The Most Stable Class of Benzenoid Hydrocarbons and Their Topological Characteristics − Total Resonant Sextet Benzenoids Revisited

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Polycyclic aromatic hydrocarbons that we previously called total resonant sextet (TRS) benzenoids are revisited within the framework of recent experimental findings. A benzenoid transformation called leapfrogging generates TRS benzenoids. There are 13, 30, and 114 TRS benzenoid isomers with formulas $C_{72}H_{26}$, $C_{96}H_{30}$, and $C_{102}H_{32}$, respectively. "The leapfrogs of benzenoids are 2-factorable" is a stronger statement than "the leapfrogs of benzenoids are closed-shell."

INTRODUCTION

Mullen and co-workers have recently synthesized large to super-large benzenoid hydrocarbons[1−4] of the type that we have previously called total resonant sextet (TRS) benzenoids,[5−14] and this success has revived our interest in these systems. In 1987, we enumerated and compiled a list of large benzenoid isomers that were presumed to be capable of being structurally characterized once detected in the environment or synthesized.[5] Supplements to this compilation subsequently became available.[7,8,11,14] Clar[15] recognized that members of any given set of benzenoid isomers can possess a different maximum number of resonant sextets (Clar π-sextets) and that the stability of a given benzenoid was related to this maximum number. TRS benzenoids were called fully benzenoid by Clar[15] and are represented by formulas in which the number of carbons are divisible by six and by structures totally covered by Clar π-sextets (disjoint hexagonal rings with three mutually permutable pπ-bonds). The work of Mullen and co-workers[1−4] has also renewed the interest of Randić who uses his conjugated conjugate circuit theory to identify regularities in large benzenoids.[16]

Mullen and co-workers have synthesized the matching D_{2h} $C_{54}H_{22}$ and $C_{78}H_{26}$ TRS benzenoids[1,4] that we depicted in Figure 3 of our previous work.[13] Each of these benzenoid structures represents one of a set of four possible TRS isomers, which are first-generation members of the respective TRS constant-isomer series.[10,13] Mullen and co-workers[1] have also reported the synthesis of one of the 11 $C_{54}H_{26}$ TRS benzenoids depicted in our 1987 book (the C_{2h} isomer on page 92).[5] In the discussion of our topological paradigm, we illustrated the enumeration of the 16 first-generation members of the $C_{132}H_{34}$ TRS benzenoid constant-isomer series,[8] and Mullen and co-workers have now described the synthesis of the D_{2h} isomer.[2] This D_{2h} $C_{132}H_{34}$ TRS benzenoid can be obtained by augmented circumscribing of the D_{2h} $C_{48}H_{22}$ TRS benzenoid depicted in our 1987 book (ref 5, page 90). More spectacular is the recent synthesis of the fourth generation ($C_{222}H_{42}$) member of the one-isomer D_{6h} TRS constant-isomer series.[3] The recent synthesis of a D_{2h} $C_{72}H_{26}$ TRS benzenoid by this group[4] gives us the op-

portunity to depict the remaining 12 TRS isomers and discuss their topological characteristics while we review and further examine this important subset of fused benzenoids.

DEFINITIONS AND TERMINOLOGY

The molecular graph is the C−C σ-bond skeleton representation of a fully conjugated polyene chemical structure. A total resonant sextet (TRS) benzenoid structure corresponds to a polyhex graph whose number of vertexes is divisible by six and has a 2-factor subgraph (a spanning subgraph having solely cyclic components with only degree-2 vertexes) composed exclusively of hexagons. The molecular graph of a TRS benzenoid may be depicted by a polyhex with $N_C/6$ ($n = N_C$ = no. of formula carbons = no. of molecular graph vertexes) nonadjacent inscribed circles separated by $(1/6)(2N_C + 6 − 3N_H)$ empty rings, where $s = N_H$ corresponds to the number of formula hydrogens (or no. of molecular graph degree-2 vertexes). A single-cycle 2-factor subgraph is called a Hamiltonian subgraph. A Hamiltonian benzenoid has a molecular graph with a Hamiltonian subgraph. A benzenoid Kekulé structure is isomorphic to a 1-factor subgraph (a spanning subgraph composed solely of K_2 or disjoint edge components) of the corresponding molecular graph. Circumscribing a benzenoid is a construction process involving surrounding the perimeter of a benzenoid C_nH_s with a chain of $2s+6$ carbon atoms plus 6 additional hydrogens in such a way as to generate only hexagonal rings giving a successor $C_{n+2s+6}H_{s+6}$ benzenoid; the reverse of this process is excising. Other conjugated polyenes can analogously be circumscribed. Augmented circumscribing of a strain-free TRS benzenoid is a construction process involving replacing all perimeter Hs on a TRS by =CH_2 units and then circumscribing the resultant structure.[6,8]

CIRCUMSCRIBING ALGORITHM

The successive circumscribing of qualified conjugated hydrocarbons with hexagonal rings leads to constant-isomer series. Constant-isomer series are polycyclic aromatic hydrocarbon sets of successively increasing formulas where the number of isomers remain unchanged. Symmetry between

