

The Most Stable Class of Benzenoid Hydrocarbons—New Topological Correlations of Strain-Free Total Resonant Sextet Benzenoids

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While briefly reviewing how the concepts of strictly pericondensed, strain-free, Clar's aromatic sextet, and symmetry are interconnected in the topological correspondence between strictly pericondensed and total resonant sextet (TRS) benzenoid hydrocarbons, new structural correlations in isomer numbers, symmetry distributions, and empty rings between various strain-free TRS benzenoids made up of only fused hexagonal rings are presented. These correlations are made evident by the Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons [Table PAH6(sextet)] and application of the leapfrog operation. A new perimeter topology relationship for fused strain-free TRS benzenoids is derived. This work represents a contribution toward understanding formula/structure relationships of benzenoid hydrocarbons.

INTRODUCTION

The sextet rule of Clar¹ is an extension of aromaticity from monocyclic to fused polycyclic molecular systems. Clar's sextet rule in benzenoid chemistry is equivalent to Lewis' octet rule (or more generally, noble gas electronic configuration rule) in inorganic chemistry. Maximizing the number of Clar's sextets is analogous to maximizing the outer-shell electrons to a noble gas electronic configuration. Clar's book¹ summarizes a considerable amount of experimental support for the exceptional stability associated with the presence of sextets in benzenoid hydrocarbons. According to the ISI Web of Science (1995 to present), Clar's book¹ has been cited well over 500 times in the literature. The benzenoid hydrocarbons that we call total resonant sextet (TRS) benzenoid hydrocarbons were called fully benzenoid by Clar,¹ all-benzenoid by Cyvin, Gutman, and co-workers,² and, in his recent review, fully aromatic by Randić.³ Using his conjugated circuit theory, Randić has shown that TRS benzenoid hydrocarbon isomers have the highest resonance energy (RE) and states: "Benzenoid(s) having a single Clar structure with only aromatic sextets (indicated by inscribed circles) and empty rings, the fully benzenoid systems (i.e., TRS benzenoids) described by Clar, are most stable; benzenoids having several Clar structures are next most stable; and benzenoids having a single Clar structure with rings and isolated (fixed) CC double bonds are least stable."³ Randić recently presented a novel view of Clar's structures that the reader might find informative as background.³

The research of Müllen and his group in Mainz, Germany has shown that TRS benzenoid hydrocarbons having carbon atoms of 54, 60, 66, 72, 78, 84, and larger still behave like discreet molecular structures and do not look graphitic in their electronic or spectral behavior.^{4,5} These compounds show the distinct benzenoid bands in their UV and fluorescence spectra. These TRS benzenoid hydrocarbons are made through condensation reaction of polyphenyl structures which are themselves total resonant sextet systems. The simplest of these reactions is an $\text{AlCl}_3/\text{CuCl}_2$ induced cyclodehydro-

genation (a type of chemical pyrolysis) of hexaphenylbenzene to D_{6h} hexabenzob[bc,ef,hi,kl,no,qr]coronene ($\text{C}_{42}\text{H}_{18}$), and the largest TRS benzenoid synthesized by the Müllen group is a D_{6h} $\text{C}_{222}\text{H}_{42}$ structure.^{4,5} These D_{6h} TRS benzenoids synthesized by the Müllen group are the second ($\text{C}_{42}\text{H}_{18}$) and fourth ($\text{C}_{222}\text{H}_{42}$) generation members of our constant one-isomer D_{6h} TRS series generated by successively supercircumscribing benzene with a polyphenylene "beaded" necklace.

A fundamental premise made early in our study of benzenoid hydrocarbons of environmental consequence was that during their pyrolytic formation the most highly condensed forms would be preferred.⁶ Also, our book and prior published results enumerated for the first time all the possible strain-free TRS benzenoid hydrocarbons which the Müllen group has synthesized.^{4,5} The success of the Müllen group in synthesizing the largest known benzenoid hydrocarbons to date are the results both of the above fundamental premise and Clar's sextet principle. The concepts of strictly pericondensed,² strain-free [ref 6, p 85],^{7,8} Clar's sextet principle,¹ and molecular symmetry were key to our discovery of the many spectacular topological properties of these systems^{7–15} which were subsequently verified and elaborated further by Cyvin and co-workers.¹⁶ These four S's (strictly pericondensed, strain-free, sextet, and symmetry) are intricately related through an organizational framework called a Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (Table PAH6) (see Table 2).^{7–15} Strictly pericondensed benzenoid hydrocarbons have connected excised internal structures and are devoid of catacondensed appendages, the smallest of which would be a benzo moiety. Strictly pericondensed benzenoids without adjacent bay regions (i.e., coves or fjords) are by their very nature strain-free, and as we will see, strain-free TRS are devoid of adjacent or proximate bay regions; a cove has two (e.g., like benzo[c]-phenanthrene) and a fjord has three (e.g., like dibenzo[c,g]-phenanthrene) adjacent bay regions and hexaheicene has four adjacent bay regions. We will briefly review these concepts and then present some new topological correspondences among what we call strain-free total resonant sextet (TRS) benzenoid hydrocarbons having only fused hexagonal rings.

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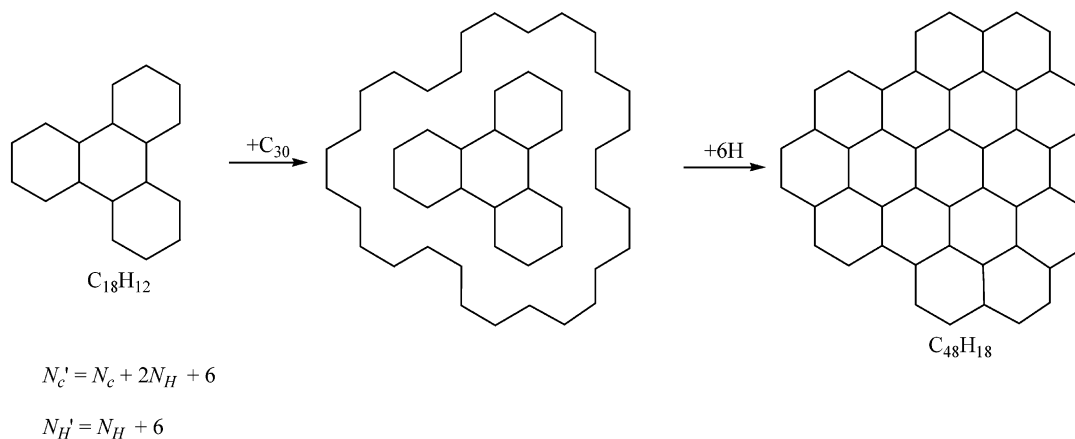


Figure 1. Circumscribing triphenylene with a ring of 30 carbons and incrementing with 6 more hydrogens gives circum(30)triphenylene.

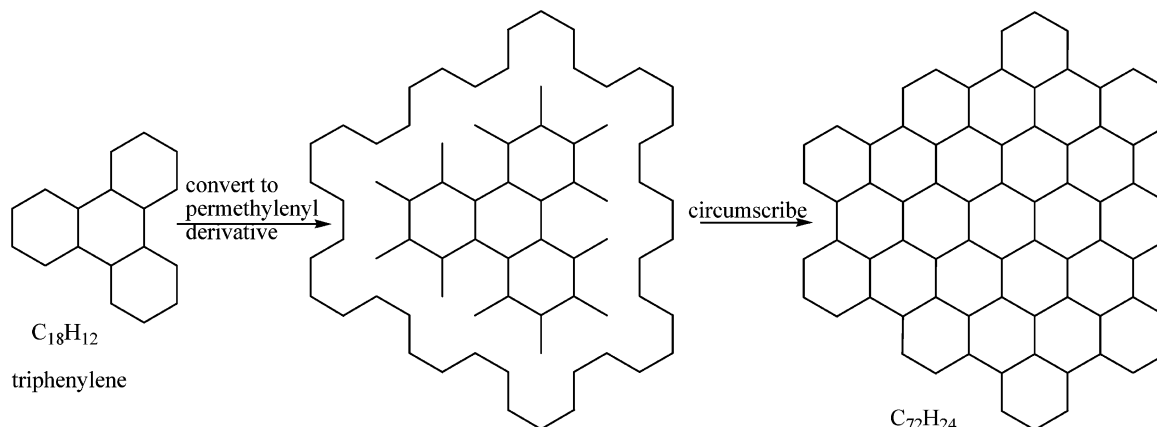


Figure 2. Augmented circumscribing a TRS benzenoid involves first converting to a permethylenyl derivative followed by circumscribing to give a larger TRS benzenoid.

