Topological Characteristics of Strictly Pericondensed Constant-Isomer Benzenoid Series

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Our previous constant-isomer series are supplemented and extended. Two distinct classes of constant-isomer benzenoid groups have been identified. One class is topologically unique and the other one forms a pairwise topologically equivalent class.

Introduction

Generally, as the number of carbons in alkanes increases, so does the number of isomers [1]. There exist, however, special benzenoid series in which the number of isomers remains constant as the number of carbons increases [2]. Through the recent availability of the benzenoid isomer table of Stojmenović and coworkers it was possible to extend these results [3].

Results and Discussion

Conceptual Tools

Using the formula periodic table for benzenoids (Table PAH6 = Table 1 in [4]) and the excised internal structure concept, several new strictly peri-condensed series possessing an identical number of isomers have been identified [5]. Strictly peri-condensed benzenoids have the property that the graph spanned by their internal carbon vertices (i.e., their excised internal structure) is connected. Pyrene ($C_{16}H_{10}$) has ethene, coronene ($C_{24}H_{12}$) has benzene, and ovalene ($C_{32}H_{14}$) has naphthalene ($C_{10}H_8$) as excised internal structures and are strictly peri-condensed benzenoids that are members of the one-isomer series found in Tables 1 and 2. All constant-isomer strictly peri-condensed benzenoids are found on the extreme left-hand edge of Table PAH6 and are devoid of adjacent or proximate bay regions (fjords and coves). This translates into benzenoids with perimeters having everywhere two-carbon-atom gaps or greater, which means that all these even carbon strictly peri-condensed benzenoids can serve as excised internal structures for other successor (larger) strictly peri-condensed benzenoids. Other strictly peri-condensed benzenoids on this edge possess some isomers with doublet bay regions (coves) and are antecedents, but not members, of constant-isomer series. Herein, we present a refinement of our previously published algorithm [2, 4–6] which allows us to identify this subset of benzenoids that can not serve as excised internal structures. The use of the excised internal structure in generating the $C_{22}H_{12}$ constant-isomer series is illustrated in Fig. 1 of [4].

Constant-Isomer Series of Strictly Peri-condensed Benzenoids

Tables 1 and 2 present all known benzenoid constant-isomer series in which the latter are now reported for the first time. Each table reveals the same distinct pattern in which the number of isomers alternate between singlet and doublet occurrence. Also, the pattern for the progressive increase in the first member formula of each series should be evident and will allow one to extend these tables even further.

Tables PAH6 and PAH6 (odd) have been published before and are not repeated here [4]. To determine when a formula C_nH_s ($n = N_c$ and $s = N_H$) is compatible with a strictly peri-condensed benzenoid occurring along the left-hand staircase edge of Table PAH6, one can use the mathematical results given by Harary and Harborth [7]. If a possible value n of N_c is given, then an integer s is a possible value of N_H if and only if

$$2\left\{\tfrac{1}{2}\left(n+\sqrt{6n}\right)\right\} - n \leqq s \leqq n+2-2\left\{\frac{n-2}{4}\right\}, \qquad (1)$$

where $\{x\}$ is used to denote the smallest integer larger than or equal to x. Thus, in the following algorithm

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Table 1. Constant-isomer series of even strictly peri-condensed benzenoids.

