

# Perimeter Topology of Benzenoid Polycyclic Hydrocarbons

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The equivalence of the perimeter topological equations derived by Dias and the 13 possible modes of hexagon adjacency in fused benzenoid systems subsequently presented by Cyvin, Gutman, and collaborators is shown. The aufbau principle for generation of all fused total resonant sextet (TRS) benzenoid hydrocarbons is proved. The precise distinction and topological properties between fused, nonfused, strain-free, strained, helical, and nonhelical benzenoid hydrocarbons are carefully delineated. The TRS benzenoid isomers have the maximum number of bay regions, and expressions for the number of bay regions that any given TRS benzenoid will have are given.

## INTRODUCTION

The perimeter topology of a benzenoid hydrocarbon determines much of its chemistry. All the hydrogens are located on the perimeter of a benzenoid, the different perimeter (hydrogen) groups have distinct IR absorption bands due to characteristic out-of-plane bending vibrations and  $^1\text{H}$  NMR chemical shifts,<sup>1</sup> electrophilic aromatic substitution occurs solely at the perimeter of a benzenoid, and the benzenoid perimeter has a strong influence on the crystal packing structure. Many of the computer enumerations of polyhexes are based on a boundary code algorithm.<sup>2–4</sup> The generation of constant-isomer series by repetitive circumscribing with hexagonal rings is a perimeter phenomenon. Also, the odd carbon (radical) benzenoids have  $4n = N_{pc} + N_H = q_p$  perimeters, and the more stable even carbon benzenoids have  $4n + 2 = q_p$  perimeters ( $n = 1, 2, 3, \dots$ ). Thus, the perimeter topology of benzenoids manifests itself in a variety of ways requiring its thorough understanding.

We will start by tracing the evolution of relationships that define the perimeter topology of polycyclic aromatic hydrocarbons composed exclusively of hexagonal rings (fused benzenoid system = PAH6).<sup>1–6</sup> Then the evolution of our aufbau building-up principles will be discussed. How these two ideas are intricately related will then be exposed. In route, a number of definitions are presented and a number of properties are treated.

## PRELIMINARIES

Polyhexes consist of mutually connected congruent regular hexagons in a geometrically planar arrangement. These systems correspond to what we refer to as molecular graphs of benzenoid hydrocarbons. Thus, the hexagon is a line/vertex depiction of benzene that corresponds to its  $\sigma$ -bond molecular graph but which omits the C/H atoms and  $p\pi$ -bonds. Herein we will have to carefully distinguish between fused, nonfused (benzenoids having a bridging bond joining two benzenoid units), strain-free, strained, helical, and nonhelical benzenoid hydrocarbons. Helical benzenoids have

four or more adjacent (proximate) bay regions and cannot be excised out from the graphite lattice. Hexahelicene ( $\text{C}_{26}\text{H}_{16}$ ) cannot be cut out from the graphite infinite lattice and is the smallest helical benzenoid. We will be concerned only with nonhelical fused benzenoids in all the following sections except the last one.

Let the chemical formula of a benzenoid be denoted by  $\text{C}_n\text{H}_s \equiv (n;s)$ . Its polyhex molecular graph has only degree-2 and degree-3 vertices interconnected by lines (or edges). Let  $e(i, j)$  equal the number of edges with end points (vertices) of degree- $i$  and degree- $j$ , then a polyhex molecular graph has only  $e(2,2)$ ,  $e(2,3)$ , and  $e(3,3)$  types of edges where  $e(2,2)$  occurs only on the perimeter,  $e(3,3)$  occurs internally or on bay regions, and  $e(2,3)$  occurs between the other two types of edges. The total number of carbon atoms ( $N_c = n$ ), hydrogen atoms ( $N_H = s$ ), and C–C  $\sigma$ -bonds [ $q = \frac{1}{2}(3N_c - N_H)$ ] in a benzenoid hydrocarbon ( $\text{C}_n\text{H}_s$ ) is the total number of vertices ( $n$ ), degree-2 vertices ( $s$ ), and interconnecting lines (edges), respectively, in the corresponding polyhex molecular graph. Thus, of special importance in regard to the benzenoid perimeter topology are the invariants of  $C$  (no. of coves = two proximate bay regions),  $F$  (no. of fjords = three proximate bay regions),  $f$  (fissures),  $e(2,2)$  = no. of free edges,  $N_H$  = no. of hydrogens,  $N_{pc}$  = no. of perimeter degree-3 molecular graph vertices, and  $q_p$  = no. of perimeter molecular graph edges which will be defined more completely in the following sections.

## PERIMETER TOPOLOGY OF FUSED (ORDINARY) BENZENOID HYDROCARBONS

The perimeter topology of a benzenoid contains plenty of useful information. For example, as mentioned above, a number of computer polyhex enumerations uses a so-called boundary code.<sup>2–4</sup> The number of peripheral degree-3 vertices,  $N_{pc}$ , on the perimeter of a benzenoid (polyhex) molecular graph is  $N_{pc} = N_H - 6$ . There can be 0, 1, 2, 3, and 4 successive degree-2 vertices between any two nearest peripheral degree-3 vertices designated as bay, solo, duo, trio, and quarto regions, respectively.  $\eta_0$ ,  $\eta_1$ ,  $\eta_2$ ,  $\eta_3$ , and  $\eta_4$  designate the number of bay, solo, duo, trio, and quarto peripheral regions on a given benzenoid molecular graph.<sup>1,5</sup>

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The perimeter topology of any benzenoid molecular graph is described by eq 1

$$-\eta_0 + 0\eta_1 + \eta_2 + 2\eta_3 + 3\eta_4 = 6 \quad (1)$$

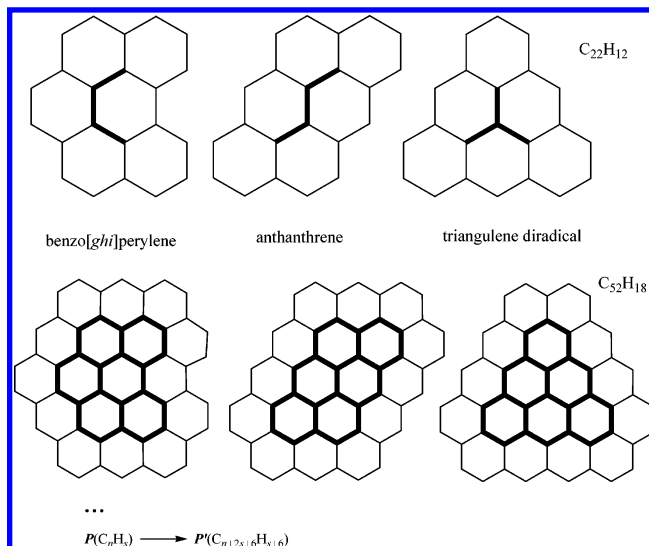
which is independent of the number of solo regions ( $\eta_1$ ); also  $N_H = 0\eta_0 + \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4$ ; we include here the  $0\eta_1$  (i.e., zero solos) in eq 1 and  $0\eta_0$  to make the numeric pattern more obvious to the reader. The molecular graph of a strictly pericondensed benzenoid hydrocarbon has all its internal edges (edges between two adjoined hexagons) and internal degree-3 vertices ( $N_{Ic}$ ) mutually connected and a perimeter topology that is defined by  $-\eta_0 + \eta_2 + 2\eta_3 = 6$  where  $\eta_4 = 0$ . All second generation and higher members of our constant-isomer series have the perimeter topology of  $-\eta_0 + \eta_2 = 6$ . The molecular graph of a catacondensed benzenoid has  $\eta_3 = 0$ , every internal edge disconnected from any other internal edge, and a perimeter topology defined by  $-\eta_0 + \eta_2 + 3\eta_4 = 6$ . We derived eq 1 in 1984 by subtracting  $N_{pc} = \eta_0 + \eta_1 + \eta_2 + \eta_3 + \eta_4$  from  $N_H = \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4$  and noting  $6 = N_H - N_{pc}$ .<sup>1,5</sup> Alternatively, the perimeter circumference length ( $q_p$ ) was obtained by adding these two equations to give  $\eta_0 + 2\eta_1 + 3\eta_2 + 4\eta_3 + 5\eta_4 = N_H + N_{pc} = q_p$  where  $q_p$  equals  $4n$  ( $n = 1, 2, 3, \dots$ ) for odd carbon and  $4n + 2$  for even carbon benzenoids.<sup>1,5</sup>

All constant-isomer benzenoids are extremal benzenoids. A constant-isomer benzenoid has the following properties. For a given number of hexagons ( $r$ ), it has a minimum perimeter length [ $\min(q_p)_r$ ], a maximum number of internal vertices [ $\max(N_{Ic})_r$ ], and a minimum number of vertices [ $\min(N_c)_r$ ], edges [ $\min(q)_r$ ], and degree-2 vertices [ $\min(N_H)_r$ ].