BRIEF REVIEW

The essence of structural chemistry is the combinatorics of atoms according to definite rules in which stability plays a significant role. Given a particular chemical formula, the range of structure types that it can correspond to it can be deduced. What is usually lacking is a systematic process or set of algorithms by which one can arrive at a corresponding isomer set. Much of our work has been directed toward developing formula/structure algorithms which systematizes all benzenoid hydrocarbons in such a way as to help us extract the maximum amount structural information from their chemical formulas. To fully appreciate the results reported herein, the reader may benefit by reading the sequels to this work in chronological order.¹³

Here we review our standard terminology. Recall that a molecular (polyhex) graph is the C–C σ -bond skeleton of a (benzenoid) conjugated hydrocarbon where the C and H atoms and C–H and $p\pi$ -bonds are omitted. A TRS Clar graph is a molecular graph with disjoint inscribed circles separated by so-called empty rings (rings without inscribed circles) where each circle represents three $p\pi$ -bonds that are mutually permutable just as it frequently is used for benzene in standard textbooks. In Figures 1–3 the molecular graph of triphenylene is given; its TRS Clar graph would possess three disjoint inscribed circles in the three equivalent outer rings. To convert the molecular graph of triphenylene into one of its 9 Kekulé structures ($K = 9$) one would have to draw-in 9 lines representing $p\pi$ -bonds in such a way as to

not violate valence. $N_c = n$ and $N_H = s$ denote the number of carbon (molecular graph vertices) and hydrogen (molecular graph degree-2 vertices) atoms, respectively. N_{pc} and N_{lc} denote the number of degree-3 vertices that are on the perimeter at the juncture of two hexagons and inside at the juncture of three hexagons of the polyhex molecular graph ($N_c = N_{pc} + N_{lc} + N_H$), respectively. r denotes the number of rings and d_s denotes the net number of disconnections among the internal edges between two hexagons ($N_{lc} + d_s = r - 2$). For triphenylene ($C_{18}H_{12}$), $N_c = 18$, $N_H = 12$, $N_{pc} = 6$, $N_{lc} = 0$, $r = 4$, and $d_s = 2$.

Let us review the structural organization of Table PAH6- (sextet) (see Table 2) that was previously published.¹³ The formulas in each row are successively incremented by $C_{12}H_6$ and each column by C_6H_2 . All the molecular graphs corresponding to TRS benzenoid structures having formulas in the same row possess the same number of internal third degree vertices and in each column have the same net number of disconnections (d_s). Thus, N_{lc} at the right end of each row and d_s at the top of each column are invariants providing structural information on members of the respective rows and columns. Members belonging to the same row or column are said to belong to the same row or column series according to the specified N_{lc} or d_s value.

Previously we showed that circumscribing benzenoids as illustrated with triphenylene in Figure 1 was analogous to augmented circumscribing of strain-free TRS benzenoids as illustrated in Figure 2.^{9–15} Figure 3 shows an equivalent

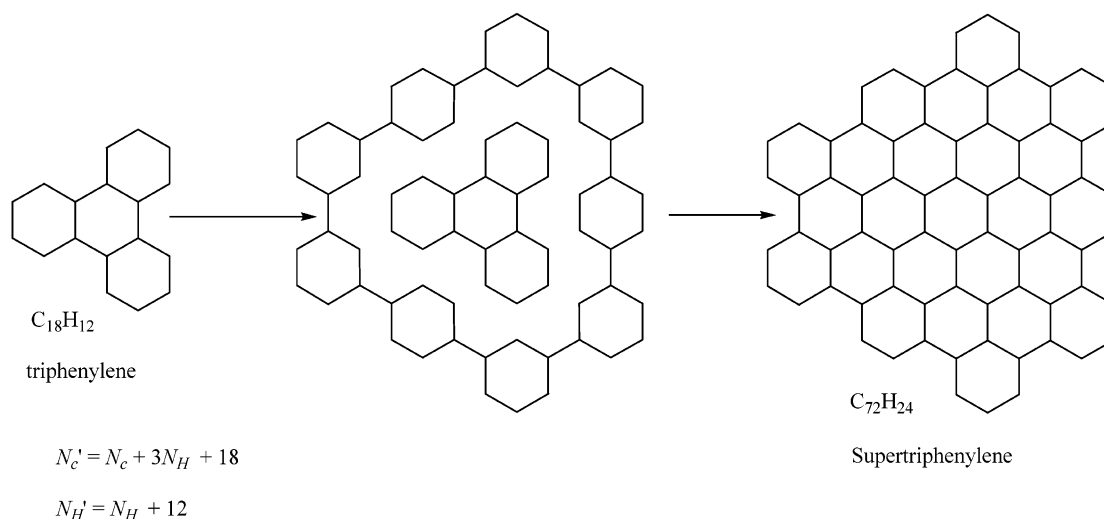


Figure 3. Supercircumscribing a TRS benzenoid with a polyphenylene beaded necklace gives a larger TRS benzenoid of the next generation in a TRS constant-isomer series. Supercircumscribing is equivalent to augmented circumscribing.

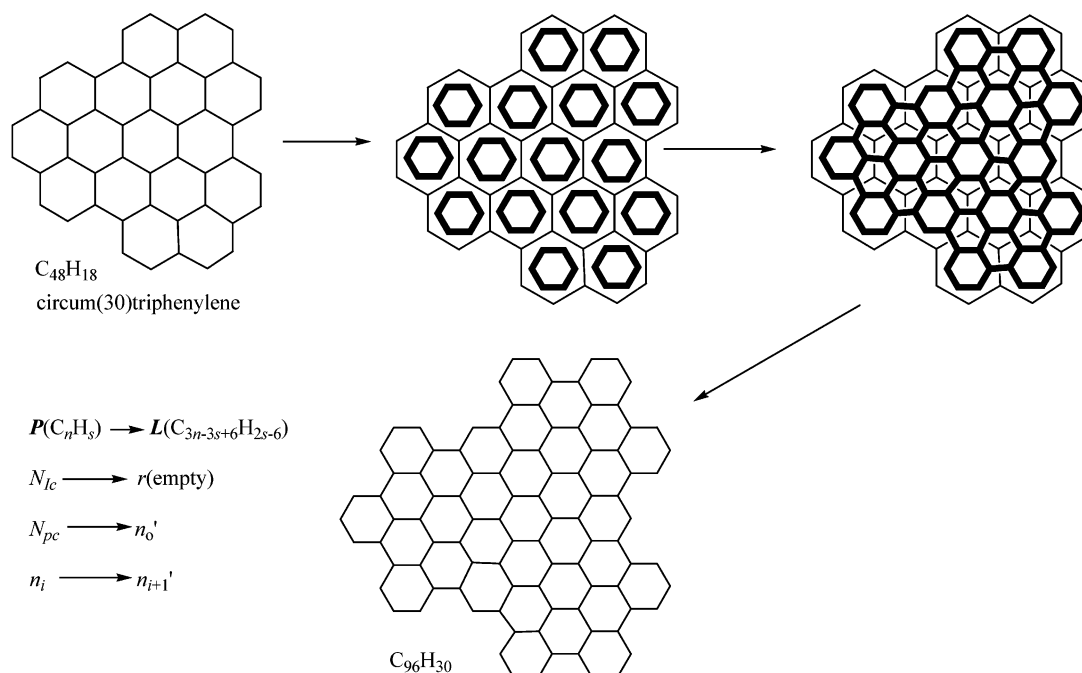


Figure 4. Leapfrog transformation of circumtriphenylene ($C_{48}H_{18}$) generates the TRS $C_{96}H_{30}$ benzenoid synthesized by Mullen and co-workers.⁴⁵