Initial term (P=1)	Series N_c	N_H	Number of isomers
C_6H_6	$6p^2$	$6p$	1
$C_{10}H_8$	$6p^2+4p$	$6p+2$	1
$C_{16}H_{10}$	$6p^2+8p+2$	$6p+4$	1
$C_{22}H_{12}$	$6p^2+12p+4$	$6p+6$	2(1) [a]
$C_{30}H_{14}$	$6p^2+16p+8$	$6p+8$	3(1)
$C_{40}H_{16}$	$6p^2+20p+14$	$6p+10$	3(1)
$C_{50}H_{18}$	$6p^2+24p+20$	$6p+12$	7(2)
$C_{62}H_{20}$	$6p^2+28p+28$	$6p+14$	12(4)
$C_{76}H_{22}$	$6p^2+32p+38$	$6p+16$	12(4)
$C_{90}H_{24}$	$6p^2+36p+48$	$6p+18$	27(12)
$C_{106}H_{26}$	$6p^2+40p+60$	$6p+20$	38(19)
$C_{124}H_{28}$	$6p^2+44p+74$	$6p+22$	38(19)
$C_{142}H_{30}$	$6p^2+48p+88$	$6p+24$	86(47)
$C_{162}H_{32}$	$6p^2+52p+104$	$6p+26$	128(71)
$C_{184}H_{34}$	$6p^2+56p+122$	$6p+28$	128(71)
$C_{206}H_{36}$	$6p^2+60p+140$	$6p+30$	264(164)
$C_{230}H_{38}$	$6p^2+64p+160$	$6p+32$	373(243)
$C_{256}H_{40}$	$6p^2+68p+182$	$6p+34$	373(243)
$C_{282}H_{42}$	$6p^2+72p+204$	$6p+36$	749(516)
$C_{310}H_{44}$	$6p^2+76p+228$	$6p+38$	1055(245)
$C_{340}H_{46}$	$6p^2+80p+254$	$6p+40$	1055(745)

[a] Number of radical isomers is given in parentheses.

Table 2. Constant-isomer series of odd strictly peri-condensed benzenoids.

Initial term (P=1)	Series N_c	N_H	Number of isomers
$C_{13}H_9$	$6p^2+6p+1$	$6p+3$	1
$C_{19}H_{11}$	$6p^2+10p+3$	$6p+5$	1
$C_{27}H_{13}$	$6p^2+14p+7$	$6p+7$	1
$C_{35}H_{15}$	$6p^2+18p+11$	$6p+9$	2
$C_{45}H_{17}$	$6p^2+22p+17$	$6p+11$	4
$C_{57}H_{19}$	$6p^2+26p+25$	$6p+13$	4
$C_{69}H_{21}$	$6p^2+30p+33$	$6p+15$	13
$C_{83}H_{23}$	$6p^2+34p+43$	$6p+17$	20
$C_{99}H_{25}$	$6p^2+38p+55$	$6p+19$	20
$C_{115}H_{27}$	$6p^2+42p+67$	$6p+21$	48
$C_{133}H_{29}$	$6p^2+46p+81$	$6p+23$	74
$C_{153}H_{31}$	$6p^2+50p+97$	$6p+25$	74
$C_{173}H_{33}$	$6p^2+54p+113$	$6p+27$	174
$C_{195}H_{35}$	$6p^2+58p+131$	$6p+29$	258
$C_{219}H_{37}$	$6p^2+62p+151$	$6p+31$	258
$C_{243}H_{39}$	$6p^2+66p+171$	$6p+33$	550
$C_{269}H_{41}$	$6p^2+70p+193$	$6p+35$	796
$C_{297}H_{43}$	$6p^2+74p+217$	$6p+37$	796 [a]

[a] Predicted value based on induction.

Table 3. Number of isomers of near-staircase edge strictly peri-condensed benzenoids.

Formula	Number of isomers [a, b]
$C_{111}H_{27}$	490
$C_{113}H_{27}$	167
$C_{129}H_{29}$	730
$C_{131}H_{29}$	251
$C_{149}H_{31}$	761
$C_{151}H_{31}$	255
$C_{171}H_{33}$	542
$C_{193}H_{35}$	787
$C_{217}H_{37}$	793
$C_{58}H_{20}$	85(44)
$C_{72}H_{22}$	103(53)
$C_{74}H_{22}$	36(17)
$C_{88}H_{24}$	79(42)
$C_{104}H_{26}$	121(65)
$C_{120}H_{28}$	$\underline{561}$
$C_{122}H_{28}$	125(69)
$C_{138}H_{30}$	$\underline{1160}$
$C_{140}H_{30}$	$\underline{413}$
$C_{158}H_{32}$	$\underline{1688}$
$C_{160}H_{32}$	$\underline{600}$
$C_{180}H_{34}$	$\underline{1733}$
$C_{182}H_{34}$	$\underline{610}$
$C_{204}H_{36}$	$\underline{1247}$
$C_{228}H_{38}$	$\underline{1781}$
$C_{254}H_{40}$	$\underline{1793}$

[a] The numbers of less stable diradical isomers are given in parentheses.
[b] The sums of radical and nonradical isomers are underlined.

one should use (1) to confirm whether a formula is a strictly peri-condensed benzenoid or not; i.e., whether it occurs on the left-hand staircase edge of Table PAH6 or not.

