

Notes on Constant-Isomer Series

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Constant-isomer series are polycyclic aromatic hydrocarbon sets having equal numbers of isomers. While presenting an overview of constant-isomer series, general algebraic formulations of our previous results on polycyclic hydrocarbons are reported. Numerous interrelationships and properties of specific representatives are presented. The underlying similarity relationships covered by our topological paradigm provides the unifying framework for this paper. Formulas of constant-isomers correspond to fewer types of structures.

INTRODUCTION

Two approaches to isomer enumeration have been taken. They may be categorized as the *comprehensive* and the *selective*. Comprehensive enumeration of all classes of isomers corresponding to a given formula by a generation scheme is currently an active area of study.^{1,2} Our approach has been the latter. First, a selective scheme for enumeration of a particular class of compounds, namely, benzenoids, was developed.^{3,4} Now, we will show how this scheme can be expanded to include related derivative structures of chemical importance. At the same time, we will present some general formulations of our previous results. The formula periodic table and the concept of constant-isomer benzenoids will be our principal tools for accomplishing these tasks.

The recent benzenoid enumeration results of Herndon are noteworthy because for the first time they included stereoisomers.⁵ This has resulted in some improved numerical results on helicene isomer numbers.⁶ Herndon's numerical results⁵ reflect the number of enantiomers and meso diastereomers that result from nonplanarity in certain benzenoids, whereas the numerical results of Cyvin and co-workers⁶ only consider constitutional isomers. Since benzenoid members of constant-isomer series are mainly planar, their associated isomer numbers are unaffected by the complexities arising from stereoisomers.⁷

Two recent syntheses of large strictly peri-condensed benzenoids have been reported. Though a former synthesis and structure assignment of circum(26)anthracene ($C_{40}H_{16}$) proved to be incorrect,⁸ it has now been accomplished.⁹ This latter work also reports the synthesis of a related $C_{38}H_{16}$ fluoranthene. Synthesis of the largest known strictly peri-condensed benzenoid, circum(34)paraterphenyl ($C_{52}H_{20}$), via double Diels-Alder addition of maleic anhydride to dicoronene ($C_{48}H_{20}$) followed by DDQ oxidation has been accomplished.¹⁰ These interesting syntheses along with the new results on corannulene¹¹ and fullerenes,¹² in general, suggest that a new dawn for large carbon molecule chemistry has arrived [cf. with the whole issue of *Acc. Chem. Res.* 1991, 25 (3), which deals exclusively with fullerenes].

The intent of this paper is to bring together results previously published for four different classes of PAHs^{3,4,13-15} in such a way as to provide an overview which emphasizes their common unifying framework (formula periodic table and algorithms) and interrelationships. While doing this, new insights, derivations, and results of general formulations will be presented. Also, it will be shown that this same framework can be extended to include additional enumerations of other

select derivatives of PAHs. A new topological invariant for indacenoids will be presented.

RESULTS AND DISCUSSION

Basic Definitions and Terminology. Our formula periodic table⁴ for benzenoid hydrocarbons (Table PAH6) is a two-dimensional array of C_nH_s ($n = N_c$, $s = N_H$) formulas having x,y -coordinates of (d_s, N_{Ic}) where $d_s + N_{Ic} = r - 2$. This latter relationship (cf. with the Glossary) shows that one needs to know any two of the three parameters of d_s , N_{Ic} , or r in order to classify a benzenoid. The benzenoid molecular graph is a C-C σ -bond representation of the benzenoid hydrocarbon structure having only second-degree (N_H) and third-degree ($N_c - N_H = N_{pc} + N_{Ic}$) vertices. The total number of edges q is made up of the number of internal edges q_i bounded by two hexagonal rings and the number peripheral edges q_p bounded by only one hexagonal ring. The internal third-degree vertices N_{Ic} are bounded by three hexagonal rings, the net number of disconnections among the internal edges q_i is given by d_s , and the total number of rings is given by r . Table PAH6 is used both in a generic sense [Table PAH6 = Table PAH6(even) \cup Table PAH6(odd)] and, when obvious from the context, to mean Table PAH6(even). Since Table PAH6 represents a partially ordered set, many benzenoid graph-theoretical properties are not absolutely sorted into distinct sets. The total number of edges is given by $q = 1/2 (3N_c - N_H)$, and nonisomeric benzenoids with same q value will have formulas differing per $3\Delta N_c = \Delta N_H$. For example, ovalene ($C_{32}H_{14}$) and the some >446 ($>$ emphasizes that this number does not include stereoisomers)⁵ cata-condensed isomers of $C_{34}H_{20}$ have $3\Delta N_c = \Delta N_H = 3 \times 2 = 6$. Indeed, if each coordinate location (d_s, N_{Ic}) in Table PAH6 had turned out to correspond to a unique q value, as originally thought,⁴ then the locants in Table PAH6 would have represented a countable infinite set requiring only one invariant, instead of two, to totally classify a benzenoid. This is counter to the two-dimensionality criterion of a periodic table set.⁴

Two different constant-isomer series of the same class with the same isomer number and symmetry distribution among its membership are called correspondent series.¹³⁻¹⁵ Two polycyclic hydrocarbons, each belonging to the same generation of a correspondent series, having the same symmetry, number of bay regions (η_0), and relative stability ranking are called correspondents. Strictly peri-condensed benzenoid correspondents will also have the same number of selective lineations, total resonant sextet benzenoid correspondents will also have the same number of solo groups (η_1), and indacenoid correspondents will both possess either adjacent or nonadjacent

pentagonal rings. Total resonant sextet benzenoids¹³ exhibit constant-isomer series that have a one-to-one matching with strictly peri-condensed benzenoid constant-isomer series. If a constant-sextet-isomer series has an isomer number and symmetry distribution matching that of a strictly peri-condensed benzenoid constant-isomer series, then the two associated series are called associate series. If a specific total resonant sextet and strictly peri-condensed pair belonging to the same generation of associate series have the same symmetry and relative stability ranking and the number of solo groups of the former matches the number of bay regions of the latter, then the partners are called associates. These correlations will be more fully illustrated in the section on similarity and topological characteristics.

The horizontal cata-condensed benzenoid boundary in Table PAH6 is easily defined by $N_c = 2N_H - 6$ where $N_H = 8, 10, 12, \dots$. The left-hand staircase boundary also has $N_H = 8, 10, 12, \dots$, but N_c for a given N_H has more than one value for $N_H > 10$. $N_{Ic} = r_6$ for all the benzenoid structures having formulas belonging to the $d_s = -2$ ($N_c = 3N_H - 10$) column series in Table PAH6, which means that all benzenoids to the left of this column will have more internal third-degree vertices than they have hexagonal rings. Thus, the 'less than' in $r_{5\max} \leq N_{Ic}(\text{PAH6})$ applies for those benzenoid formulas located to the left of the $d_s = -2$ column series in Table PAH6.¹⁴

While interlacing Table PAH6(even) and Table PAH6(odd) does provide other insights as discussed by Cyvin,¹³ Table PAH6(even) not only has greater practical applications but the properties of Table PAH6(even), which have been listed,⁴ are different from those of Table PAH6(odd). For example, formulas in Table PAH6(odd) have no total resonant sextet benzenoid isomers and correspond to odd carbon and odd radical species with $4n$ perimeters that give antiaromatic contributions; whereas, formulas in Table PAH6(even) have total resonant sextet isomers (i.e., obeys a Clar sextet stability rule) and correspond to nonradical structures with some even radical isomers all with $4n+2$ perimeters. Clearly, on all accounts, Table PAH6(even) sorts out the more stable benzenoids. We expect these even radicals to be more stable than the odd ones, and the even carbon benzenoids to have no antiaromatic contributions, whatsoever.

Formula Periodic Table Sets. We have restricted our formula periodic tables for PAHs to fused polycyclic hydrocarbons.^{3,4} Thus, benzene, cyclopentadienyl, biphenyl, etc. only have a provisional status in these tables.^{14,15} It appears that the smallest member of a periodic table set is frequently most unique. The precise location of hydrogen in the periodic table for the elements is also troublesome.

The cata-condensed total resonant sextet formulas of our Table PAH6(sextet) is given by C_nH_s where $n = N_c = 18 + 12p$ and $s = N_H = 12 + 6p$ with $p = 0, 1, 2, \dots$. The base formulas (first generation) for the six one-isomer series can be recursively extended by $N_c' = N_c + 3N_H + 18$ and $N_H' = N_H + 12$ starting with (C_6H_6) , $(C_{12}H_{10})$, $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, and $C_{48}H_{20}$. The cata-condensed formulas define the horizontal edge of Table PAH6(sextet), and the one-isomer formulas serve as guide posts for determining the left-hand staircase edge.

