

ARTICLES

Mathematics of Periodic Tables for Benzenoid Hydrocarbons[†]

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The upper and lower bounds for invariants of polyhex systems based on the Harary and Harborth inequalities are studied. It is shown that these invariants are uniquely correlated by the Periodic Table for Benzenoid Hydrocarbons. A modified periodic table for total resonant sextet (TRS) benzenoids based on the invariants of D_s and r (empty) is presented; D_s is the number of disconnections among the empty rings for fused TRS benzenoid hydrocarbons. This work represents a contribution toward deciphering the topological information content of benzenoid formulas.

INTRODUCTION

While reviewing some mathematical relationships of polyhex systems based on the Harary and Harborth inequalities,¹ some new ones will be derived. These relationships will be linked to the periodic tables for benzenoid hydrocarbons which will require review of past work.² Key conceptual tools will include the excised internal structure/circumscribing operation as related to constant-isomer series of ordinary benzenoids,³ supercircumscribing of total resonant sextet (TRS) benzenoids,⁴ and the leapfrog operation as related to TRS benzenoids.⁵ Some recent relevant work⁶ and reviews in regard to these systems should be consulted.⁷ How these periodic tables organize the corresponding benzenoid formula/structure relationships into distinct domains will be detailed.

BRIEF REVIEW

Some Definitions. Polyhex is the discrete mathematical equivalent of a benzenoid hydrocarbon. A polyhex is a tessellation (mosaic) of hexagons which corresponds to the molecular graph of a benzenoid. A molecular graph of a benzenoid hydrocarbon (used interchangeably with the term “benzenoid”) is its σ -bond skeleton with all the hydrogens and π -bonds omitted. The benzenoid notation for the total number of carbons (N_c), hydrogens (N_H), and σ -bonds is equivalent to the polyhex (molecular graph) graph theoretical notation for total number of vertices (n), degree-2 vertices (s), and lines or edges (q), respectively. There are three distinct kinds of benzenoid carbons, the number of which are denoted by N_{pc} , N_{ic} , and N_H ($N_c = N_{ic} + N_{pc} + N_H$) where N_{pc} and N_{ic} correspond to the peripheral and internal degree-3 molecular graph vertices and N_H to the degree-2 vertices. The subscripts i or l and p denote internal and peripheral, respectively. The number of hexagonal rings is denoted by r . A benzenoid is strained if it has two or more adjacent bay

regions. Thus, benzo[*c*]phenanthrene is strained, but chrysene and triphenylene are strain-free. Recall that that strained benzenoids cannot be circumscribed and that leapfrog benzenoids are strain-free total resonant sextet (TRS) benzenoids.^{3,4,7}

Periodic Tables for Benzenoid Hydrocarbons. Table 1 is based on the equation of $d_s + N_{ic} - r = -2$ which consists of $(x, y, z) = (d_s, N_{ic}, r)$ points in a plane. Table PAH6 is a plot of d_s versus N_{ic} where the third dimension r is not explicitly shown but can be indicated by parallel lines connecting formulas with identical r values. Thus Table PAH6 (Table 1) is simply one of six different 2-dimensional projections of a 3-dimensional plane. Alternatively, the invariants d_s and N_{ic} can be replaced by N_c and N_H to give the equation $N_c - N_H - 2r = -2$. Again any two of these three invariants can be selected to give periodic tables with three different (x, y) coordinates which constitutes 2-dimensional projections of the plane $N_c - N_H - 2r = -2$ in 3-space. Our Hill index (C/H each independently increasing in magnitude) version of Table PAH6 uses N_c and N_H as invariants and accumulates all the formulas for constant-isomer benzenoids at the left and all the formulas for the catacondensed benzenoids at the right; this version is designated as Table PAH6' with a prime. The Hill index version of Table PAH6(even) can be found in several references and is useful in systematic searching of formula indexes for benzenoid structures.²

Table PAH6 (Table 1) can be partitioned into two parts separating even carbon formulas from odd carbon ones, i.e., Table PAH6 = Table PAH6(even)UTable PAH6(odd). A subset of Table PAH6(even) involving the columns having formulas divisible by six (every third column) in which TRS benzenoid isomers are only considered results in a new periodic table for fused TRS benzenoids [Table PAH6-(sextet)].^{2,4} In this regard, note that not all benzenoids in Table PAH6(even) having formulas divisible by six have TRS isomers. For example, coronene ($C_{24}H_{12}$) has no TRS isomers. The initial focus of Table PAH6(sextet) was on the more stable fused benzenoid hydrocarbons per Clar's sextet

[†] Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.

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Table 1. (Table PAH6) Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (PAH6)

$(N_C = 3 N_H - 14 - 2 d_S)$											
$d_S = -8$	$d_S = -7$	$d_S = -6$	$d_S = -5$	$d_S = -4$	$d_S = -3$	$d_S = -2$	$d_S = -1$	$d_S = 0$	$d_S = 1$	N_{Ic}	
FORBIDDEN REGION								$C_{10}H_8$	$C_{14}H_{10}$... 0	
								$C_{13}H_9$	$C_{17}H_{11}$... 1	
								$C_{16}H_{10}$	$C_{20}H_{12}$... 2	
								$C_{19}H_{11}$	$C_{23}H_{13}$... 3	
								$C_{22}H_{12}$	$C_{26}H_{14}$... 4	
$(N_C/N_H) < 2$								$C_{25}H_{13}$	$C_{29}H_{15}$... 5	
$C_{00}H_{00}$							$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$... 6	
$2 < (N_C/N_H) < 3$								$C_{27}H_{13}$	$C_{31}H_{15}$	$C_{35}H_{17}$... 7
								$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$... 8
								$C_{33}H_{15}$	$C_{37}H_{17}$	$C_{41}H_{19}$... 9
						$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$... 10	
						$C_{35}H_{15}$	$C_{39}H_{17}$	$C_{43}H_{19}$	$C_{47}H_{21}$... 11	
						$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$... 12	
				$C_{37}H_{15}$	$C_{41}H_{17}$	$C_{45}H_{19}$	$C_{49}H_{21}$	$C_{53}H_{23}$... 13		
				$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$... 14		
				$C_{43}H_{17}$	$C_{47}H_{19}$	$C_{51}H_{21}$	$C_{55}H_{23}$	$C_{59}H_{25}$... 15		
$(N_C/N_H) > 3$				$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$...	
				$C_{45}H_{17}$	$C_{49}H_{19}$	$C_{53}H_{21}$	$C_{57}H_{23}$	$C_{61}H_{25}$	$C_{65}H_{27}$...	
				$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$...	
				$C_{47}H_{17}$	$C_{51}H_{19}$	$C_{55}H_{21}$	$C_{59}H_{23}$	$C_{63}H_{25}$	$C_{67}H_{27}$	$C_{71}H_{29}$	
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	
				$C_{53}H_{19}$	$C_{57}H_{21}$	$C_{61}H_{23}$	
				$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	
				$C_{55}H_{19}$	$C_{59}H_{21}$	$C_{63}H_{23}$	
				$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	
				$C_{57}H_{19}$	$C_{61}H_{21}$	$C_{65}H_{23}$	
				$C_{60}H_{20}$	$C_{64}H_{22}$	
... $C_{59}H_{19}$	$C_{63}H_{21}$	$C_{67}H_{23}$	
... $C_{62}H_{20}$	$C_{66}H_{22}$	
... $C_{65}H_{21}$	$C_{69}H_{23}$	
... $C_{68}H_{22}$	$r = d_S + N_{Ic} + 2 = \frac{1}{2}(N_C - N_H + 2)$								
... $C_{71}H_{23}$									
...									

