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Constant-isomer benzenoid series and their polyradical subsets

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Summary. Constant-isomer benzenoids are partitioned into their nonradical or monoradical and diradical, triradical, tetraradical, et cetera subsets. It is shown that the isomer numbers for the monoradical, diradical, triradical, and tetraradical, et cetera subsets are exactly the same and that a one-to-one correspondence in symmetry, number of bay regions, and selective lineations exist between the benzenoid sets having the same isomer numbers.

Key words: Benzenoids – Isomers – Enumeration – Polyradicals – Symmetry

1. Introduction

In the previous paper [1], constant-isomer benzenoid series and their topological correspondences were described. The isomer numbers of these constant-isomer series exhibited an alternating singlet and doublet occurrence. Benzenoid members of those isomer series having the same isomer number revealed a one-to-one matching in the properties of symmetry, number of bay regions, and number of selective lineations. It was shown that even carbon diradical and odd carbon monoradical benzenoids possessed a one-to-one correspondence in isomer numbers, symmetry, number of bay regions, and selective lineations. Herein, it will be shown that this one-to-one correspondence is duplicated between the even carbon tetraradicals and the odd carbon triradical benzenoids. This led us to conjecture and verify that this same correspondence also exists between even carbon hexaradical and odd carbon pentaradical benzenoids, and so forth. Given that total resonant sextet benzenoids also have constant-sextet-isomer series with isomer numbers that are totally congruent with the isomer numbers associated with even carbon and odd carbon constant-isomer benzenoid series [2], we suggest that these correspondences may constitute the essence of a new topological paradigm.

Odd carbon strictly peri-condensed benzenoids have been observed as pyrolytic intermediates [3]. During carbonization, the onset of mesophase formation occurs concomitantly with appreciable concentrations of benzenoid free radicals [4]. Also, the presence of benzenoid free radicals in interstellar space has been alluded [5]. Thus, this study is an important contribution to the further understanding of this class of compounds [6].

The formula periodic table for benzenoids (Table PAH6) and enumeration studies provide the framework for understanding the limits of what we do and can know about benzenoid hydrocarbons. Thus, this epistemology also represents an important aspect of the results presented herein.

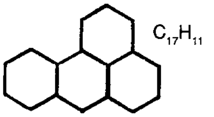
2. Definitions and terminology

In this paper a benzenoid structure is represented by a polyhex molecular graph in which all the C and H atoms and C–H and $p\pi$ bonds are omitted leaving only the C–C σ-bond skeleton having only second- and third-degree vertices [1, 7, 8]. A strictly peri-condensed benzenoid has no cata-condensed appendage or disconnected internal third-degree vertices. Benzo[α]pyrene (a well-known carcinogen) and perylene are not strictly peri-condensed because the former has a cata-condensed appendage (the benzo moiety) and the latter has disconnected internal third-degree vertices. An excised internal structure of a benzenoid hydrocarbon consists of all its connected internal third-degree vertices that remain after stripping off all the peripheral second- and third-degree vertices. Pyrene ($C_{16}H_{10}$) is a strictly peri-condensed benzenoid with an ethene excised internal structure. Since ethene is incapable of having isomers, pyrene has no other benzenoid isomer since it has only one arrangement of its internal third-degree vertices. If pyrene is circumscribed by a perimeter of carbon atoms and incremented by 6H's, one obtains the only $C_{42}H_{16}$ benzenoid isomer since its internal third-degree vertices have only one possible polyhex arrangement. Both $C_{16}H_{10}$ and $C_{42}H_{16}$ are formulas found on the left-hand staircase edge of Table PAH6. Successive repetition of this process generates the one-isomer series starting with the basis structure of pyrene. This summarizes the fundamental principle behind the constant-isomer series.

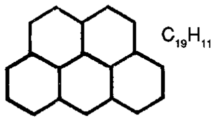
Odd carbon benzenoid hydrocarbons are odd radical species. Even carbon benzenoids can be even radical or nonradical (zero radical) species. Here it is worthwhile to note that, for example, a triradical has three nonbonding Hückel MOs (i.e., three zero eigenvalues) and a minimum number of three unpaired electron sites for any system of electron pairing. A formula periodic table for odd carbon benzenoids is referred to as Table PAH6(odd) [6]. Table PAH6 refers to the formula periodic table for even carbon benzenoids or generically to both even and odd benzenoids.