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the base excised internal structure (EIS) and its successors is preserved when one successively circumscribes with hexagonal rings to ultimately generate constant-isomer series. Previously, it was demonstrated that there exists a one-to-one correspondence between the constant-isomer benzenoid series generated by the circumscribing process and TRS constant-isomer series generated by an augmented circumscribing process.[8−11] Circumscribing benzene with a string of 18 connected carbons with 6 hydrogens gives coronene ($C_{24}H_{12}$); benzene is called the excised internal structure of coronene. Circumscribing coronene gives circum(30)-coronene ($C_{54}H_{18}$), and circumscribing this circumcoronene gives dicircum(30,42)coronene ($C_{96}H_{24}$). Successive repetition of this process gives the coronene D_{6h} one-isomer series. Note that each one of these formulas appears on a protruding ridge of the left-hand staircase boundary in our Formula Periodic Table for Benzenoid Hydrocarbons (Table PAH6).[5,9,14] Circumscribing naphthalene ($C_{10}H_8$) gives ovalene ($C_{32}H_{14}$), and circumscribing pyrene ($C_{16}H_{10}$) gives circum(26)pyrene ($C_{42}H_{16}$). These are the first two-generation members to the ovalene and pyrene D_{2h} matching one-isomer series, respectively. All the formulas corresponding to constant-isomer benzenoid series will be found along the left-hand staircase edge in Table PAH6. Successive augmented circumscribing of benzene gives the hexa-*peri*-benzocoronene TRS D_{6h} one-isomer series. Similarly, successive augmented circumscribing of biphenyl and dibenzo[*fg,op*]tetracene give the respective TRS D_{2h} matching one-isomer series. All the formulas corresponding to TRS constant-isomer series appear on the left-hand staircase edge of Table PAH6(sextet) which is a subset of Table PAH6.[8] Here it is of interest to note that both Stein and Randić and their co-workers have studied D_{6h} series, which includes our coronene and hexa-*peri*-benzo-coronene one-isomer series without knowing it.[17,18] No doubt, these series have quite naturally been the objects of numerous model studies of graphite.

The circumscribing process of a benzenoid system with hexagonal rings is denoted by P → circum-P = P′. It has been previously shown that $N_{pc} = N_H - 6$, $q_p = N_H + N_{pc} = 2N_H - 6$, and $r = (^1/_2)(N_C - N_H) + 1$ where $N_C = N_{pc} + N_{Ic} + N_H$ and N_{pc} and N_{Ic} and q_p are the number of perimeter and internal degree-3 vertexes and perimeter edges, respectively. For P → P′, $N_C → N_{Ic}′$ and $N_H → N_{pc}′$. Thus, for circum-P, $N_{pc}′ = N_H′ - 6 = N_H$, giving $N_H′ = N_H + 6$ and, similarly, $q_p′ = N_{pc}′ + N_H′$ and $N_C′ = q_p′ + N_C$ giving $N_C′ = N_C + N_{pc}′ + N_H′ = N_C + 2N_H + 6$. These recursive equations are useful for monitoring the progress of successive circumscribing.

## COMPARISON OF THE CIRCUMSCRIBING AND LEAPFROG ALGORITHMS

The circumscribing and leapfrog algorithms are based on operations that transform planar and polyhedral 3-connected structures into other structures by systematically increasing the number of hexagonal rings while preserving symmetry.[12,19] Both the TRS benzenoid and leapfrog fullerene structures are smaller subsets of the possible number of isomers. The leapfrog operation on dodecahedron (C_{20}) gives buckminsterfullerene (C_{60}).[19] The leapfrog rule says that for every isomer of a fullerene with n carbon atoms (C_n), there is a corresponding unique closed-shell isomer of the fullerene

C_{3n}.[19] This C_{3n} isomer has the same point-group symmetry as its C_n precursor and can be constructed from it by a two-stage leapfrogging process that involves omnicapping and subsequently taking the face dual. In the leapfrog procedure, symmetry is conserved, the number of pentagons remains fixed, and all pentagons in the product are nonadjacent. Any benzenoid, open-shell or closed-shell, can be transformed by the leapfrog algorithm into a successor TRS benzenoid (either totally fused or aryl substituted) with a maximum number of Clar sextets and same point-group symmetry. Fullerene leapfrogs and TRS benzenoids are always closed-shell systems. The augmented circumscribing algorithm generates successive members of the TRS constant-isomer series, whereas the leapfrog algorithm associates a given set of benzenoids with a specific set of TRS benzenoids.