#### CIRCUMSCRIBING AND CONSTANT-ISOMER BENZENOID SERIES

Strictly pericondensed benzenoid sets that have the same number of isomers at each stage of increasing formula are known as constant-isomer series and have formulas only found on the left-hand staircase boundary edge of Table PAH6 (Periodic Table for Benzenoid Hydrocarbons).<sup>1,5,6</sup> Successive circumscribing with hexagonal rings generates constant-isomer benzenoids.<sup>6</sup> Adding a perimeter of carbon and six hydrogen atoms to give a successor  $C_{n+2s+6}H_{s+6}$  benzenoid circumscribes a  $C_nH_s$  benzenoid. Consider the known  $C_{22}H_{12}$  benzenoid isomers<sup>1</sup> given in Figure 1. Circumscribing these isomers with a perimeter of hexagonal rings generates the  $C_{52}H_{18}$  benzenoid isomers as shown. Successive repetition of this process leads to the corresponding three-isomer series. Note that in circumscribing with hexagonal rings, the number of bay regions and symmetry is preserved between the original benzenoid and its successor.

Denote circumscription of a benzenoid by  $P \rightarrow \text{circum}P = P'$ . It has been shown for benzenoids that  $N_{pc} = N_H - 6$  and  $r = (1/2)(N_c - N_H) + 1$  where  $N_c = N_{pc} + N_{Ic} + N_H$ . For  $P(C_nH_s) \rightarrow P'(C_{n+2s+6}H_{s+6})$ ,  $\eta_0 \rightarrow \eta'_0$ ,  $\eta_1 \rightarrow 0$ ,  $\eta_2 \rightarrow \eta'_2$ ,  $\eta_3 \rightarrow 2\eta'_2$ ,  $\eta_4 \rightarrow 3\eta'_2$ , and the number of fissures  $\rightarrow \eta'_1$ ; also,  $N_c \rightarrow N'_{Ic}$  and  $N_H \rightarrow N'_{pc}$  giving  $N'_c = N'_{Ic} + N'_{pc} + N'_H = N_c + 2N_H + 6$  and  $N'_H = N_H + 6$ . The latter two relationships are recursions for the number of carbons and hydrogens resulting after each successive circumscribing step.

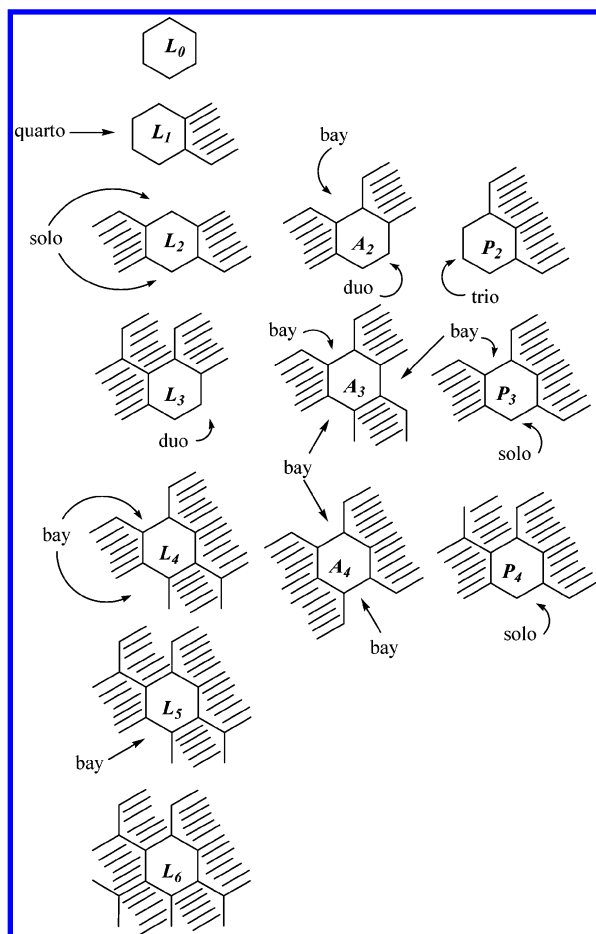


**Figure 1.** Circumscribing the only 3 conjugated isomers of  $C_4H_6$  (shown in bold in the upper row) with hexagonal rings gives the only  $C_{22}H_{12}$  benzenoid isomers. Circumscribing the only  $C_{22}H_{12}$  benzenoid isomers (shown in bold in the lower row) gives the only  $C_{52}H_{18}$  benzenoid isomers. Successive repetition of this process leads to the respective 3-isomers series— $C_{22}H_{12}$ ,  $C_{54}H_{18}$ ,  $C_{96}H_{24}$ ,  $C_{150}H_{30}$ ,  $C_{216}H_{36}$ , ....

#### TYPES OF HEXAGON ADJACENCY IN FUSED BENZENOID HYDROCARBONS

Gutman and Cyvin proposed that with respect to the number of immediately adjacent hexagon neighbors and their mutual positions, one can distinguish 13 distinct modes, denoted as  $L_j$  ( $j = 0-6$ ),  $A_k$ , and  $P_k$  ( $k = 2-4$ ) where the numerical subscript gives the number of adjacent hexagons.<sup>7</sup> These 13 modes are presented in Figure 2. Using Pólya's theorem,<sup>8</sup> one can derive the configuration counting series of  $C(x) = 1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6$  for the hexagon in which the superscripts denotes the number of adjacent hexagons and the coefficients sum to 13 proving that this is the complete list of possibilities. For additional clarity, Figure 3 illustrates a specific polyhex with the various hexagon adjacency codes (except  $L_0$  for the null case of benzene itself) displayed within the relevant hexagon rings. Catacondensed benzenoids can only have  $L_1$ ,  $L_2$ ,  $A_2$ , and  $A_3$  types of hexagon adjacency, and strictly pericondensed benzenoids can only have  $L_3$ ,  $L_5$ ,  $L_6$ ,  $P_2$ , and  $P_4$  types of hexagon adjacency.

From Figure 2, it is seen that  $L_1$  and  $P_2$  each correspond exclusively to a quarto and trio perimeter region, respectively. If we let  $|L_1|$  and  $|P_2|$  with vertical bars represent the respective cardinalities, then  $\eta_4 = |L_1|$  and  $\eta_3 = |P_2|$ . Recall that catacondensed benzenoid molecular graphs *must* have quarto perimeter regions ( $\eta_4 \geq 2$ ) and only pericondensed benzenoid molecular graphs *may* have trio perimeter regions ( $0 \leq \eta_3$ ).<sup>1,5</sup> Only  $A_2$  and  $L_3$  have a duo perimeter region. Only  $L_2$ ,  $P_3$ , and  $P_4$  have solo perimeter regions, and  $A_2$ ,  $A_3$ ,  $P_3$ ,  $L_4$ ,  $A_4$ , and  $L_5$  have bay perimeter regions.  $L_2$  has two solo perimeter regions,  $P_3$  has a solo and a bay perimeter region, and  $P_4$  has a single solo perimeter region.  $L_5$  has a single,  $A_4$  has two, and  $A_3$  has three bay perimeter regions. The connection between our perimeter topology terminology<sup>1,5</sup> and Gutman and Cyvin's hexagon adjacency  $L/A/P$  terminology<sup>7</sup> will now be established.