What is important about Table PAH6 in regard to isomer enumeration is that the formulas along the left-hand staircase-like extreme edge correspond to a relatively small number of benzenoid isomers. It will be shown that by manually enumerating a few isomers corresponding to the smaller formulas on this edge, one can then conceptually enumerate the isomers corresponding to the remaining formulas along this edge.

Figure 1 depicts all 35 of the $C_{41}H_{17}$ benzenoid isomers previously published [2], except the last triradical having inadvertently been omitted. They were generated by enumerating their excised internal structures shown in bold. Subtracting C_4H_2 from $C_{41}H_{17}$, one obtains $C_{37}H_{15}$, which is the second generation of the first one-isomer series (starting with $C_{13}H_9$) given in Table 2. Use of our aufbau algorithm on this $C_{37}H_{15}$ benzenoid gives the ultimate $C_{41}H_{17}$ benzobenzenoid isomer (Fig. 1) which is not strictly peri-condensed. Only one of these $C_{41}H_{17}$ benzenoids has a cove and can not serve as an excised internal structure. Subtracting CH from $C_{41}H_{17}$ gives $C_{40}H_{16}$ which corresponds to 4 benzenoid isomers [2, 6]. All combinatorial attachments of CH methylenyl units (done by replacing a hydrogen by CH and placing this H onto the CH) in these 4 isomers avoiding less than two carbon-atom gaps that occur at the edge of bay regions generates 34 methylenylbenzenoid isomers of

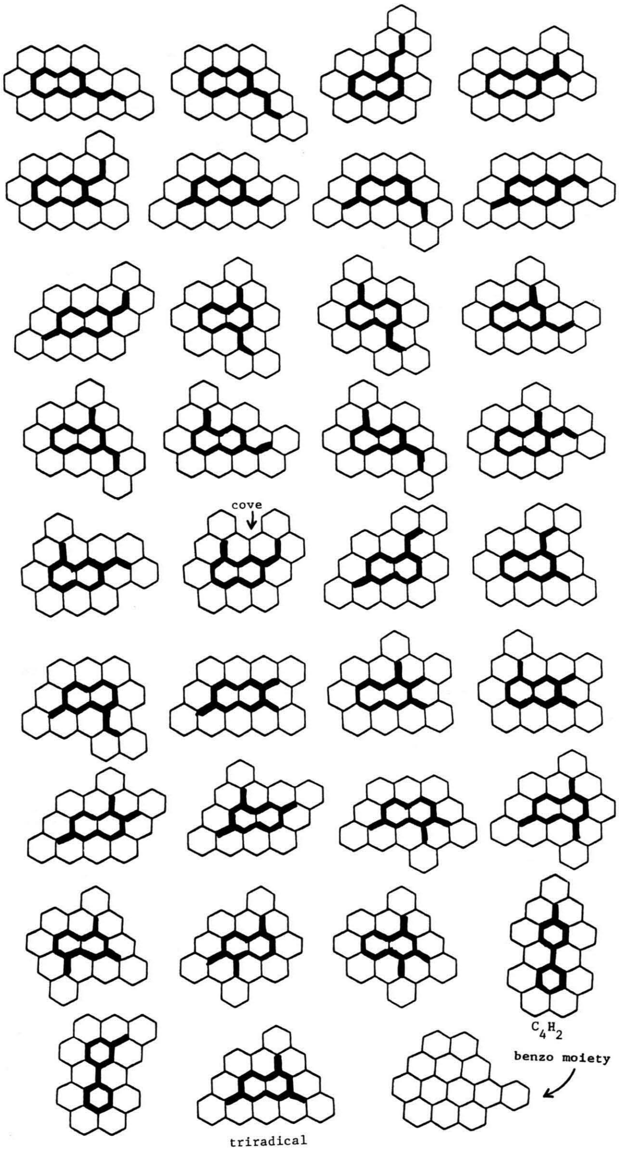


Fig. 1. The 35 $C_{41}H_{17}$ isomers with their excised internal structures shown in bold.