Since the recursion pattern characteristic of Table II [Table PAH6(sextet)' in ref 13] may not be obvious, we now present one method for generating this table. Arranging the formulas of the six one-isomer series in ascending numerical order, one obtains the left column below. Now, fill in between all the formulas having a number of carbons divisible by six. Next, assign the number of hydrogens that is equal to the number

of hydrogens of the immediate lower one-isomer formula. The final result (right column) corresponds to the sextet formulas on the left-hand staircase edge of Table PAH6(sextet).

$C_{18}H_{12}$		$C_{18}H_{12}$
$C_{24}H_{14}$		$C_{24}H_{14}$
$C_{30}H_{16}$		$C_{30}H_{16}$
...	$\leftarrow C_{36}H_{18}$	$C_{36}H_{18}$
$C_{42}H_{18}$		$C_{42}H_{18}$
$C_{48}H_{20}$		$C_{48}H_{20}$
...	$\leftarrow C_{54}H_{22}$	$C_{54}H_{22}$
$C_{60}H_{22}$		$C_{60}H_{22}$
...	$\leftarrow C_{66}H_{24}$	$C_{66}H_{24}$
$C_{72}H_{24}$		$C_{72}H_{24}$
...	$\leftarrow C_{78}H_{26}$	$C_{78}H_{26}$
$C_{84}H_{26}$		$C_{84}H_{26}$
...	$\leftarrow C_{90}H_{28}$	$C_{90}H_{28}$
$C_{96}H_{28}$		$C_{96}H_{28}$
...	$\leftarrow C_{102}H_{30}$	$C_{102}H_{30}$
...	$\leftarrow C_{108}H_{30}$	$C_{108}H_{30}$
$C_{114}H_{30}$		$C_{114}H_{30}$
...	$\leftarrow C_{120}H_{32}$	$C_{120}H_{32}$
$C_{126}H_{32}$		$C_{126}H_{32}$
...	$\leftarrow C_{132}H_{34}$	$C_{132}H_{34}$
...	$\leftarrow C_{138}H_{34}$	$C_{138}H_{34}$
$C_{144}H_{34}$		$C_{144}H_{34}$
...		...

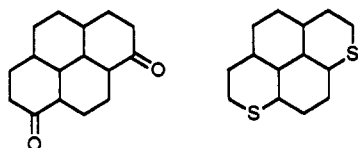
One should note that Table PAH6 is based on the invariants of (d_s, N_{Ic}) per equation $d_s + N_{Ic} = r - 2$. Needless to say, any pair of the invariants d_s , N_{Ic} , and r can be used as the (x, y) coordinates for construction of a different version of a *formula periodic table for benzenoids*. For example, C_nH_s benzenoid formulas can alternatively be arranged in a (N_{Ic}, r) coordinate system. This leads to a table where all the formulas in the columns have the same N_{Ic} values and all the formulas in the rows have the same number of rings (r), i.e., all the cata-condensed formulas now form a vertical left-hand edge and the constant-isomer benzenoid series are now located on a right-hand staircase edge. The criteria for a periodic table set is that it is a partially ordered set, forming a two-dimensional array of infinite extent, and complies with the triad principle where the middle element has a metric property which is the arithmetic mean of two oppositely adjacent elements.^{4,16} This leads to hierarchical ordering of the properties and edge effects where elements on the edge are more unique. Clearly, any alternative pair of coordinate invariants chosen from d_s , N_{Ic} , and r will not produce any substantive change in our formulation of Table PAH6. In other words, Table PAH6 consists of points with (x, y, z) coordinates of (d_s, N_{Ic}, r) on a plane defined by equation $d_s + N_{Ic} - r = -2$. 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 is simply one of six different two-dimensional projections of a plane in three dimensions.

Isomer Enumeration. While it is true that approximately 500 benzenoids have been recorded with certainty,¹⁶ one can only surmise that many times more derivatives must be known. One of the goals of this work is to show how the enumeration results of benzenoids and other related polycyclic hydrocarbons can be used to obtain isomer enumeration data for well-defined groups of derivatives. Our formula periodic tables will play a key role in the algorithm for accomplishing this task. Also, it will be shown that constant-isomer formulas have far fewer possible structure types and usually represent the end points of this algorithm.^{3,13}

Enumeration of methylenylbenzenoid isomers is an important part of our algorithm.³ Our prior work on enumeration of benzenoid quinones has application to the enumeration of

dimethylenylbenzenoids, which is also important to this algorithm. The concept of permethylenylbenzenoids as an intermediate step in the enumeration of essentially strain-free total resonant sextet benzenoids, called augmented circumscription, was crucial to our discovery of the spectacular congruency that exists between strictly peri-condensed and total resonant sextet constant-isomer benzenoid series.¹³

In the quest for an organic conductor, dithia analogs of benzenoids have been studied.¹⁷ The simplistic rationale here is that dithia analogs of benzenoids are isoelectronic to dianions of benzenoids without being charged. We show here that our previous relationships for determining the number of nonradical benzenoid quinones¹⁸ can be used to determine the number of nonradical dithia benzenoid analogs. Consider the pyrene skeleton of D_{2h} symmetry. The number of nonradical pyrene monoquinone isomers is identical to the number of nonradical dithiapyrene isomers. This parallelism is obvious from the following comparison of the third most stable isomer of each.



$$Iq(D_{2h}(v_2)) = (n+2)^2/16 = 9 \text{ nonradical isoskeletal isomers}$$

To review how our algorithm summarized in Scheme I (in ref 3) works, we outline the enumeration of all $C_{58}H_{20}$ benzenoid isomers. To obtain all $C_{24}H_{14}$ ($r = 6$) excised internal structures, we enumerate all $C_{24}H_{14}$ benzenoids ($N_{ic} = 2$) without coves, all methylenyl $C_{23}H_{13}$ ($N_{ic} = 3$) isomers with at least two carbon gaps, and all ethenyl and dimethylenyl $C_{22}H_{12}$ ($N_{ic} = 4$) isomers with at least two carbon gaps. All these $C_{24}H_{14}$ isomers are then circumscribed with a perimeter of 34 carbons and incremented with six hydrogens. An additional isomer is obtained by attaching a benzo group to circumcoronene ($C_{54}H_{18}$). There are nine qualified nonradical $C_{24}H_{14}$ benzenoids. There are 23 nonradical and 13 diradical $C_{24}H_{14}$ methylenylbenzenoids. The total number of dimethylenyl derivatives of the $C_{22}H_{12}$ benzenoids is given by Polya's theorem from which nonqualified isomers having less than two carbon gaps must be subtracted. Figure 1 shows two types of dimethylenyl $C_{22}H_{12}$ benzenoids that must be disqualified, one where at least one methylenyl group is proximate to a bay region and the other where two methylenyl groups are 1,3 about a tertiary third-degree peripheral carbon vertex. The number of nonradical isomeric dimethylenyl derivatives are obtained by using our previously published relationships for determining nonradical quinone derivatives¹⁸ for $C_{22}H_{12}$ benzenoids. Note that the above 1,3-dimethylenyl grouping about a tertiary third-degree carbon vertex always produces a radical species from a nonradical precursor benzenoid. Polya's theorem gives 36 dimethylenylantranthrenes, and our previously published relationship for C_{2h} benzenoids gives 21 nonradical dimethylenylantranthrenes.¹⁸ The difference is 15 diradical dimethylenylantranthrenes from which three diradical isomers are subtracted owing to the dimethylenyl 1,3-grouping about a third-degree carbon vertex as shown in Figure 1. Thus, there are 12 diradical and 21 nonradical dimethylenylantranthrene $C_{24}H_{14}$ isomers capable of being circumscribed. Similarly, by Polya's theorem, there are 36 total, and, by our previously published relationships for C_{2v} benzenoids, 21 nonradical dimethylenylbenzo[ghi]perylene. Among these, there are one nonradical isomer with