**Figure 2.** The 13 possible arrangements of hexagons in benzenoid systems consistent with the counting polynomial of  $C(x) = 1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6$  where the coefficients count the number of row entries above; their  $L/A/P$  notations are given where the numerical subscripts gives the number of adjacent hexagons shown in hatch. The perimeter designations (bay, solo, duo, trio, and quarto) are also given.

#### CONNECTION BETWEEN THE DIAS PERIMETER TOPOLOGY EQUATIONS AND THE GUTMAN-CYVIN HEXAGON ADJACENCY EQUATIONS

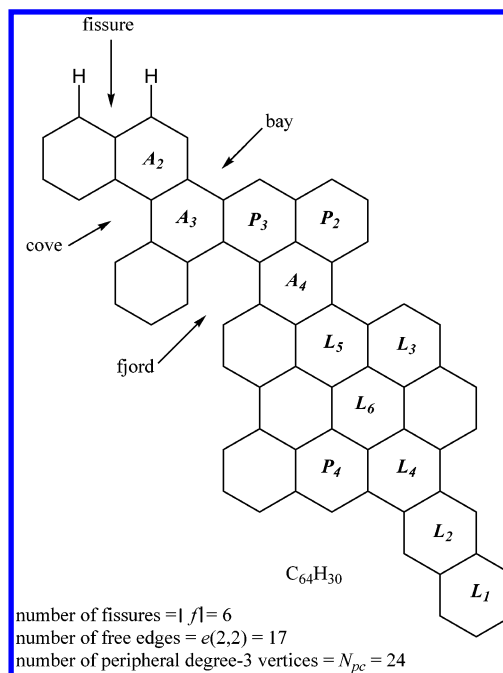
Recall eq 1 above. We will now match term-by-term the perimeter topology terms ( $\eta_0, \eta_1, \eta_2, \eta_3, \eta_4$ ) with the hexagon adjacency terms [ $|L_j|$  ( $j = 1-6$ ),  $|A_k|$ , and  $|P_k|$  ( $k = 2-4$ )]. Examining Figure 2, it can be seen that the number of bay regions correspond to  $\eta_0 = |A_2| + 3|A_3| + 2|A_4| + 2|L_4| + |L_5| + |P_3|$ . The number of solo regions correspond to  $\eta_1 = 2|L_2| + |P_3| + |P_4|$ , and the number of duo regions correspond to  $\eta_2 = |A_2| + |L_3|$ . The number of trio and quarto regions correspond to  $\eta_3 = |P_2|$  and  $\eta_4 = |L_1|$ , respectively. Inserting these equalities into eq 1 gives

$$-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = -3|A_3| - 2|A_4| + 3|L_1| + |L_3| - 2|L_4| - |L_5| + 2|P_2| - |P_3| = 6 \quad (2)$$

Equation 2 is in agreement with that given by John<sup>9,10</sup> which is simply another expression of our prior eq 1.<sup>1,5</sup>

#### FURTHER PERIMETER PARAMETERS

Gutman and Cyvin defined<sup>7</sup> a free edge as an edge between two vertices of degree-2, the number of which was previously defined as  $e(2,2)$  on page 28 of our book.<sup>1</sup> Among



**Figure 3.** Illustration of notation from Figure 2.

the other relationships defined<sup>1</sup> on pages 28–29 are  $q_p = \eta_0 + 2\eta_1 + 3\eta_2 + 4\eta_3 + 5\eta_4$  and  $e(2,2) = 6 + e(3,3)_p = 6 + \eta_0$  where the former is perimeter length. Using the relationships determined in the prior section between our topological perimeter terms and the Gutman and Cyvin hexagon adjacency terms, we obtain the following equation for the perimeter length

$$q_p = \eta_0 + 2\eta_1 + 3\eta_2 + 4\eta_3 + 5\eta_4 = 4|A_2| + 3|A_3| + 2|A_4| + 5|L_1| + 4|L_2| + 3|L_3| + 2|L_4| + |L_5| + 4|P_2| + 3|P_3| + 2|P_4| \quad (3)$$

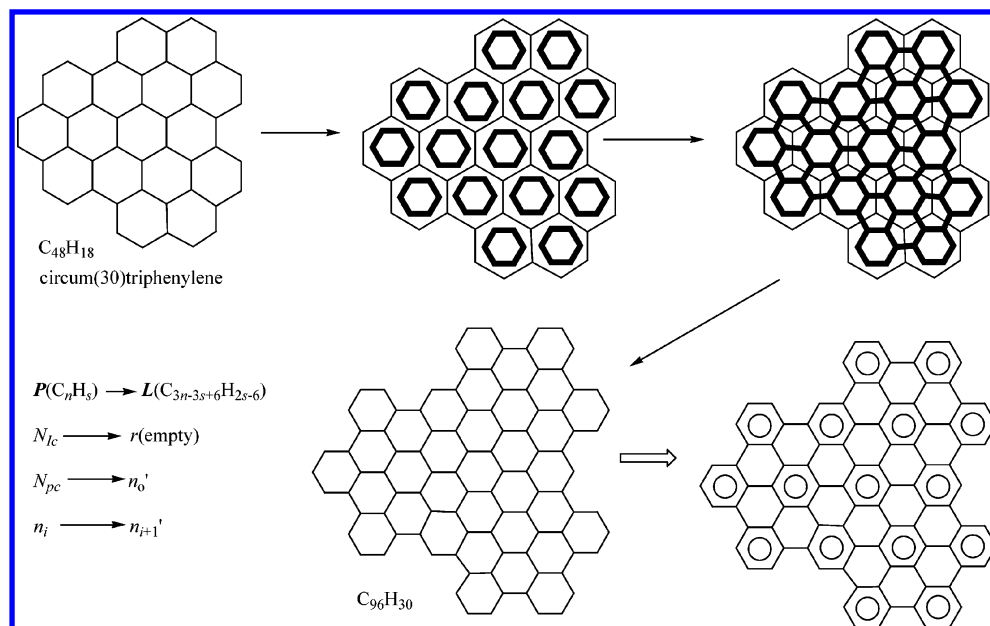
that agrees with eq 9 in Cyvin's et al. prior paper.<sup>11</sup> The next equation also agrees with eq 10 in the same paper:<sup>11</sup>

$$e(2,2) = 6 + \eta_0 = |A_2| + 3|L_1| + |L_3| + 2|P_2| \quad (4)$$

Thus, our prior equations<sup>1</sup> for perimeter length and number of free edges in terms of our perimeter topology parameters have fewer terms but are otherwise equivalent to the equations by Gutman and Cyvin<sup>10,11</sup> expressed in terms of their hexagon adjacency parameters.