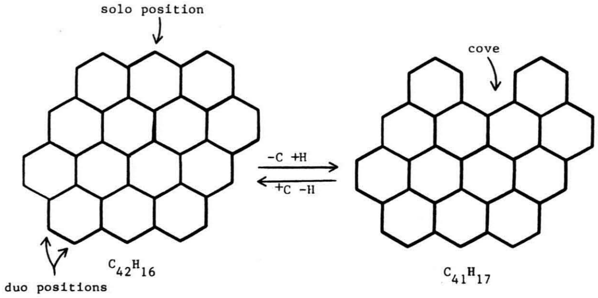
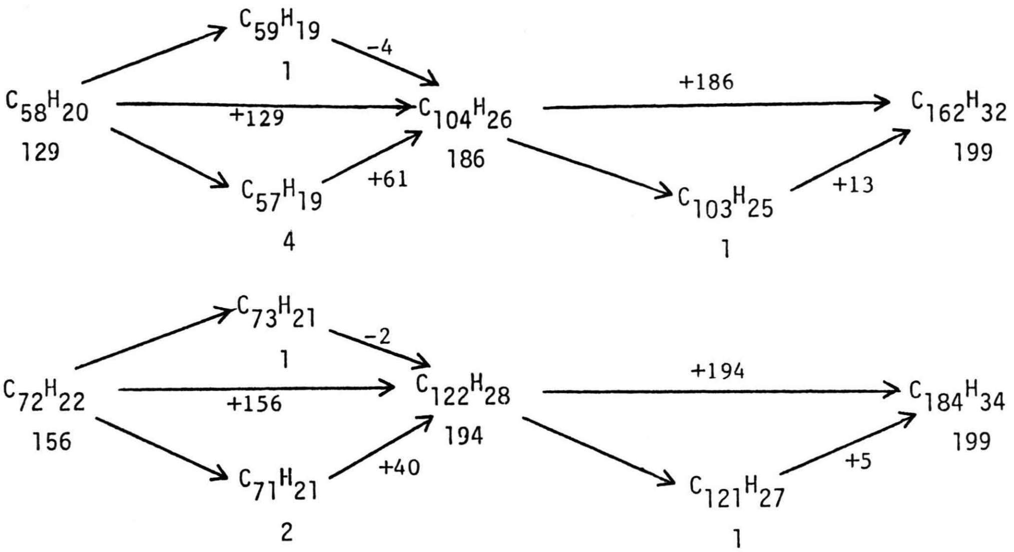


Fig. 2. Algorithmic determination of strictly peri-condensed benzenoid isomers having doublet bay regions (coves).

$C_{41}H_{17}$. Circumscribing a 40-carbon atom perimeter around these 68 $C_{41}H_{17}$ isomers and incrementing with 6 Hs gives 68 $C_{81}H_{23}$ benzenoid isomers. As determined by (1) $C_{77}H_{21}$ is not found on Table PAH6 (odd) and, therefore, does correspond to a benzenoid. This means there are no benzo isomers of the formula $C_{81}H_{23}$. Subtracting CH from $C_{81}H_{23}$ gives $C_{80}H_{22}$ which corresponds to the third formula of the one-isomer series commencing with pyrene. All combinatorial attachments of a CH methylenyl unit to this dicircumpyrene gives 6 $C_{81}H_{23}$ methylenylbenzenoid isomers. Circumscribing a 52-carbon atom perimeter around these $68+6=74$ isomers and incrementing with 6 Hs gives the base members of the constant-isomer series beginning with $C_{133}H_{29}$. Subtracting CH from $C_{133}H_{29}$ gives $C_{132}H_{28}$, which is not found in Table PAH6 as determined by (1). Thus, there are only 74 strictly peri-condensed benzenoid isomers of the formula $C_{133}H_{29}$ which serve as base members for the relevant constant-isomer series. Suppose one did not have the 35 $C_{41}H_{17}$ benzenoid depictions. How would one know how may benzenoids possessed coves and could not serve as excised internal structures? The answer is quite simple and represents a new refinement to our published algorithm [2, 4] summarized by this example. Add one carbon and subtract one hydrogen from $C_{41}H_{17}$ to get $C_{42}H_{16}$ which is circumpyrene shown in Figure 2. If any of the four equivalent solo positions are deleted, one obtains the $C_{41}H_{17}$ structure having a cove (Figs. 1 and 2).