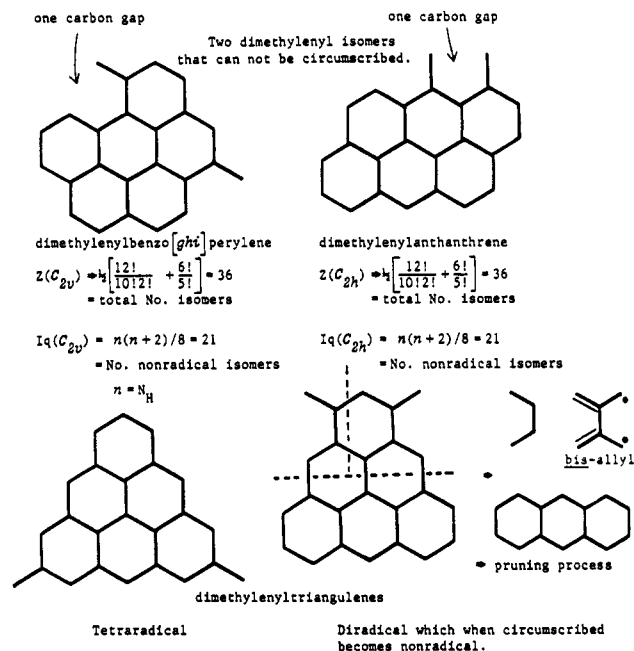


Figure 1. Determining and classifying dimethylenyl ultimate excised internal structures of $C_{58}H_{20}$ benzenoid isomers.

both methylenyl groups proximate to the bay region, five nonradical and five diradical isomers with a single methylenyl group proximate to the bay region, and two diradicals with the dimethylenyl 1,3-grouping (Figure 1). This gives eight diradical and 15 nonradical dimethylenylbenzo[ghi]perylene isomers capable of being circumscribed. There are six nonradical and seven radical dimethylenyltriangulenes and two diradical ethenyltriangulene isomers; one of the radical dimethylenyltriangulenes is a tetradiradical and another is diradical but becomes nonradical upon circumscribing. There are six nonradical ethenylantranthrenes and ethenylbenzo[ghi]perylene, each. Summing all the above values leads to $1 + 9 + 23 + 21 + 15 + 6 + 6 + 6 + 1 = 88$ nonradical and $13 + 12 + 8 + 6 + 2 = 41$ radical $C_{58}H_{20}$ benzenoid isomers.¹⁹

This example illustrates several important points concerning our algorithm. First, our general relationships for determining the number of nonradical benzenoid quinones¹⁸ are quite useful in determining the number of nonradical dimethylenylbenzenoids. In the application of these relationships, one must eliminate all isomers possessing one or two methylenyl groups proximate to a bay region because they result in less than two carbon gaps. Dimethylenylbenzenoids having the two methylenyl groups located 1,3 to each other about a third-degree peripheral carbon vertex are always diradical and must be disqualified from circumscribing because there is only a one-carbon gap between the methylenyls. Second, our previous discussions regarding diradical excised internal structures that can be pruned of even-carbon fragments to yield a bis-allyl diradical formed by joining to allyl radicals through their nonstarred positions are relevant.²⁰ Circumscribing these types of diradicals leads to nonradical successor benzenoids as occurred with the dimethylenyltriangulene structures in Figure 1. This was previously illustrated with bis-allyl, which yields bisanthrene.²⁰ Third, our work on the smallest tetradiradical members of our constant-isomer series is germane.²¹

Isomer Enumeration of Select PAH Derivatives. Understanding the range of structure types that can correspond to a particular benzenoid formula will aid our archiving, retrieving, and ultimate managing of chemical information.⁵ Consider the formula $C_{34}H_{18}$ that corresponds to more than 333 benzenoids of which at least 14 are known. Can there

be alkyl, vinyl, or phenyl benzenoids (one benzenoidyl unit) with this formula? Our algorithm for answering this question is quite straightforward.²² Successively subtract C_2H_4 (for ethyl or dimethyl), C_2H_2 (for vinyl), or C_6H_4 (for phenyl), respectively, from $C_{34}H_{18}$ and check our Table PAH6(even) to see if the successor formula still belongs to Table PAH6(even). If it does, then the answer is affirmative. Subtraction of C_2H_4 from $C_{34}H_{18}$ gives $C_{32}H_{14}$, which corresponds to ovalene. Subtracting C_2H_4 from $C_{32}H_{14}$ gives $C_{30}H_{10}$, which is not found on Table PAH6(even). Thus, $C_{34}H_{18}$ can have four ethyl- or 28 dimethylovalene isomers; this latter isomer number was determined by using Polya's equation listed in our benzenoid quinone paper.¹⁸ Similarly, subtraction of C_2H_2 twice from $C_{34}H_{18}$ gives $C_{30}H_{14}$, which corresponds to three nonradical benzenoids; further subtraction of C_2H_2 from $C_{30}H_{14}$ gives a formula not on Table PAH6(even). Thus, $C_{34}H_{18}$ can have 168 divinyl benzenoid isomers as determined by Polya's equation. Subtraction of C_6H_4 from $C_{34}H_{18}$ gives $C_{28}H_{14}$, which corresponds to eight nonradical benzenoids; a second C_6H_4 subtraction gives $C_{22}H_{10}$, which cannot correspond to a benzenoid. From our published depictions,¹⁶ it can easily be determined that there are 68 nonradical phenylbenzenoids of the formula of $C_{34}H_{18}$. In these examples, note that the number of rings $r = (1/2)(N_c + 2 - N_H)$ remained constant and that the final valid formula belonged to the extreme left-hand staircase edge of Table PAH6(even), which is either constant-isomer benzenoids or antecedents to constant-isomer benzenoids.

Determining the compatibility of a benzenoid formula with other structure types follows the same strategy as illustrated in the preceding paragraph. For example, how many naphthylbenzenoids are compatible with the formula of $C_{34}H_{18}$? Subtracting $C_{10}H_6$ from $C_{34}H_{18}$ gives $C_{24}H_{12}$, which is coronene. Thus, α -naphthyl- and β -naphthylcoronene have the same $C_{34}H_{18}$ benzenoid formula. However, subtracting $C_{14}H_8$ from $C_{34}H_{18}$ gives $C_{20}H_{10}$, which does not exist on Table PAH6. This means that larger arylbenzenoids of the formula $C_{34}H_{18}$ do not exist. In these examples, the N_c/N_H ratio of the successor formula increases and is located closer the staircase edge of Table PAH6. This is always true for these substituents. In the next example, the N_c/N_H ratio of the successor formula will decrease and move toward the cata-condensed benzenoid edge of Table PAH6. Can the $C_{34}H_{18}$ benzenoid formula correspond to an ethynyl benzenoid? Subtracting C_2 from $C_{34}H_{18}$ twice gives $C_{30}H_{18}$ and subtracting a third time gives $C_{28}H_{18}$ where only the former is on Table PAH6; $C_{30}H_{18}$ corresponds to >123 ($>$ emphasizes that this number does not include stereoisomers)⁵ cata-condensed benzenoids. Thus, there are a large number of diethynylbenzenoid isomers of the formula $C_{34}H_{18}$. Exactly the same algorithm can be used to obtain the number of alkyl-, alkenyl-, alkynyl-, and aryl-substituted fluorenoids/fluoranthenoids¹⁴ and indacenoids¹⁵ where Table PAH5,6(F/F) and Table PAH5,6(I) would replace Table PAH6. In general, it can be concluded from the above examples that the formulas of constant-isomers cannot correspond to alkyl-, alkenyl-, or aryl-substituted PAH molecules.

The above algorithmic approach can be applied to mixed substituents. Also, this section demonstrates that our overall enumeration results can be easily extended to the enumeration and classification of many types of related substituted polycyclic hydrocarbon structures, as well as for isoskeletal heteroatom analogs.²² It is worth emphasizing at this point that the formulas belonging to constant-isomer series correspond to far fewer types of molecular structures.

Contreras and co-workers have shown that, for a specific molecular formula, a dramatic decrease in the number of isomers occurs by replacing rings with double bonds and isolated rings by condensed ones.² These observations concur with benzenoid enumeration results, which show that more condensed benzenoids tend to have fewer benzenoid isomers. The phenomenon of constant-isomer series is an ultimate expression of this tendency.