Randić and Trinajstić restrict their use of *benzenoid* to nonradical polyhex molecular structures [8], whereas Cyvin and Gutman are less restrictive and classify benzenoid hydrocarbons into Kekulean (having at least one 1-factor subgraph) and non-Kekulean (radical benzenoids) [9]. While it is true that small free radical ($< C_{50}$) polyhex molecules have never been characterized, it is also true that free radicals play a very important role in reaction chemistry [3–6]. Given the universe of possible free radicals that temporarily form during the course of a chemical reaction, the conjugated polyhex radicals are among the more stable ones, i.e., they are the benzenoids of radical species. The existence of a polyhex Kekule structure does not guarantee that the corresponding molecule will stably exist. It is well known that relatively large acenes and zethrenes, the latter for which $K = 9$, do not stably exist. But even Randić and Trinajstić refer to these unstable species as benzenoid hydrocarbons [8]. Thus, the benzenoid definition of Randić and Trinajstić does not always identify species that are chemically stable.

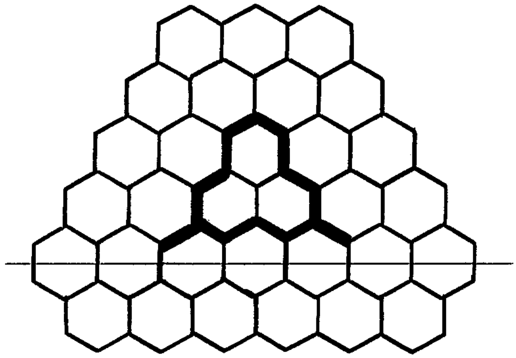
One conceptual barrier that the advocates for exclusive use of the term *benzenoid* for only even carbon nonradical conjugated polyhexes must overcome is that of overlapping nomenclature. For example, the following molecules below are illustrative. Since the general practitioner will find it difficult to psychologically accept that these monoradicals are not benzenoid hydrocarbons but yet are still named according to benzenoid nomenclature, this paper follows the Cyvin and Gutman definition of a benzenoid.


$C_{17}H_{11}$

Benzo [*de*] anthryl


$C_{19}H_{11}$

Dibenzo [*def,jk*] phenanthryl
(Benzo [*cd*]pyrenyl)


$C_{83}H_{23}, C_{2v}$

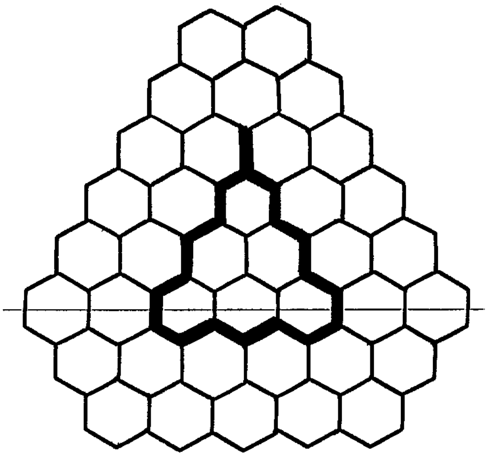

$C_{99}H_{25}, C_{2v}$

Fig. 1. The triradical benzenoids of $C_{83}H_{23}$ and $C_{99}H_{25}$ with their ultimate excised internal structures shown in *bold*

Table 1. Constant-isomer series of monoradical strictly peri-condensed benzenoid hydrocarbons

Series	No. of monoradical isomers	Symmetry distributions[a]
$C_{13}H_9$ $C_{37}H_{15}$ ...	1	$D_{3h}(0, 1^3)$
$C_{19}H_{11}$ $C_{47}H_{17}$ ...	1	$C_{2v}(0, 1)$
$C_{27}H_{13}$ $C_{59}H_{19}$ ...	1	$C_{2v}(0, 1)$
$C_{35}H_{15}$ $C_{71}H_{21}$ ...	2	$C_s(0)$, $C_s(1, 1^2)$
$C_{45}H_{17}$ $C_{85}H_{23}$ ...	4	$C_{2v}(0, 1)$, $C_s(1, 1^2) - 2$, $C_s(1)$
$C_{57}H_{19}$ $C_{101}H_{25}$ ...	4	
$C_{69}H_{21}$ $C_{117}H_{27}$ ...	12	$C_s(1) - 2$, $C_s(1, 1) - 4$, $C_s(1, 1^2) - 2$, $C_{2v}(2, 1) - 2$ $C_{2v}(2, 1^4)$, $C_s(2, 1)$
$C_{83}H_{23}$ $C_{135}H_{29}$ ...	19	$C_s(0)$, $C_s(1) - 3$, $C_s(1, 1) - 4$, $C_s(1, 1^2) - 2$, $C_{2v}(2, 1^2)$, $C_{2v}(2, 1^3) - 2$, $C_s(2, 1) - 5$, $C_s(2, 1^3)$
$C_{99}H_{25}$ $C_{155}H_{31}$ ...	19	
$C_{115}H_{27}$ $C_{175}H_{33}$ ...	46	$C_{3h}(3)$, $C_{2v}(0, 1) - 2$, $C_s - 43$

