{20}$ | $C_{60}H_{22}$ | ... | | | | | | | |
| $C_{50}H_{16}$ | $C_{54}H_{18}$ | $C_{58}H_{20}$ | $C_{62}H_{22}$ | ... | | | | | | | | |
| $C_{56}H_{18}$ | $C_{60}H_{20}$ | $C_{64}H_{22}$ | ... | | | | | | | | | |
| $C_{62}H_{20}$ | $C_{66}H_{22}$ | ... | | | | | | | | | | |
| | ... | | | | | | | | | | | |

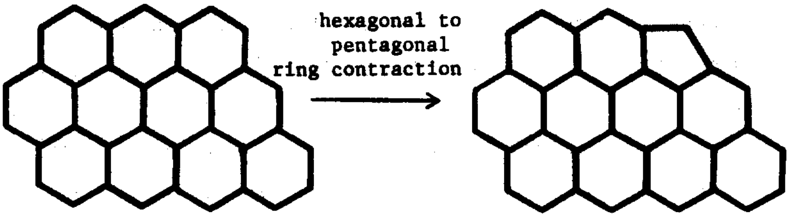
PCH5 structures with formulas in the same column of Table 1 will have the same number of third degree vertices $N_{Ic}$(PCH5). Thus in regard to $N_{Ic}$, Table PAH6 and Table PCH5 are orthogonal sets. Since odd carbon polypentagonal and polyhexagonal conjugated hydrocarbons are invariably less stable radical species, Table 1 only lists even carbon formulas. The odd carbon formulas can be obtained in each column by adding or substracting $C_3H$ from the formulas listed. In the recursive generation of benzenoid hydrocarbon isomers per our aufbau principle, three elementary aufbau units, $C_2$, $C_3H$, and $C_4H_2$, were demonstrated to be sufficient [12].

*Formula/Structure Relationships Defined by Table 1.* As one can see, Table 1 defines three major domains; the upper-left fullerene derived region (here we also include $C_{12}H_8$ and $C_{18}H_{10}$), the middle polypentagonal region, and the lower-right polyhexagonal (benzenoid) region. The first domain contains formulas that must correspond to polycyclic structures possessing $\leq 12$ pentagonal rings in addition to hexagonal ones. The second domain contains formulas that must correspond to structures having pentagonal or pentagonal and hexagonal fused rings. The third domain contains formulas that must correspond to structures having hexagonal or pentagonal and hexagonal fused rings. The intersection region which contains formulas to the left of the double vertical lines and below the staircase dashed line can have a range of polycyclic structures from fused polypentagonal (PCH5) to polyhexagonal (PAH6) conjugated hydrocarbons. Formulas to the right of the double vertical lines can not correspond to structures containing exclusively fused pentagonal rings, and formulas located to the left of the vertical double lines and above the dashed staircase line can not correspond to structures containing exclusively fused hexagonal rings. To illustrate these relationships, consider the structures given in Figure 1. Circum(26)anthracene ($C_{40}H_{16}$) has recently been synthesized [13] and is a member of the four-isomer benzenoid series ($C_{40}H_{16}$, $C_{78}H_{22}$, ...) located on the staircase edge of Table PAH6 as defined by the dashed line in Table 1. One example polypentagonal isomer of circumanthracene is also shown in Figure 1. Immediately above this formula in Table 1 is $C_{34}H_{14}$ which is also above the dashed line belonging to the middle domain. No benzenoid structure can correspond to the formula of $C_{34}H_{14}$. However, there are 34 fluoranthenoid (PAHs with one pentagonal ring among



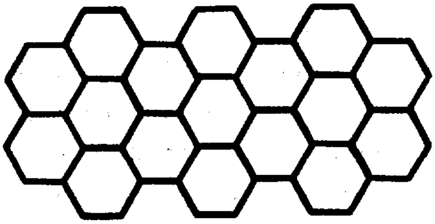
$C_{40}H_{16}$, circum(26)anthracene

a polypentagonal isomer of $C_{40}H_{16}$



$C_{35}H_{15}$

a fluoranthenoid $C_{34}H_{14}$ isomer



$C_{52}H_{20}$, circum(34)paraterphenyl

Figure 1. Representative polypentagonal/polyhexagonal conjugated hydrocarbons.