The aufbau principle and formula periodic table and circumscribing, augmented circumscribing, and leapfrog algorithms form the tool set of our topological paradigm. In brief, this topological paradigm consists of the following elements: (1) a corresponding formula periodic table contains formulas on the edge of a 2-dimensional array that belong to constant-isomer series generated by successive circumscribing (or augmented circumscribing); (2) as the formula of the first-generation members to each successive constant-isomer series increases, so does the corresponding number of isomers; (3) the number of isomers increases according to a regular pattern where some of the isomer numbers repeat; (4) in those constant-isomer series having the same number of isomers, there is a one-to-one matching between the structures; (5) the topological invariants in this one-to-one matching of structures are symmetry, 1-factorability, 2-factorability, number of bay regions and selective lineations, and the adjacency/nonadjacency of pentagonal rings; (6) the formula periodic tables and constant-isomer series for strictly pericondensed monoradical, diradical, triradical, tetraradical, etc. benzenoids are totally isomorphic; (7) the formula periodic tables and constant-isomer series for strictly pericondensed and strain-free TRS benzenoids are totally isomorphic; the leapfrog algorithm associates any given benzenoid with its TRS isomorph.[8−11,13]

LEAPFROG ALGORITHM

Application of the leapfrog algorithm on all noncatacondensed benzenoid isomer sets culled of members with catacondensed appendages (benzo, naphtho, etc.) or bridging units (like that in zethrene) and four or more adjacent bay regions will generate all possible isomeric strain-free TRS benzenoids; strain-free TRS benzenoids have nonhelical structures devoid of adjacent bay regions.[6,11] Any fused benzenoid (C_nH_s) can be transformed into a successor (fused or nonfused) benzenoid ($C_{3n−3s+6}H_{2s−6}$) with a maximum number of Clar sextets by the leapfrog algorithm.[12] The successor leapfrog L is constructed from the precursor benzenoid P in two stages. First the hexagonal rings are omnicapped to produce a deltagonal polycyclic **D**. The inner dual of **D** is taken by putting a central point inside each trigonal ring and connecting the points in adjacent rings with lines (cf. with Figures 1 and 2). An alternative description of the leapfrog transformation involves drawing a smaller ring in a staggered orientation within each ring of the original molecular graph and joining the new rings by lines crossing
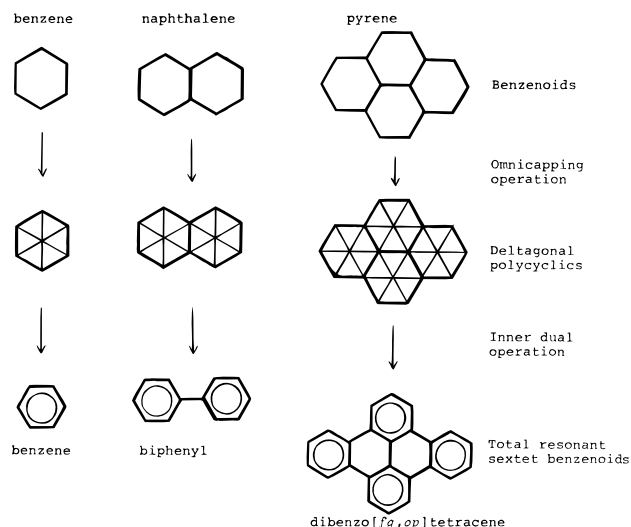
Figure 1. Illustration of the leapfrog algorithm in the transformation of benzenoids into total resonant sextet benzenoids.
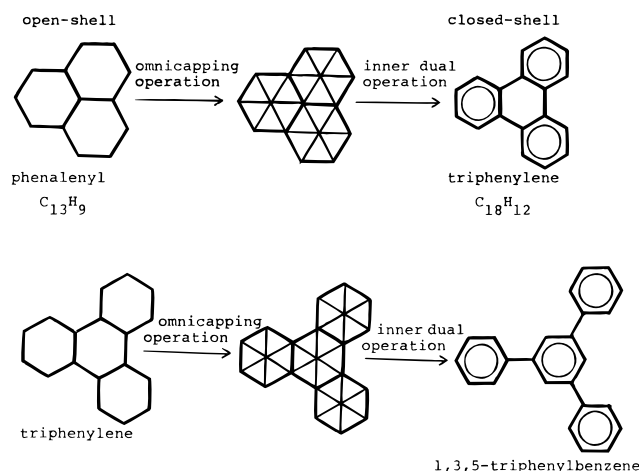
Figure 2. Application of the leapfrog algorithm on phenalenyl two successive times. Note that this operation always give species with closed-shell electronic configurations.

the internal edges of the original graph at right angles.[19] Benzene is the smallest TRS benzenoid and the leapfrog on benzene gives benzene back and is a null operation (Figure 1). In the leapfrog operation on pyrene to give dibenzo[*fg,op*]-tetracene, the internal third degree vertexes of the former ($N_{Ic} = 2$) become empty rings (hexagonal rings without inscribed circles) in the latter (Figure 1). The leapfrog on phenalenyl, which is open-shell, gives the TRS benzenoid triphenylene, which is closed-shell (Figure 2). TRS benzenoids are always closed-shell. Iteration of the leapfrog on triphenylene in Figure 2 illustrates that successive application of the leapfrog eventually leads to a group of disconnected benzenes and terminates at this point because the leapfrog on benzene is a null operation. Figures 1 and 2 show that the symmetry of the precursor and successor benzenoids is preserved by the leapfrog operation.