[a] Symmetry group (η_0, No. selective lineations) – No. of benzenoid members. η_0 is the number of bay regions. For each selective lineation, the benzenoid molecular graph possesses an eigenvalue of $\varepsilon = \pm 1$

[b] Number of bay regions and selective lineations were not determined

Benzenoid hydrocarbons have highly ordered arrangements of hexagonal rings analogous to a mosaic constructed from a single tile shape. The repeating motif of benzenoids is the hexagonal ring of carbon atoms. According to well-established theorems of polyhexagonal systems, only a small list of rotational symmetries is possible for benzenoids [10]. They can have twofold, threefold, or sixfold axes of rotational symmetry and no other possibilities.

Topology is a branch of mathematics which studies those properties of objects that do not change when the object is elastically deformed. A circle, triangle, and a square are all topologically equivalent. Symmetry defines an equivalence relationship among the vertices of a molecular graph and is a graphical invariant since elastic deformation does change this equivalence, but only makes it less obvious depending on the presentation. All planar benzenoids are homeomorphic. Topology forgets all the hexagonal rings, (carbon) vertices,

Table 2. Constant-isomer series of even carbon strictly peri-condensed benzenoids and their diradicals

Series	No. of diradical isomers	Series	No. of diradical isomers
$C_{22}H_{12}$ $C_{52}H_{18}$ ...	1	$C_{184}H_{34}$ $C_{258}H_{40}$ ...	70
$C_{30}H_{14}$ $C_{64}H_{20}$ ...	1	$C_{206}H_{36}$ $C_{284}H_{42}$ ...	162
$C_{40}H_{16}$ $C_{78}H_{22}$ ...	1	$C_{230}H_{38}$ $C_{312}H_{44}$ ...	239
$C_{50}H_{18}$ $C_{92}H_{24}$ ...	2	$C_{256}H_{40}$ $C_{342}H_{46}$ ...	239
$C_{62}H_{20}$ $C_{108}H_{26}$ ...	4	$C_{282}H_{42}$ $C_{372}H_{48}$ ...	504
$C_{76}H_{22}$ $C_{126}H_{28}$ ...	4	$C_{310}H_{44}$ $C_{404}H_{50}$ ...	726
$C_{90}H_{24}$ $C_{144}H_{30}$ ...	12	$C_{340}H_{46}$ $C_{438}H_{52}$ ...	726
$C_{106}H_{26}$ $C_{164}H_{32}$ ...	19	$C_{370}H_{48}$ $C_{472}H_{54}$ ...	1471[a]
$C_{124}H_{28}$ $C_{186}H_{34}$ ...	19	$C_{402}H_{50}$ $C_{508}H_{56}$ ...	2062[a]
$C_{142}H_{30}$ $C_{208}H_{36}$ ...	46	$C_{436}H_{52}$ $C_{546}H_{58}$ ...	2062[a]
$C_{162}H_{32}$ $C_{232}H_{38}$ ...	70		

[a] Derived from data in Ref. [13]

et cetera – it forgets all the interesting chemical and graphical properties. When two benzenoids have the same isomer number, symmetry, number of bay regions, and number of selective lineations, they are said to be *isotopological.* Since all benzenoids trivially have the same topology, this definition is stronger, and coincides more closely with the usual intuitive chemical meaning of *shape* for topology. Benzenoid correspondents belonging to the constant-isomer series are isotopological.

3. Enumeration of constant-isomer benzenoid series

The enumeration of constant-isomer benzenoid series utilizes our excised internal structure concept [11]. The algorithm has been published and is not repeated

Table 3. Constant-isomer series of even carbon strictly peri-condensed benzenoids and their tetraradicals

Series	No. of tetraradical isomers	Series	No. of tetraradical isomers
$C_{142}H_{30}$ $C_{208}H_{36}$ ...	1	$C_{282}H_{42}$ $C_{372}H_{48}$ ...	12
$C_{162}H_{32}$ $C_{232}H_{38}$ ...	1	$C_{310}H_{44}$ $C_{404}H_{50}$ ...	19[a]
$C_{184}H_{34}$ $C_{258}H_{40}$ ...	1	$C_{340}H_{46}$ $C_{438}H_{52}$ ...	19
$C_{206}H_{36}$ $C_{284}H_{42}$ ...	2	$C_{370}H_{48}$ $C_{472}H_{54}$ ...	46
$C_{230}H_{38}$ $C_{312}H_{44}$ ...	4	$C_{402}H_{50}$ $C_{508}H_{56}$ ...	70
$C_{256}H_{40}$ $C_{342}H_{46}$ ...	4	$C_{436}H_{52}$ $C_{546}H_{58}$ ...	70