$$r = d_S + N_{Ic} + 2 = \frac{1}{2}(N_C - N_H + 2)$$

rule; this table was shown to correlate the number of fused strain-free isomers and their symmetry.⁴ If we permit phenyl or TRS aryl substituted TRS benzenoids, then Table PAH6-(sextet) must be expanded. The formulas in this table above the catacondensed TRS formulas have formulas surrounded by parentheses. This expanded version we will denote as Table PAH6(sextet,expanded).⁸ This “expanded” emphasis is necessary because our initial studies was on the fused TRS subset, and in the employment of Table PAH6(sextet), it was originally stated that biphenyl ($C_{12}H_{10}$), terphenyl ($C_{18}H_{14}$), quaterphenyl ($C_{24}H_{18}$), etc. had provisional status in Table PAH6(sextet) without their explicit inclusion. With this proviso Table PAH6(sextet) is a subset of Table PAH6(even). There is a one-to-one isomorphism among the isomers belonging to Table PAH6 (Table 1) and Table PAH6(sextet,-expanded). The partitioning of Table PAH6 into Table PAH6(even) and Table PAH6(odd) separates the formulas corresponding to the more stable even carbon systems from the less stable odd radical benzenoids having only fleeting existence as intermediates in pyrolytic processes. Sorting out the TRS benzenoid class from Table PAH6(even) gives the most stable subset of the even carbon benzenoids.

In 1990, we discovered an astounding one-to-one correspondence between the benzenoid structures which have their formulas located on the left-hand staircase boundary of both Table PAH6 (Table 1) and Table PAH6(sextet) in

regard to the number of isomers in their constant-isomer series, the distribution of symmetry in the structures of these isomers, and other topological characteristics.^{2,4} The constant-isomer series in Table PAH6 (Table 1) are generated by successive circumscription of C_nH_s benzenoids to generate $C_{n+2s+6}H_{s+6}$ benzenoids and in Table PAH6(sextet) by successive supercircumscription of TRS C_nH_s benzenoids to generate $C_{n+3s+18}H_{s+12}$ TRS benzenoids.

Constant-isomer benzenoid series belonging to Table PAH6 are generated by successively circumscribing a first generation set of benzenoid polyhex structures having a given formula with cyclic polyenes. For example, consider the first generation benzenoid members of a constant-isomer series of formula C_nH_s where $n = N_C$ and $s = N_H$ are either both even or odd. Circumscribing these first generation members with a hydrogen deficient cyclic polyene ($C_{2s+6}H_6$) perimeter concurrent with transfer of the s peripheral hydrogens gives the second generation members of the formula $C_{n+2s+6}H_{s+6}$; i.e., the C/H recursion equations for the formulas resulting from circumscribing a (N_C, N_H) parent to give the next (N'_C, N'_H) successor is $N'_C = N_C + 2N_H + 6$ and $N'_H = N_H + 6$. Repetition of this process gives a series of benzenoid structures with the same number of isomers at each circumscribing step. If C_nH_s is the chemical formula of a first generation member of a constant isomer series, then the formulas of succeeding members is given by C_mH_t where m

$= n + 6j^2 - 12j + 6 + 2js - 2s$ and $t = s + 6j - 6$ with j passing through all integers (i.e., the generation number, $j = 1, 2, 3, \dots$). The analog operation for generating constant-isomer TRS benzenoid series belonging to Table PAH6-(sextet) involves successive supercircumscribing a first generation set of TRS benzenoid polyhex structures having a given formula with polyphenylene necklaces. For example, consider the first generation TRS benzenoid members of a constant-isomer series of formula C_nH_s . Supercircumscribing these first generation members with a hydrogen deficient cyclic polyphenylene ($C_{3s+18}H_{12}$) perimeter concurrent with transfer of the s peripheral hydrogens gives the second generation members of the formula $C_{n+3s+18}H_{s+12}$; i.e., the C/H recursion equations for the formulas resulting from circumscribing a (N_c, N_H) parent to give the next (N'_c, N'_H) successor is $N'_c = N_c + 3N_H + 18$ and $N'_H = N_H + 12$. Repetition of this process gives a series of TRS benzenoid structures with the same number of isomers at each supercircumscribing step.

The periodic table for benzenoid hydrocarbons [Table PAH6] is an array of C_nH_s formulas having a right-hand horizontal edge defined by $C_{4r+2}H_{2r+4}$ with $r = 2, 3, 4, \dots$ (r = no. rings) for the catacondensed benzenoids and a left-hand staircase edge on which the formulas for the constant-isomer benzenoid series exclusively appear; stair bottom rung formulas ($C_{25}H_{13}$, $C_{33}H_{15}$, $C_{38}H_{16}$, ...) on this staircase edge correspond to immediate precursors to the first generation constant-isomer sets. The left-hand staircase-like boundary of Table PAH6 (Table 1) starts with a six-formula step followed by a four-formula step, and all subsequent steps thereafter hold three and two formulas each. Each stair of this staircase edge is composed of the upper protrusive corner edge with the formulas of $C_{10}H_8$, $C_{24}H_{12}$, $C_{32}H_{14}$, and so on, and the lower corner junction between two adjacent steps has the formulas of $C_{25}H_{13}$, $C_{33}H_{15}$, $C_{38}H_{16}$, and so on. The extreme-left benzenoids have formulas at the extreme left of the rows in Table PAH6 (Table 1). Protrusive benzenoids have formulas with nothing either above or to left of them in Table PAH6. Extremal benzenoids have molecular graphs with the maximum number of internal vertices (n_i) for a given number of hexagons (r) and are extreme-left benzenoids; they also cannot have adjacent bay regions (coves, fjords, etc.) and therefore are strain-free. With the exception of naphthalene (if we exclude benzene), only second and higher generation benzenoid isomer sets have formulas located at the protrusive corner of the staircase edge of Table PAH6. Members of the one-isomer benzenoid series have the largest number of hexagonal rings for a given perimeter length $q_p = 2s - 6$ or s value. The first generation members of nonunique (possessing more than one isomer) constant-isomer benzenoids have formulas first appearing under the protrusive formulas of one-isomer series. Thereafter, the second and higher generation benzenoid isomer members have formulas located at the protrusive corner of the staircase edge of Table PAH6.

The smallest even carbon benzenoid is benzene (C_6H_6), and the smallest odd carbon benzenoid is phenalenyl ($C_{13}H_9$); since benzene is not a fused benzenoid, it only has a provisional status in Table PAH6. The formulas to the first generation members to the one-isomer series are C_6H_6 , $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, and $C_{27}H_{13}$ all of which have no bay regions on the perimeters. The number of benzenoid hydro-

gens ($N_H = s$) possible are $s = 6$ and $s \geq 8$. First generation members of constant-isomers pass through all possible numbers of hydrogen ($s = 6$ and $s \geq 8$).