method to augmented circumscribing called supercircumscribing. Both the successive circumscribing of strictly pericondensed benzenoids and the successive supercircumscribing of TRS benzenoids lead to constant isomers series. The constant-isomer series of these two different benzenoid classes have precisely the same isomer numbers where there is a one-to-one symmetry correspondence between the two associated memberships with the same isomer numbers. While Cyvin and co-workers verified our results, they concluded that “A rigorous proof of the general validity of these patterns has so far not been given.”¹⁶ Later we proved this topological correspondence by using Fowler’s leapfrog algorithm¹⁷ as illustrated in Figure 4 which shows that circumtriphenylene is the progenitor of the TRS benzenoid which Müllen and co-workers trivially named superphenylene.^{5,18} A more appropriate trivial name for this D_{3h} $C_{96}H_{30}$ TRS benzenoid would be “leapfrogcircumtriphenylene” or “super(1,3,5-triphenylbenzene)” since it can be derived by

leapfrogging circumtriphenylene ($C_{48}H_{18}$) or supercircumscribing 1,3,5-triphenylbenzene, respectively.^{13,18} To perform the leapfrog operation (Figure 4) one simply redraws a slightly smaller hexagon in each hexagon of the precursor polyhex molecular graph with a relative 30 degree rotation from the initial outer hexagon and then connect the newly formed hexagons to form the leapfrog polyhex.

To further illustrate this topological correspondence between strain-free strictly pericondensed benzenoids and TRS benzenoids, consider Figure 5. Depicted in the upper portion of Figure 5 at the left is a portion of the right-hand staircase boundary edge of Table PAH6 which contains both odd and even benzenoid formulas and at the right is a portion of the right-hand staircase boundary edge of Table PAH6(sextet).^{10–13} At the lower left of Figure 5 are depicted the polyhex molecular graphs of the strictly pericondensed benzenoids (with the exception of naphthalene) corresponding to the formulas immediately above and at the lower right are the

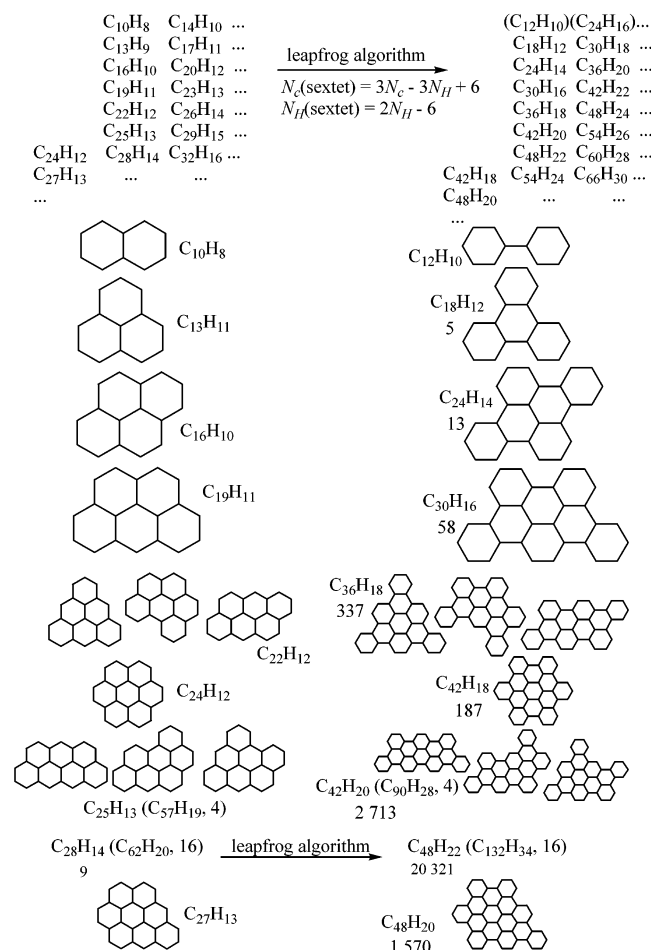


Figure 5. Comparison of the first generation members of the constant-isomer series having formulas on the left-hand staircase boundary edge of Table PAH6 (left side of Figure 5) and the associated total resonant (TRS) benzenoids having formulas on the left-hand staircase boundary of Table PAH6(sextet) (right side of Figure 5).

polyhex molecular graphs of the TRS benzenoids. Leapfrogging the polyhex molecular graphs at the left give the corresponding molecular graphs at the right. In comparing the molecular graphs at the left with those at the right, note the correspondence in symmetry. Recall that the TRS sextet isomers at the right are just a subset of all benzenoids of that given formula; the total number of benzenoid isomers is also given below each TRS formula, and the total number of TRS isomers is depicted. For example, leapfrogging the only $C_{27}H_{13}$ benzenoid isomer shown at the bottom left of Figure 5 gives the only $C_{48}H_{20}$ TRS benzenoid isomer shown at the right out of 1570 possible benzenoid isomers. The correspondence between the formulas of $C_{27}H_{13}$ and $C_{48}H_{20}$ is given by the above equations [$N_c(\text{sextet}) = 3N_c - 3N_H + 6 = 3 \times 27 - 3 \times 13 + 6 = 48$; $N_H(\text{sextet}) = 2N_H - 6 = 2 \times 13 - 6 = 20$]. Thus the equations listed below the upper arrow in Figure 5 and the leapfrog algorithm allows us to determine the TRS isomers at the right from known benzenoid isomers at the left without requiring us to know what the rest of the isomers look like. The leapfrogs of all the catacondensed benzenoids are polyphenylenes which are not fused benzenoids and, therefore, only have provisional status in Table PAH6(sextet) as indicated by the formulas in parentheses in the upper right-hand corner of Figure 5.

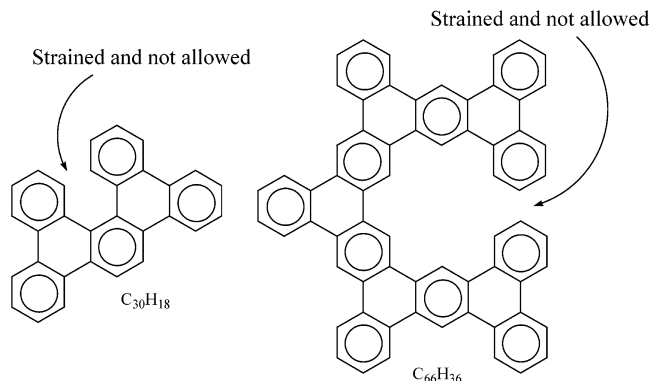


Figure 6. Two principal types of strain interaction that are not allowed because thermally induced oxidative cyclodehydrogenation can lead to less strained systems with increased resonance stabilization.

Müllen and co-workers have synthesized a $C_{72}H_{26}$ TRS benzenoid which is the leapfrog of circobiphenyl ($C_{38}H_{16}$) [cf. with p 68 of ref 6] that they gave the trivial name of supernaphthalene;^{4,5} here again a more appropriate trivial name would be that of “leapfrogcircobiphenyl”. Supernaphthalene is only one of 13 TRS.¹³ They also synthesized a D_{2h} $C_{78}H_{26}$ TRS benzenoid that is the leapfrog of circum(38)-anthracene ($C_{40}H_{16}$) [cf. with p 68 of ref 6] that could be called “leapfrogcircumanthracene” which is one member of four belonging to our TRS constant-isomer series;¹³ this D_{2h} $C_{78}H_{26}$ TRS benzenoid can also be obtained by supercircumscribing *p*-terphenyl and could be named “super (*p*-terphenyl)”. Their D_{2h} $C_{132}H_{34}$ TRS benzenoid is one of 16 belonging to the first generation members belonging to another of our TRS constant-isomer series;¹³ this D_{2h} $C_{132}H_{34}$ TRS benzenoid can be obtained by leapfrogging dibenzo-[*fg,op*]anthanthrene ($C_{28}H_{14}$, phenanthro[1,10,9,8-*opqra*]-perylene) and supercircumscribing the resulting TRS benzenoid.