otherwise hexagonal ones) isomers [14] that do correspond to this formula, one which is shown in Figure 1. Deletion of any two end rings of the $C_{40}H_{16}$ PCH5 structure in Figure 1 will give a $C_{34}H_{14}$ PCH5 structure. For another example, the benzenoid, circum(30)coronene ($C_{54}H_{18}$), and one of its possible PCH5 structures can be found in Figure 1 of reference 6. The $C_{52}H_{20}$ benzenoid structure in Figure 1 has its formula two lines below $C_{40}H_{16}$ and has recently been synthesized [15]. Pyrene has its $C_{16}H_{10}$ formula to the right of the double vertical lines in Table 1. The 4 fluoranthenoid and 13 indacenoid isomers of pyrene have been depicted [16], but no PCH5 structures are possible for $C_{16}H_{10}$. It has been shown [6,10] that the maximum number of pentagonal rings in addition to hexagonal ones that a benzenoid (PAH6) isomer can possess is given by $r_{5_{max}} \leq N_{Ic}(PAH6)$. For pyrene, $N_{Ic}(PAH6)=2$ and therefore polypentagonal/polyhexagonal isomers of pyrene can have structures with no more than two pentagonal rings in addition to hexagonal ones. If we lift the polypentagonal/polyhexagonal restriction, then by expanding one hexagonal ring to a heptagonal one another hexagonal ring will simultaneously contract to a pentagonal one. This would give a pyrene cata-condensed isomer having three pentagonal rings and one heptagonal ring, but this is not polypentagonal/polyhexagonal system. For additional results concerning PAH5 structures, one should refer to the recent work of Cyvin and collaborators [17].

As the above illustrates, Table 1 contains all the possible formulas for benzenoids, fluoranthenoids, indacenoids, fullerenes, and related polypentagonal/polyhexagonal systems. Its organization has allowed us to identify regions which collect formulas that correspond to well defined ranges of structures. In general, the benzenoid domain possesses structures of greater (aromatic) stability. The thermal formation of strictly peri-condensed benzenoids (and to a certain extent fluoranthenoids) from less condensed carbon systems requires the liberation of hydrogen which serves to increase the system entropy. As one moves through the polypentagonal domain toward and into the fullerene domain, there is general trend toward less stable structures with more or less increasing antiaromatic and strain contributions. At the edge of the fullerene domain, formation of gas phase fullerene clusters of nearly spherical shape leads to further increase in the system entropy, relaxation of strain through curving, and the removal of the need for end groups. The study of stable and usually unknown molecular species along with more stable and known molecular species helps one to understand more fully the variables that contribute to structural stability of molecules, and here it is seen that the construction of Table 1 incorporates stability as a factor.

In the next section, we will demonstrate how to sort out the more stable benzenoid isomers without requiring knowledge of all the isomers having a given formula [18].

## *The Circumscribing and Leapfrog Algorithms*

*Circumscribing.* The circumscribing of the perimeter of a benzenoid $C_nH_s$ with a chain of 2s+6 carbon atoms plus 6 additional hydrogens in such a way as to only generate hexagonal rings gives a successor $C_{n+2s+6}H_{s+6}$ benzenoid [4,19]. Figure 1 shows anthracene ($C_{14}H_{10}$, in bold) being circumscribed to give circum(26)anthracene ($C_{40}H_{16}$). Fluoranthenoids and indacenoids can be similarly circumscribed by a perimeter of hexagonal rings [5,9]. Constant-isomer series are generated by the circumscribing algorithm and are sets of polycyclic conjugated hydrocarbons with increasing numbers of carbon and hydrogen atoms which have equal numbers of isomers at each stage of increasing formula. Two fundamental premises that are embodied in our master algorithm [8] have been explicitly iterated by Cyvin and coworkers as theorems [17]. Among a given class of PCHs with a specified formula $C_nH_s$, there exists at least one isomer which can be circumscribed with hexagonal rings arbitrarily many times. Any such $C_nH_s$ PCH structure when circumscribed sufficiently many times gives an ultimate successor structure belonging to the first generation isomer set of a constant-isomer series.