Lets now apply this algorithm to the data provided by Stojmenović and coworkers [3]. Consider $C_{58}H_{20}$, which has 129 benzenoid isomers [3]. Adding C and subtracting H from $C_{58}H_{20}$ gives $C_{59}H_{19}$, which corresponds to the second generation of the third one-isomer series in Table 2, which has 4 different solo positions [5], the deletion of which gives 4 $C_{58}H_{20}$ benzenoid isomers with coves. Subtracting 4 from 129 gives 125 benzenoid $C_{58}H_{20}$ isomers that serve as excise internal structures. Subtracting CH from $C_{58}H_{20}$ gives $C_{57}H_{19}$, which corresponds to the first numbers of the second four-isomer series in Table 2. These 4 $C_{57}H_{19}$ isomers give 61 $C_{58}H_{20}$ methylenylbenzenoids. Circumscribing a 46-carbon atom perimeter around these $125+61=186$ $C_{58}H_{20}$ isomers and incrementing with 6 Hs gives 186 $C_{104}H_{26}$ ben-



Scheme 1. Algorithmic determination of the number of isomers of $C_{162}H_{32}$ and $C_{184}H_{34}$.

zenoid isomers. This derived isomer number of 186 for $C_{104}H_{26}$ agrees with the one given by the data of Stojmenović and coworkers [3] and constitutes verification of our algorithm. Since the formulas of $C_{100}H_{24}$ and $C_{105}H_{25}$ do not exist in Tables PAH6 and PAH6 (odd), there are no benzobenzenoid or benzenoid isomers with coves corresponding to $C_{104}H_{26}$. Subtracting CH from $C_{104}H_{26}$ gives $C_{103}H_{25}$ which corresponds to the third generation of the last one-isomer series in Table 2, to which attaching a CH methylenyl group gives 13 methylenylbenzenoids corresponding to $C_{104}H_{26}$. Circumscribing these $186+13=199$ $C_{104}H_{26}$ isomers with a 58-carbon perimeter and incrementing with 6 Hs gives 199 $C_{162}H_{32}$ strictly peri-condensed benzenoid base members of the relevant constant-isomer series. Consider $C_{72}H_{22}$ which has 156 isomers [3].

Repeating our algorithm starting with this formula gives 194 $C_{122}H_{28}$ isomers and finally 199 isomers for the base members of the constant-isomer series commencing with $C_{184}H_{34}$. Scheme 1 summarizes these results. It should be noted that $C_{59}H_{19}$ and $C_{103}H_{25}$ used in the algorithmic determination of the isomer number for $C_{162}H_{32}$ belong to the same one-isomer series, and $C_{73}H_{21}$ and $C_{121}H_{27}$ used in the algorithmic determination of the isomer number for $C_{184}H_{34}$ belong to the same one-isomer series. This correspondence is general for this algorithm. All the isomer numbers presented in Tables 1 to 3 were derived via application of the algorithm summarized in the above examples and are by-and-large not present in previously published work [2–6]. Thus, from our depictions for the constant-isomer series having smaller isomer numbers previously published [2, 5, 6], using our algorithm, and the numerical data of Stojmenović and coworkers [3], we have been able to deduce isomer numbers that were heretofore unknown.