RESULTS AND DISCUSSION

Derivation of Some Mathematical Relationships. According to Harary and Harborth [their eqs 36 and 39],¹ benzenoid hydrocarbons (which they called hexagonal animals) exist if and only if n (number of vertices) and r (number of rings) are integers within the ranges of

$$2r + 1 + \lceil (12r - 3)^{1/2} \rceil \leq n \leq 4r + 2 \quad (1)$$

$$\lceil 1/4(n - 2) \rceil \leq r \leq n + 1 - \lceil 1/2(n + 6^{1/2}n^{1/2}) \rceil \quad (2)$$

where $\lceil x \rceil$ is the ceiling function and corresponds to the smallest integer not smaller than x . The two sides of these equations define the extreme values (upper and lower bounds) for n and r for polyhexes. The right-hand of eq 1 corresponds to the catacondensed benzenoids located on the right-hand horizontal edge of Table PAH6, and the left-hand of eq 1 corresponds to benzenoids having formulas on the extreme left-hand staircase edge of Table PAH6. The following additional extremal relationships were given in this key paper. The maximum number of internal edges q_i (edges between two adjoining hexagons) and the minimum number of edges q for a benzenoid with r rings is

$$q_i(\max) = 3r - \lceil (12r - 3)^{1/2} \rceil \quad (3)$$

$$q(\min) = 3r + \lceil (12r - 3)^{1/2} \rceil \quad (4)$$

where in general $q + q_i = 6r$. Because $q = q_l + q_p$, subtracting (3) from (4) gives

$$q_p(\min) = 2\lceil (12r - 3)^{1/2} \rceil \quad (5)$$

Thus, for a given r the range of q , q_l , and q_p is given by the following inequalities

$$3r + \lceil (12r - 3)^{1/2} \rceil \leq q \leq 5r + 1 \quad (6)$$

$$3r - \lceil (12r - 3)^{1/2} \rceil \leq q_l \leq r - 1 \quad (7)$$

$$2\lceil (12r - 3)^{1/2} \rceil \leq q_p \leq 4r + 2 \quad (8)$$

where the right-hand side of these equations corresponds to catacondensed benzenoids.

From eq 1, the minimum number of carbons n and maximum number of internal degree-3 carbon vertices n_i for a given number of rings r is derived as

$$n(\min) = 2r + 1 + \lceil (12r - 3)^{1/2} \rceil \quad (9)$$

$$n_i(\max) = 2r + 1 - \lceil (12r - 3)^{1/2} \rceil \quad (10)$$

where the latter evolves from $n_i = 4r + 2 - n$; note that the minimum/maximum switch is the result of the negative sign. Both $n(\min)$ and $n_i(\max)$ occur for the formulas on the extreme left-hand staircase edge of Table PAH6; benzenoids having $n_i(\max)$, i.e., those having a maximum number of internal (third degree) vertices for a given number of hexagons, are called extremal benzenoids. Thus, for a given

r the range of n_i is given by the following inequality

$$0 \leq n_i \leq 2r + 1 - \lceil (12r - 3)^{1/2} \rceil \quad (11)$$

where $n_i(\min) = 0$ pertains to the catacondensed and $n_i(\max)$ to the extremal benzenoids. To illustrate application of eq 11, consider $r = 19$. This inequality gives $0 \leq n_i \leq 2 \times 19 + 1 - \lceil (12 \times 19 - 3)^{1/2} \rceil$ or $0 \leq n_i \leq 24$, i.e., from the catacondensed benzenoids ($C_{78}H_{42}$, $n_i = 0$) to the third generation member to the D_{6h} one-isomer series ($C_{54}H_{18}$, $n_i = 24$). Using eqs 1 and 11, from $N_c - N_{lc} = N_{pc} + N_H$, we get

$$2\lceil (12r - 3)^{1/2} \rceil \leq n - n_i = n_p + s = 2s - 6 \leq 4r + 2 \quad (12)$$

where $n_p + s = q_p = q - q_l = 2s - 6$ (s = number of degree-2 vertices and n_p = number of peripheral degree-3 vertices) corresponds to the size of the periphery of a benzenoid polyhex. Thus eq 12 can be reduced to the following inequality

$$\lceil (12r - 3)^{1/2} \rceil + 3 \leq s \leq 2r + 4 \quad (13)$$

In general, for a given r : $n(\max)$, $q(\max)$, $q_l(\min)$, $q_p(\max)$, and $s(\max)$ pertain to the catacondensed benzenoids (given by the right-hand side of the inequalities (1), (6), (7), (8), and (13), respectively), while $n(\min)$, $q(\min)$, $q_l(\max)$, $q_p(\min)$, and $s(\min)$ pertain to extremal benzenoids (given by the left-hand side of the inequalities (1), (6), (7), (8), and (13), respectively).

These extremal relationships are deemed more convenient if they can be recast in terms of the chemical formulas C_nH_s , namely in terms of n and s exclusively. For that purpose the following relationships will be useful: $q = 1/2(3N_c - N_H)$, $r = q + 1 - N_c = 1/2(N_c - N_H + 2)$, $N_{pc} = N_H - 6$, $N_c = N_{lc} + N_{pc} + N_H$, and $N_c + N_{lc} = 4r + 2$; note that for the catacondensed benzenoids $N_c = 4r + 2$ for which $N_{lc} = 0$. Reversing the order of eq 2 gives

$$n + 1 - \lceil 1/2(n + 6^{1/2}n^{1/2}) \rceil \geq r \geq \lceil 1/4(n - 2) \rceil$$

Using $r = 1/2(n - s + 2)$ and multiplying throughout by 2 gives

$$2n + 2 - 2\lceil 1/2(n + 6^{1/2}n^{1/2}) \rceil \geq n - s + 2 \geq 2\lceil 1/4(n - 2) \rceil$$

Subtracting $n + 2$ throughout this inequality gives

$$n - 2\lceil 1/2(n + 6^{1/2}n^{1/2}) \rceil \geq -s \geq -n - 2 + 2\lceil 1/4(n - 2) \rceil$$

Multiplying this inequality by minus throughout reverses the inequality signs to give

$$2\lceil 1/2(n + 6^{1/2}n^{1/2}) \rceil - n \leq s \leq n + 2 - 2\lceil 1/4(n - 2) \rceil \quad (14)$$

Equation 14 gives the range for the number of hydrogens (s) for a given number of carbons (n) found in benzenoids. For example, consider $n = 54$. Application of eq 14 gives

$2\lceil 1/2(54 + 6^{1/2}54^{1/2}) \rceil - 54 \leq s \leq 54 + 2 - 2\lceil 1/4(54 - 2) \rceil$ or $18 \leq s \leq 30$, i.e., $C_{54}H_{18}$ to $C_{54}H_{30}$ where $C_{54}H_{18}$ is the third generation member, circumcoronene, belonging to the D_{6h} one-isomer series and $C_{54}H_{30}$ corresponds to the 314 075 catacondensed isomers.