Iteration of the leapfrog transformation on a given set of fullerenes of the same n leads to a series of closed-shell leapfrog isomers where the symmetry-related properties follow from those of the precursor parents. This process is analogous to that of successive circumscribing of isomeric benzenoids, which leads to a series of circumscribed isomers with the same distributions of symmetry-related properties

as the initial parents (first generation). The reverse to circumscribing, called excising, gives the excised internal structure. Although constant-isomer series are the ultimate result of successive circumscribing, successive leapfrogging of fullerenes does not cause convergence to constant-isomer series.

There are 114 326 benzenoid isomers[20] with the formula $C_{48}H_{24}$, and it is predicted that the TRS benzenoid subset are the more stable ones. To find these more stable benzenoid structures, we need to identify the appropriate precursor benzenoids that will give us these more stable species upon application of the leapfrog operation. To accomplish this, one will need the following equations:

$$N_C = (1/3)N_C(\text{sextet}) + (^1/_2)N_H(\text{sextet}) + 1$$

$$N_H = (^1/_2)N_H(\text{sextet}) + 3$$

Thus, for $C_{48}H_{24}$ it is determined that $N_C = 29$ and $N_H = 15$, giving $C_{29}H_{15}$ ($N_{Ic} = 5$, $r = 8$) as the formula of the benzenoid structures we need for the leapfrog operation. In previously published benzenoid depictions,[21] one finds that there are 21 $C_{29}H_{15}$ benzenoids. After eliminating all the structures with benzo appendages, one is left with four $C_{29}H_{15}$ benzenoid structures that via the leapfrog operation gives four $C_{48}H_{24}$ TRS benzenoids that have been previously depicted.[5] Our previous work[8,12] demonstrated that there exists a one-to-one topological matching between strictly pericondensed and TRS constant-isomer series. In going from the parent P to its leapfrog L, the following correspondences hold:

$$P(C_nH_s) \rightarrow L(C_{3n-3s+6}H_{2s-6}) \qquad n_0 \rightarrow n_1'$$

$$N_{Ic} \rightarrow r(\text{empty}) \qquad n_1 \rightarrow n_2'$$

$$N_{pc} \rightarrow n_0' \qquad n_2 \rightarrow n_3'$$

$$n_3 \rightarrow n_4'$$

$$n_4 \rightarrow n_5'$$

where N_{Ic}, N_{pc}, $r(\text{empty})$, and n_i are the number of internal degree-3, peripheral degree-3, rings without Clar sextets, and perimeter units ($i = 0$ for bay region, $i = 1$ for solo, $i = 2$ for duo, $i = 3$ for trio, $i = 4$ for quarto, and $i = 5$ for phenyl), respectively.

STRAIN-FREE TOTAL RESONANT SEXTET BENZENOIDS

It is important to distinguish strain-free TRS benzenoids from other kinds. The strain-free concept was absolutely essential to the discovery of the topological isomorphism that exists between strictly pericondensed and TRS benzenoids,[8–11] underlies the synthetic strategy employed by Mullen and co-workers,[1–4] and eliminates steric interaction as a variable in the conjugated circuit studies of Randić and co-workers.[16] Strain-free TRS benzenoids have nonhelical structures devoid of adjacent bay regions and are incapable of undergoing further cyclodehydrogenation to more condensed systems, as illustrated in Figure 3. As we noted
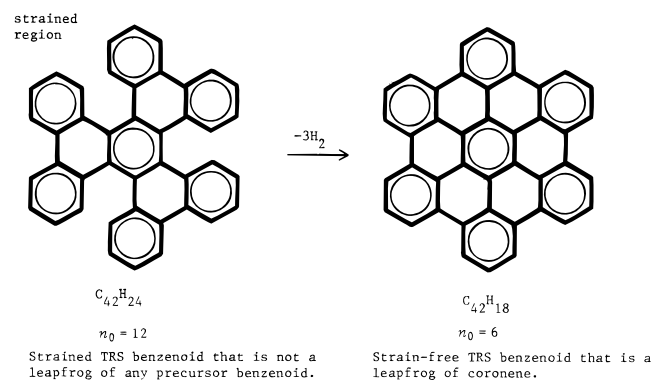
Figure 3. Minimization of the number of bay regions (n_0) by cyclodehydrogenation.