[a] This value and those below were determined by induction

here [12]. This algorithm is a logical construct whose validity has been corroborated by Cyvin and Brunvoll [13]. Constant-isomer series are strictly peri-condensed benzenoids (except for benzene and naphthalene) whose formulas are located at the extreme left-hand staircase edge of Table PAH6; they are the species that have maximal ratios of C to H. Circumscribing a set of isomeric basis structures (first generation excised internal structures) having formulas on this staircase edge with a perimeter of carbon atoms and incrementing with 6H's gives the total isomer set of successor (second generation) benzenoids. Our algorithm allows one to systematically derive the complete set of basis structures from isomeric sets having formulas not found on the staircase edge of Table PAH6.

Figure 1 gives an example of the excised internal structure concept showing the ultimate excised internal structure. If a strictly peri-condensed benzenoid has N_c' carbons and N_H' hydrogens and its excised internal structure has N_c carbons and N_H hydrogens, then $N_c' = N_c + 2N_H + 6$ and $N_H' = N_H + 6$ represent useful recursion relationships for obtaining successive strictly peri-condensed formulas [12, 14].

Table 1 gives the number of monoradical benzenoids and the associated symmetry distributions of these isomers; note that last three series of Table 1 have triradical isomers that are not included. These results were previously presented where it was established that the diradical even carbon benzenoids (Table 2) have a one-to-one correspondence to the monoradical odd carbon benzenoids in regard to their isomer numbers and topological characteristics of the benzenoid members. The topological characteristics defined were number of bay regions (η_0), selective lineations, (lines scored through structures that

Table 4. Constant-isomer series and odd carbon strictly peri-condensed benzenoids and their triradicals

Series	No. of triradical isomers	Series	No. of triradical isomers
$C_{69}H_{21}$ $C_{117}H_{27}$ ...	1	$C_{219}H_{37}$ $C_{299}H_{43}$ ...	19
$C_{83}H_{23}$ $C_{135}H_{29}$ ...	1	$C_{243}H_{39}$ $C_{327}H_{45}$ ...	46
$C_{99}H_{25}$ $C_{155}H_{31}$ ...	1	$C_{269}H_{41}$ $C_{357}H_{47}$ ...	70
$C_{115}H_{27}$ $C_{175}H_{33}$ ...	2	$C_{297}H_{43}$ $C_{389}H_{49}$ ...	70
$C_{133}H_{29}$ $C_{197}H_{35}$ ...	4	$C_{325}H_{45}$ $C_{421}H_{51}$ ...	162
$C_{153}H_{31}$ $C_{221}H_{37}$ ...	4	$C_{355}H_{47}$ $C_{455}H_{53}$ ...	239
$C_{173}H_{33}$ $C_{245}H_{39}$ ...	12	$C_{387}H_{49}$ $C_{491}H_{55}$ ...	239
$C_{195}H_{35}$ $C_{271}H_{41}$ ...	19[a]		

[a] This value and those below were determined by induction

correspond to ±1 eigenvalues), and symmetry. If a monoradical belonging to a constant-isomer series has N_H hydrogens and N_c carbons and its diradical correspondent has N''_H hydrogens and N''_c carbons, then $N''_H = N_H + 3$ and $N''_c = N_H + N_c$.

Using the previously published algorithm [12], it will now be shown that the same isomer numbers present in Tables 1 and 2 appear when the even carbon tetraradical (Table 3) and odd carbon triradical (Table 4) benzenoids are sorted out from the constant-isomer series and that the corresponding benzenoid members exhibit the same one-to-one matching in regard to the topological characteristics defined above. Figures 2 to 6 give the ultimate excised internal structures of the tetraradical (left side) and triradical (right side) correspondents to the constant-isomer series in Tables 3 and 4. There is only one triradical and tetraradical for each (Fig. 2) of the series beginning with $C_{142}H_{30}$ and $C_{69}H_{21}$, $C_{162}H_{32}$ and $C_{83}H_{23}$, and $C_{184}H_{34}$ and $C_{99}H_{25}$, and, as it can be seen from Fig. 2, there is a one-to-one matching in topological characteristics between the members belonging to each of these odd carbon and even carbon series; both $C_{142}H_{30}$ and $C_{69}H_{21}$ have D_{3h} symmetry while the other pairs have C_{2v} symmetry. While the symmetries are evident in the ultimate excised internal structures