IMPORTANCE STRAIN-FREE CONCEPT

It is important that one understands what is meant by essentially strain-free TRS benzenoid hydrocarbons. Strain-free benzenoids have no immediately adjacent or proximate bay regions (or large looped helical-related structures that coil back on itself). Figure 5 illustrates the one-to-one structural correspondence between the strain-free strictly pericondensed benzenoids (structures shown at the left in Figure 5) having formulas on the left-hand staircase boundary edge of Table PAH6 and the strain-free TRS benzenoids (structures shown at the right in Figure 5) having formulas on the left-hand staircase boundary edge of Table PAH6(sextet). Table PAH6(sextet) and the associated TRS benzenoids are a subset of Table PAH6 and all benzenoids. Strain-free strictly pericondensed benzenoids can have no concave regions (i.e., adjacent bay regions) on the perimeter of their structures.¹⁹ Strained hexahelicene-related structures are purposely excluded in our enumeration studies. Figure 6 identifies the smallest strained TRS benzenoid hydrocarbons that are representative of two types of systems excluded in our treatment of TRS benzenoid hydrocarbons.⁸ The smaller $C_{30}H_{18}$ TRS structure can be regarded as a pentahelicene related structure, and the larger $C_{66}H_{36}$ TRS structure can be regarded as a large looped helicene.¹⁹ It is topologically impossible for any TRS benzenoid to have two adjacent

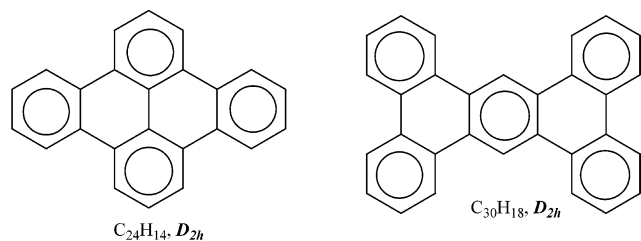


Figure 7. Matching $C_{24}H_{14}$ and $C_{30}H_{18}$ strain-free TRS benzenoid sets.

bay regions but as the strained $C_{30}H_{18}$ TRS structure in Figure 6 shows, strained TRS benzenoids may have a triplet of adjacent bay regions. The strained $C_{30}H_{18}$ TRS structure has no leapfrog precursor and cannot be circumscribed, and the larger $C_{66}H_{36}$ TRS structure can be generated by the leapfrog operation on a pentabenzohexahelicene and cannot be supercircumscribed. Pentahelicene and hexahelicene related benzenoid structures have never been detected in combustion/environmental analyte samples. Thus we presume that both types of strained TRS systems in Figure 6 cannot be isolated in nature because they can undergo further oxidative cyclo-dehydrogenation under pyrolytic conditions.

In general, hexahelicene related benzenoid structures are not relevant in our topological studies of strictly pericondensed benzenoid systems, and pentahelicene related TRS benzenoid structures have been excluded in our topological studies of TRS benzenoid systems.^{6,8,13} A two carbon gap must exist everywhere on the perimeter of a strictly pericondensed benzenoid before it can be circumscribed. The consequence of this is that a necessary and sufficient condition for benzenoid to be circumscribable is that it contains no adjacent bay regions.¹⁹ For example, chrysene ($C_{18}H_{12}$) with its two nonadjacent bay region can be circumscribed (cf. with p 72 of ref 6), but benzo[*c*]phenanthrene ($C_{18}H_{12}$) with its two adjacent bay regions cannot be circumscribed. Since the leapfrog of benzo[*c*]phenanthrene is *s-cis-m,m'*-quaterphenyl the following is an equivalent restriction for being able to supercircumscribe a TRS benzenoid. Whenever a TRS benzenoid possesses an edge section in which a *s-cis-m,m'*-quaterphenyl substructure can be embedded, then that TRS benzenoid cannot be supercircumscribed.¹³ The D_{3h} $C_{132}H_{42}$ TRS benzenoid trivially called supertriphenylene by Müllen and co-workers^{4,5} possesses three peripheral regions that can be embedded by *s-cis-m,m'*-quaterphenyl substructures and therefore cannot be supercircumscribed.

NEW CORRELATIONS OF STRAIN-FREE TRS BENZENOIDS

The strain-free criterion was essential for the recognition of the strictly pericondensed constant-isomer benzenoid series and their associated one-to-one correspondence in isomer count and structure symmetry with the constant-isomer series of the TRS benzenoids as illustrated in Figures 1–5. This one-to-one correspondence is for structures having formulas on the staircase boundary edges of Table PAH6 and Table PAH6(sextet). We now present another correspondence that exists among strain-free TRS benzenoids having formulas not on the staircase boundary edges that was not previously recognized.

Taking data from Table 1 in a paper⁸ by Dias, Cyvin, and Brunvoll on the numbers of isomers of strain-free total

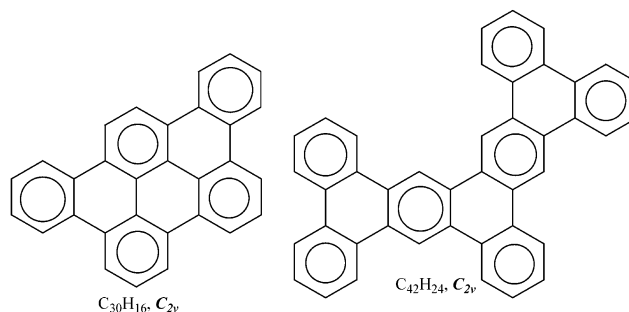


Figure 8. Matching $C_{30}H_{16}$ and $C_{42}H_{24}$ strain-free TRS benzenoid sets.

Table 1. Numbers of Strain-Free TRS Benzenoids Classified According to Symmetry

formula	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s
$d_s = 2, N_{lc} = 0$						
$C_{18}H_{12}$	1					
$C_{24}H_{14}, C_{30}H_{18}$			1			
$C_{30}H_{16}, C_{42}H_{24}$					1	
$C_{36}H_{18}, C_{54}H_{30}$	1			1	1	
$C_{42}H_{20}, C_{66}H_{36}$					1	2
$C_{48}H_{22}, C_{78}H_{42}$			1	2	2	3
$C_{54}H_{24}, C_{90}H_{48}$		1			2	9
$C_{60}H_{26}, C_{102}H_{54}$				5	5	16
$d_s = 5, N_{lc} = 2$						
$C_{36}H_{20}$					1	
$C_{42}H_{22}, C_{48}H_{26}$	1					1
$C_{48}H_{24}, C_{60}H_{32}$					1	3
$C_{54}H_{26}, C_{72}H_{38}$				1	2	8
$C_{60}H_{28}, C_{84}H_{44}$					1	24
$d_s = 8, N_{lc} = 4$						
$C_{54}H_{28}$					3	2
$C_{60}H_{30}, C_{66}H_{34}$			1	1	2	9

resonant sextet benzenoid and inserting them into Table PAH6(sextet) (see Table 2),¹³ the following correlations will be noted: The known isomers numbers in the $N_{lc} = 0$ row coincide with those in the $d_s = 2$ column, namely 1, 1, 1, 3, 3, 8, 12, ...; the known isomers numbers in the $N_{lc} = 2$ row coincide with those in the $d_s = 5$ column, namely 1, 1, 2, 4, 11, 25, ...; the known isomers numbers in the $N_{lc} = 4$ row coincide with those in the $d_s = 8$ column, namely 1, 2, 5, 13, 35, ...; the known isomers numbers in the $N_{lc} = 6$ row coincide with those in the $d_s = 11$ column, namely 3, 4, 13, 36, 112, ...; the known isomers numbers in the $N_{lc} = 8$ row coincide with those in the $d_s = 14$ column, namely 3, 11, 35, 112, ...; and the known isomers numbers in the $N_{lc} = 10$ row coincide with those in the $d_s = 17$ column, namely 8, 25, Note that these correlations occur for the section of Table PAH6(sextet) (see Table 2) which is subtended by the $d_s = 2$ column and the $N_{lc} = 0$ row (i.e., the formulas to the right of and including the $d_s = 2$ column).