Previously, it was shown that the benzenoids of successive formulas in a constant-isomer series possessed the same topological features in regard to the number of bay regions, selective lineations, and symmetry (cf. Fig. 1 in [4]). We now show that there is a one-to-one topological correspondence between the member benzenoids of constant-isomer series with the same isomer number.

Topological Characteristics

The one-isomer series (Table 1) beginning with benzene is unique and has corresponding benzenoids with D_{6h} symmetry. The other two one-isomer series starting with naphthalene and pyrene have benzenoids with D_{2h} symmetry. The constant-isomer series starting with $C_{22}H_{12}$ is unique [4]. Both the constant-isomer series starting with $C_{30}H_{14}$ and $C_{40}H_{16}$ have benzenoids that are pairwise equivalent in their topology. Even carbon strictly peri-condensed benzenoids up to $C_{46}H_{18}$ can only possess nonradical and di-

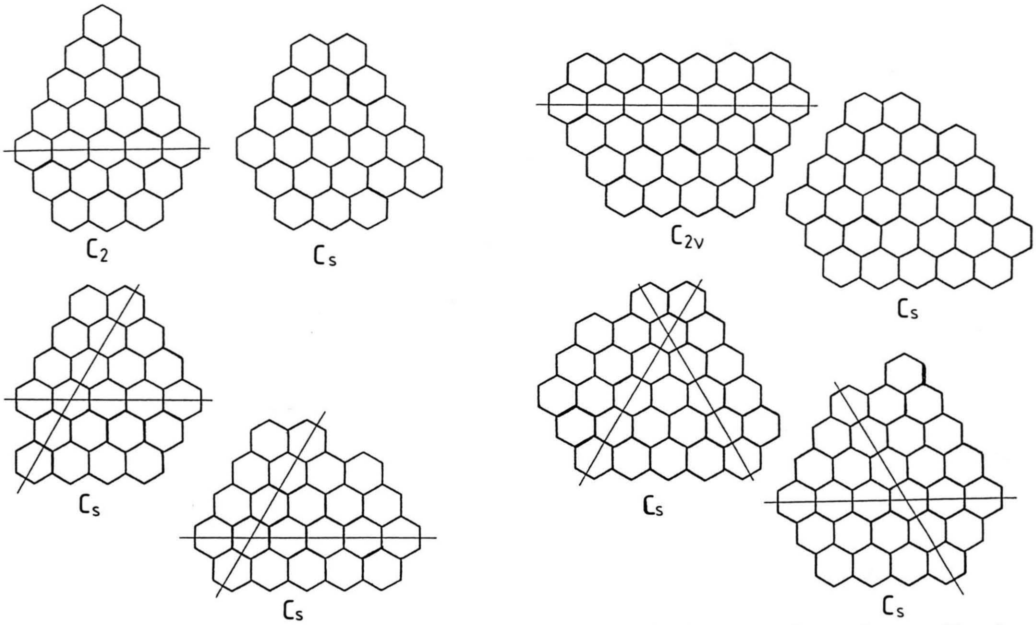


Fig. 3. Diradical base members of the $C_{62}H_{20}$ (left) and $C_{76}H_{22}$ (right) constant-isomer benzenoid series.