Table 1. Number of Benzenoid Hydrocarbon Isomers

formula	$N_{Ic}{}^a$	$d_s{}^a$	total no. isomers	no. strain-free TRS isomers
$C_{30}H_{16}$	4	2	58	1
$C_{42}H_{18}$	12	−1	187	1
$C_{54}H_{22}$	16	−1	13 286	4
$C_{54}H_{26}$	8	5	947 291	11
$C_{72}H_{26}$	26	−4	643 859	13
$C_{78}H_{26}$	32	−7	319 258	4
$C_{96}H_{30}$	42	−10	≫123 790	30
$C_{102}H_{32}$	44	−10	≫123 790	114
$C_{132}H_{34}$	70	−22	extremely large	16
$C_{222}H_{42}$	144	−55	extremely large	1

^{a} $d_s + N_{Ic} = r - 2$; d_s = net disconnections of internal edges, N_{Ic} = no. of internal degree − 3 vertices, r = no. rings.

previously,[11] TRS benzenoids cannot have coves (two adjacent bay regions) and the strain-free constraint excludes fjords (three adjacent bay regions). These conditions were subsequently elaborated as theorems by Gutman and Babic.[22]

Cyclodehydrogenation can occur pyrolytically or chemically with copper (II) salts mixed with anhydrous $AlCl_3$ in CS_2 at room temperature.[1−4] Our fundamental premise is that polycyclic aromatic hydrocarbons tend to become more condensed under pyrolytic conditions via cyclodehydrogenation.[5,6] Part of the driving force for this condensation is decreasing steric strain and increasing π-electronic energy.

## ENUMERATION OF TRS BENZENOID ISOMERS OF RECENT CHEMICAL INTEREST

Table 1 lists all the formulas for the TRS benzenoids synthesized by Mullen and co-workers.[1−4] The total number of benzenoid isomers of the specified formulas in the first column appears in the fourth column and the subset number of TRS benzenoid isomers follows in the fifth column. Depictions of the structures for all the TRS benzenoid isomers of the formulas $C_{30}H_{16}$ to $C_{54}H_{26}$ can be found in our 1987 book.[5] The four $C_{78}H_{26}$ TRS benzenoid isomers were previously depicted.[11,13] Both the $C_{54}H_{26}$ and $C_{78}H_{26}$ structures are first-generation members of the respective TRS constant-isomer series that possess a one-to-one matching in point group symmetry among the four isomers per our previously published topological paradigm.[7−11,13]