Not only is there a commonality in isomer numbers between the strain-free TRS benzenoid members belonging to the *i*th column and *i*th row of Table PAH6(sextet) (see Table 2) but there is also a one-to-one matching in the symmetry distributions and the number of empty rings between the members of these perpendicular sets having the same isomer numbers. Further results are summarized in Table 1 along with their symmetry distributions. In regard to the number of isomers and symmetry distributions, the TRS structures having formulas along the diagonal, $C_{18}H_{12}$ (1), $C_{36}H_{20}$ (1), $C_{54}H_{28}$ (5), $C_{72}H_{36}$ (36), ..., of these perpendicular sets are unique. Figures 7–12 show the TRS

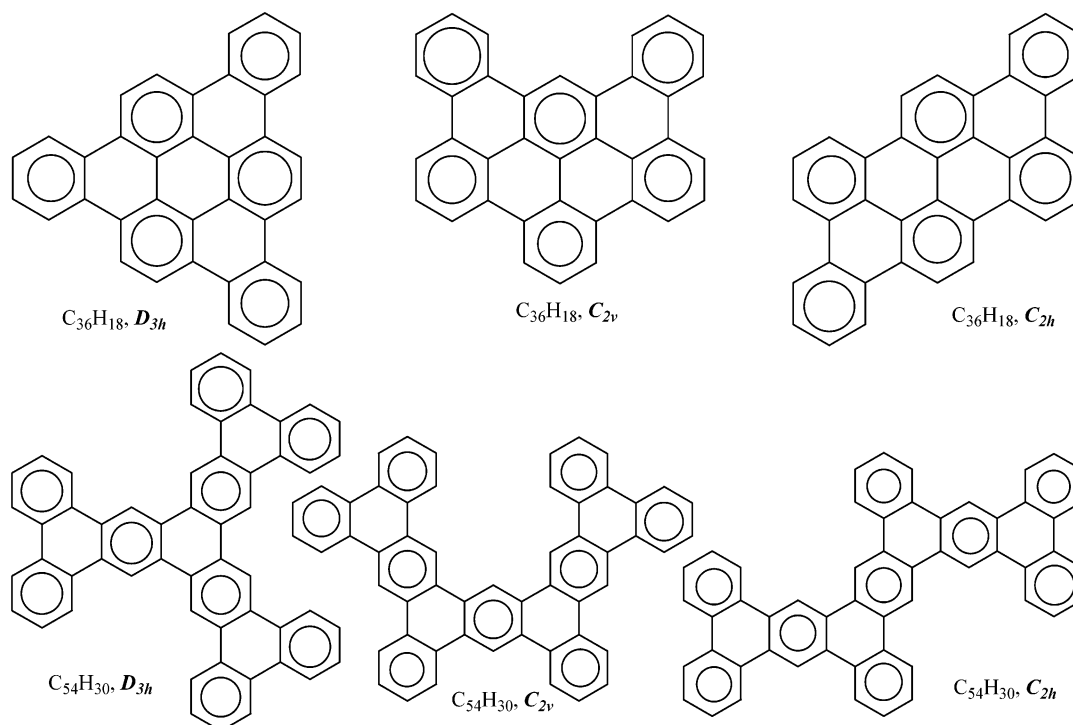


Figure 9. Matching $C_{36}H_{18}$ and $C_{54}H_{30}$ strain-free TRS benzenoid sets.

Table 2. Table PAH6 (Sextet): Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons

$d_s = -13$	$d_s = -10$	$d_s = -7$	$d_s = -4$	$d_s = -1$	$d_s = 2$	$d_s = 5$	$d_s = 8$	$d_s = 11$	$d_s = 14$	$d_s = 17$	$d_s = 20$	N_{lc}
					$C_{18}H_{12}$ (1)	$C_{30}H_{18}$ (1)	$C_{42}H_{24}$ (1)	$C_{54}H_{30}$ (3)	$C_{66}H_{36}$ (3)	$C_{78}H_{42}$ (8)	$C_{90}H_{48}$ (12)	... 0
					$C_{24}H_{14}$ (1)	$C_{36}H_{20}$ (1)	$C_{48}H_{26}$ (2)	$C_{60}H_{32}$ (4)	$C_{72}H_{38}$ (11)	$C_{84}H_{44}$ (25)	$C_{96}H_{50}$... 2
					$C_{30}H_{16}$ (1)	$C_{42}H_{22}$ (2)	$C_{54}H_{28}$ (5)	$C_{66}H_{34}$ (13)	$C_{78}H_{40}$ (35)	$C_{90}H_{46}$ 4
					$C_{36}H_{18}$ (3)	$C_{48}H_{24}$ (4)	$C_{60}H_{30}$ (13)	$C_{72}H_{36}$ (36)	$C_{84}H_{42}$ (112) 6
					$C_{42}H_{20}$ (3)	$C_{54}H_{26}$ (11)	$C_{66}H_{32}$ (35)	$C_{78}H_{38}$ (112) 8
					$C_{48}H_{22}$ (8)	$C_{60}H_{28}$ (25)	$C_{72}H_{34}$ (100)10
				$C_{42}H_{18}$ (1)	$C_{54}H_{24}$ (12)	$C_{66}H_{30}$ (63)	$C_{78}H_{36}$ (257)12
				$C_{48}H_{20}$ (1)	$C_{60}H_{26}$ (26)	$C_{72}H_{32}$ (144)
				$C_{54}H_{22}$ (4)	$C_{66}H_{28}$ (48)
				$C_{60}H_{24}$ (9)	$C_{72}H_{30}$ (114)
				$C_{66}H_{26}$ (24)
				$C_{60}H_{22}$ (1)	$C_{72}H_{28}$
				$C_{66}H_{24}$ (2)	$C_{78}H_{30}$
				$C_{72}H_{26}$ (13)
				$C_{78}H_{28}$ (34)	$C_{84}H_{30}$
				$C_{72}H_{24}$ (1)	$C_{84}H_{30}$
				$C_{78}H_{26}$ (4)
				$C_{84}H_{28}$ (16)
				$C_{90}H_{30}$
				$C_{84}H_{26}$ (1)	$C_{96}H_{32}$
				$C_{90}H_{28}$ (4)
				$C_{96}H_{30}$ (30)	$C_{102}H_{32}$ (114)
				$C_{102}H_{32}$ (114)
				$C_{96}H_{28}$ (1)	$C_{108}H_{34}$
				$C_{102}H_{30}$ (9)

structures for the matching sets of $C_{24}H_{14}$ and $C_{30}H_{18}$, $C_{30}H_{16}$ and $C_{42}H_{24}$, $C_{36}H_{18}$ and $C_{54}H_{30}$, $C_{42}H_{20}$ and $C_{66}H_{36}$, $C_{42}H_{22}$ and $C_{48}H_{26}$, and $C_{48}H_{24}$ and $C_{60}H_{32}$, respectively. Based on the observed correlations displayed in Table PAH6(sextet) (see Table 2) for the known strain-free TRS benzenoid isomer numbers, we predict the following isomer numbers: $C_{102}H_{54}$ (26), $C_{114}H_{60}$ (48), $C_{126}H_{66}$ (114), $C_{96}H_{50}$ (63), $C_{108}H_{56}$ (144), $C_{90}H_{46}$ (100), and $C_{102}H_{52}$ (257).

All strain-free TRS benzenoid structures having 60 carbons or less have been previously depicted in our prior work.^{6,20} Our aufbau for construction of these strain-free TRS benzenoids involved two attachment modes:^{6,8,20} (1) attachment of benzenetetrayl (C_6H_2) to a bay region of a smaller TRS benzenoid to generate a TRS successor having a molecular

graph with two more internal third degree vertices ($\Delta N_{lc} = 2$) and (2) attachment of a biphenylenetetrayl ($C_{12}H_6$) to a benzo edge of a smaller TRS benzenoid to generate a TRS successor having no change in the number of internal third degree vertices ($\Delta N_{lc} = 0$). This latter aufbau is illustrated in Figure 13 for the generation of the strain-free $C_{66}H_{36}$ TRS benzenoids in Figure 10 from the strain-free $C_{54}H_{30}$ TRS benzenoids in Figure 9; the various attachments of the biphenylenetetrayl are represented by the hexagons without inscribed circles. In Figure 13 structures 2 and 5 are excluded because of strain and one of the duplicates 3 and 8 and two of the triplicates 1, 4, and 6 and are discarded leaving a grand total of three strain-free $C_{66}H_{36}$ TRS benzenoids.