Constant-Isomer Series. Constant-isomer series are a series of C_nH_s ($n = N_c$, $s = N_H$) formulas corresponding to specified classes of polycyclic conjugated hydrocarbons having an equal number of isomers. These series are generated by successive circumscribing with a perimeter of carbon atoms and incrementing with a specific number of hydrogens.^{3,4,13-15}

Circumscribing a PAH gives a successor PAH' having the same symmetry and number of bay regions (η_0) and selective lineations ($1'$). Both PAH and PAH' are chemically isotopological. A pair of correspondents are also isotopological. Augmented circumscribing of a total resonant sextet benzenoid gives a successor total resonant sextet having the same symmetry and number of solo groups (η_1), and both these molecules are isotopological.

If any formula on Table PAH6 of N_c carbon atoms and N_H hydrogen atoms is selected and all associated structures are circumscribed with a perimeter of $2N_H + 6$ carbon atoms incrementing the hydrogens by six, a set of successor benzenoid structures is obtained. When other structures (benzobenzenoids, methylenylbenzenoids, dimethylenylbenzenoids, ethenylbenzenoids) of the same formula, if they exist, are added to this set, the set can again be circumscribed to obtain another set of benzenoids. This process is repeated successively, where the number of isomers increases at each step, until a formula is obtained on the protrusive left-hand staircase edge of Table PAH6. Once this occurs, further circumscribing leads to the same number of benzenoid isomers because there can be no other related structures of this formula. Thus, a set of strictly peri-condensed benzenoids which have no other related isomeric structures (benzobenzenoids, methylenylbenzenoids, dimethylenylbenzenoids, ethenylbenzenoids) with a formula on the staircase edge of Table PAH6 can be successively circumscribed to give successor benzenoids with the same number of isomers; benzenoids with this property are called constant-isomer series. Again, we see that constant-isomer formulas correspond to far fewer types of molecular structures.

While our tables for constant-isomer series are quite complete for the range of formulas corresponding to practical PAHs, we now present equations which will allow one to determine the base formulas for all constant-isomer series, no matter how large the initial formula. We call these equations floating functions. These floating functions were derived algorithmically from the successive differences in the N_c and N_H values of the base formulas for the relevant constant-isomer series summarized in Table I. As will become evident, these floating functions represent a collection of sums of arithmetic series derived from the recursions present in Table I.

It was stated in our previous paper³ that "Also, the pattern for the progressive increase in the first member formula of each (constant-isomer) series should be evident and will allow one to extend these tables even further". Subsequently, Cyvin and co-workers published²³ an analytical expression containing a floor function parameter which they claim to be more mathematically rigorous than the obvious recursion present in Table I. A number of patterns among the various ΔN_c

Table I. Base Formulas of Constant-Isomer Series

strictly peri-condensed		total resonant sextet		fluorenoids/fluoranthenoids		indacenoids	
initial formula	successive ΔN_c	initial formula	successive ΔN_c	initial formula	successive ΔN_c	initial formula	successive ΔN_c
C ₆ H ₆		C ₆ H ₆		C ₅ H ₅			
(C ₉ H ₇) ^a	3	(C ₁₂ H ₈) ^a	6	(C ₈ H ₆) ^a	3	(C ₅ H ₅) ^a	
C ₁₀ H ₈	1	C ₁₂ H ₁₀	0	C ₉ H ₇	1	C ₈ H ₆	3
C ₁₃ H ₉	3	C ₁₈ H ₁₂	6	C ₁₂ H ₈	3	C ₁₁ H ₇	3
C ₁₆ H ₁₀	3	C ₂₄ H ₁₄	6	C ₁₅ H ₉	3	C ₁₄ H ₈	3
C ₁₉ H ₁₁	3	C ₃₀ H ₁₆	6	C ₁₈ H ₁₀	3	C ₁₇ H ₉	3
C ₂₂ H ₁₂	3	C ₃₆ H ₁₈	6	C ₂₃ H ₁₁	5	C ₂₂ H ₁₀	5
C ₂₇ H ₁₃	5	C ₄₈ H ₂₀	12	C ₂₆ H ₁₂	3	C ₂₇ H ₁₁	5
C ₃₀ H ₁₄	3	C ₅₄ H ₂₂	6	C ₃₁ H ₁₃	5	C ₃₂ H ₁₂	5
C ₃₅ H ₁₅	5	C ₆₆ H ₂₄	12	C ₃₆ H ₁₄	5	C ₃₇ H ₁₃	5
C ₄₀ H ₁₆	5	C ₇₈ H ₂₆	12	C ₄₁ H ₁₅	5	C ₄₄ H ₁₄	7
C ₄₅ H ₁₇	5	C ₉₀ H ₂₈	12	C ₄₈ H ₁₆	7	C ₅₁ H ₁₅	7
C ₅₀ H ₁₈	5	C ₁₀₂ H ₃₀	12	C ₅₃ H ₁₇	5	C ₅₈ H ₁₆	7
C ₅₇ H ₁₉	7	C ₁₂₀ H ₃₂	18	C ₆₀ H ₁₈	7	C ₆₅ H ₁₇	7
C ₆₂ H ₂₀	5	C ₁₃₂ H ₃₄	12	C ₆₇ H ₁₉	7	C ₇₄ H ₁₈	9
C ₆₉ H ₂₁	7	C ₁₅₀ H ₃₆	18	C ₇₄ H ₂₀	7	C ₈₃ H ₁₉	9
C ₇₆ H ₂₂	7	C ₁₆₈ H ₃₈	18	C ₈₃ H ₂₁	9	C ₉₂ H ₂₀	9
C ₈₃ H ₂₃	7	C ₁₈₆ H ₄₀	18	C ₉₀ H ₂₂	7	C ₁₀₁ H ₂₁	9
C ₉₀ H ₂₄	7	C ₂₀₄ H ₄₂	18	C ₉₉ H ₂₃	9	C ₁₁₂ H ₂₂	11
C ₉₉ H ₂₅	9	C ₂₂₈ H ₄₄	24	C ₁₀₈ H ₂₄	9	C ₁₂₃ H ₂₃	11
C ₁₀₆ H ₂₆	7	C ₂₄₆ H ₄₆	18	C ₁₁₇ H ₂₅	9	C ₁₃₄ H ₂₄	11
C ₁₁₅ H ₂₇	9	C ₂₇₀ H ₄₈	24	C ₁₂₈ H ₂₆	11	C ₁₄₅ H ₂₅	11
C ₁₂₄ H ₂₈	9	C ₂₉₄ H ₅₀	24	C ₁₃₇ H ₂₇	9	...	
C ₁₃₃ H ₂₉	9	C ₃₁₈ H ₅₂	24	C ₁₄₈ H ₂₈	11		
C ₁₄₂ H ₃₀	9	C ₃₄₂ H ₅₄	24	C ₁₅₉ H ₂₉	11		
C ₁₅₃ H ₃₁	11	C ₃₇₂ H ₅₆	30	C ₁₇₀ H ₃₀	11		
C ₁₆₂ H ₃₂	9	C ₃₉₆ H ₅₈	24	...			
C ₁₇₃ H ₃₃	11	C ₄₂₆ H ₆₀	30				
C ₁₈₄ H ₃₄	11	C ₄₅₆ H ₆₂	30				
C ₁₉₅ H ₃₅	11	C ₄₈₆ H ₆₄	30				
C ₂₀₆ H ₃₆	11	C ₅₁₆ H ₆₆	30				
C ₂₁₉ H ₃₇	13	C ₅₅₂ H ₆₈	36				
C ₂₃₀ H ₃₈	11	C ₅₈₂ H ₇₀	30				
C ₂₄₃ H ₃₉	13	C ₆₁₈ H ₇₂	36				
C ₂₅₆ H ₄₀	13	C ₆₅₄ H ₇₄	36				
C ₂₆₉ H ₄₁	13	C ₆₉₀ H ₇₆	36				
C ₂₈₂ H ₄₂	13	C ₇₂₆ H ₇₈	36				
C ₂₉₇ H ₄₃	15	C ₇₆₈ H ₈₀	42				
C ₃₁₀ H ₄₄	13	C ₈₀₄ H ₈₂	36				
C ₃₂₅ H ₄₅	15	C ₈₄₆ H ₈₄	42				
C ₃₄₀ H ₄₆	15	C ₈₈₈ H ₈₆	42				
C ₃₅₅ H ₄₇	15	C ₉₃₀ H ₈₈	42				
C ₃₇₀ H ₄₈	15	C ₉₇₂ H ₉₀	42				
...		...					