Figure 4 depicts the 13 $C_{72}H_{26}$ TRS benzenoid structures for the first time, but this isomer number has been published.[11] The $\boldsymbol{D}_{2h}$ isomer (first structure in Figure 4) synthesized by Mullen and co-workers[4] is the leapfrog of
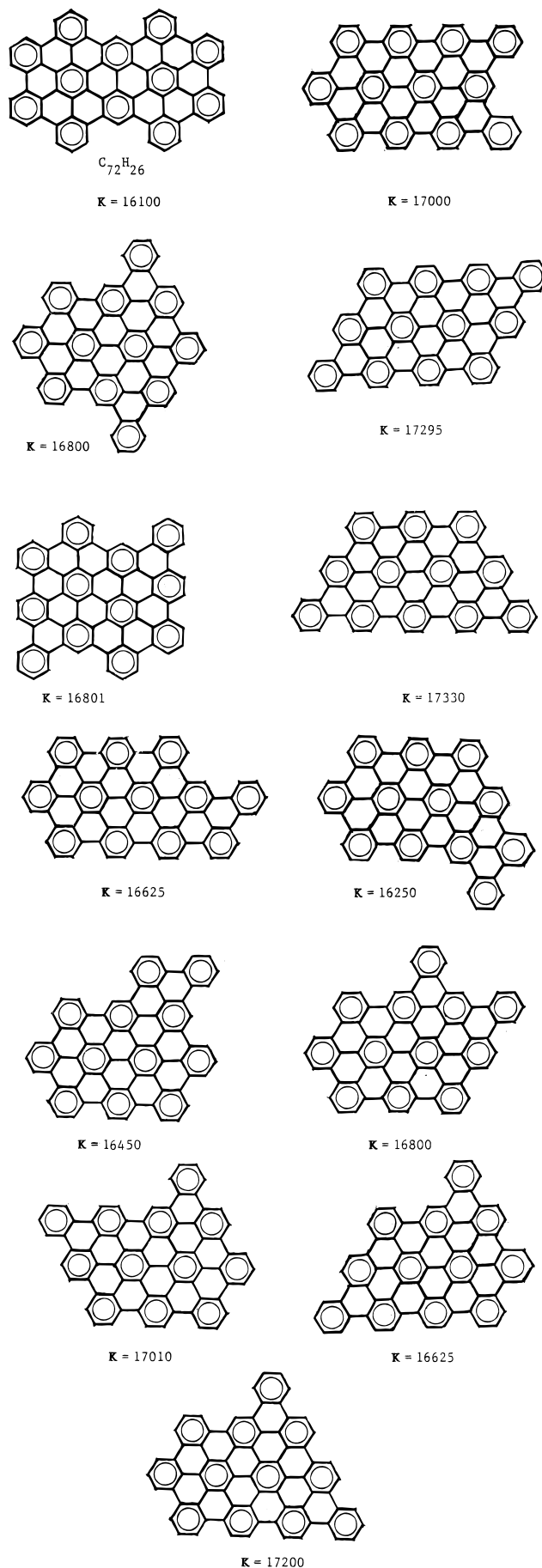
Figure 4. All possible $C_{72}H_{26}$ total resonant sextet benzenoid isomers.
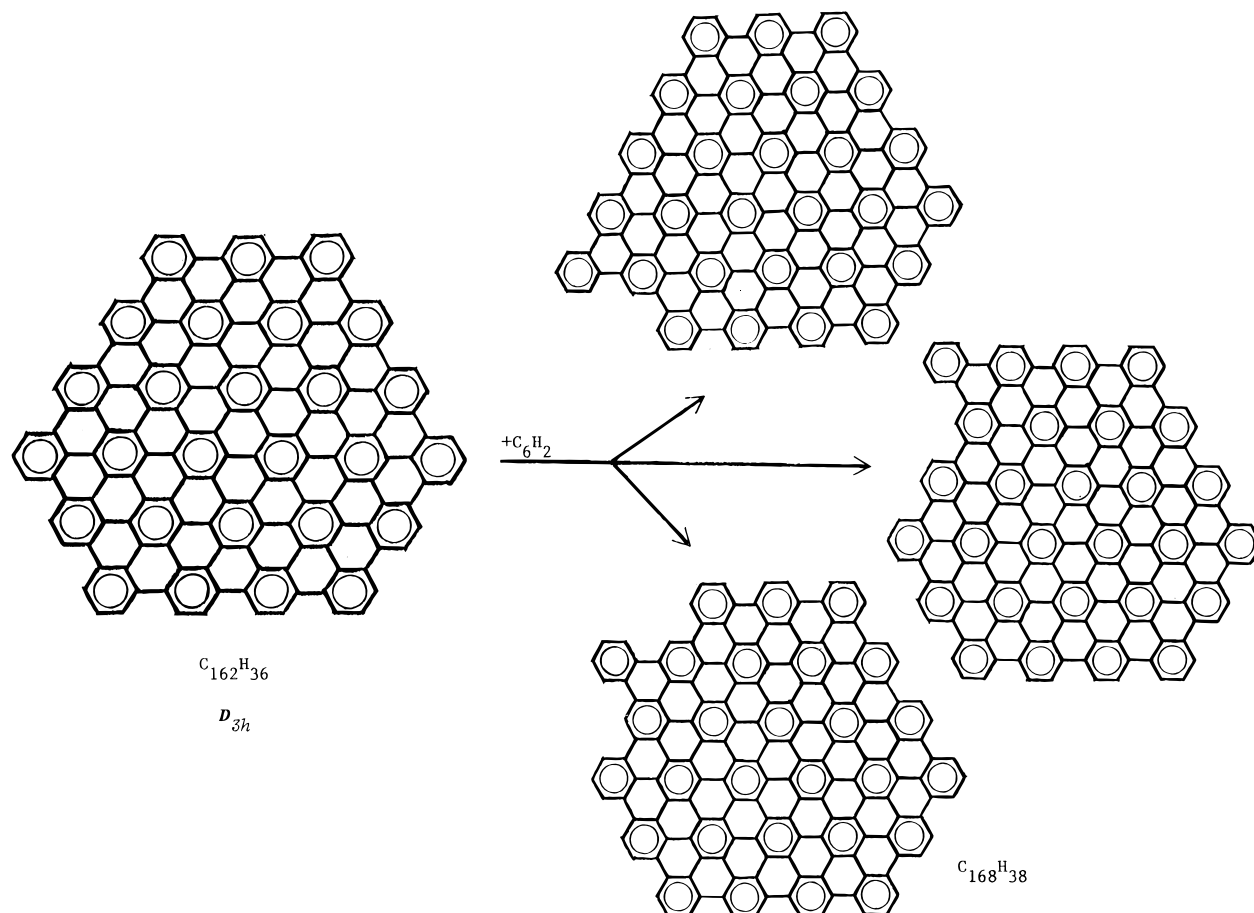
Figure 5. Three isomers belonging to one of the TRS 16-isomer series.

circobiphenyl (ref 5, page 68). These 13 $C_{72}H_{26}$ TRS structures are precursors to the 16 $C_{168}H_{38}$ TRS benzenoid isomers that are first-generation members of the respective TRS constant-isomer series.[8,23] Subtraction of C_6H_2 from $C_{168}H_{38}$ gives $C_{162}H_{36}$, which corresponds to the third-generation member (Figure 5) of the D_{3h} TRS one-isomer series. There are three distinct attachments of benzenetetrayl (C_6H_2) to the D_{3h} $C_{162}H_{36}$ structure in Figure 5 that give three TRS $C_{168}H_{38}$ isomers. Furthermore, augmented circumscribing of the 13 $C_{72}H_{26}$ structures in Figure 4 gives a grand total of 16 TRS $C_{168}H_{38}$ isomers that are the first-generation members of the respective TRS constant-isomer series.[8,23] The 16 isomers of the $C_{132}H_{34}$ TRS constant-isomer series are correspondents to the 16 isomers of the $C_{168}H_{38}$ TRS constant-isomers series, and there is a one-to-one matching between the structures of these two sets.[8,11,23]