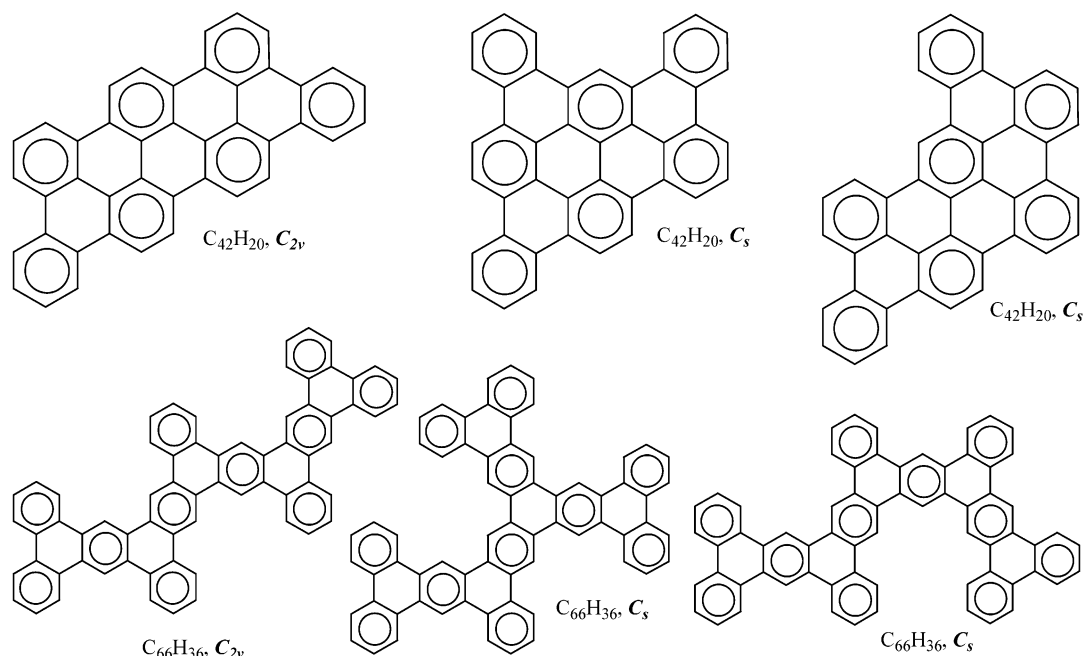


Figure 10. Matching $C_{42}H_{20}$ and $C_{66}H_{36}$ strain-free TRS benzenoid sets.

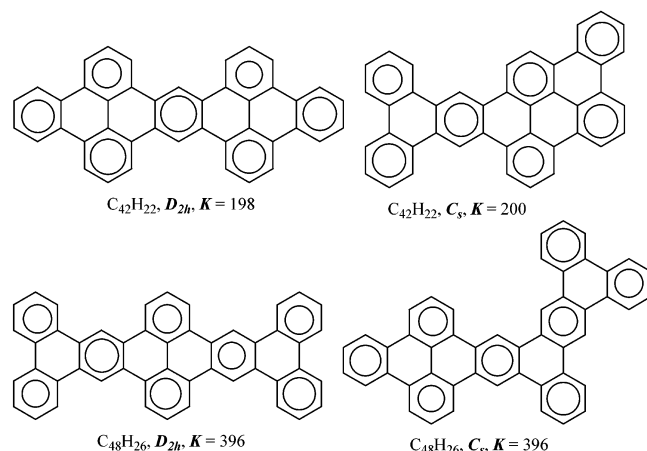


Figure 11. Matching $C_{42}H_{22}$ and $C_{48}H_{26}$ strain-free TRS benzenoid sets.

The results of Table PAH6(sextet) can be transferred to Table PAH6 for all benzenoid hydrocarbons. To identify the precursor formulas corresponding to structures from which leapfrogging results in the TRS benzenoid structures, the following equations are applicable:

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

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

These equations form the basis of what we regard as reverse leapfrogging. Recall that the empty rings in the Clar structure of a TRS benzenoid leapfrog correspond to the internal third degree vertices and that the sextet rings correspond to the rings of the precursor molecular graph (cf. with Figure 4). Using these equations, reverse leapfrogging of the smallest catacondensed strain-free TRS benzenoid, triphenylene ($C_{18}H_{12}$, $d_s = 2$, $N_{lc} = 0$), leads easily to the smallest strictly pericondensed benzenoid, phenalenyl ($C_{13}H_9$, $d_s = 0$, $N_{lc} = 1$). Next consider reverse leapfrogging on the strain-free $C_{30}H_{18}$ TRS structure in Figure 7. Using the above equations

the precursor (reverse leapfrog) benzenoid structures must have the formula of $C_{20}H_{12}$ which correspond to benzo[*a*]-pyrene, benzo[*e*]pyrene, and perylene [p 205–206, ref 6] with the molecular graph invariants of $d_s = 1$ and $N_{lc} = 2$. The leapfrog operation on the first two $C_{20}H_{12}$ benzenoids (Figure 14) generates 2-phenyl-dibenzo[*fg,op*]naphthacene and 6-phenyl-dibenzo[*fg,op*]naphthacene, respectively, which are excluded in this work because they are not totally fused benzenoids systems. This is also why the formulas in the upper right-hand corner of Figure 5 are placed in parentheses because the corresponding structures of biphenyl and all other polyphenylene members ($C_{12}H_{10}$, $C_{24}H_{16}$, ...) of this row series are not fused TRS benzenoids. In general, all leapfrog precursors with benzo or other catacondensed related appendages will generate phenyl or TRS aryl substituted TRS benzenoids that must be excluded because they are not totally fused systems. The leapfrog of perylene (Figure 14) gives the TRS benzenoid, tetrabenzo[*a,c,h,j*]anthracene, that is shown in Figure 7. Note that the strained $C_{30}H_{18}$ TRS benzenoid in Figure 6 has no leapfrog precursor.

It is informative to examine reverse leapfrogging of the next catacondensed TRS benzenoid having the formula of $C_{42}H_{24}$ ($d_s = 8$, $N_{lc} = 0$). Application of the above equations to this formula gives $C_{27}H_{15}$ ($d_s = 2$, $N_{lc} = 3$) which corresponds to 25 benzenoid isomers that have been listed.²¹ Two of these isomers are given in Figure 15 along with their leapfrogs shown in bold. The first one gives the $C_{42}H_{24}$ strain-free TRS benzenoid in Figure 8, and the second one gives a TRS biaryl which is excluded because it is not a totally fused benzenoid. Of the 25 $C_{27}H_{15}$ benzenoid leapfrog precursors, 21 are excluded because of their benzo appendages which give leapfrogs with phenyl substituents and 3 are excluded because they give TRS biaryls leapfrogs. These two examples (Figure 15) show what happens when molecular graphs with disconnected internal third degree vertices are separated by one ring (perylene-like substructures) versus more than one ring. In the latter case, one obtains TRS biaryl leapfrogs. The perylene substructure has a central ring with the two