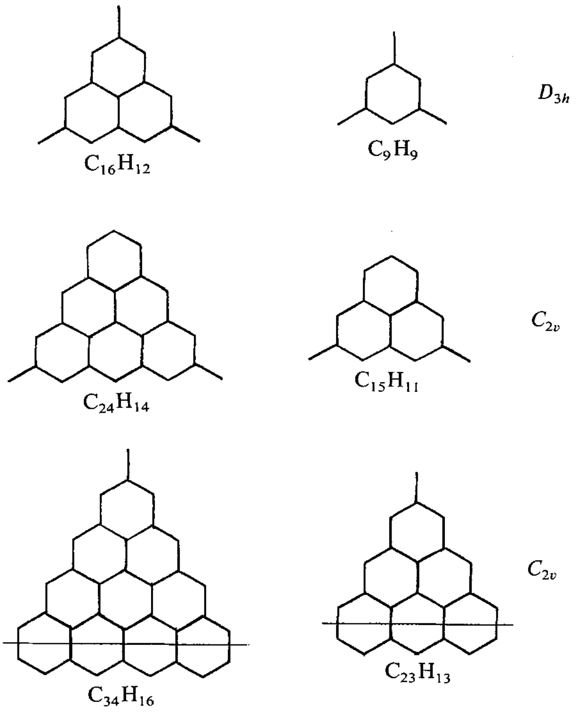


Fig. 2. Ultimate excised internal structures of the tetraradical (*left*) and triradical (*right*) series starting with the respective formulas of $C_{142}H_{30}$, $C_{162}H_{32}$, $C_{184}H_{34}$ (*left*) and $C_{69}H_{21}$, $C_{83}H_{23}$, $C_{99}H_{25}$ (*right*)

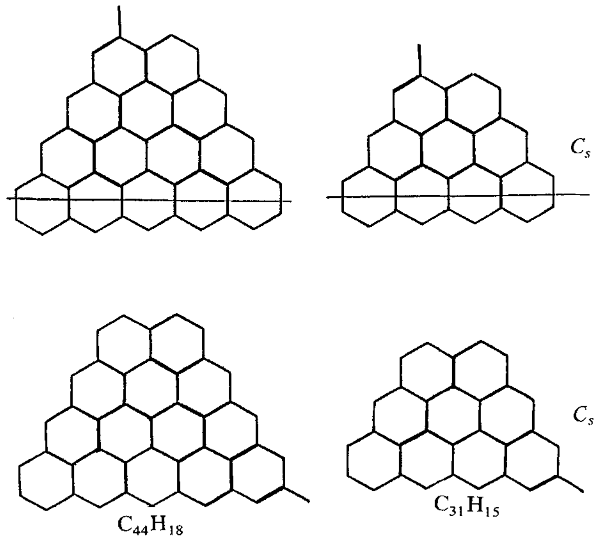


Fig. 3. Ultimate excised internal structures of the tetraradical $C_{206}H_{36}$ (*left*) and triradical $C_{115}H_{27}$ (*right*) benzenoid series

shown in Figs. 2 to 6, the total number of bay regions and selective lineations are only evident in the fully circumscribed benzenoid structures (cf. with Fig. 1). None of the benzenoids associated with the ultimate excised internal structures in Fig. 2 have bay regions, and each of the benzenoids corresponding to the C_{2v}

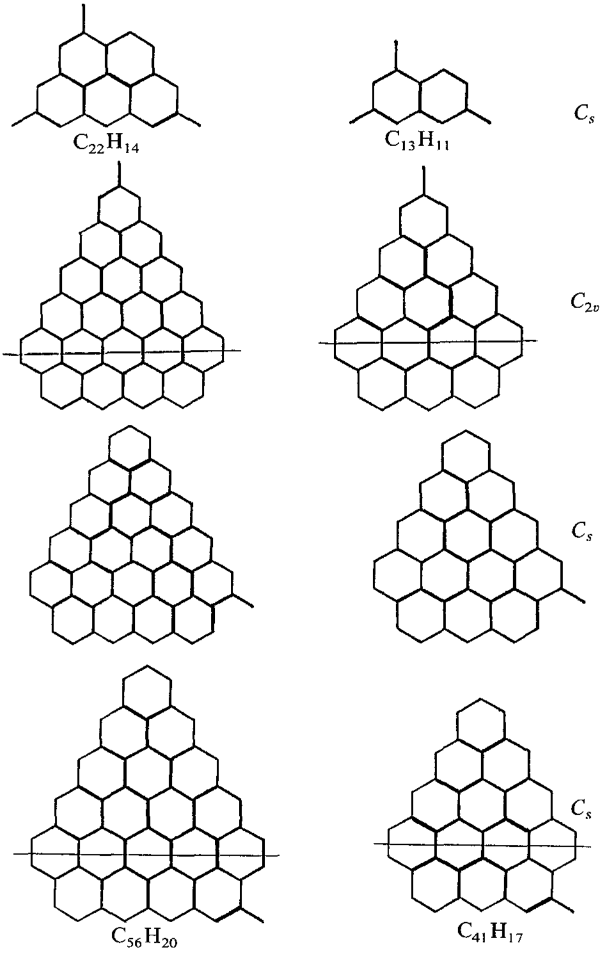


Fig. 4. Ultimate excised internal structures of the tetraradical $C_{230}H_{38}$ (*left*) and triradical $C_{133}H_{29}$ (*right*) benzenoid series