^a Phantom formulas.

columns exist. Since the total resonant sextet constant-isomer series are totally isomorphic to the strictly peri-condensed constant-isomer series, any relationship obtained for one can be obtained directly for the other.¹³ For the strictly peri-condensed column, ΔN_c contains successive odd numbers repeated six times with a pattern of ...abaaaaca...; for the fluorenoids/fluoranthenoids column, ΔN_c contains successive odd numbers repeated five times with a pattern of ...abaaaaca...; and for the indacenoids column, ΔN_c contains successive odd numbers repeated four times with a pattern of ...aaaa.... This regularity is more than a coincidence. Starting with naphthalene (C₁₀H₈), take every sixth initial formula in the first column of Table I. This gives

N_c	ΔN_c	$\Delta\Delta N_c$	N_H	ΔN_H
10			8	
30	20		14	6
62	32	12	20	6
106	44	12	26	6
162	56	12	32	6
230	68	12	38	6
310	80	12	44	6

The first difference (ΔN_c) is an arithmetic series with the common difference of 12. This means that N_c can be

represented by the arithmetic sum of $6w^2 + 14w + 10$, and N_H can be represented by $6w + 8$ ($w = 0, 1, 2, \dots$). Starting with C₁₃H₉ and thereafter every sixth initial formula from Table I, we obtained the arithmetic sum of $N_c = 6w^2 + 16w + 13$ with $N_H = 6w + 9$. Repeating this derivation a total of six times gives six related equations which can be combined to give the floating functions summarized in the next paragraph.

The base formulas (first generation) for all the constant-isomer benzenoid series (except for the series starting with benzene) can be obtained from the following general relations:

$$N_c = 6w^2 + 14w + 10 + (2w + 3)v + u \quad (1)$$

$$N_H = 6w + 8 + v$$

$$v = (0, 1, 2, 3, 4, 5) \text{ and } u = (0, 0, 0, 0, 0, 2)$$

$$w = 0, 1, 2, \dots$$

where each specified positive integer value of w , v and u in unison, successively takes on the values given in the parentheses. Our published tables for constant-isomer benzenoid series end

before $w = 7$. For example, consider $w = 6$ for $v = u = 0$, $N_c = 310$, and $N_H = 44$. The next five formulas (Table I) are obtained by successively assigning v and u , the value in their parentheses in sequence order:

N_c	N_H	v	u
325	45	1	0
340	46	2	0
355	47	3	0
370	48	4	0
387	49	5	2

If one makes the following change of variables $j = w$, $\delta = v + 1$, and $2[\delta/6] = u$ ($[x]$ is the floor function where the largest integer smaller than or equal to x is chosen) in eq 1, then the previously derived expressions of Cyvin and co-workers are obtained.²³ Thus, the above constitutes an alternative derivation of general expressions for obtaining the base (first generation) formulas of constant-isomer benzenoid series. This agreement demonstrates the validity of both our recursion algorithm by which the original results were obtained^{3,4} and the subsequent expressions of eqs 3 and 4 for fluorenoids/fluoranthenoids and indacenoids, respectively, which were derived in the same manner. Table I summarizes the recursion patterns used to derive all the original results.^{3,4}

To determine all the base formulas of the total resonant sextet benzenoid constant-isomer series (except for the series starting with benzene), the following general relations can be used:

$$N_c(\text{sextet}) = 18w^2 + 24w + 12 + 3(2w + 2)v + 3u \quad (2)$$

$$N_H(\text{sextet}) = 12w + 10 + 2v$$

$$w = 0, 1, 2, \dots$$

$$v = (0, 1, 2, 3, 4, 5) \text{ and } u = (0, 0, 0, 0, 0, 2)$$

where each integer value of w , v and u in unison, takes on the successive values given in the parentheses. For example, one obtains the following for $w = 6$ (Table I):

N_c	N_H	w	v	u
804	82	6	0	0
846	84	6	1	0
888	86	6	2	0
930	88	6	3	0
972	90	6	4	0
1020	92	6	5	2

The successive ΔN_c differences (Table I) between the base formulas of the fluorenoid/fluoranthenoid constant-isomer series (Table III in ref 14) is given by 3, 1, 3, 3, 3, 5, 5, 5, 7, 5, 7, 7, 7, 9, 9, 9, 11, and 9. Clearly, the next series of numbers not shown is 11, 11, 11, 13, 11, Although, this apparent series allows the generation the base formulas for all possible fluorenoid/fluoranthenoid constant-isomer series, the following floating function can be alternatively employed to generate these base formulas:

$$N_c = 5w^2 + 12w + 9 + (2w + 3)v + u \quad (3)$$

$$N_H = 5w + 7 + v$$

$$w = 0, 1, 2, 3, \dots$$

$$v = (0, 1, 2, 3, 4)$$

$$u = (0, 0, 0, 0, 2)$$

In the application of this floating function, each value of w , v and u in unison takes on the values shown in their parentheses set. For example, for $w = 3$ the following is obtained:

N_c	N_H	w	v	u
90	22	3	0	0
99	23	3	1	0
108	24	3	2	0
117	25	3	3	0
128	26	3	4	2

To determine the base formulas of all the indacenoid constant-isomer series, the following floating function can be used where each value of w and v takes on the successive values given in the parentheses:

$$N_c = 4w^2 + 10w + 8 + (2w + 3)v \quad (4)$$

$$N_H = 4w + 6 + v$$

$$w = 0, 1, 2, 3, \dots$$

$$v = (0, 1, 2, 3)$$

Equations 1, 3, and 4 can be intuitively generalized as follows:

$$N_c = (6 - r_5)w^2 + 2(7 - r_5)w + (10 - r_5) + (2w + 3)v + [1 - (1/2)r_5(r_5 - 1)]u$$

$$N_H = (6 - r_5)w + (8 - r_5) + v$$

$$v = (0, 1, 2, \dots, 5 - r_5)$$

$$u = (0, 0, \dots, 0, 2)$$

where r_5 can equal 0, 1, or 2. This generalization again emphasizes the uniformity of the recursion relationships used to obtain the original results.^{3,14,15} Recently Cyvin has put forth a conjecture proposing a relationship that might engulf our eq 3.²⁴ However, we claim that the derivation outlined herein, which is based on the sum of an arithmetic series determined within a unified framework, constitutes the essence of an analytical proof.

Figure 7 of ref 21 presents the ultimate excised internal structures and corresponding base formulas for the smallest unique polyradical members of the benzenoid constant-isomer series. From a practical point of view, these results are quite complete. However, if these results are to be extended further, then note that these ultimate excised internal structures have formulas given by $N_c = \Delta^2$ and $N_H = 3\Delta$, where Cyvin's notation²⁴ of $\Delta = 1, 2, 3, 4, \dots$ now corresponds to monoradical (CH_3), diradical (C_4H_6), triradical (C_9H_9), tetradical ($\text{C}_{16}\text{H}_{12}$), and so on. From the Figure 7 recursion pattern, it can be shown that the specific number of times, y , which these ultimate excised internal structures must be circumscribed to become base members of the constant-isomer series is given by $y = (1/4)(\Delta^2 - 2\Delta + 5)$ for odd formulas which have odd values for Δ or $y = (1/4)(\Delta^2 - 2\Delta + 4)$ for even formulas ($\Delta = \text{even}$) where both equations were derived from arithmetic series using our original results.²¹ These relationships for y along with the corresponding N_c and N_H values of the ultimate excised internal structure can be inserted into $N_c + 2yN_H + 6y^2 = N'_c$ and $N_H + 6y = N'_H$ where N'_c and N'_H correspond to the formula of the base polyradical members.²³ Thus, the formulas for the smallest unique