#### CLAR'S SEXTET PRINCIPLE AND STRAIN-FREE TRS BENZENOID HYDROCARBONS

Clar's sextet principle states that a TRS benzenoid (called fully benzenoid by Clar) is, in general, kinetically more stable.<sup>12</sup> A TRS benzenoid is characterized by the fact that its number of carbons is divisible by six and has a molecular graph **totally** covered by disjoint inscribed circles. A molecular graph is the C–C  $\sigma$ -bond representation of a benzenoid structure and each inscribed circle represents a benzene **resonant** sextet of  $p\pi$ -electrons. The inscribed circles are separated by so-called empty rings because all the  $p\pi$ -electrons have been formally assigned to the adjoining sextets (circles). All empty rings have exactly three adjacent resonant sextet rings and have hexagon adjacency of  $A_3$ ,  $L_4$ ,  $L_5$ , or  $L_6$ . Polyphenylenes and related nonfused benzenoid



**Figure 4.** Leapfrog transformation of circumtriphenylene ( $C_{48}H_{18}$ ) generates the TRS  $C_{96}H_{30}$  benzenoid synthesized by Mullen and co-workers.

systems represent a special subclass of TRS benzenoids. Benzenoids that are not TRS benzenoids are said to be ordinary. It will be important to make the distinction between fused and nonfused and strained and strain-free TRS benzenoid systems and their topological characteristics. Thus there are four categories of TRS benzenoids—strained and strain-free TRS made up of only fused hexagonal rings and strained and strain-free TRS having phenyl, polyphenylenyl, and/or TRS aryl substituents.<sup>13</sup> The major premise of our early work on these systems was that only fused strain-free TRS benzenoid hydrocarbons would survive the pyrolytic condition under which they were formed.<sup>1,14</sup> Strain-free TRS benzenoids are devoid of fjords (3 adjacent bay regions) on their perimeters. As it turned out, this strain-free premise was essential for our discovery of the topological paradigm concerning ordinary benzenoids and the TRS benzenoids.<sup>14,15</sup> That strain-free TRS benzenoids are the only leapfrog successors of ordinary benzenoids is a key discovery.<sup>16</sup>

#### PERIMETER TOPOLOGY OF TOTAL RESONANT SEXTET BENZENOID HYDROCARBONS

We pointed out that a cove (two adjacent bay regions) never occurs in a TRS benzenoid.<sup>14,17</sup> Subsequently, Gutman and Babić not only proved this but went further and proved that benzenoid and linked benzenoid systems which do not possess fissures or coves are TRS benzenoid hydrocarbons;<sup>18</sup> a fissure ( $f$ ) is a peripheral degree-3 vertex bounded by degree-2 vertices (cf. with Figure 3). In addition, strain-free TRS benzenoids cannot possess fjords (three adjacent bay regions). Also, the absence of coves and/or fjords is a prerequisite for being able to circumscribe a benzenoid (vide infra). At this juncture recall that hexahelicene ( $C_{26}H_{16}$ ) has four adjacent bay regions, and it and higher helical systems are excluded in all the following sections except the last one because they cannot be cut out from the graphite sheet.

#### PERIMETER TOPOLOGY OF BENZENOID HYDROCARBONS, CLAR'S SEXTET PRINCIPLE, AND LEAPFROG ALGORITHM

If we let  $\eta_5$  be the number of phenyl groups, eq 1 for the perimeter topology can further be generalized as

$$-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 + 4\eta_5 = 6 \quad (5)$$

Also,  $N_H = \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4 + 5\eta_5$ . Figure 4 illustrates the leapfrog procedure. In general, let the overall leapfrog transformation be denoted by  $P(C_nH_s) \rightarrow L(C_{3n-3s+6}H_{2s-6})$ . In going from  $P$  to  $L$ , the following correspondences hold:  $N_{lc} \rightarrow r(\text{empty})$ ,  $N_{pc} \rightarrow \eta_0'$ , and  $\eta_j \rightarrow \eta_{j+1}'$  where  $j = 0, 1, 2, 3$ , and  $4$ . The conversion of peripheral degree-3 vertices to bay regions causes fissures to disappear. The previous perimeter topology relationship for all benzenoids becomes  $-\eta_1' + \eta_3' + 2\eta_4' + 3\eta_5' = 6$  where the prime emphasizes that this latter equation is only valid for strain-free (leapfrog) TRS benzenoids and  $\eta_5'$  is the number of phenyl groups. By equating the perimeter topology relationship for all benzenoids with that for strain-free TRS benzenoids, we obtain eq 6

$$-\eta_0' + \eta_1' + \eta_2' + \eta_3' + \eta_4' + \eta_5' = 0 \quad (6)$$

which is valid only for the perimeter topology of leapfrog TRS benzenoid hydrocarbons. All strain-free TRS benzenoids are leapfrogs, but leapfrogs of hexahelicene-related species are strained and are not regarded as ordinary benzenoids.<sup>13</sup> Since this equation is an expression of the perimeter topology, its application to requires one to go completely around the perimeter of any benzenoid while counting the various successive degree-2 vertices between any two nearest peripheral degree-3 vertices. Thus, bridging edges between two polyhex units will be counted twice, once for each traversal direction. For example, encircling biphenyl gives  $\eta_0' = 2$  and  $\eta_5' = 2$  because in this process one passes over the bridging edge twice in different directions and once for



each phenyl group; application of the relevant equation gives  $-\eta_0' + \eta_1' + \eta_2' + \eta_3' + \eta_4' + \eta_5' = -2 + 2 = 0$ .

This perimeter topological equation says that the number of bay regions must cancel out the sum of the other perimeter types, i.e., when the number of carbons are divisible by 6, there must be a maximum number of bay regions for the TRS benzenoid isomer subset. For example, triphenylene has 3 bay regions ( $\eta_0' = 3$ ) whereas its 4 other  $C_{18}H_{12}$  benzenoid isomers have two to zero bays. Similarly, dibenzo[*fg,op*]-naphthacene has  $\eta_0' = 4$ , and its 13 other  $C_{24}H_{14}$  benzenoid isomers (12 nonradical and 1 diradical) have  $\eta_0' = 3$  to 1. In addition, strain-free TRS benzenoid isomers have the same maximum number of bay regions. This explains the requisite type of perimeter topology a TRS benzenoid must have, but which very few benzenoids comply.

Further insight can be gained by application of the perimeter topological eq 6 to 1-phenyltriphenylene and 2-phenyltriphenylene. 1-Phenyltriphenylene is a strained TRS because it has a fjord-like region and consequently can be thermally cyclodehydrogenated to dibenzo[*fg,op*]naphthacene, and it is not a leapfrog. In contrast, 2-phenyltriphenylene is a strain-free TRS which is the leapfrog successor of benzo[*de*]anthracene. For 1-phenyltriphenylene,  $-\eta_0' + \eta_1' + \eta_2' + \eta_3' + \eta_4' + \eta_5' = -6 + 0 + 0 + 1 + 2 + 1 \neq 0$ , and for 2-phenyltriphenylene  $-\eta_0' + \eta_1' + \eta_2' + \eta_3' + \eta_4' + \eta_5' = -5 + 1 + 1 + 0 + 2 + 1 = 0$ . In the first case, the equation does not equate to zero, whereas in the second case it does equate to zero. Clearly application of this perimeter topological equation represents an important diagnostic difference between strained and strain-free TRS benzenoids that are not derived from leapfrogging hexahelicene-related benzenoids.

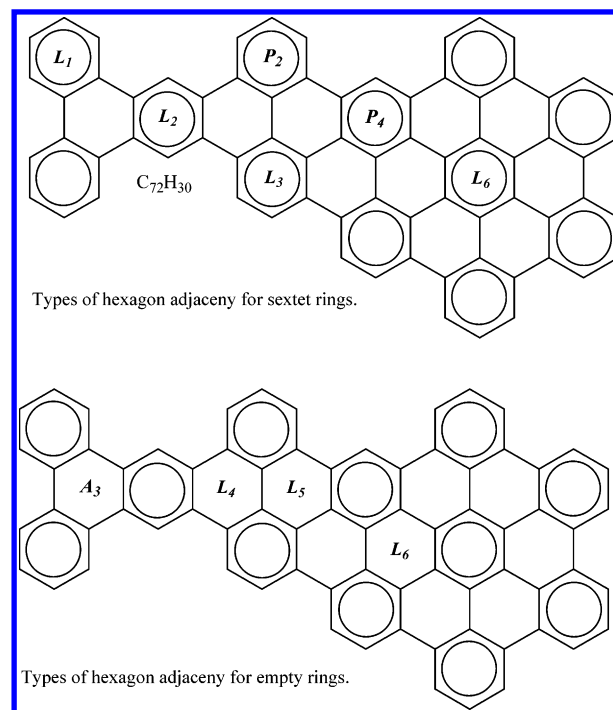
Previously we derived eq 7 that gives the number of bay regions ( $\eta_0$ ) any fused strain-free TRS benzenoid must have<sup>14</sup>

$$\eta_0(\max) = (1/6)N_c + 1/3(d_s - 2) = 1/2N_H - 3 \quad (7)$$

This is also the upper bound for the maximum number of bay regions any constant-isomer benzenoid can have. The latter equality in eq 7 results from our parameter relationship of  $d_s = (1/2)(3N_H - N_c - 14)$ .<sup>5</sup>