*Total Resonant Sextet Benzenoids.* Total resonant sextet benzenoids have formulas in which the number of carbons are divisible by six and structures totally covered by Clar sextets (hexagon rings with three mutually permutable p$\pi$-bonds) [9]. Total resonant sextet (TRS) benzenoids have the largest p$\pi$ electron energy and are kinetically the more stable isomers. Figure 2 shows the $\sigma$-bond skeletons for the first generation members of the three even carbon one-isomer series and their associate TRS benzenoids; the resonant sextets are indicated by inscribed circles. Circumscribing benzene gives coronene ($C_{24}H_{12}$). Circumscribing coronene gives circum(30)coronene ($C_{54}H_{18}$), and circumscribing circumcoronene gives dicircum(30,42)coronene ($C_{96}H_{24}$). Successive repetition of this process gives the coronene one-isomer series. Note that each one of these formulas appears along the dashed staircase line in Table 1. All the formulas corresponding to constant-isomer

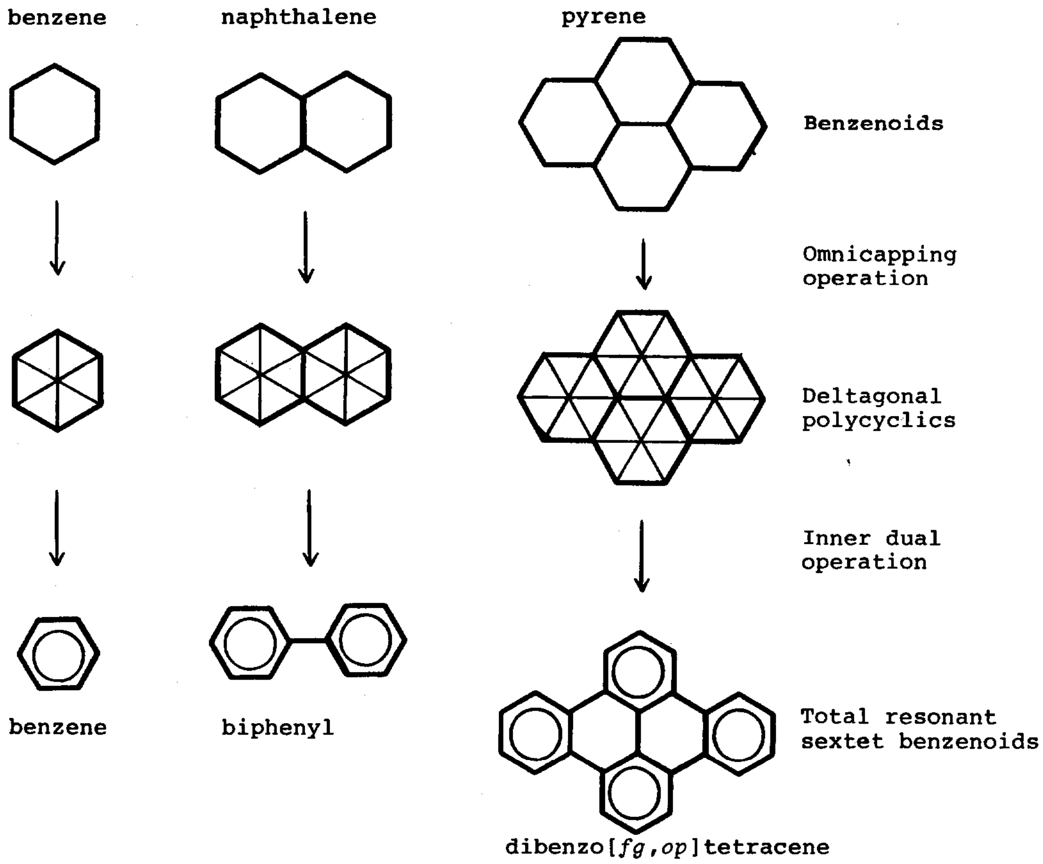


Figure 2. Illustration of the leapfrog algorithm in the transformation of benzenoids into total resonant sextet benzenoids.

benzenoid series will be found along the dashed staircase line in Table 1. Circumscribing naphthalene ($C_{10}H_8$) gives ovalene ($C_{32}H_{14}$), and circumscribing pyrene ($C_{16}H_{10}$) gives circum(26)pyrene ($C_{42}H_{16}$). These are the first two members to the ovalene and pyrene one-isomer series, respectively. Previously, it was demonstrated that there exists a one-to-one correspondence between the constant-isomer benzenoid series and constant-sextet-isomer series defined by an augmented circumscribing process called supercircumscribing [9]. We will now show how this correspondence is connected by the leapfrog algorithm.