There are 30 $C_{48}H_{18}$ strictly pericondensed benzenoids, and the 22 nonradical isomers were depicted in our book.[5] Performing the leapfrog[12] on the published depictions, which include the eight radical structures,[24] gives 30 $C_{96}H_{30}$ TRS benzenoids. From the work of Stojmenović and Tošić, we know that there are 117 $C_{51}H_{19}$ benzenoid isomers;[21] subtracting C_4H_2 gives $C_{47}H_{17}$ (Figure 6), which is the second-generation member of the C_{2v} one-isomer series. Attachment of the C_4H_2 (1,3-butadienetetrayl) aufbau to the three distinct edges of this $C_{47}H_{17}$ structure gives three $C_{51}H_{19}$ structures with catacondensed appendages that will give three phenyl-substituted leapfrog $C_{102}H_{32}$ structures.[12] This number must be subtracted from 117 to give the number of fused TRS benzenoids corresponding to the formula of $C_{102}H_{32}$.

Thus, without knowing what the $C_{51}H_{19}$ structures look like, we deduce that there are 114 $C_{102}H_{32}$ TRS benzenoid structures.

EMPTY RING CONFIGURATION OF TRS BENZENOIDS

The TRS benzenoids with formulas in the $d_s = 2$ column series of Table PAH6(sextet) have empty ring configurations that look like catacondensed benzenoids. The TRS benzenoids with formulas toward the left of this column ($d_s = -1, -4, -7, ...$) have empty ring configurations that correspond to benzenoids with $N_{Ic} = 6, 12, 18, ...,$ and those formulas in columns to the right ($d_s = 5, 8, 11, ...$) possess empty ring configurations comprised of 2, 3, 4, ... disconnected catacondensed benzenoids. If a TRS benzenoid has N_C' carbons and N_H' hydrogens, then the empty ring configuration corresponds to benzenoids of $N_C = N_C' - N_H'$ carbons and $N_H = N_H' - 6$ hydrogens; for empty ring configurations composed of two or more components (in columns $d_s = 5, 8, 11, ...$), these equations give the sums of the number of carbons and hydrogens.

These relationships are easily verified by the TRS benzenoids given in Figures 1−5. For example, benzene ($N_C = 18 - 12 = 6$ and $N_H = 12 - 6 = 6$) and naphthalene ($N_C = 24 - 14 = 10$ and $N_H = 14 - 6 = 8$) are the catacondensed empty ring configurations for triphenylene (Figure 2) and dibenzo[*fg,op*]tetracene (Figure 1), respectively. Coronene is the empty ring configuration for hexa-*peri*-benzocoronene (Figure 3), and the first $C_{72}H_{26}$ TRS benzenoid structure in Figure 4 ($K = 16\ 100$) has a bicoronene empty ring configuration.
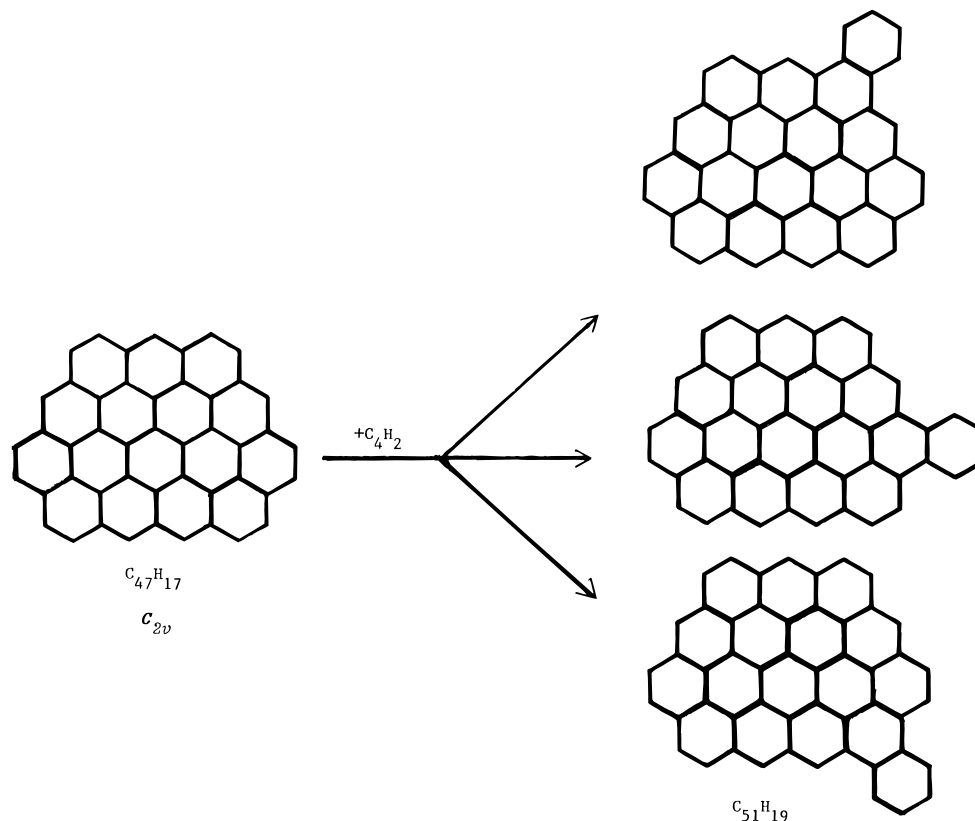
Figure 6. The only $C_{51}H_{19}$ benzenoids with benzo appendages.