excised internal structures have one selective lineation while the ones with D_{3h} have three selective lineations.

There are two tetraradical and two triradical isomers in the benzenoid series beginning with $C_{206}H_{36}$ and $C_{115}H_{27}$, respectively, in Tables 3 and 4. Figure 3 shows that the corresponding benzenoids all have C_s symmetry; one tetraradical and triradical isomer member has one bay region and two selective lineations and the other has neither. The four tetraradical benzenoids for each of the series beginning with $C_{230}H_{38}$ and $C_{256}H_{40}$ in Tables 3 and 4 triradical benzenoids for each of the series beginning with $C_{133}H_{29}$ and $C_{153}H_{31}$ in Table 4 have ultimate excised internal structures shown in Figs. 4 and 5. In each series there is one benzenoid member with C_{2v} symmetry and there are three benzenoid members with C_s symmetry. Figure 6 gives the 3 C_{2v} and 9 C_s tetraradical (left) and triradical ultimate excised internal structures corresponding to the benzenoid series starting with $C_{282}H_{42}$ and $C_{173}H_{33}$, respectively. In general, if a constant-isomer series triradical has N_H hydrogens and N_c carbons and its tetraradical

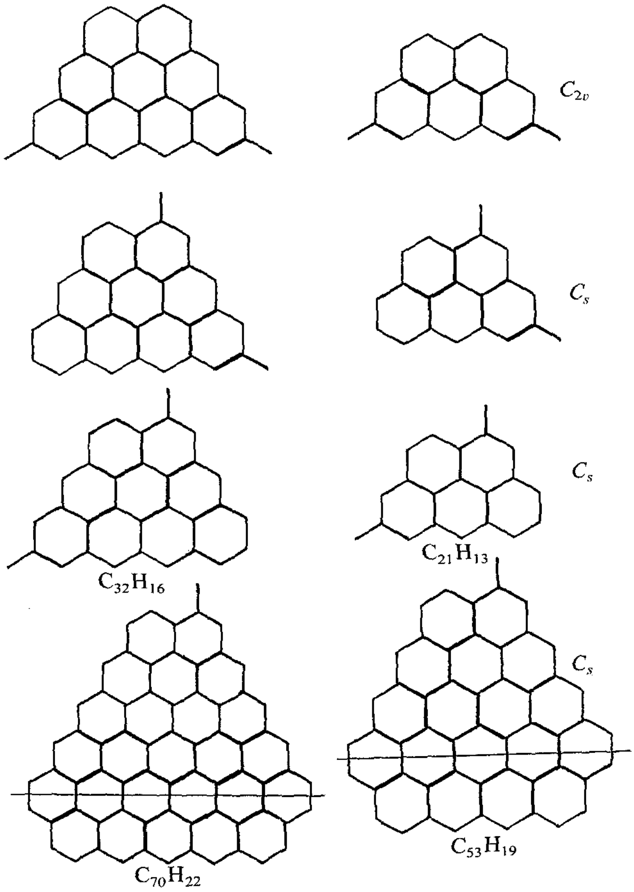


Fig. 5. Ultimate excised internal structures of the tetraradical $C_{256}H_{40}$ (*left*) and triradical $C_{153}H_{31}$ (*right*) benzenoid series

correspondent has N_H'''' hydrogens and N_c'''' carbons, then $N_H'''' = N_H + 9$ and $N_c'''' = 3N_H + N_c + 10$.