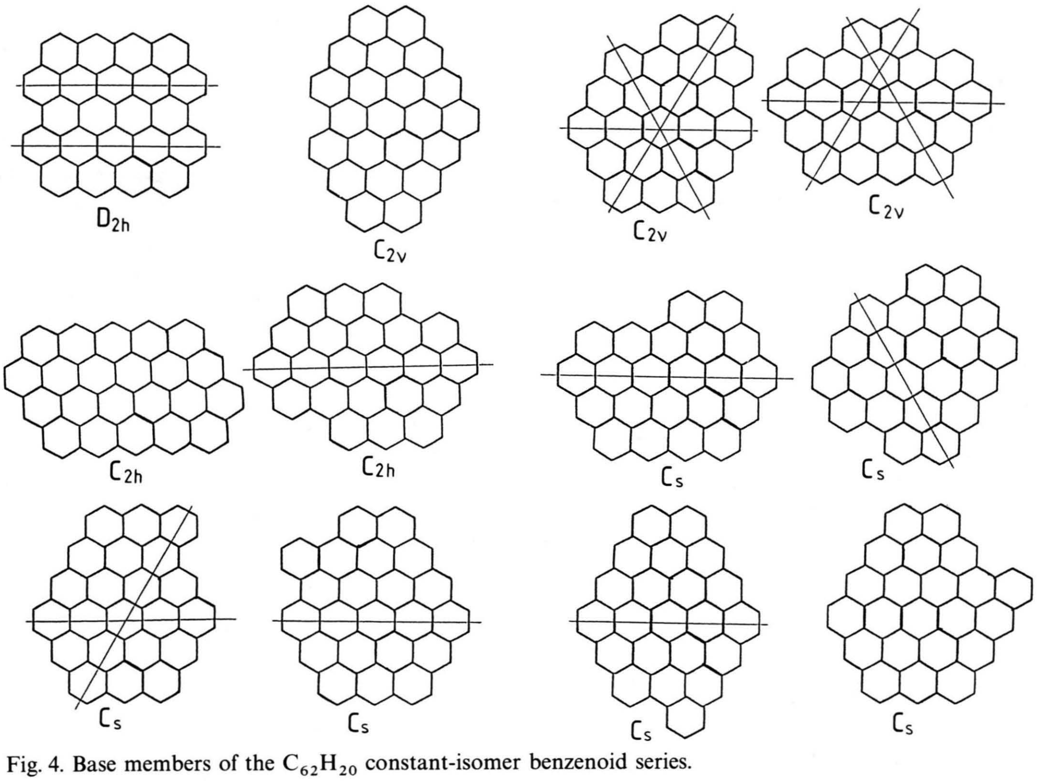


Fig. 4. Base members of the $C_{62}H_{20}$ constant-isomer benzenoid series.