It now remains to determine the first generation formula for any given constant-isomer series. This was done by exploiting the behavior and properties of the one-isomer series on the staircase edge of Table PAH6 and our aufbau principle. The one-isomer benzenoids have the largest number of hexagon rings for a given perimeter length ($q_p = 2s - 6$ or s value). Using this property and eq 13, we get the following successive equations

$$s = \lceil (12r - 3)^{1/2} \rceil + 3$$

$$s \leq (12r - 3)^{1/2} + 3$$

$$(s - 3)^2 \leq (12r - 3)$$

$$s^2 - 6s + 9 \leq 12r - 3$$

$$s^2 - 6s + 12 \leq 12r$$

$$r \geq 1/12(s^2 - 6s + 12)$$

$$r(\max) = \lfloor 1/12(s^2 - 6s + 12) \rfloor = 1/2(n + 2 - s)$$

$$n = 2\lfloor 1/12(s^2 - 6s) \rfloor + s \quad (15)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x . Since one-isomer formulas pass through all possible numbers of hydrogen ($s = 6$ and $s \geq 8$), starting with benzene eq 15 gives all the formulas belonging to the members of the 6 one-isomer benzenoid series. To use eq 15 just simply input successively the number of benzenoid hydrogens possible ($s = 6, 8, 9, 10, 11, 12, 13 \dots$). For example, these 7 values for s gives C_6H_6 , $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, $C_{24}H_{12}$, $C_{27}H_{13}$, ..., respectively. After the first step, the second and successive higher generation members to the one-isomer series occur on a protrusive location of the staircase edge of Table PAH6 (Table 1). Immediately beneath these protrusive one-isomer formulas of subscript coefficients (n', s'), one finds the formulas of subscript coefficients (n, s) for the first-generation members of the constant-isomer series with higher numbers of isomers. Using the elementary aufbau of C_3H on these protrusive one-isomer formulas, we can get the formula for all the first-generation constant-isomer series. Performing a retro-aufbau operation ($n-3, s-1$) = (n', s') on the first-generation formula of a higher constant-isomer, transforms eq 15 to

$$n - 3 = 2\lfloor 1/12[(s - 1)^2 - 6(s - 1)] \rfloor + (s - 1)$$

where n and s now correspond to the formula of the higher constant-isomers immediately beneath a one-isomer formula (n', s'). Simplification of this latter equation gives

$$n = s + 2\lfloor 1/12(s^2 - 8s + 19) \rfloor \quad (16)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest

integer not larger than x . Equation 16 determines the first generation formula for any given constant-isomer series. To use eq 16 successively input the number of benzenoid hydrogens possible ($s = 6, 8, 9, 10, 11, 12, \dots$). For example, $s = 11$ gives $n = 11 + 2\lfloor 4.333 \rfloor = 11 + 2 \times 4 = 19$ which gives $C_{19}H_{11}$ as the first generation formula for the C_{2v} one-isomer monoradical benzenoid series. The second ($j = 2$), third ($j = 3$), fourth ($j = 4$), etc. generation formulas are given by the above relationships in a prior paragraph as $C_{47}H_{17}$, $C_{87}H_{23}$, $C_{139}H_{29}$, etc. As another example, $s = 14$ and 16 gives $n = 14 + 2\lfloor 8.58 \rfloor = 14 + 2 \times 8 = 30$ and $n = 16 + 2\lfloor 12.25 \rfloor = 16 + 2 \times 12 = 40$ which gives $C_{30}H_{14}$ and $C_{40}H_{16}$, respectively, as the first generation formulas for the matching pair of 4-isomer series. In this way eq 16 generates all 39 formulas ($\dots, C_{10}H_8, C_{13}H_9, C_{16}H_{10}, C_{19}H_{11}, C_{27}H_{13}, \dots$) in ref 2.

Isomorphism between Table PAH6 between all Benzenoids and Table PAH6(Sextet,Expanded) for Strain-Free Total Resonant Sextet Benzenoid Hydrocarbons. Strain-free total resonant sextet (TRS) benzenoids constitute a subclass of benzenoids that comply with Clar's sextet principle.⁹ Among other things, TRS benzenoids have N_c divisible by six, are devoid of coves and fissures, and have a maximum number of bay regions given by $\eta_o(\text{TRS}) = \frac{1}{2}N_H - 3$. An adaptation of Fowler's leapfrog algorithm¹⁰ provided a second proof of this isomorphism.⁵ Application of the retro-leapfrog expressions $[(\frac{1}{3}n' + \frac{1}{2}s' + 1, \frac{1}{2}s' + 3) \rightarrow (n, s)]$ to equation to eq 16 gives

$$\frac{1}{3}n' + \frac{1}{2}s' + 1 = \frac{1}{2}s' + 3 + 2\lfloor \frac{1}{12}[(\frac{1}{2}s' + 3)^2 - 8(\frac{1}{2}s' + 3) + 19] \rfloor$$

After dropping the primes, this equation can be simplified to eq 17

$$n = 6\lfloor \frac{1}{48}(s^2 - 4s + 64) \rfloor \quad (17)$$

which gives the first-generation formula to strain-free total resonant sextet (TRS) benzenoid constant-isomer series. Unlike the prior equations only an even number of hydrogens are permissible, i.e., $s = (6, 10), 12, 14, 16, 18, 20, \dots$ where the first two numbers pertain to benzene and biphenyl which only have provisional status in Table PAH6(sextet) because they are not fused benzenoids. To illustrate the use of eq 17 consider $s = 12$. Application of eq 17 gives $n = 6\lfloor \frac{1}{48}(12^2 - 4 \times 12 + 64) \rfloor = 6\lfloor \frac{1}{48}(144 - 48 + 64) \rfloor = 6\lfloor 3.33 \rfloor = 6 \times 3 = 18$ which corresponds to triphenylene $C_{18}H_{12}$, the first generation member of the D_{3h} one-isomer total resonant sextet series. In a like manner, eq 17 generates the 39 pertinent formulas ($C_6H_6, C_{12}H_{10}, C_{18}H_{12}, C_{24}H_{14}, C_{30}H_{16}, C_{36}H_{18}, C_{48}H_{20}, \dots$) found in ref 2.

Previously we showed that our benzenoid periodic tables can be based on any two of the invariants (d_s, N_{lc}, r).² By virtue of the leapfrog algorithm, the following correlations can be shown to be applicable:



$$N_{lc} \rightarrow r(\text{empty})$$

$$r \rightarrow r(\text{sextet})$$

$$N_{pc} \rightarrow \eta_o'$$

$$\eta_j \rightarrow \eta_{j+1}'$$

$$d_s \rightarrow D_s$$

Here d_s is the net number of disconnection among the internal edges, and D_s is the net disconnection of empty rings. The recognition of $d_s \rightarrow D_s$ is new. Since $[d_s, N_{lc}, r] \rightarrow [D_s, r(\text{empty}), r(\text{sextet})]$, it will emerge any two invariants from $[D_s, r(\text{empty}), r(\text{sextet})]$ will fully characterize the general topology of TRS benzenoids.