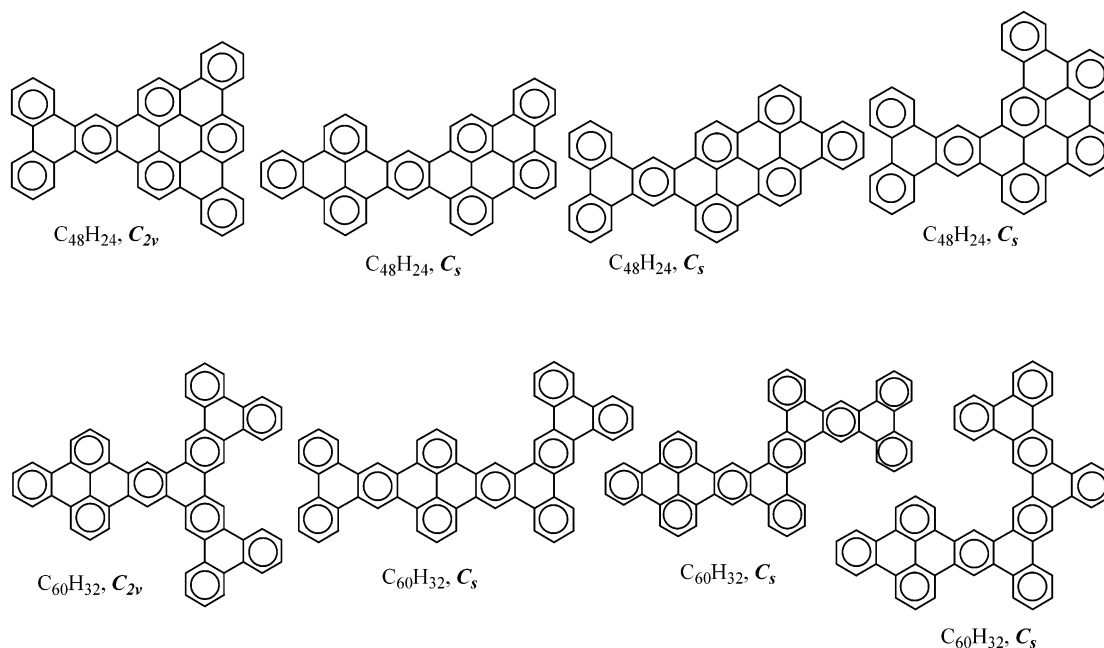


Figure 12. Matching $C_{48}H_{24}$ and $C_{60}H_{32}$ strain-free TRS benzenoid sets.

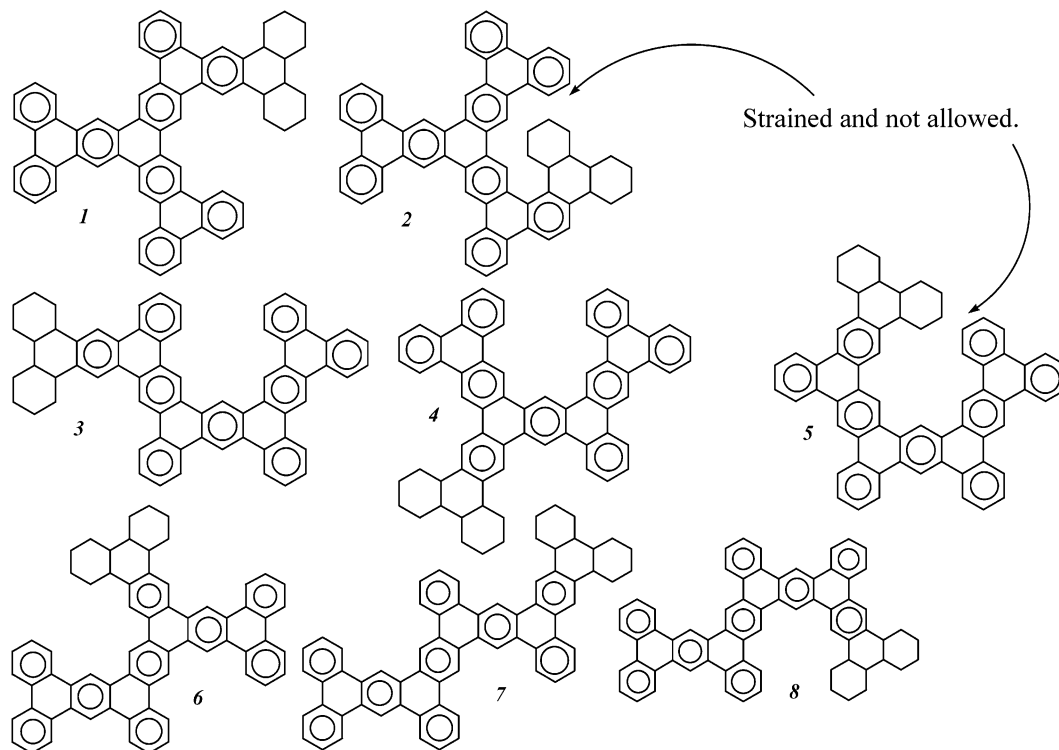


Figure 13. Biphenylene aufbau construction of the strain-free $C_{66}H_{36}$ TRS in Figure 10 benzenoids from the strain-free $C_{54}H_{30}$ TRS benzenoids in Figure 9.

internal third degree vertices located para on its molecular graph which upon leapfrogging become empty rings separated by a fused sextet ring. Even more dramatic is $C_{34}H_{18}$ which corresponds to 396 benzenoids,²¹ but only 3 of them generate totally fused strain-free TRS benzenoid leapfrogs shown in Figure 9.

As a final example, let us consider the $C_{66}H_{36}$ catacondensed strain-free TRS benzenoids in Figure 10. These three TRS benzenoids result from leapfrogging the appropriate precursor $C_{41}H_{21}$ benzenoids ($d_s = 4$, $N_{lc} = 5$) out of a total of 6405 isomers.²² Reverse leapfrogging these three $C_{66}H_{36}$ TRS benzenoids identifies the only benzenoids of this $C_{41}H_{21}$

formula that have no catcondensed appendages or internal third degree vertices separated by more than two rings. It was easier to enumerate the $C_{66}H_{36}$ strain-free TRS benzenoids, and this reverse leapfrog process allowed us to determine these structures without having to know what the rest of the $C_{41}H_{21}$ benzenoids look like.

It needs to be emphasized at this juncture that as the leapfrog operation has clearly demonstrated, there is a one-to-one matching between all the benzenoid structures encompassed by Table PAH6 and all the strain-free TRS encompassed by Table PAH6(sextet) if we include all the phenyl and aryl substituted TRS benzenoids such as those

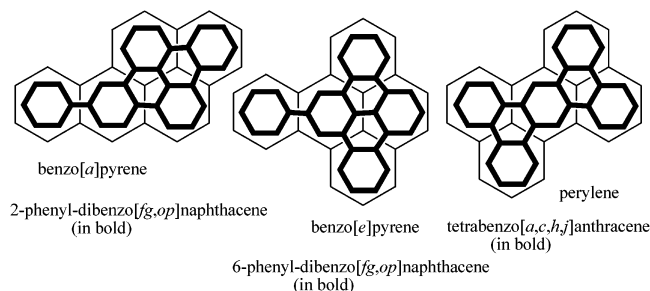


Figure 14. The $C_{20}H_{12}$ benzenoid isomers and their $C_{30}H_{18}$ TRS leapfrogs shown in bold.

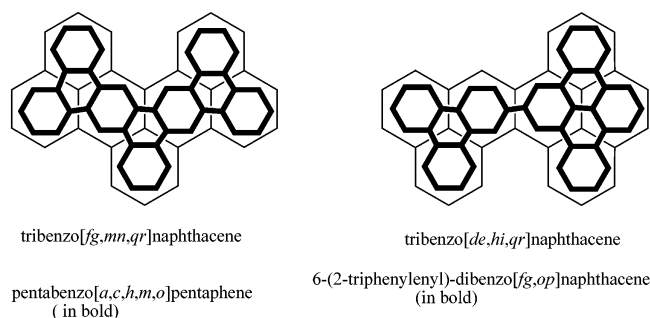


Figure 15. Two example leapfrogs in bold of $C_{27}H_{15}$ benzenoids.

in Figures 14 and 15. 1-Phenyl- and 5-phenyldibenzo[fg,op]-naphthacene are not leapfrogs and are excluded by our strain-free criterion because under pyrolytic conditions one should expect that they will undergo oxidative cyclodehydrogenation to more condensed TRS systems as shown in Figure 16. In this paper, we have been concerned with the subset of strain-free TRS benzenoid that are totally fused benzenoid systems.

It is important to note that both refs 21 and 22 only enumerate hexagonal systems that can be cut out from the graphite lattice. Thus hexahelicene and larger helicenes and their related leapfrogs are excluded. This graphite lattice criterion and the exclusion adjacent bay regions criterion for circum-

scribing of strictly pericondensed benzenoids and the equivalent criteria for TRS benzenoids and supercircumscribing is illustrated by the leapfrogs for pentabenzo[de,hi,qr]naphthacene and benzo[c]phenanthrene shown in Figure 17, respectively.