*Leapfrogging.* The leapfrog rule says that for every isomer of a fullerene with n carbon atoms ($C_n$), there is a corresponding unique closed-shell isomer of the fullerene $C_{3n}$. This $C_{3n}$ isomer has the same point-group symmetry as its $C_n$ precursor and can be constructed from it by a two-stage "leapfrogging" process which involves omnicapping and subsequently taking the face dual [11]. Herein, it will be shown that any benzenoid, open-shell or closed-shell, can be transformed by the leapfrog algorithm into a successor benzenoid with a maximum number of Clar sextets and same point-group symmetry. Application of the leapfrog algorithm on all noncatacondensed benzenoid isomer sets culled of members with catacondensed appendages or bridging units and four or more adjacent bay regions will generate all possible strain-free total resonant sextet benzenoids; strain-free TRS benzenoids have nonhelical structures devoid of two or more adjacent bay regions.

A distinction between dual and inner dual needs to be made. The former is used with polyhedra and the latter is used with polygons. To construct a dual or inner dual, a point is placed in the center of every face or ring and the points in adjacent faces or rings are connected by lines, respectively. A dual graph of a polygonal system would possess one more point than its inner dual; this additional point would be located in the outer infinite region with lines passing through the periphery of the polygon. Two polyhedra are duals when the vertices of one correspond to the face-centers of the other. The tetrahedron is self-dual and the cube and octahedron are duals. The leapfrog operation on dodecahedron ($C_{20}$) which is open-shell gives buckminsterfullerene ($C_{60}$) which is closed-shell. The dual of a 3-connected spherical polyhedron with twelve pentagons and $r_6$ hexagonal faces is a spherical deltahedron with triangular faces, twelve 5-coordinate and $r_6$ 6-coordinate vertices. Exactly twelve pentagons are required to give a geometrically closed shape. In the leapfrog procedure, symmetry and the number of pentagons remains fixed and nonadjacent. Since the

Schlegel representation of dodecahedron, the smallest fullerene, has eleven independent pentagonal rings, the structures corresponding to smaller formulas in the fullerene derivative domain in Table 1 are limited to a maximum of eleven pentagonal rings.

Any fused benzenoid ($C_nH_s$) can be transformed into a successor (fused or nonfused) benzenoid ($C_{3n-3s+6}H_{2s-6}$) with a maximum number of Clar sextets by the leapfrog algorithm [18]. The successor leapfrog L is constructed from the precursor benzenoid P in two stages. First the hexagonal rings are omnicapped to produce a deltagonal polycyclic D. The inner dual of D is taken by putting a central point inside each trigonal ring and connecting the points in adjacent rings with lines. This is illustrated by the transformation of the benzene, naphthalene, and pyrene in Figure 2 to TRS benzenoids. Note that benzene is the smallest TRS benzenoid and that the leapfrog on benzene is a null operation. Observe that in the leapfrog operation on pyrene to give dibenzo[*fg,op*]tetracene, the internal third degree vertices of the former ($N_{Ic}=2$) become empty rings (hexagonal rings without inscribed circles) in the latter. Figure 3 shows that the leapfrog on an open-shell benzenoid, phenalenyl which is a monoradical species, gives the TRS benzenoid, triphenylene. TRS benzenoids are always closed-shell. Iteration of the leapfrog on triphenylene in Figure 3 illustrates that successive application of the leapfrog eventually leads to a group of disconnected benzenes. Both Figures 2 and 3 show that symmetry of the precursor and successor benzenoids is preserved by the leapfrog operation.

Iteration of the leapfrog transformation on a given set of polyhedra of the same n leads to a series of closed-shell leapfrog isomers where the symmetry-related properties follow from those of the precursor parents [11]. This is analogous to the process of successive cicumscribing of isomeric benzenoids which leads to a series of circumscribed isomers (cf. with anthracene and circumanthracene in Figure 1) with the same distributions of symmetry-related properties as the initial parents (first generation) [4,8]. Note that the reverse to circumscribing gives the excised internal structure, and that constant-isomer series are the ultimate result of successive circumscribing.