Thus, the number of even carbon tetraradical and odd carbon triradical constant-isomer benzenoids possess a one-to-one matching in regard to their number of isomers and topological characteristics. It can be shown by induction that the even carbon hexaradical benzenoids will also have same one-to-one matching with the odd carbon pentaradical benzenoids, and so on. Also, using the isomer numbers deduced in Tables 2 and 3, one can add up all the even carbon diradicals and tetraradicals and substract them from the total number of isomers previously published [1, 13] for the constant-isomer series in Table 5 to obtain the number of nonradical benzenoids. Note here that pentaradicals first appear in the $C_{325}H_{45}$, $C_{355}H_{47}$, and $C_{387}H_{49}$ constant-isomer series. Similarly, hexaradical benzenoids first appear in the $C_{582}H_{60}$, $C_{622}H_{62}$, and $C_{664}H_{64}$ constant-isomer series [1]. Figure 7 gives the ultimate excised internal structures of the smallest monoradical and polyradical constant-isomer benzenoid series; note that they all have D_{3h} symmetry. By a similar uniform construction process, it can be inductively shown that this congruency in isomer number, symmetry,

Table 5. Constant-isomer series of even carbon strictly peri-condensed benzenoids

Series	No. of isomers	Series	No. of isomers
$C_{206}H_{36}$ $C_{284}H_{42}$ ...	264 (164)[a]	$C_{340}H_{46}$ $C_{438}H_{52}$ ...	1055 (745)
$C_{230}H_{38}$ $C_{312}H_{44}$ ...	373 (243)	$C_{370}H_{48}$ $C_{472}H_{54}$ ...	2022 (1517)[b]
$C_{256}H_{40}$ $C_{342}H_{46}$ ...	373 (243)	$C_{402}H_{50}$ $C_{508}H_{56}$ ...	2765 (2132)[b]
$C_{282}H_{42}$ $C_{372}H_{48}$ ...	749 (516)	$C_{436}H_{52}$ $C_{546}H_{58}$ ...	2765 (2132)[b]
$C_{310}H_{44}$ $C_{404}H_{50}$ ...	1055 (745)		

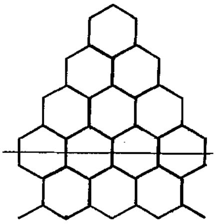
[a] The number of less stable radical isomers is given in parentheses
[b] Derived from data in Ref. [13]

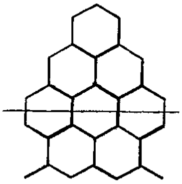
and number of bay regions and selective lineations must persist for all polyradicals belonging to the constant-isomer benzenoid series. Since the isomer number sequence for the monoradicals (Table 1), diradicals (Table 2), triradicals (Table 4), tetraradicals (Table 3), pentaradicals, et cetera are exactly identical, one can use the recursion pattern evident in Tables 1 to 4 to extend these results even further.

4. Conclusion

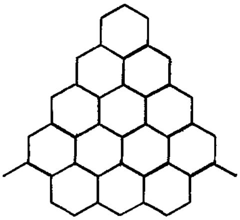
This work further characterizes constant-isomer benzenoid series according to their radical properties, symmetry, and number of isomers, bay regions, and selective lineations. Additional isomer numbers for nonradical constant-isomer benzenoid series have been determined. A spectacular congruency between the above characteristics for constant-isomer benzenoids has been elaborated.

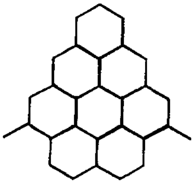
This work is a further contribution toward our comprehensive study of benzenoids. Study of less stable radical benzenoids is important because they probably occur as reactive intermediates. Also, the study of less stable species enhances our understanding of more stable ones through intercomparison of their characteristics. An important component of this process is the enumeration of all possible isomers which allows one to compare known species against this list so that one can begin to speculate why some isomers occur and others do not.



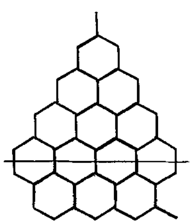


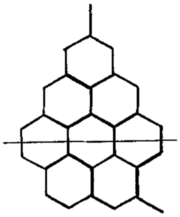
C_{2v}



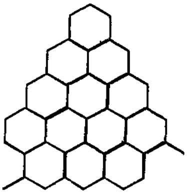


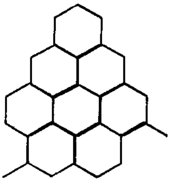
C_{2v}



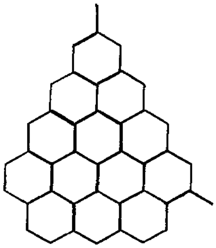


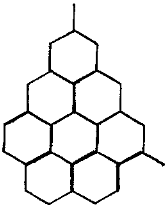
C_s





C_s





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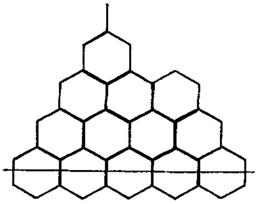