#### CONNECTION BETWEEN THE DIAS PERIMETER TOPOLOGY EQUATIONS AND THE GUTMAN-CYVIN HEXAGON ADJACENCY EQUATIONS FOR FUSED STRAIN-FREE TRS BENZENOID

In this section and the following sections, we restrict our discussion to exclusively fused TRS benzenoid hydrocarbons, i.e., no phenyl or TRS aryl substituted TRS benzenoids are allowed. Gutman considered the effect of sextet rings on the total  $\pi$ -electron energy for a series of TRS benzenoid hydrocarbons and found complete agreement with Clar's aromatic sextet theory.<sup>19</sup> This study examined the consequence of sextets in all of the hexagon adjacencies shown in Figure 2. All these hexagon adjacencies are possible if one includes both strained and strain-free TRS benzenoids, as done by Gutman.<sup>19</sup> If we restrict ourselves to only fused strain-free TRS benzenoids, then a shorter list of hexagon adjacencies results. In addition, we will consider hexagon adjacency for the empty and sextet rings separately. Figure 5 shows all the possible hexagon adjacencies for fused strain-



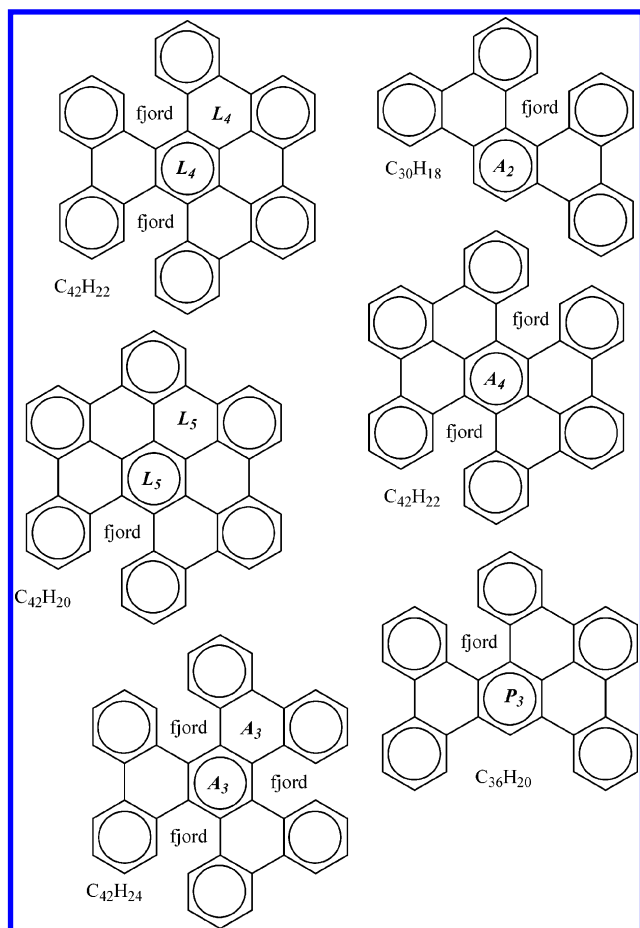
**Figure 5.** Types of hexagon adjacency in strain-free TRS benzenoid hydrocarbons. For sextet rings, only  $L_1$ ,  $L_2$ ,  $L_3$ ,  $L_6$ ,  $P_2$ , and  $P_4$  are possible. For the empty rings, only  $A_3$ ,  $L_4$ ,  $L_5$ , and  $L_6$  are possible. For strain-free TRS benzenoids,  $A_2$ ,  $A_4$ , and  $P_3$  types of hexagon adjacency are not possible for either the sextet or empty rings.

free TRS benzenoids. The upper TRS structure gives the relevant  $L/A/P$  labels for the sextet rings and the lower one for the empty rings. As shown by Figure 6, the hexagon adjacency types  $A_2$ ,  $A_4$ , and  $P_3$  can only occur in sextet rings of strained TRS benzenoids which necessarily must have fjords; note that the  $C_{30}H_{18}$ ,  $C_{42}H_{24}$ , and  $C_{42}H_{22}$  strained TRS benzenoids in Figure 6 are known.<sup>1</sup> For strained or strain-free TRS benzenoids, the  $L/A/P$  labels of  $L_1$ ,  $L_2$ ,  $L_3$ ,  $A_2$ ,  $A_4$ ,  $P_2$ ,  $P_3$ , and  $P_4$  can never occur in empty rings, i.e., empty rings are always of the  $A_3$ ,  $L_4$ ,  $L_5$ , and  $L_6$  type. Only  $L_6$  can occur in a sextet or empty ring in both strained and strain-free systems but is never found on a benzenoid perimeter. Examining Figure 2 and excluding the hexagon adjacency types  $A_2$ ,  $A_4$ , and  $P_3$ , it can be seen that the number of bay regions correspond to  $\eta_0 = 3|A_3| + 2|L_4| + |L_5|$ . The number of solo regions correspond to  $\eta_1 = 2|L_2| + |P_4|$ , and the number of duo regions correspond to  $\eta_2 = |L_3|$ . The number of trio and quarto regions still correspond to  $\eta_3 = |P_2|$  and  $\eta_4 = |L_1|$ , respectively. Inserting these equalities into eq 1 gives

$$-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = -3|A_3| + 3|L_1| + |L_3| - 2|L_4| - |L_5| + 2|P_2| = 6 \quad (8)$$

for fused strain-free TRS benzenoids. Alternatively, using  $-\eta_1' + \eta_3' + 2\eta_4' = 6$ , which is only valid for fused strain-free (leapfrog) TRS benzenoids, gives

$$-\eta_1' + \eta_3' + 2\eta_4' = 2|L_1| - 2|L_2| + |P_2| - |P_4| = 6 \quad (9)$$



**Figure 6.** Strained TRS benzenoid hydrocarbons have fjords and cannot be leapfrogs. Example strained TRS benzenoids and their relevant hexagon adjacency term.

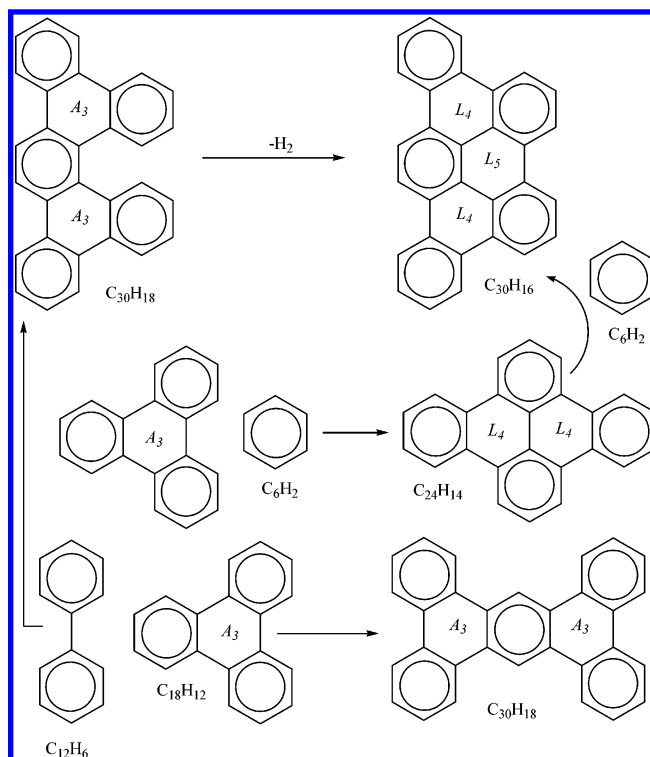
Either equating eqs 8 and 9 or inserting the  $L/A/P$  relationships into eq 6 gives the following eq 10