Using the leapfrog correlations $P \rightarrow L$, we can derive a number of interesting relationships for TRS benzenoids from those previously listed for all benzenoids (Table 2).¹¹ In order to derive those given in Table 2, the following relationships in which the invariants $X(\text{TRS})$ for leapfrogs are equated to the invariants X for their precursor or parent benzenoid systems will be needed:

$$N_c(\text{TRS}) = 3N_c - 3N_H + 6$$

$$N_H(\text{TRS}) = 2N_H - 6$$

$$q(\text{TRS}) = 6r + 2N_{lc} + d_s + 1 = 7r + N_{lc} - 1$$

$$r(\text{empty}) = N_{lc}$$

$$r(\text{sextet}) = r$$

$$\eta_o(\text{TRS}) = N_{pc}$$

$$\eta_{j+1}(\text{TRS}) = \eta_j$$

$$D_s = d_s$$

Thus, from the isomorphism that exists between all benzenoid systems and the TRS subset of benzenoids, we can easily derive a number of mathematical relationships.

Since the invariants of $[D_s, r(\text{empty}), r(\text{sextet})]$ are easily discerned by simple visual inspection of a TRS benzenoid structure, we now study their relationships in regard to the Harary and Harborth inequalities. Using the leapfrog operation on eq 10, we immediately obtain

$$r(\text{empty})_{\max} = 2r(\text{sextet}) + 1 - \lceil [12r(\text{sextet}) - 3]^{1/2} \rceil \quad (18)$$

for a given number of sextet rings. In analogy to the definition of ordinary extremal benzenoids, TRS benzenoids having $r(\text{empty})_{\max}$, i.e., those having a maximum number of empty rings for a given number of sextet rings, can be called extremal TRS benzenoids; but note that external TRS benzenoids are not extremal benzenoids, per se. Performing the leapfrog operation on eq 11 gives, in general,

$$0 \leq r(\text{empty}) \leq 2r(\text{sextet}) + 1 - \lceil [12r(\text{sextet}) - 3]^{1/2} \rceil \quad (19)$$

where the zero for $r(\text{empty})_{\min}$ at the left of the inequality

occurs for the polyphenylenes in Table PAH6(sextet,expanded).⁹ To obtain $r(\text{empty})_{\min}$ where only fused TRS benzenoids are allowed, we perform the following analysis. This $r(\text{empty})_{\min}$ occurs for catacondensed systems ($\text{C}_{12n+6}\text{H}_{6n+6}$, $n = 1, 2, 3, \dots$). Triphenylene ($\text{C}_{18}\text{H}_{12}$) and tetrabenz[a,c,h,j]anthracene ($\text{C}_{30}\text{H}_{18}$) are the smallest members of the catacondensed TRS benzenoids and have $r(\text{empty}) = 1$ and 2 and $r(\text{sextet}) = 3$ and 5, respectively. In general, for the catacondensed TRS benzenoids, we have $r(\text{empty}) = 1, 2, 3, \dots, n$ and $r(\text{sextet}) = 3, 5, 7, \dots, 2n + 1$. Using the floor function $r(\text{empty})_{\min} = \lfloor (1/2)r(\text{sextet}) \rfloor$, we can amend the left-hand side of eq 19 as

$$\lfloor (1/2)r(\text{sextet}) \rfloor \leq r(\text{empty}) \leq 2r(\text{sextet}) + 1 - \lceil [12r(\text{sextet}) - 3]^{1/2} \rceil \quad (20)$$

which gives the range (the upper and lower bound) of the number of empty rings for a given number of sextet rings for fused TRS benzenoids in Table PAH6(sextet).

We now obtain the upper and lower bound for the number of sextet rings for a given number of empty. Since $r(\text{empty}) \leq r(\text{empty})_{\max}$, from eq 18 it is obtained

$$r(\text{empty}) \leq 2r(\text{sextet}) + 1 - \lceil [12r(\text{sextet}) - 3]^{1/2} \rceil$$

$$2r(\text{sextet}) + 1 - r(\text{empty}) \geq \lceil [12r(\text{sextet}) - 3]^{1/2} \rceil$$

Since $\lceil [12r(\text{sextet}) - 3]^{1/2} \rceil \geq [12r(\text{sextet}) - 3]^{1/2}$, this latter gives

$$2r(\text{sextet}) + 1 - r(\text{empty}) \geq [12r(\text{sextet}) - 3]^{1/2}$$

Squaring both sides of this inequality gives

$$[2r(\text{sextet}) + 1 - r(\text{empty})]^2 \geq 12r(\text{sextet}) - 3$$

which can be rearranged to

$$r(\text{sextet})^2 - [r(\text{empty}) + 2]r(\text{sextet}) + \frac{1}{4}[r(\text{empty})^2 - 2r(\text{empty}) + 4] \geq 0$$

The roots of this quadratic equation are given by

$$r(\text{sextet}) = \frac{1}{2}[r(\text{empty}) + 2 \pm \{6r(\text{empty})\}^{1/2}]$$

Trial solutions on the smallest TRS benzenoids [$\text{C}_{24}\text{H}_{14}$ with $r(\text{sextet}) = 4$ and $r(\text{empty}) = 2$ versus $\text{C}_{30}\text{H}_{16}$ with $r(\text{sextet}) = 5$ and $r(\text{empty}) = 3$] leads to the following ceiling function:

$$r(\text{sextet})_{\min} = \lceil \frac{1}{2}[r(\text{empty}) + 2 + \{6r(\text{empty})\}^{1/2}] \rceil \quad (21)$$

In general, the extreme-left TRS benzenoids in Table PAH6(sextet) have the fewest sextet rings for a given number of empty rings. To obtain $r(\text{sextet})_{\max}$ where only fused TRS benzenoids are allowed, we perform the following analysis. The catacondensed TRS benzenoids have the largest number of sextet rings [$r(\text{sextet})_{\max}$] for a given number of empty rings. For the catacondensed TRS benzenoids, we have $r(\text{empty}) = 1, 2, 3, \dots, n$ and $r(\text{sextet}) = 3, 5, 7, \dots, 2n + 1$. From these relationships it is easily deduced that $r(\text{sextet})_{\max} = 2r(\text{empty}) + 1$. This with eq 21 leads to the following inequality

$$\lceil \frac{1}{2}[r(\text{empty}) + 2 + \{6r(\text{empty})\}^{1/2}] \rceil \leq r(\text{sextet}) \leq 2r(\text{empty}) + 1 \quad (22)$$

where the quantity at the right of this inequality occurs for catacondensed TRS benzenoids in Table PAH6(sextet).

Previously we showed that $d_s = r - N_{lc} - 2 = N_{pc} - r$ is the net number of disconnection among the internal edges. Using eq 11 with the relationship of $N_{lc} = r - d_s - 2$, we obtain

$$\begin{aligned} 0 \leq n_i = r - d_s - 2 &\leq 2r + 1 - \lceil (12r - 3)^{1/2} \rceil \\ -r + 2 &\leq -d_s \leq r + 3 - \lceil (12r - 3)^{1/2} \rceil \\ \lceil (12r - 3)^{1/2} \rceil - r - 3 &\leq d_s \leq r - 2 \end{aligned} \quad (23)$$

Using the leapfrog operation on eq 23, we immediately obtain

$$\lceil [12r(\text{sextet}) - 3]^{1/2} \rceil - r(\text{sextet}) - 3 \leq D_s \leq r(\text{sextet}) - 2 \quad (24)$$

which gives the lower and upper bounds between the number of empty ring disconnections for a given number of sextet rings.