*Sorting Out the More Stable Benzenoids.* Suppose in the analysis of an environmental sample you observe a GC/MS ion peak which corresponds to a $C_{48}H_{24}$ benzenoid. There are 114,326 benzenoid isomers with this formula [20], and it is predicted that the TRS benzenoid subset are the more stable ones. To find these more stable benzenoid structures, we need

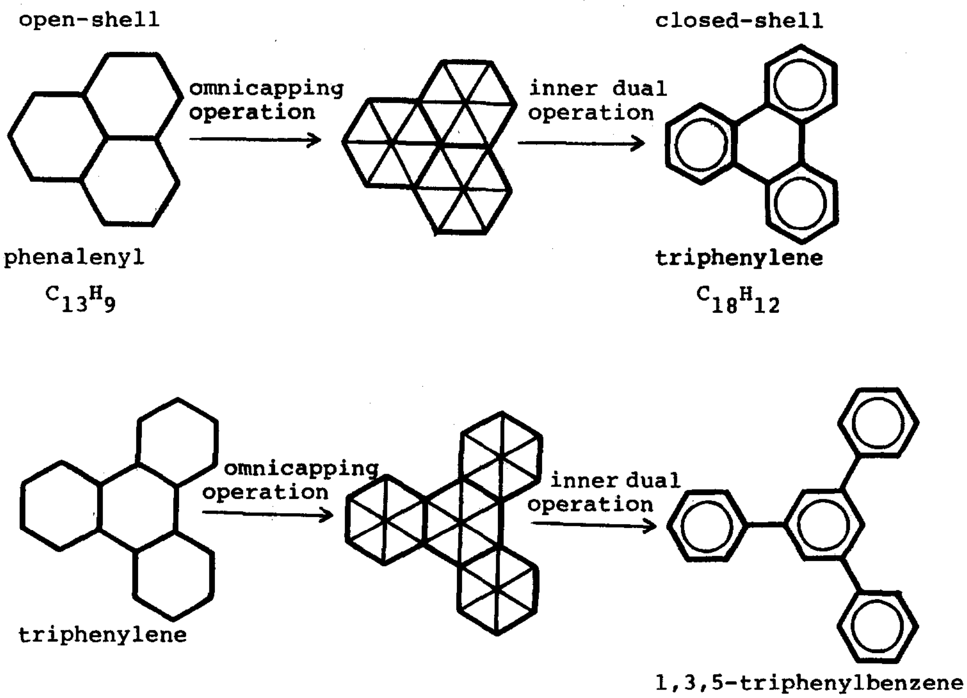


Figure 3. Application of the leapfrog algorithm on phenalenyl two succesive times. Note that this operation always give species with closed-shell electronic configurations.

to identify the appropriate precursor benzenoids upon which the application of the leapfrog operation will give us these more stable species. To accomplish this one will need the following equations:

$$N_c=(1/3)N_c(\text{sextet})+(1/2)N_H(\text{sextet})+1$$

$$N_H=(1/2)N_H(\text{sextet})+3$$

Thus, for $C_{48}H_{24}$ it is determined that $N_c=29$ and $N_H=15$ giving $C_{29}H_{15}$ as the formula of the benzenoid structures we need for the leapfrog operation. In previously published benzenoid depictions [21], one finds that there are 21 $C_{29}H_{15}$ benzenoids. After eliminating all the structures with benzo appendages, one is left with four $C_{29}H_{15}$ benzenoid structures which via the leapfrog operation gives four $C_{48}H_{24}$ TRS benzenoids that have been previously depicted [19]. To obtain the more stable benzenoid isomers for the formulas not having $N_c$ divisible by 6, one can use the aufbau process on the closest located TRS benzenoids as generated above.

## CONCLUSION

This is a contribution directed toward the development of a unified structure theory of polycyclic conjugated hydrocarbons. While presenting an overview of our prior results, it has been shown that one can extract far more structural information from large chemical formulas than previously realized. The new concepts of periodic table set, the aufbau and excised internal structure/circumscribing principles, constant-isomer series, and Fowler's leapfrog algorithm have been exploited in organizing and understanding formula/structure relationships. Well over 600 benzenoids, fluoranthenoids, indacenoids, and fullerenes ($C_{60}$, $C_{70}$, $C_{76}$, $C_{78}$, and $C_{84}$) that have formulas found in Table 1 have been characterized in the literature [11,16,19].

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