$$(|L_1| + 2|L_2| + |L_3| + |P_2| + |P_4|) - \text{sextet ring terms} \\ (3|A_3| + 2|L_4| + |L_5|) = 0 \quad (10) \\ \text{empty ring terms}$$

where the first set of hexagon adjacency terms in parentheses are for sextet rings and the second set of terms in parentheses are for empty rings. Note that eq 10 is independent of  $L_6$  which may be either an empty or sextet ring. For catacondensed strain-free TRS benzenoids eq 10 reduces to  $(|L_1| + 2|L_2|) - (3|A_3|) = 0$  and for strictly pericondensed strain-free TRS benzenoids it reduces to  $(|L_3| + |P_2|) - (|L_5|) = 0$ .

The coefficients in each parentheses of eq 10 sum to six. The coefficient of 1 to the  $|L_1|$ ,  $|L_3|$ ,  $|P_2|$ , and  $|P_4|$  terms of eq 10 means there is a single cluster of adjacent empty rings, the coefficient of 2 to the  $|L_2|$  term means there are two nonadjacent empty rings, the coefficient of 3 to the  $|A_3|$  term means there are three nonadjacent sextet rings, the coefficient of 2 to the  $|L_4|$  term means there are two nonadjacent groups consisting of one isolated sextet ring and a cluster of three adjacent hexagons composed of two disjoint sextets, and coefficient of 1 to the  $|L_5|$  term means that there is a single cluster of five adjacent hexagons composed of three disjoint sextets (cf. with Figure 5).

Recall that the molecular graph of a strictly pericondensed benzenoid hydrocarbon has all its internal edges and degree-3



**Figure 7.** Three modes of aufbau construction of TRS benzenoid hydrocarbons are necessary and sufficient.

vertices mutually connected and a perimeter topology that is defined by  $-\eta_0 + \eta_2 + 2\eta_3 = 6$  where  $\eta_4 = 0$ . Thus, eq 2 becomes

$$-\eta_0 + \eta_2 + 2\eta_3 = -|L_5| + |L_3| + 2|P_2| = 6 \quad (11)$$

which is independent of  $\eta_1 = |P_4|$ ; also  $N_H = \eta_1 + 2\eta_2 + 3\eta_3 = 2|L_3| + 3|P_2| + |P_4|$ . All second generation and higher members of our constant-isomer series have the perimeter topology of  $-\eta_0 + \eta_2 = 6 = |L_3| - |L_5|$  where  $N_H = \eta_1 + 2\eta_2 = 2|L_3| + |P_4|$ . The reader may verify these relationships using the first two-generation members of the three-isomer series in Figure 1.

#### BUILDING-UP (AUFBAU) OF FUSED TOTAL RESONANT SEXTET BENZENOID HYDROCARBONS

There are three types of addition of hexagons which are sufficient for generating all fused total resonant sextet benzenoids.<sup>13,19</sup> All total resonant sextet benzenoids can be generated by additions of one, two, or three hexagons at a time. These five, three, and one contact hexagon additions occur in fjords, on bay regions, or on free edges, respectively. These aufbau constructions involve closing-up a fjord with concurrent loss of  $H_2$ , the addition of the  $C_6H_2$  benzenetetrayl sextet aufbau unit to a bay region with concurrent transfer of two hydrogens, and the addition of the  $C_{12}H_6$  biphenyltetrayl double sextet aufbau unit to a free edge with concurrent transfer of two hydrogens. Figure 7 illustrates these aufbau constructions with the smallest known TRS benzenoids.<sup>1</sup> Note that the first hexagon addition increases the number of internal third degree vertices by four ( $\Delta N_{ic} = 4$ ), the attachment of a benzene sextet piece to a bay region increases the number of internal third degree vertices by two ( $\Delta N_{ic} = 2$ ), and the attachment of the biphenyl sextet piece to a free edge does not change the number of internal third degree

vertices ( $\Delta N_{lc} = 0$ ) in the successor strain-free TRS benzenoid. The aufbau generation of all catacondensed benzenoids only requires successive attachment of the biphenyl sextet piece.<sup>14,20</sup> The contact regions for all three constructions become empty rings. We now state this fundamental building-up principle in sharper form.

**Principle 1.** Starting with benzene or biphenyl all fused TRS benzenoids are obtained through a repetitive process by forming a hexagon region within fjords, attaching a benzene sextet piece to bay regions, and a biphenyl sextet piece to a free edges with the proximate formation of  $L_5$ ,  $A_3$ , and  $L_4$  type of empty rings, respectively.

To demonstrate this principle it should first be ascertained that every TRS benzenoid has appropriate empty rings. Equation 10 [also confer with Figure 4] demonstrates that every strain-free (and strained) TRS benzenoid must have  $A_3$ ,  $L_4$ , and  $L_5$  types of empty rings.

**Proposition 1.** Any fused TRS benzenoid with  $r > 2$  has one or more empty hexagons of  $A_3$ ,  $L_4$ , and  $L_5$  types.

By virtue of Proposition 1, it is clear that one, two, or three hexagons joined through  $A_3$ ,  $L_4$ , and  $L_5$  types of empty hexagon can be removed from any TRS benzenoid with  $r > 2$  so as to produce a smaller TRS benzenoid. In this way it must be possible to tear down any fused TRS benzenoid completely to benzene or biphenyl. It is implied that one, two, or three hexagons are removed every time in this tearing-down process, which is opposite to the building-up. Therefore it is also possible to build up any TRS benzenoid by successively attaching a benzene or biphenyl sextet piece or closing a fjord through  $A_3$ ,  $L_4$ , and  $L_5$  empty ring modes every time. This completes the demonstration of the sufficiency of Principle 1.

Principle 1 states the sufficiency of adding one, two, or three hexagons at a time. It is easy to prove the necessity of Principle 1 for building up a TRS benzenoid in general. To begin with, joining the two smallest TRS benzenoids, benzene and biphenyl, gives triphenylene with concurrent formation of the  $A_3$  empty ring type. Figure 7 shows the next three smallest strain-free TRS benzenoids (ref 1, page 86) of each empty ring type which establish their necessity. Attachment of the benzene sextet piece ( $C_6H_2$ ) to one of the bay regions of triphenylene ( $C_{18}H_{12}$ ) gives dibenzo[fg,op]-tetracene ( $C_{24}H_{14}$ , also named dibenzo[fg,op]naphthacene) resulting in the concurrent formation of another  $L_4$  empty ring and conversion of the  $A_3$  empty ring mode in triphenylene to a  $L_4$  empty ring mode. Note that formation an empty ring mode adjacent to another causes a change in the mode of the latter and that the number of internal third degree vertices increased by two. Alternatively, triphenylene can be converted to tetrabenzo[a,c,h,j]naphthacene or dibenzo[fg,j]picene ( $C_{30}H_{18}$ ) by attachment of a biphenyl sextet piece ( $C_{12}H_6$ ) to one of its three 1,2 or 3,4 equivalent free edges, respectively, resulting in concurrent formation of another  $A_3$  empty ring mode. In this example, the mode of the nonadjacent empty ring and the number of internal third degree vertices do not change as in the previous example. As a final example, attachment of a benzene sextet piece to one of the four equivalent bay regions of dibenzo[fg,op]naphthacene gives tribenzo[fg,ij,rs]pentaphene ( $C_{30}H_{16}$ ) with the concurrent formation of a  $L_4$  empty ring mode and an increase in the number of internal third degree vertices from two to four. In this example, the newly formed empty ring

causes a change of the adjacent empty ring mode from  $L_4$  to  $L_5$ , whereas the more remote  $L_4$  empty ring remains unchanged. Alternatively, closing up the fjord in dibenzo[fg,j]picene with concurrent expulsion of  $H_2$  will also give tribenzo[fg,ij,rs]pentaphene and is analogous to our premise that all related benzenoid systems with fjords will not survive pyrolytic conditions.<sup>1,14</sup> This completes the proof of our aufbau for TRS benzenoids.