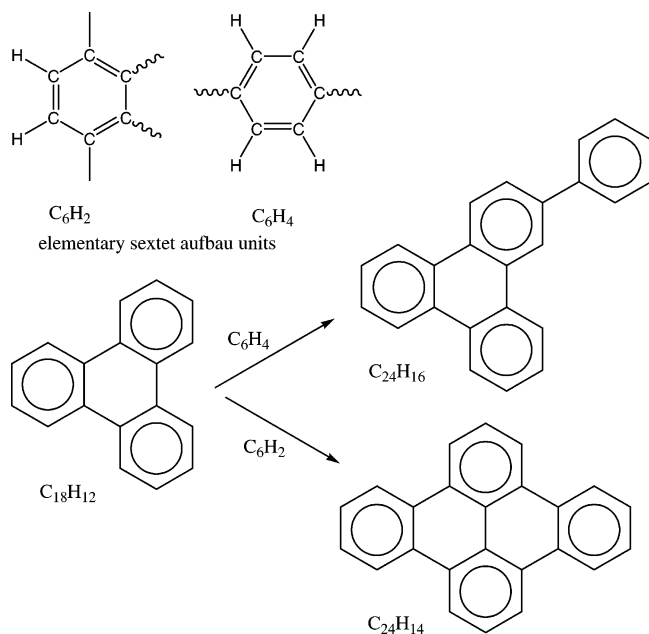
Properties of TRS Benzenoids Belonging to Table PAH6(Sextet,Modified). The distinction between benzenoids having formulas in Table PAH6, Table PAH6(even), Table PAH6(odd), Table PAH6(sextet), and Table PAH6(sextet,expanded) which are based on the coordinates of $(x,y) = (d_s, N_{lc})$ have been systematically reviewed. Using correlations between all benzenoids and leapfrog subset, we now present a modified version of Table PAH6(sextet,expanded) based on the coordinates of $(x,y) = [D_s, r(\text{empty})]$ where D_s is the net number of disconnections among the empty rings and/or bridging bonds. This new periodic table is denoted as Table PAH6(sextet,modified) and is shown in Table 3. Basically it is the same as Table PAH6(sextet,expanded) with the rows skewed down. All the TRS structures belonging to formulas in the same row of Table 3 have the same number of empty rings, and all TRS structures having formulas in the same column have the same number of disconnections among their empty rings and/or bridging bonds. All the formulas with parentheses cannot have any TRS structures that made up of totally fused rings but must be TRS structures with TRS aryl substituents. As one goes along a column or row the number of carbons change by six and the number of hydrogens change by two or four, respectively. Take the formulas of $\text{C}_{48}\text{H}_{22}$, $\text{C}_{48}\text{H}_{24}$, and $\text{C}_{48}\text{H}_{26}$ in Table 3, having 8, 4, and 2 TRS isomers, respectively, all with 6 sextet rings. It is clear from the table that $\text{C}_{48}\text{H}_{22}$ has 6 connected empty rings, $\text{C}_{48}\text{H}_{24}$ has 5 empty rings with a single sepa-

Table 2. Mathematical Expressions Derived from Those Valid for All Benzenoids by Leapfrogging to Give Those Valid for the Strain-Free TRS Subset

all benzenoids	strain-free TRS benzenoids
$N_{pc} = N_H - 6$	$\eta_o(\text{TRS}) = \frac{1}{2}N_H(\text{TRS}) - 3$
$N_c = N_{lc} + N_{pc} + N_H$	$N_c(\text{TRS}) = 3\eta_o(\text{TRS}) + 3r(\text{empty}) + 6$
$r = \frac{1}{2}(N_c + 2 - N_H)$	$r(\text{sextet}) = N_c(\text{TRS})/6$
$d_s = N_{pc} - r$	$D_s = \eta_o(\text{TRS}) - r(\text{sextet})$
$d_s = r - N_{lc} - 2$	$D_s = r(\text{sextet}) - r(\text{empty}) - 2$
$q = \frac{1}{2}(3N_c - N_H)$	$q(\text{TRS}) = 7r(\text{sextet}) + r(\text{empty}) - 1$

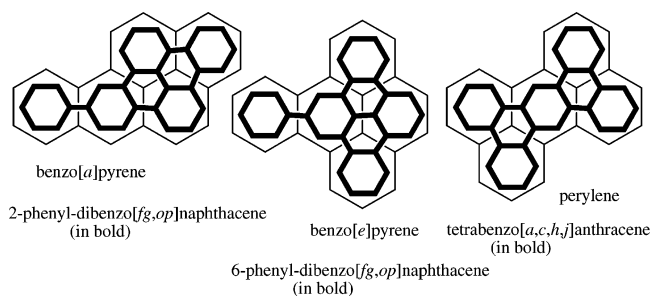
Table 3. [Table PAH6 (Sextet, Modified)] Formula Periodic Table for Total Resonant Sextet (TRS) Benzenoid Hydrocarbons^a

...	$D_S = -4$	$D_S = -3$	$D_S = -2$	$D_S = -1$	$D_S = 0$	$D_S = 1$	$D_S = 2$	$D_S = 3$	$D_S = 4$... $r(\text{empty})$
					(C ₁₂ H ₁₀)	(C ₁₈ H ₁₄)	(C ₂₄ H ₁₈)	(C ₃₀ H ₂₂)	(C ₃₆ H ₂₆)	... 0
					C ₁₈ H ₁₂	(C ₂₄ H ₁₆)	(C ₃₀ H ₂₀)	(C ₃₆ H ₂₄)	(C ₄₂ H ₂₈)	... 1
					C₂₄H₁₄	C ₃₀ H ₁₈	(C ₃₆ H ₂₂)	(C ₄₂ H ₂₆)	(C ₄₈ H ₃₀)	... 2
					C ₃₀ H ₁₆	C ₃₆ H ₂₀	C ₄₂ H ₂₄	(C ₄₈ H ₂₈)	(C ₅₄ H ₃₂)	... 3
					C₃₆H₁₈	C₄₂H₂₂	C₄₈H₂₆	C₅₄H₃₀	(C ₆₀ H ₃₄)	... 4
					C ₄₂ H ₂₀	C ₄₈ H ₂₄	C ₅₄ H ₂₈	C ₆₀ H ₃₂	C ₆₆ H ₃₆	... 5
					C₄₂H₁₈	C₄₈H₂₂	C₅₄H₂₆	C₆₀H₃₀	C₆₆H₃₄	... 6
					C ₄₈ H ₂₀	C ₅₄ H ₂₄	C ₆₀ H ₂₈	C ₆₆ H ₃₂ 7
					C₅₄H₂₂	C₆₀H₂₆	C₆₆H₃₀ 8
					C ₆₀ H ₂₄	C ₆₆ H ₂₈ 9
					C₆₀H₂₂	C₆₆H₂₆ 10
					C₆₆H₂₄	C₇₂H₂₈ 11
					C₇₂H₂₆ 12
					C ₇₂ H ₂₄	C ₇₈ H ₂₈ 13
					C₇₈H₂₆	C₈₄H₃₀ 14
					C ₈₄ H ₂₈ 15
					C₈₄H₂₆	C₉₀H₃₀ 16
					C ₉₀ H ₂₈	C ₉₆ H ₃₂ 17
					C₉₆H₃₀ 18
...					C ₁₀₂ H ₃₂ 19

^a D_S = net number disconnections among the empty rings.**Figure 1.** Illustration of the aufbau construction of TRS systems.

ration, and $C_{48}H_{26}$ has 4 empty rings with two disconnections, all without knowing what these TRS structures look like.