Table II. Indacenoid Hydrocarbon Constant-Isomer Series

series	no. of isomers	pseudo-symmetry ^a distribution	no. of IPR ^b isomers	pseudo-symmetry ^a distribution
(C ₅ H ₅) ^c C ₁₉ H ₉ C ₄₁ H ₁₃ ...	1	C _{2v}	0	
C ₈ H ₆ C ₂₄ H ₁₀ C ₄₈ H ₁₄ ...	1	D _{2h}	0	
C ₁₁ H ₇ C ₂₉ H ₁₁ C ₅₃ H ₁₅ ...	1	C _{2v}	0	
C ₁₄ H ₈ C ₃₄ H ₁₂ C ₆₂ H ₁₆ ...	3	D _{2h} (2), C _s (1)	1	D _{2h}
C ₁₇ H ₉ C ₃₉ H ₁₃ ...	6	C _{2v} (2), C _s (4)	2	C _{2v} , C _s
C ₂₂ H ₁₀ C ₄₆ H ₁₄ ...	7	D _{2h} (1), C _{2v} (4), C _s (2)	3	D _{2h} , C _{2v} (2)
C ₂₇ H ₁₁ C ₅₃ H ₁₅ ...	6	C _{2v} (2), C _s (4)	2	C _{2v} , C _s
C ₃₂ H ₁₂ C ₆₀ H ₁₆ ...	12	D _{2h} (1), C _{2v} (4), C _s (7)	5	D _{2h} , C _{2v} (2), C _s (2)
C ₃₇ H ₁₃ C ₆₇ H ₁₇ ...	28	C _{2v} (5), C _s (23)	11	C _{2v} , C _s (10)
C ₄₄ H ₁₄ C ₇₆ H ₁₈ ...	26	C _{2v} (8), C _{2h} (3), C _s (15)	14	C _{2v} (7), C _{2h} (3), C _s (4)
C ₅₁ H ₁₅ C ₈₅ H ₁₉ ...	28	C _{2v} (5), C _s (23)	11	C _{2v} , C _s (10)
C ₅₈ H ₁₆ ...	51	D _{2h} (4), C _{2v} (6), C _{2h} (2), C _s (39)	24	D _{2h} (3), C _{2v} (4), C _{2h} , C _s (16)

^a Pseudosymmetry assumes that these molecules are perfectly planar.^b Isolated pentagonal rings. ^c To obtain successive formulas, use the following recursions of $N_c' = N_c + 2N_H + 4$ and $N_H' = N_H + 4$.

polyradical members of the constant-isomer series are given directly by $N_c' = (1/8)(3\Delta^4 + 26\Delta^2 + 75)$ and $N_H' = (3/2)(\Delta^2 + 5)$ for odd polyradicals ($\Delta = 1, 3, 5, \dots$) and $N_c' = (1/8)(3\Delta^4 + 20\Delta^2 + 48)$ and $N_H' = (3/2)(\Delta^2 + 4)$ for even polyradicals ($\Delta = 0, 2, 4, \dots$). These simple relationships give the base formulas for all the smallest unique polyradicals of the constant-isomer series. For $\Delta = 0$ one obtains C₆H₆; that is, the benzene formula is the base formula for the smallest unique "zero even radical" member of the constant-isomer series. Cyvin and co-workers²⁴ have derived by a different method a single floor function expression comparable to the above two final equations and stated, "It is very plausible, although not strictly proved, that the method of Example 2 produces the title systems (extremal benzenoids with maximum color excess) in general. Dias ... came to an equivalent conclusion".²⁴ This agreement is a validation of our results.

Identifying the formula of the smallest unique polyradical member of the constant-isomer series is useful because the isomer number sequence for each specified polyradical subset is identically 1, 1, 1, 2, 4, 4, 12, 19, 19, 46, 70, 70, 162, 239, 239, 504, 726, 726, 1471, 2062, 2062,²¹ For example, what is the smallest tetraradical base formula? From the above equations for even radicals, $N_c = 142$ and $N_H = 30$ is obtained. Thus, the constant-isomer series with the base formula of C₁₄₂H₃₀ has one tetraradical benzenoid isomer,

and the subsequent constant-isomer series with base formulas³ of C₁₆₂H₃₂, C₁₈₄H₃₄, C₂₀₆H₃₆, C₂₃₀H₃₈, C₂₅₆H₄₀, C₂₈₂H₄₂, ... have 1, 1, 2, 4, 4, 12, 19, ... tetraradical benzenoid isomers.

Rule of Nonadjacent Pentagonal Rings. The preference for isolated pentagonal rings (IPR) in polycyclic species was espoused by Kroto.¹² The fusion of two pentagons to form a pentalene substructure is energetically unfavorable as a result of increased σ -bonding ring strain and the formation of an antiaromatic ($4n = 8$) $p\pi$ electronic contribution. Nonadjacent pentagonal rings make smaller antiaromatic contributions. Thus, in this section we examine how the application of this constraint affects our previous results on constant-isomer indacenoids. The exclusion of adjacent pentagonal ring-containing indacenoids is summarized in Table II and shows that the constant-isomer series having the same isomer number exhibits not only a one-to-one matching in their symmetry distributions but also in whether the pentagonal rings are adjacent or not. With this IPR constraint, the one-isomer formulas which appear on the left-hand staircase edge of Table PAH5,6(I) (Table II in ref 15) will have to be deleted. Also, note that the previously observed isomer sequence of ... a b a c ... is still retained.

Similarity and Topological Characteristics. Similarity is a measure of the degree of overlap between two or more molecules. Recognition of recurring molecular substructures is important in appraising similarity. For example, corannulene ([5]circulene), coronene ([6]circulene), and [7]circulene all have the same recurring unit (elementary substructure).²⁵ All three of these known molecules are subspectral in the HMO $p\pi$ energy levels of 2.6751, 1.5392, -1.0, and -1.2143 (in β units). If these energy levels had included the frontier MOs (i.e., the HOMO and LUMO), this similarity would have been stronger since these orbitals govern the major chemistry associated with such molecules.

Polycyclic hydrocarbon members of the constant-isomer series with the same isomer number exhibit a pairing of their molecular membership according symmetry and other specific topological invariants. This is a type of similarity phenomenon that we call a topological paradigm. Figure 2 gives the base members of the two matching four-isomer benzenoid series, and Figure 3 gives the two associated four-sextet-isomer total resonant benzenoid series. Figure 4 gives the base members of the two nine-isomer fluorenoid/fluoranthenoid series, and Figure 5 gives the base members of the two six-isomer indacenoid series. Comparison of the appropriate invariants between the correspondents and associates in these figures will allow the similarity of the various partners to be verified.

The principal graph theoretical invariants which determine the total $p\pi$ energy (E_π) of benzenoids (PAH6) have been discussed by Hall.²⁶ The number of carbon vertices (N_c) and CC bonds (q) are dominant quantities. The number of bay regions (η_0) also makes a small but significant contribution, as does the number of Kekulé structures. When isomer groups are compared, N_c and q remain fixed, and a relative ranking between the two sets can be accomplished by using E_π , if known. Alternatively, a decisive ranking can frequently be achieved by using η_0 and K (or SC for nonalternants). For example, the one-to-one matching between the C₃₆H₁₄/C₄₈H₁₆ base members of the nine-isomer fluorenoid/fluoranthenoid series in Figure 4 has not yet been completely determined using only symmetry and bay regions. The first C_{2v} structure in each set has no bay region and is uniquely matched. However, the second and third C_{2v} structures in each set can only be uniquely matched by knowledge of their relative E_π (or SC) values. The remaining C_s structures are also not