#### MODIFIED BUILDING-UP (AUFBAU) OF FUSED TOTAL RESONANT SEXTET BENZENOID HYDROCARBONS

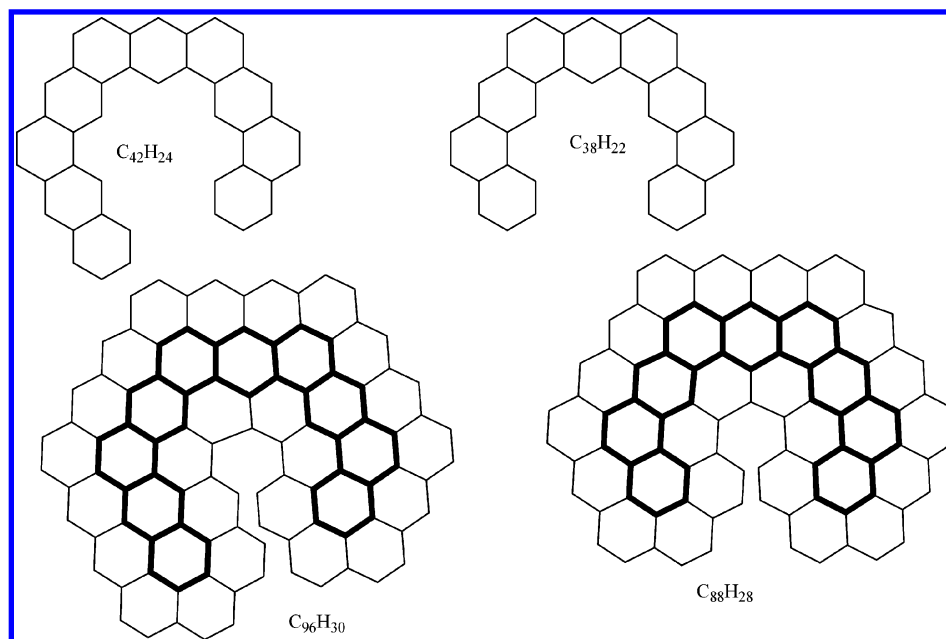
Our modified aufbau for building-up TRS benzenoids replaces the one hexagon addition operation which involves the closing-up of fjords with the extrusion of  $H_2$  by enumerating strictly pericondensed TRS benzenoids instead. These latter macromolecular TRS benzenoids ( $C_{n+3s+18}H_{s+12}$ ) are constructed from a smaller TRS benzenoid ( $C_nH_s$ ) by replacing all  $\geq C-H$  peripheral units by  $>C=CH_2$  ( $C_{n+s}H_{2s}$ ) and circumscribing the resulting excised internal structure. In this way benzene ( $C_6H_6$ ) becomes hexamethylenebenzene ( $C_{12}H_{12}$ ) which when circumscribed gives hexabenzob[bc,ef,hi,kl,no,qr]coronene ( $C_{42}H_{18}$ ).<sup>14,20</sup> This overall process is called augmented circumscribing. Augmented circumscribing of biphenyl ( $C_{12}H_{10}$ ) and triphenylene ( $C_{18}H_{12}$ ) gives the next two smallest strictly pericondensed TRS benzenoids  $C_{60}H_{22}$  and  $C_{72}H_{24}$ , respectively.<sup>14</sup> Using this modified aufbau all strain-free TRS benzenoids up to and including 60 carbons were enumerated and displayed by the author.<sup>14,17</sup> All strained TRS benzenoids were excluded in this enumeration because it was one of our fundamental premises that this system would not survive pyrolytic formation due to relief of strain by extrusion of  $H_2$  to close-up the fjord.

#### GENERAL AUFBAU PRINCIPLE

Our fundamental aufbau principle was proven by Cyvin and co-workers.<sup>10</sup> It states that all fused benzenoid isomers of a given formula of  $C_nH_s$  are generated by all combinatorial attachments (with concurrent transfer of two hydrogens) of  $C_2$  aufbau units to the bay regions,  $C_3H$  aufbau units to the vee-shaped fissure regions, and  $C_4H_2$  aufbau units to free edges to all benzenoid isomers of formulas  $C_{n-2}H_s$ ,  $C_{n-3}H_{s-1}$ , and  $C_{n-4}H_{s-2}$ , respectively.<sup>6</sup> Starting with benzene, all the catacondensed benzenoids are generated by repetitive combinatorial attachment of the  $C_4H_2$  aufbau unit. The  $C_2$  (ethenetetrayl),  $C_3H$  (allyltetrayl), and  $C_4H_2$  (1,3-butadiene-tetrayl) are elementary aufbau units since all other aufbau units are some combination of them. For example, the  $C_6H_2$  benzene and  $C_{12}H_6$  biphenyl sextet pieces for construction of TRS benzenoid systems as described above have the equivalency of  $C_6H_2 = C_2 + C_4H_2$  and  $C_{12}H_6 = 3C_4H_2$ ; i.e., by appropriate sequential attachment of the elementary aufbau units, one can duplicate the action of these sextet pieces in construction of TRS benzenoids.

#### MODIFIED AUFBAU PRINCIPLE

In our original studies,<sup>1,21</sup> we employed our modified aufbau which uses two elementary aufbau units ( $C_3H$  and  $C_4H_2$ ) and the circumscribing operation. While isomorphic duplicates, which must be deleted, are necessarily generated



**Figure 8.** Two benzenoid hydrocarbons which can be circumscribed only once.

by the aufbau construction, circumscribing is exclusive. Thus, some reduction in the generation of isomorphic duplicates occurs in the use of the of our modified aufbau enumeration.

#### NONHELICAL STRAINED BENZENOID SYSTEMS

Recall that hexahelicene ( $C_{26}H_{16}$ ) possessing 4 adjacent bay regions and related helical polyhexes that cannot be cut out from the infinite graphite sheet are excluded herein in our use of strained and strain-free benzenoid system. Nonhelical strained benzenoid systems are defined as having fjords (3 adjacent bay regions). Furthermore, leapfrogs of benzenoids are invariably strain-free TRS benzenoids, TRS benzenoids are topologically unable to possess coves (2 adjacent bay regions), and benzenoids with coves cannot be circumscribed. Strained TRS benzenoids have fjords (Figure 6). Since eqs 6, 7, and 10 are only valid for strain-free TRS benzenoids (e.g., Figures 4 and 5), we now present modified versions of these equations which are valid for all TRS benzenoids, both strain-free and strained. Let the number of fjords in a benzenoid be designated by  $F$ . Equation 6 becomes

$$-\eta'_0 + \eta'_1 + \eta'_2 + \eta'_3 + \eta'_4 + \eta'_5 + 2F = 0 \quad (12)$$

Application of eq 12 to the strained  $C_{42}H_{22}$  TRS benzenoid (Figure 6) having  $F = 2$  gives  $-10 + 0 + 0 + 2 + 4 + 0 + 4 = 0$ . Similarly, eq 7 can also be modified to give

$$\eta_0(\text{TRS}) = (1/6)N_c + 1/3(d_s - 2) + F = 1/2N_H(\text{sextet}) - 3 + F \quad (13)$$

which is valid for strain-free and strained TRS benzenoids. The reader again can test the validity of this equation on the strained TRS benzenoids in Figure 6.