We will now explain Table 3 further. The aufbau construction of TRS benzenoids is illustrated in Figure 1. Starting with benzene which has a provisional status in Table 3, attaching benzenediyl (C_6H_4) and simultaneously transferring hydrogen from the site of attachment gives biphenyl ($C_{12}H_{10}$). Successively continuing this process generates the first row of Table 3, all of which comprise of the polyphenylenes. The polyphenylenes are all devoid empty rings, biphenyl has a single bridging bond between the phenyl moieties of zero disconnection ($D_S = 0$), the terphenyl isomers have two bridging bonds between the phenylene and phenyl moieties that have a single disconnection ($D_S = 1$), the

**Figure 2.** The $C_{20}H_{12}$ benzenoid isomers and their $C_{30}H_{18}$ TRS leapfrogs shown in bold.

quaterphenyl isomers have three bridging bonds between the phenylene and phenyl moieties with two disconnections ($D_S = 2$), and so forth. Recall that bridging bonds are regarded as being equivalent to two bay regions,³ e.g., for biphenyl $\eta_0(\text{TRS}) = \frac{1}{2}N_H(\text{TRS}) - 3 = 5 - 3 = 2$. Attaching benzenetetracyl (C_6H_2) to biphenyl with the transfer of two hydrogens from the biphenyl moiety to the benzenetetracyl unit gives triphenylene ($C_{18}H_{12}$). Triphenylene can be converted in similar way to give the TRS $C_{24}H_{16}$ and $C_{24}H_{14}$ systems shown in Figure 1. The TRS benzenoids in obtrusive locations of Table 3 ($C_{42}H_{18}$, $C_{60}H_{22}$, $C_{72}H_{24}$, $C_{84}H_{26}$, etc.) can be generated by supercircumscribing ($C_nH_s \rightarrow C_{n+3s+18}H_{s+12}$) with polyphenylene necklaces. Supercircumscribing benzene, biphenyl, triphenylene, dibenzo[fg,op]tetracene ($C_{24}H_{14}$), etc. gives hexabenzo[bc,ef,hi,kl,no,qr]coronene ($C_{42}H_{18}$, superbenzene), superbiphenyl, ($C_{60}H_{22}$), supertriphenylene ($C_{72}H_{24}$), superdibenzo[fg,op]tetracene ($C_{84}H_{26}$), etc., respectively.⁴

This algorithm constitutes the essence of our modified aufbau construction of TRS benzenoids previously described.³

The enumeration of the $C_{30}H_{18}$ TRS systems which are leapfrogs of the $C_{20}H_{12}$ benzenoids (Figure 2) is further illustrative. This formula is not in parentheses because it has one fused TRS benzenoid (tetrabenzo[a,c,h,j]anthracene, third bold structure in Figure 2 and top structure in Figure 3) which

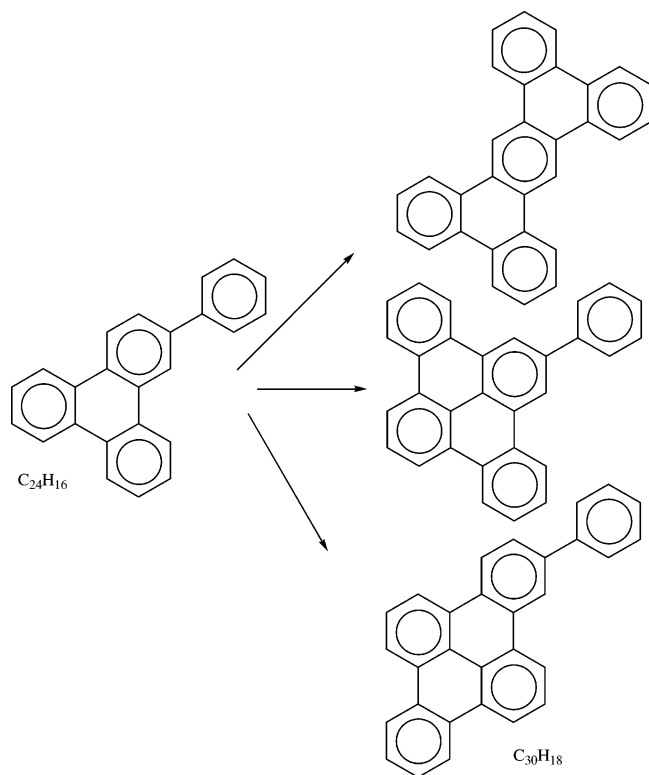


Figure 3. The C_6H_2 aufbau construction of the strain-free TRS systems from 2-phenyltriphenylene.

can be generated from the formula above ($C_{24}H_{16}$) but not from the formula at the left ($C_{24}H_{14}$). The two phenyl substituted dibenzo[*fg,op*]tetracene isomers in Figure 3 can also be generated from the left formula by benzenediyl attachment. The three top isomers in Figure 4 are not allowed as they are strained systems capable of undergoing pyrolytic cyclodehydrogenation to the even more stable TRS benzenoid ($C_{30}H_{16}$) shown.

The full definition of D_s is now clarified by examination of these TRS systems. In Figure 1, triphenylene ($C_{18}H_{12}$, $[D_s, r(\text{empty})] = [0,1]$) has a single empty ring and dibenzo-

[*fg,op*]tetracene ($C_{24}H_{14}$, $[D_s, r(\text{empty})] = [0,2]$) has two empty rings both of which exhibit zero disconnections among their empty rings, and 2-phenyltriphenylene ($C_{24}H_{16}$, $[D_s, r(\text{empty})] = [1,1]$) has an empty ring in the triphenylene moiety disconnected from the bridging bond to the phenyl moiety. In Figures 2 and 3, the phenyl dibenzo[*fg,op*]tetracene isomers and tetrabenzo[*a,c,h,j*]anthracene have the equivalent of two empty rings. In the former, the two empty rings are adjacent but disconnected from the bridging bond to the phenyl moiety, and in the latter the empty rings are not adjacent and no bridging bond exists in the structure ($[D_s, r(\text{empty})] = [1,2]$). In Figure 4, the bottom $C_{30}H_{16}$ TRS structure has three mutually adjacent empty rings ($[D_s, r(\text{empty})] = [0,3]$). The range of D_s values is given by eq 24. For example, with the input of ten sextet rings, eq 24 gives $-2 < D_s < 8$ for $C_{60}H_{22}$ (superbiphenyl) to $C_{60}H_{42}$ (decaphenyl). For superbene (hexabenzo[*bc,ef,hi,kl,no,qr*]coronene, $C_{42}H_{18}$), the empty rings form a hexagonal circuit thereby accounting for the net disconnection of empty rings as being minus one ($D_s = -1$).