In general, the empty ring configurations of TRS benzenoids correspond to those benzenoids that are among the more stable ones of an isomer set. The number of Kekulé structures for the empty ring configuration is highest for those TRS benzenoid isomers with the highest number of Kekulé structures. TRS benzenoids with empty ring configurations that correspond to TRS benzenoids should allow one to identify the most "empty" of the empty rings. For example, tribenzo[a,g,m]coronene ($C_{36}H_{18}$) is a D_{3h} TRS benzenoid with an empty ring configuration corresponding to triphenylene. Its most center ring is an empty ring to both TRS systems, and the ring resonance energy results of Randić and Guo[16] show it to be the most empty ring in tribenzo-[a,g,m]coronene.

OTHER TOPOLOGICAL CHARACTERISTICS OF TRS BENZENOID HYDROCARBONS

There are two relevant generalizations in benzenoid chemistry; they are, the more Kekulé structures (1-factor subgraphs) that a benzenoid has the more stable it is, and the more Clar sextets that a benzenoid has the more stable it is. A corollary to the latter generalization is that the most stable benzenoid isomer will be totally covered by Clar sextets (i.e., its molecular graph will have a 2-factor subgraph composed exclusively of hexagons). Any graph that is not 1-factorable cannot be 2-factorable. Odd carbon benzenoids are illustrative of this last statement. If a molecular graph is 2-factorable, then it is 1-factorable, but not all 1-factorable molecular graphs have 2-factor subgraphs. For example, consider the three $C_{22}H_{12}$ benzenoid isomers. Both anthanthrene and benzo[ghi]perylene have molecular graphs with 1-factor subgraphs, but only the latter has a 2-factor

subgraph and triangulene has neither. Thus, 1-factor and 2-factor graph theoretical properties have considerable relevance to benzenoid structure theory.

It has been shown that Table PAH6 [more precisely Table PAH6(even)] correlates many aspects of these generalizations. As one moves to the left in a row or down in a column of Table PAH6, the benzenoid molecular graphs corresponding to a given formula have increasing numbers of Kekulé structures and Clar sextets. All the catacondensed benzenoids ($N_{Ic} = 0$ row) have molecular graphs that are both 1-factorable and 2-factorable; the circumference of catacondensed benzenoids corresponds to a single-component 2-factor (cyclic) subgraph, and, therefore, all catacondensed benzenoids are Hamiltonian benzenoids. Starting with the catacondensed benzenoid row, 2-factor subgraphs of molecular graphs with formulas falling in the alternant rows of $N_{Ic} = 0$, 4, 8, 12, ... [i.e., $N_C \equiv 2 \pmod 4$] are either Hamiltonian or have an odd number of components and those with formulas falling in the other set of rows [i.e., $N_C \equiv 0 \pmod 4$] have an even number of components. 1-Factor subgraphs of molecular graphs with formulas falling in the alternate rows of $N_{Ic} = 0$, 4, 8, 12, ... [i.e., $N_C \equiv 2 \pmod 4$] have an odd number of components and those with formulas falling in the other set of rows [i.e., $N_C \equiv 0 \pmod 4$] have an even number of components. Thus, the number of 1-factor components in benzenoids and 2-factor components in TRS benzenoids is odd or even depending on whether $N_C/2$ and $N_C/6$ is odd or even, respectively.

Circumscribing a 2-factorable benzenoid gives a 2-factorable successor benzenoid. If a benzenoid molecular graph has no 2-factor subgraph, then its circumscribed successor will have no 2-factor subgraphs. The leapfrog of any

benzenoid is 2-factorable, which is a stronger statement than the leapfrog of any benzenoid is closed-shell (nonradical).

CONCLUSION

In circumscribing a benzenoid, symmetry, 1-factorability, 2-factorability, the number of bay regions, and the number of selective lineations are preserved. In leapfrogging a benzenoid, symmetry is preserved while 1-factorabilty, 2-factorability, and the number of bay regions increase. It has been noted numerous times that as the number of benzenoid bay regions increase, relative stability and the number of Kekulé structures and Clar sextets increase. For large benzenoids, this relationship may be regarded as a perimeter edge effect.

The largest benzenoid hydrocarbons synthesized to date are TRS benzenoids. This observation and the isomorphism that exists between strictly pericondensed and TRS benzenoids gives further testimony to the Clar sextet principle.

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