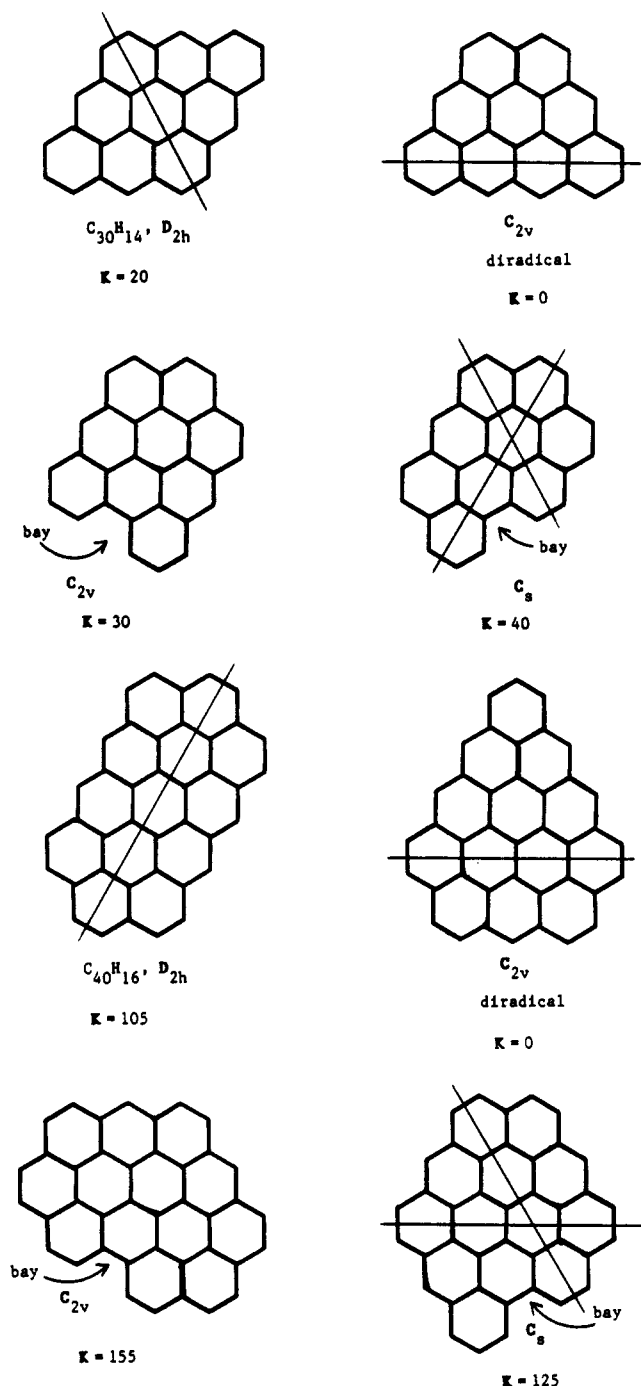


Figure 2. Base (first generation) strictly peri-condensed benzenoid structures belonging to the two corresponding four-isomer series in parallel order according to their matching topological characteristics.

uniquely matched since we do not know their E_π values. The constant-isomer benzenoid series have the additional invariant of selective lineations in the one-to-one matching between correspondents of series having the same isomer number, and the constant-isomer indacenoid series have the additional invariant associated with the adjacency/nonadjacency of their pentagonal rings. Figures 2 and 5 show the one-to-one matching between these invariants and the correspondent series.

Other important features are brought out by the results summarized in Figures 2 and 3. Although, correspondent series have the same isomer number with a one-to-one matching among their membership in regard to symmetry and other appropriate topological invariants, no overall one-to-one matching in their relative stabilities was found. This can be

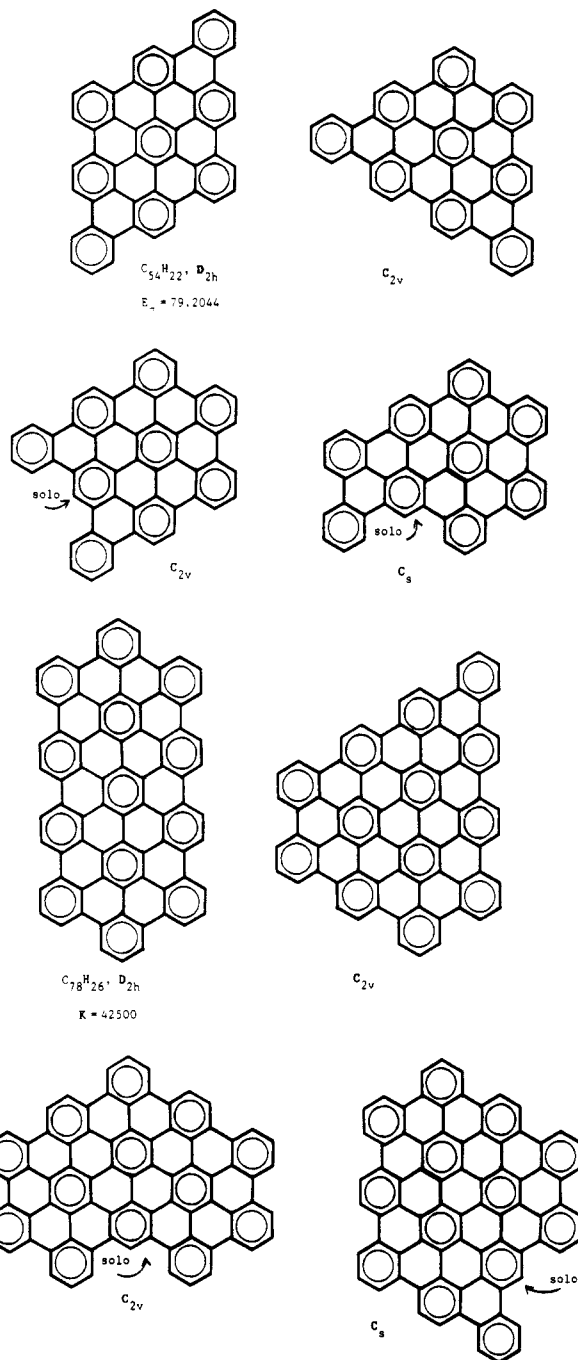


Figure 3. Base (first generation) total resonant sextet benzenoid structures belonging to the two corresponding four-sextet-isomer series arranged in parallel order according to their matching topological characteristics.

seen by comparing the relative magnitude of the K values given for the $C_{30}H_{14}$ isomers versus the $C_{40}H_{16}$ isomers. The relative stability order assigned to the base members of constant-isomer benzenoids according to K is preserved on circumscribing. For the four-isomer series starting with $C_{30}H_{14}$, in going from the first generation ($C_{30}H_{14}$) to the second ($C_{64}H_{20}$), the respective K values change according to $20 \rightarrow 1764$, $0 \rightarrow 0$, $30 \rightarrow 3136$, and $40 \rightarrow 3626$; similarly, for the four-isomer series starting with $C_{40}H_{16}$, the corresponding $K(C_{40}H_{16}) \rightarrow K(C_{78}H_{22})$ changes are $105 \rightarrow 14112$, $0 \rightarrow 0$, $155 \rightarrow 22932$, and $125 \rightarrow 20580$. It is important to distinguish here between the overall matching of two correspondent sets according to their relative stability and the expected unique matching of correspondent subsets having all other topological invariants the same.

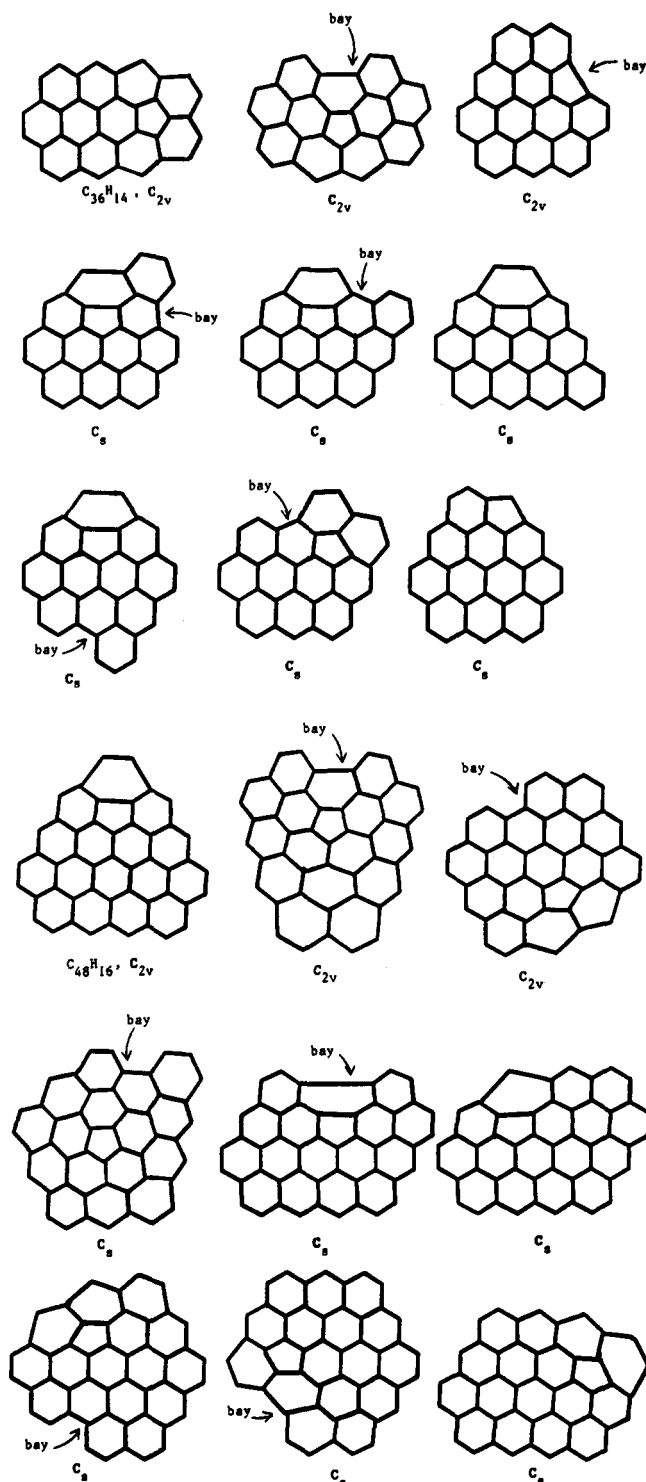


Figure 4. First-generation members of the two nine-isomer fluorenoid/fluoranthenoid constant-isomer series in parallel order according to their topological invariants.