We now illustrate the applications of eqs 17, 18, and 21. The first-generation formulas for TRS constant-isomers are given by eq 17 which is a floor function. If we allow TRS benzenoids to have bridging bonds to TRS substituents, then from Table 3 it is evident that $N_H = s = 6, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, \dots$, but it should be recalled that only biphenyl which have provisional status in Table PAH6-(sextet) has a bridging bond and all other first generation members of the TRS constant-isomer series are necessarily fused TRS benzenoids. Solving eq 17 for these s values gives $n = 6, 12, 18, 24, 30, 36, 48, 54, 66, 78, 90, \dots$ which correspond to C_6H_6 (benzene), $C_{12}H_{10}$ (biphenyl), $C_{18}H_{12}$ (triphenylene), $C_{24}H_{14}$ (tetrabenzo[*a,c,h,j*]anthracene), $C_{30}H_{16}$ (bottom TRS in Figure 4), $C_{36}H_{18}$, $C_{48}H_{20}$, $C_{54}H_{22}$, $C_{66}H_{24}$, $C_{78}H_{26}$, $C_{90}H_{28}$, and so on. A number of observations are warranted at this point. The first step on the left-hand staircase boundary of Table 3 has six formulas, the second step has four formulas, and the steps thereafter have three and two formulas. Starting with $C_{66}H_{24}$, the second formula

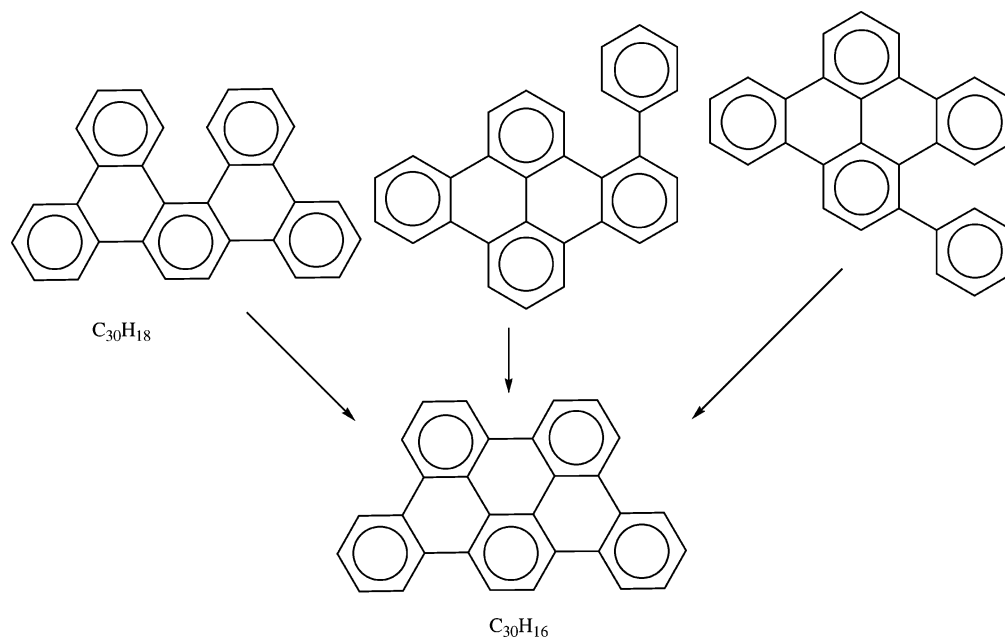


Figure 4. Pyrolytic conversion of strained TRS benzenoids to more condensed strain-free TRS benzenoids.

occurring on the three-formula steps corresponds to the first generation TRS constant-isomer series. Except for biphenyl, the formulas ($C_{42}H_{18}$, $C_{60}H_{22}$, $C_{72}H_{24}$, $C_{84}H_{26}$, ...) at the obtrusive locations (corner of each step) are second generation formulas corresponding to the TRS constant-isomer series.

The maximum number of empty rings for a given number of sextets is given by eq 18 which is a ceiling function. The number of sextets is simply given by the number of carbons divided by six. For $r(\text{sextet}) = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, \dots$, eq 18 gives $r(\text{empty}) = 0, 0, 1, 2, 3, 4, 6, 7, 8, 10, 11, 13, 14, 16, \dots$ which correspond to C_6H_6 , $C_{12}H_{10}$, $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, $C_{36}H_{18}$, $C_{42}H_{18}$, $C_{48}H_{20}$, $C_{54}H_{22}$, $C_{60}H_{22}$, $C_{66}H_{24}$, $C_{72}H_{24}$, $C_{78}H_{26}$, $C_{84}H_{26}$, ... all which are first and second generation members of TRS constant-isomers that occur on the left-hand staircase boundary.

The minimum number of sextet rings for a given number of empty rings is given by eq 21 which is a ceiling function. It is easy to show that this equation gives every formula on the left-hand staircase boundary of Table 3. With few exceptions, it should be apparent from known data that as the ratio of the number of sextet rings to empty rings increases for a given number of carbons, the HOMO energy increases.^{6,11}

CONCLUSION

While comprehensively summarizing upper/lower bound mathematical expressions derived from the Harary and Harborth inequalities, some of which were previously given by Cyvin and co-workers in various papers,¹ we have derived some new mathematical expressions especially for TRS benzenoid systems. Also, some new mathematical expressions have been derived (Table 2) using correlations between ordinary benzenoids and leapfrog benzenoids, the latter which are also the strain-free TRS benzenoids. Some believe that one can only have true knowledge if that knowledge can be expressed by a mathematical equation. Load Kelvin said, "When you can measure what you are speaking about and express it in numbers you know something about it; but when you cannot express it in numbers, your knowledge is a meager and unsatisfactory kind." A key historical insight has emerged—our original algorithmic generation of the periodic table for benzenoid hydrocarbons and Harary/Harborth spiral analysis both relied on the geometry of one-isomer benzenoid series. Their purely geometrical construct took on chemical meaning with our formulation of a periodic table for benzenoid hydrocarbons and our definition and subsequent evolution of constant-isomer series. It is our conviction that mathematics is usually ahead of physical/scientific principles. If one discovers a new phenomenon, the mathematics applicable to this phenomenon probably already exists—it is just a matter of finding it.

Table 3 [Table PAH6(sextet,modified)] organizes the formulas having corresponding structures according to their structural invariants of $(x,y) = [D_s, r(\text{empty})]$ which then segregates the formulas having structures with strictly fused hexagonal rings (left-hand triangular region) from those that do not (right-hand triangular region). This table easily reveals the number of empty rings and the number of disconnections

among them. The polyphenylenes are sorted onto the upper right-hand boundary, and the TRS constant-isomer series are sorted onto the left-hand staircase boundary. These and other topological/structural properties are given a systematic arrangement by Table PAH6(sextet,modified). Thus, Table PAH6(sextet,modified) is a partially ordered set of infinite extension, complies with the triad principle, and has a least member ($C_{12}H_{10}$). Its organization leads to hierarchical ordering of properties and exhibits edge effects characterized by the polyphenylene (formulas on the right-hand horizontal boundary) and constant-isomer series (formulas on the left-hand staircase boundary). For the invariants of D_s , d_s , η_o , N_c , N_{Ic} , N_H , N_{pc} , $r(\text{empty})$, r , and $r(\text{sextet})$ have the same values for every member of a given set of strain-free TRS isomers. Thus, we expect that the members of a fused strain-free TRS isomer set are to be more similar than members belonging to an ordinary benzenoid isomer set. This should be particularly true for members of any TRS constant-isomer set. The more invariants that a set of molecular graphs have in common, the more similar are the corresponding set of molecules.

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