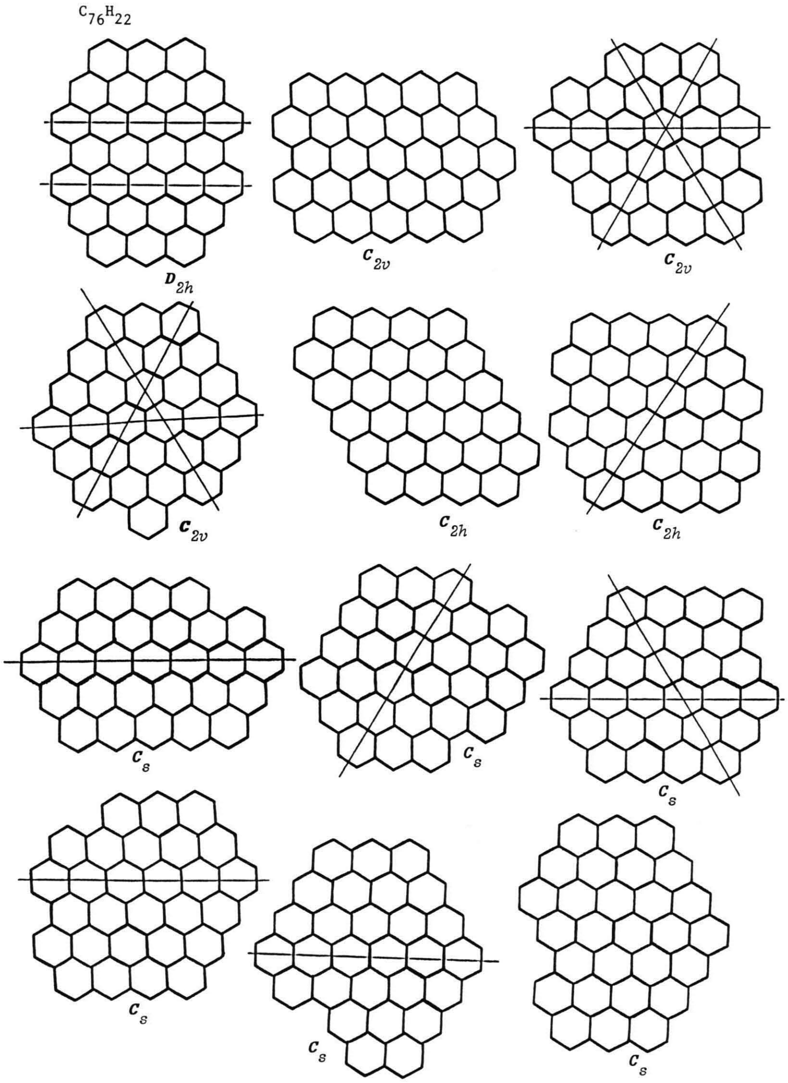


Fig. 5. Base members of the $C_{76}H_{22}$ constant-isomer benzenoid series.

radical isomers. Both the diradicals, dibenzo[*bc*, *hi*]-coronene ($C_{30}H_{14}$) and phenalenyl[2,3,4,5-*hijk*]ovalene ($C_{40}H_{16}$), have C_{2v} symmetry, no bay regions, and one selective lineation [6]. Naphtho[1,8,7-*abc*]coronene ($C_{30}H_{14}$) and anthra[2,1,9,8-*hijkl*]ovalene ($C_{40}H_{16}$) both have C_s symmetry, one bay region, and two selective lineations. Dibenzo[*bc*, *ef*]coronene ($C_{30}H_{14}$) and phenanthro[3,4,5,6-*efghi*]ovalene ($C_{40}H_{16}$) both have C_{2v} symmetry, one bay region, and no selective lineation. Finally, dibenzo[*bc*, *kl*]coronene and circumanthracene both have D_{2h} symmetry, no bay region and one selective lineation [6]. Figures 3 to 5 give all the benzenoids of the constant-isomer series starting with $C_{62}H_{20}$ and $C_{76}H_{22}$, and it can be verified that each group has a topological one-to-one correspondence.

The one-isomer series (Table 2) beginning with phenalenyl ($C_{13}H_9$) is unique and has benzenoids with D_{3h} symmetry. The one-isomer series starting with $C_{19}H_{11}$ and $C_{27}H_{13}$ have benzenoids with C_{2v} symmetry, no bay regions, and one selective lineation. The constant-isomer series starting with $C_{45}H_{17}$ and $C_{57}H_{19}$ form topologically equivalent benzenoid groups. The constant-isomer series starting with $C_{83}H_{23}$ and $C_{99}H_{25}$ both have 16 C_s and 4 C_{2v} benzenoids. These two strictly peri-condensed benzenoids can only possess mono- and triradical isomers, the relative number of which is the same. Note that no odd carbon or even carbon diradical strictly peri-condensed benzenoid can have C_{2h} symmetry.

Tables 1 and 2 greatly extend the isomer numbers found in previous work of benzenoid hydrocarbons [2–6]. As is has been herein demonstrated, these strictly peri-condensed benzenoids having formulas along the left-hand staircase boundary of Table PAH6 have unique characteristics and form alternating pairs of topologically equivalent sets of benzenoid structures with the nonidentical invariants of N_c, N_H, q, and r. This work again demonstrates the power of Table PAH6 to sort benzenoid formulas into a hierarchal order forming series with unique characteristics.

Summary

Our conceptual tools of the excised internal structure, strictly peri-condensed, and formula periodic table for benzenoids have led to our recognition of these constant-isomer series and their topological properties. Given that strictly peri-condensed benzenoids can not have helicenic isomers or isomers with benzenoid holes (circulene isomers), these isomer numbers have no ambiguity. Even carbon nonradical strictly peri-condensed benzenoids have been speculated to be ultimate pyrolytic constituents, and thus these constant-isomer series represent a relatively more important group [4, 6, 8]. Strictly peri-condensed benzenoids on the left-hand staircase edge of Table PAH6 form two classes of constant-isomer series: a topologically unique singlet class and a topologically equivalent doublet class. Herein, we specifically claim that our algorithm has generated new isomer numbers, has led to the identification of new constant-isomer series, and has led to the identification of a new topological paradigm that may have universal implications since the polyhex system is a fundamental structure of nature.

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