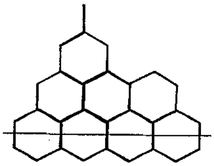

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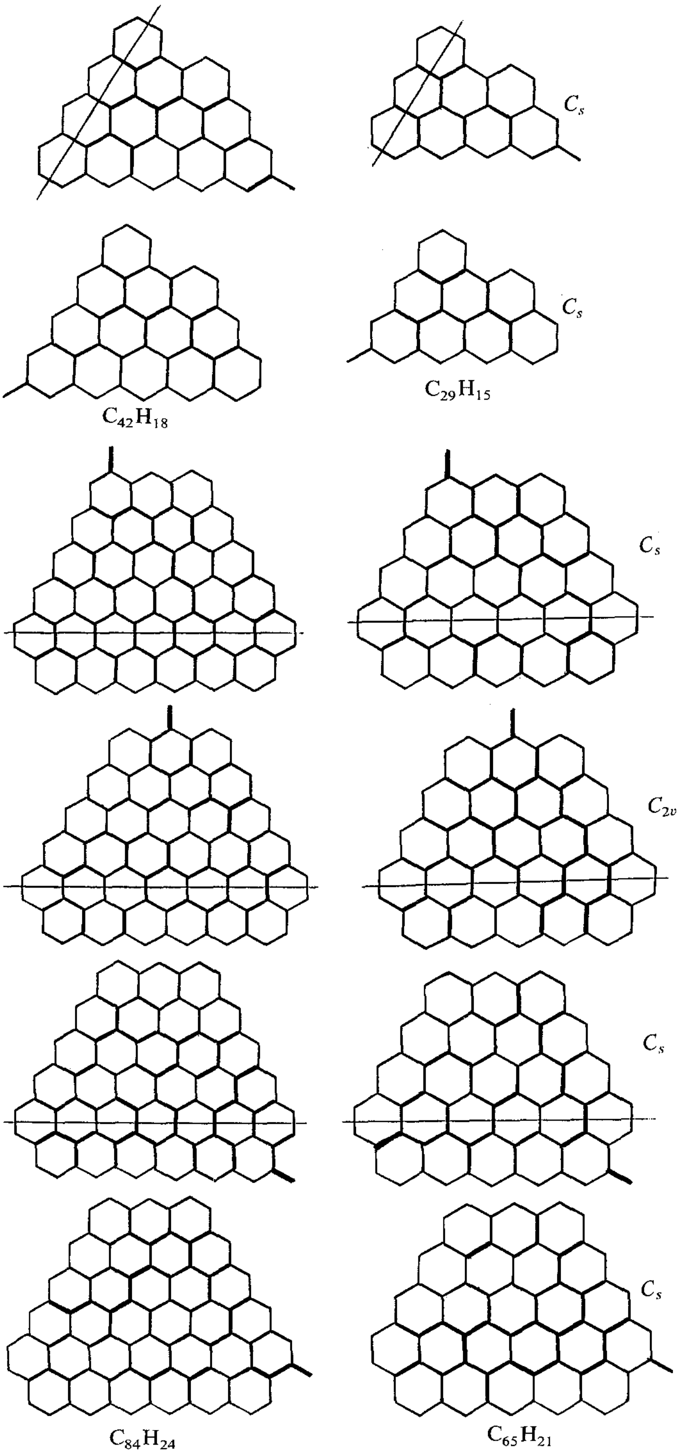

Fig. 6. Ultimate excised internal structures of the tetraradical $C_{282}H_{42}$ (*left*) and triradical $C_{173}H_{33}$ (*right*) benzenoid series

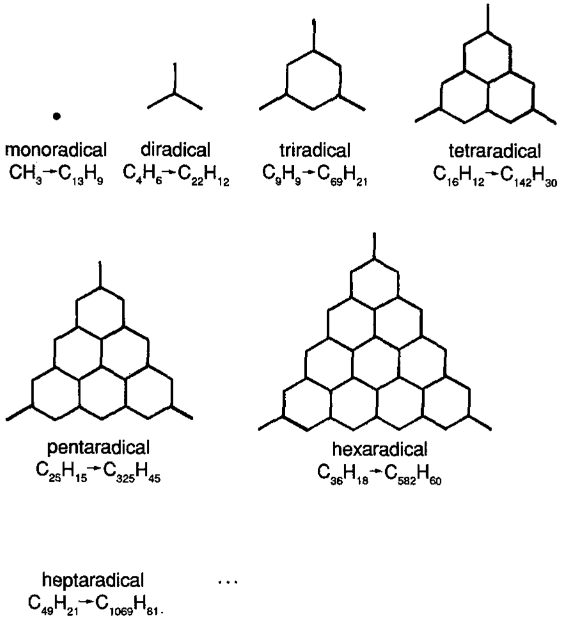

Fig. 7. Ultimate excised internal structures of the smallest monoradical and polyradical constant-isomer benzenoid series

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