The relationship between the number of coves  $C$ , fjords  $F$ , free edges  $e(2,2)$ , bay regions  $\eta_0$ , and fissures  $|f|$  is

$$N_H = e(2,2) + |f| + \eta_0 - C - 2F \quad (14)$$

Equation 13 is a new perimeter topology expression valid for nonhelical benzenoids.

#### HELICAL POLYCYCLIC AROMATIC HYDROCARBONS

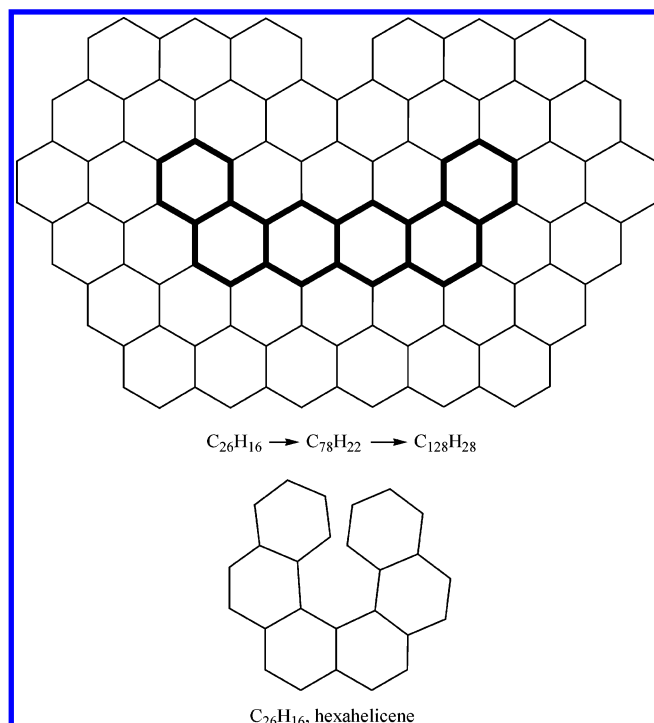
The term helical is used for PAH6 systems that have a quartet (four adjacent) or larger multiple of proximate bay regions. Thus, pentahelicene (dibenzo[*c,g*]phenanthrene,  $C_{22}H_{14}$ ) with three proximate bay regions (i.e., fjord) is nonhelical, whereas hexahelicene (phenanthro[3,4:*d*]phenanthrene,  $C_{26}H_{16}$ ) with four proximate bay regions is helical. PAH6s possess two characteristic types of perimeter curvatures—convex and concave. A concave region is a PAH6 perimeter section with zero, one, or more solo units bounded by bay regions, otherwise it is a convex region. A proximate multiple of bay regions (coves, fjords, etc.) is concave. Constant-isomer benzenoids can only possess convex curvatures. When circumscribing a benzenoid once, the number of bay regions are conserved ( $\Delta\eta_0 = 0$ ), the number of duo regions is either conserved or increases ( $\Delta\eta_2 = 2\eta_3 + 3\eta_4$ ), and the number of trio and quarto regions disappear ( $\eta_3, \eta_4 \rightarrow 0$ ) in the successor benzenoid.<sup>22</sup>

**Theorem 1.** When circumscribing a benzenoid once, the number of solo perimeter regions increases in convex regions and decreases in concave regions.

Benzenoids with a doublet (cove) or higher multiple of adjacent bay regions cannot be circumscribed because the concave region is devoid of solo units. Figure 8 illustrates the circumscription of benzenoids with both convex and concave regions where the concave regions contain solo units. Circumscribing the benzenoids shown in bold once leads to successor PAH6s in which the solo units have disappeared and the four bay regions have been merged. Because these successor PAH6s now have four proximate bay regions, they cannot be further circumscribed per Theorem 1.

**Theorem 2.** If the concave region contains  $l$  fissures, then the corresponding benzenoid can only be circumscribed  $(l + 1)$  times.





**Figure 9.** Dibenzo[*a,l*]tetracene (in bold) has two solo groups within its (upper) convex region and can only be circumscribed with hexagonal rings twice before the disappearance of these solo groups resulting in a cove. Its isomer, hexahelicene, without solo groups within the convex region cannot be circumscribed.

Figure 9 shows dibenzo[*a,l*]tetracene in bold which has a single fissure within its concave region. Circumscribing it twice ( $l + 1 = 2$ ) results in a successor benzenoid having a cove which cannot be circumscribed further.

We will now generalize eq 13 to include helical PAH6s. Let  $i$  be the number of bay regions that are adjacent within a given group. The number of such aggregates will be designated as  $(\eta_0)_i$  where  $i \geq 2$ . Then the number of coves  $C$  and fjords  $F$  would be designated by  $C = (\eta_0)_2$  and  $F = (\eta_0)_3$ , respectively. For hexahelicene  $\eta_0 = 4$  and  $(\eta_0)_4 = 1$ . With this notation eq 14 can be generalized as

$$N_H = e(2,2) + |f| + \eta_0 - \sum (i-1)(\eta_0)_i \quad (15)$$

For example, application of eq 15 to hexahelicene ( $C_{26}H_{16}$ ) gives  $N_H = 10 + 5 + 4 - 3 = 16$ .

Previously,<sup>5</sup> we derived the following relationship for the difference in the eighth coefficient to the characteristic polynomial of (nonhelical) catacondensed benzenoids in regard to their acene reference:

$$\Delta a_8(\text{cata-isomers}) = (5r - 9)\eta_0 - 2\eta_4 - C - 2F + 4 \quad (16)$$

Equation 16 can now be generalized helical PAH6s as

$$\Delta a_8(\text{cata-PAH6 isomers}) = (5r - 9)\eta_0 - 2\eta_4 + 4 - \sum (i-1)(\eta_0)_i \quad (17)$$

To illustrate eq 17 consider the  $C_{26}H_{16}$  ( $r = 6$ ,  $\eta_4 = 2$ ) isomers in Figure 9. It is known<sup>23,24</sup> that  $a_8 = 16\,222$  for hexacene ( $\eta_0 = 0$ ),  $a_8 = 16\,264$  for dibenzo[*a,l*]tetracene ( $\eta_0 = 2$ ), and  $a_8 = 16\,303$  for hexahelicene ( $\eta_0 = 4$ ,  $(\eta_0)_4 = 1$ ). Thus, for dibenzo[*a,l*]tetracene  $\Delta a_8 = 16\,264 - 16\,222$

$= 21 \cdot 2 - 2 \cdot 2 + 4 - 0 - 0 - 0 = 42$ , and for hexahelicene  $\Delta a_8 = 16\,303 - 16\,222 = 21 \cdot 4 - 2 \cdot 2 + 4 - 0 - 0 - 3 = 81$ . From eqs 16 and 17 it should be evident that the coefficients to the characteristic polynomial contain structural information associated with the perimeter of PAH6s.

## SUMMARY

The equivalence of Cyvin and Gutman's hexagon adjacency relationships to our perimeter topology relationships has been exposed. For strain-free TRS benzenoids, the number of bay regions must cancel out the number remaining perimeter types [cf. with eq 6], and the empty ring hexagon adjacency terms must cancel out the sextet ring hexagon adjacency terms [cf. with eq 10].

While eq 13 is perfectly valid for all TRS benzenoids, it can be used to give the upper bound for all benzenoids in general if one allows  $F$  to equal the sum of the number of coves and fjords. Both the circumscribing and leapfrog operations preserve symmetry between the corresponding precursor and successor benzenoids which are invariably strain-free systems. The TRS benzenoid isomers have a maximum number of bay regions. Strained TRS benzenoids, because of the presence of fjords, have more bay regions than their strain-free TRS isomers [cf. with eq 12]. There are two categories of TRS benzenoids based on strain—strain-free (leapfrogs) and strained due to fjords (cannot be generated by leapfrogging) and leapfrogs of helical PAH6s.

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