Each of the four isomers predicted to be among the most stable ones out of approximately 13286 possible $C_{54}H_{22}$ and 319258 $C_{78}H_{26}$ benzenoid isomers²⁷ are shown in Figure 3. Total resonant sextet isomers also have a minimum number of solo groups which are the most kinetically reactive among the four types of perimeter configurations (solo, duo, trio, quarto); as one can see from the examples in Figure 3, these solo groups tend to be located in a cavity which are fairly sterically hindered.

Bay regions are important topological invariants. The number of bay regions remains fixed upon successive circumscribing of polycyclic hydrocarbons. The perimeter

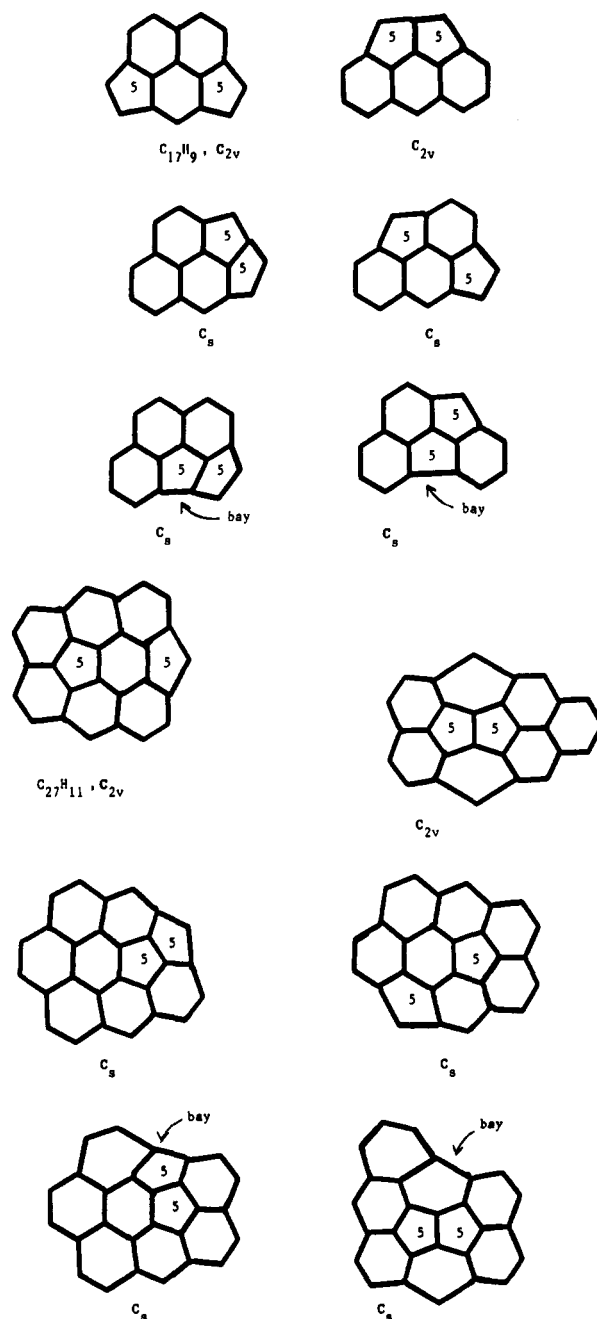


Figure 5. First-generation members of the two six-isomer indacenoid constant-isomer series in parallel order according to their topological invariants.

topology of a polycyclic hydrocarbon is prescribed by

$$-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6 - r_5$$

where the number of bay regions is given by η_0 , duo groups by η_2 , trios by η_3 , quartos by η_4 , and pentagonal rings by r_5 . This relationship is valid for all polypentagonal/polyhexagonal systems. Previously,⁴ we showed that the following correspondences exist between the perimeter topologies of benzenoids and their total resonant sextet benzenoid associates in going from the former to the latter:

$$\begin{array}{ll} \eta_0 \rightarrow \eta_1' & N_{1c} \rightarrow r(\text{empty}) \\ \eta_1 \rightarrow \eta_2' & N_{pc} \rightarrow \eta_0' \\ \eta_2 \rightarrow \eta_3' & \\ \eta_3 \rightarrow \eta_4' & \\ \eta_4 \rightarrow \eta_5' & \end{array}$$

A number of important relationships can be derived from these correspondences. The above perimeter topology rela-

tionship becomes

$$-\eta_1' + \eta_3' + 2\eta_4' + 3\eta_5' = 6$$

Combining these equations gives

$$\eta_1' + \eta_2' + \eta_3' + \eta_4' = \eta_0'$$

where the prime emphasizes that these equations are valid only for essentially strain-free total resonant sextet benzenoids. In successive augmented circumscription of total resonant sextet benzenoids, the number of solo units (η_1) remains fixed while the number of bay regions and duo groups increases.

CONCLUSION

The results summarized herein were all derived and formulated in general by an algorithmic methodology. Through the medium of a formula periodic table, one can establish a partial ordering where the range of allowable structure types associated with a given formula can be defined. Molecular stability is a component of this framework, as it should be for any significant systematic organization of chemical information. While symmetry, bay regions, selective lineations, adjacent/nonadjacent pentagonal rings, and branched/nonbranched cata-condensed rings are topological invariants that make clear contributions to the overall stability of a polycyclic conjugated hydrocarbon, other, yet undefined, invariants are still needed to more fully establish a relative ranking among isomer sets. The determination of a set of topological invariants that allows the quick establishment of a relative order of any set of molecules is an important endeavor in chemical information, and similarity is an important concept used in this process.

The formulas of constant-isomer series correspond to a smaller set of possible molecular structures. In pyrolysis as the C:H ratio increases, nature converges on a smaller set of possible structures. This phenomenon is the result of energetic/structural factors and has been exploited in our chemical information studies.

This paper in part presents a review of some of our prior results given in separate publications^{3,4,14,15} on four different classes of PAHs in order to provide a unique overview which emphasizes their common framework and corresponding interrelationships. We have provided new derivations of general formulations of constant-isomer series called floating functions based on a collection of arithmetic series sums which parallels the recursion relationships used to obtain the original results.^{3,4,14,15} Equations 3 and 4 are totally new. Exactly the same methodology was used to derive these results for strictly peri-condensed and total resonant sextet benzenoid, fluoranthenoid, and indacenoid constant-isomer series. Herein, this unified approach has been shown to be capable of extension to enumeration of select derivatives of PAHs, and an algorithm for determining the range of allowable structure types corresponding to a given PAH formula has been presented.

The interrelationships between the member structures corresponding to constant-isomer series with the same isomer number have been further elaborated. It has been shown that adjacency/nonadjacency of pentagonal rings in constant-isomer indacenoids with the same isomer number is another invariant of significance. Since no two isomers belonging to a constant-isomer series are expected to have exactly the same stability (e.g., the E_x values), the final invariant used to obtain a unique one-to-one matching among correspondents with

the same symmetry and other relevant topological properties is the relative order of stability.

GLOSSARY

d_s	net tree disconnections of internal graph edges (positive values) or connections (negative values called negative disconnection)
N_c	total number of carbon atoms in a PAH
N_H	total number of hydrogen atoms in a PAH
N_{ic}	number of internal carbon atoms in a PAH having a degree of 3
N_{pc}	number of peripheral carbon atoms in a PAH having a degree of 3
PAH6	polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings; also referred to as polyhex
$ P = p = N_c$	total number of graph points
$ Q = q$	number of graph edges (lines or C-C bonds)
q_i	number of internal graph edges
q_p	number of peripheral graph edges
r	number of rings
r_n	number of rings or cycles having n vertices
Table PAH6	table of formulas corresponding to exclusively fused benzenoid structures
Table PAH6(even)	subset of Table PAH6 which only includes even-carbon benzenoids
Table PAH6(odd)	subset of Table PAH6 which only includes odd-carbon benzenoids

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