WHY ARE THERE SO FEW TRS BENZENOID?

Kirby addressed the question,²³ “Why can so few Benzenoids be completely drawn with Clar’s Resonant Sextets?” which we will also now address. TRS benzenoids (referred to as sextet 2-factorable benzenoids by Kirby)²³ must have formulas in which the number of carbons (N_c) is divisible by six. This occurs only in every third column of Table PAH6 for only the even carbon formulas.^{7–15} Thus only 1/6th of the formulas in Table PAH6 are capable of having TRS benzenoid structures and for topological reasons only a very small fraction of the isomers of these formulas actually correspond TRS benzenoids. Why is this fraction so much less than the factor of 6? The answer to this, in part, has to do with the fact that for a benzenoid to be a TRS benzenoid, one needs the requisite type of perimeter topology that we will now explain.

The number of peripheral degree-3 vertices, N_{pc} , on the perimeter of a benzenoid 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. η_0 , η_1 , η_2 , η_3 , and η_4 designate the number of bay, solo, duo, trio, and quarto peripheral regions on a given molecular graph.^{6,13} The perimeter topology of any benzenoid molecular graph is given by the equation $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6$, which is independent of the number of solo regions (η_1); also $N_H = \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4$. The molecular graph of a strictly pericondensed benzenoid hydrocarbon has all its internal edges and degree-3 vertices mutually connected and a perimeter topology that is defined by $-\eta_0 + \eta_2 + 2\eta_3 = 6$ where $\eta_4 = 0$. The molecular graph of a

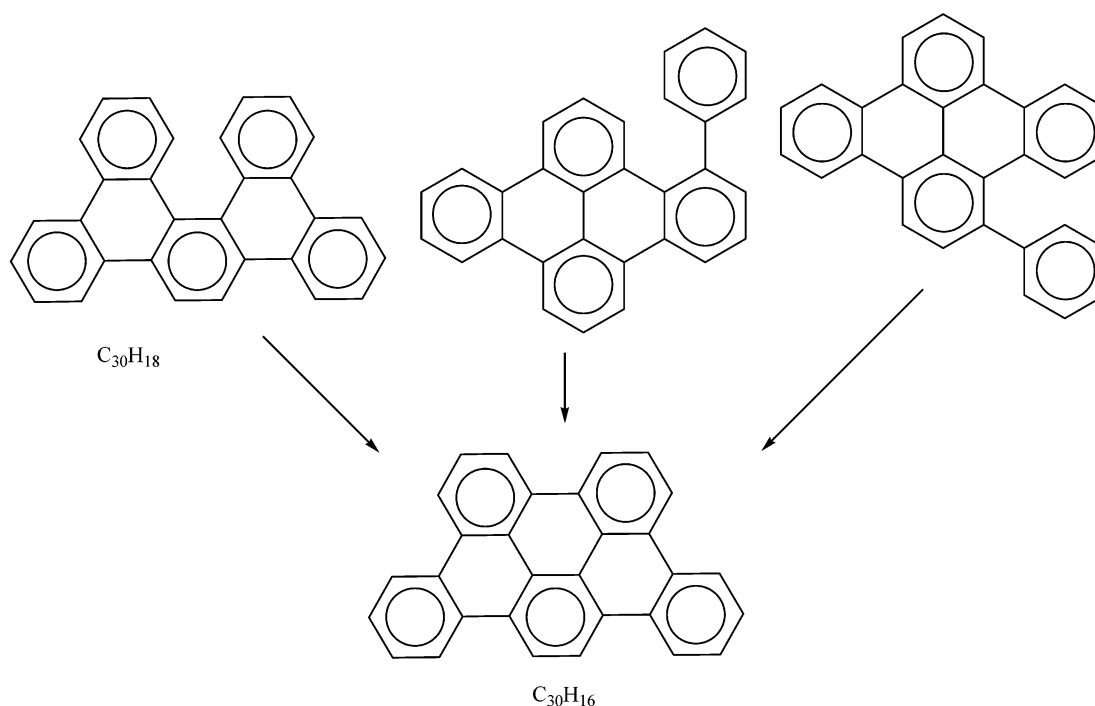


Figure 16. Pyrolytic conversion of strained TRS benzenoids to more condensed strain-free TRS benzenoids.

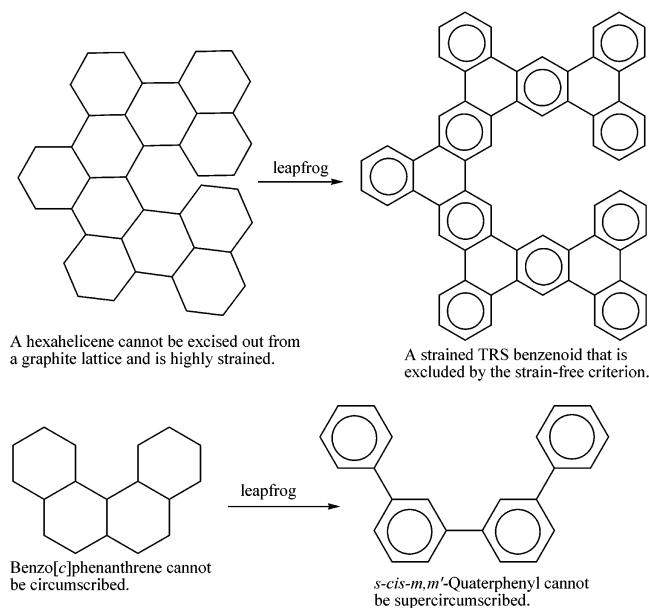


Figure 17. Equivalent restrictions for strictly pericondensed and TRS benzenoid systems.

catacondensed benzenoid has $\eta_3 = 0$ and every internal edge disconnected from any other internal edge and a perimeter topology defined by $-\eta_0 + \eta_2 + 3\eta_4 = 6$. 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 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 TRS benzenoids and η'_5 is the number of phenyl groups. By equating the perimeter topology relationship for all benzenoids with that for TRS benzenoids, we obtain $-\eta'_0 + \eta'_1 + \eta'_2 + \eta'_3 + \eta'_4 = 0$ which is valid only for the perimeter topology of fused strain-free TRS benzenoid hydrocarbons. This 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 12 other nonradical $C_{24}H_{14}$ benzenoid isomers have $\eta'_0 = 3$ to 1. This explains the requisite type of perimeter topology a TRS benzenoid must have of which very few benzenoids comply.

SUMMARY

Clar's aromatic sextet theory continues to attract the attention of researchers striving to gain a deeper insight to the fundamentals of aromaticity in large benzenoid hydrocarbons,²⁴ and our work in this area continues to find utility in the study of PAHs in flames,²⁵ asphaltenes,²⁶ and environmental analysis and synthesis.²⁷ This current work has further identified some unique topological features associated with Clar structures with particular emphasis on strain-free TRS benzenoid hydrocarbons. The Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (Table

PAH6)⁷⁻¹⁵ and the leapfrog operation are shown to be powerful graph theoretical tools for studying structural relationships among benzenoid hydrocarbons.^{13,17,18} It is suggested that the leapfrog and supercircumscribing operations could form the basis of a more formal trivial nomenclature for TRS benzenoid hydrocarbons. Specific new results reported herein include a one-to-one matching in isomer numbers, symmetry distributions, and a number of empty rings among strain-free TRS benzenoids with only fused hexagonal rings and having formulas located perpendicularly in Table PAH6(sextet). This newly observed row-column correspondence further demonstrates that casting information into a two-dimensional array leads to unique insights not made evident otherwise.²⁸ A new topological equation for fused strain-free TRS benzenoids has been derived which gives an answer to why there are relatively so few TRS benzenoid hydrocarbons.

Clar's sextet principle, our fundamental premise that pyrogenic benzenoids would have a preference for strain-free highly condensed configurations based on the graphite motif, and our aufbau/formula periodic table concepts were essential for the recognition of the spectacular congruence between all benzenoids and the TRS benzenoid subset. This unification itself attests to the validity of Clar's sextet principle. The merging of ideas and concepts from diverse origins into a unified framework leading to greater understanding constitutes the essence of knowledge.

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