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Benzenoid Series Having a Constant Number of Isomers

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By use of the formula periodic table for benzenoids and the excised internal structure concept several new strictly pericondensed benzenoid series possessing an identical number of isomers have been identified. These constant-isomer series are conjectured to be probable carbonization/pyrolytic benzenoid species.

INTRODUCTION

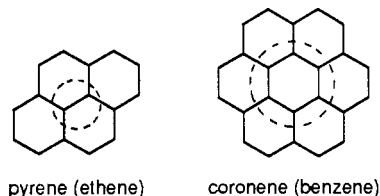
The number and identity of benzenoid (PAH6) isomers are important problems in both environmental analysis and documentation/retrieval of chemical literature of this class of compounds.¹ The knowledge of the absence and presence of benzenoid isomers in the environment should present novel insights and will allow one to speculate why. The recent availability of extended tables^{2,3} on the number of benzenoid isomers makes it now possible for us to clarify and extend our previous work on enumeration of select benzenoid families of potential importance to pyrolytic processes.^{4,5}

RESULTS AND DISCUSSION

Terminology. The formula periodic table for even-carbon benzenoids is given in Table PAH6 and for odd-carbon benzenoids in Table PAH6(odd). Throughout this paper the carbon and hydrogen atoms and the $p\pi$ and C-H bonds will be omitted, leaving only the C-C σ -bond skeleton to represent the benzenoid structure. Methine substructural units will be shown as secondary graph vertices. All the remarks and generalizations presented herein are restricted to systems that are exclusively polyhexagonal and essentially planar.

The number of carbon atom vertices will be denoted N_c , the number of internal carbon vertices bounded by three hexagonal rings N_{ic} , and the net number of disconnections (positive values) and/or rings (negative values) among the internal edges (edges bounded by two rings) d_s . For example anthracene/phenanthrene has $d_s = 1$ and $N_{ic} = 0$ and pyrene has $d_s = 0$ and $N_{ic} = 2$. A strictly pericondensed benzenoid hydrocarbon has all its internal third-degree vertices mutually connected ($d_s = 0, -1, -2, \dots$) and has no catacondensed appendages. An excised internal structure is the set of connected internal vertices usually associated with a strictly pericondensed ben-

zenoid which has a formula found at the extreme left-hand boundary of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6s).⁴ For example, the excised internal structure of pyrene is ethene and of coronene is benzene, as shown in the structures by the dotted line. Constant-isomer benzenoids have no proximate bay regions and on a per carbon basis have the fewest number of bay regions and among the highest $p\pi$ electronic energy.⁶



pyrene (ethene)

coronene (benzene)

There are only three conjugated polyene isomers of the formula C_4H_6 : rotamers *s-cis*-1,3-butadiene and *s-trans*-1,3-butadiene and trimethylenemethane diradical (Figure 1). If an 18-carbon-atom perimeter is circumscribed about each of these C_4H_6 isomers with the resulting species being incremented with 6 hydrogens, one obtains the only three $C_{22}H_{12}$ benzenoid isomers possible for this formula, i.e., benzo[ghi]perylene, anthanthrene, and triangulene.⁴ If these three latter strictly pericondensed benzenoids are circumscribed by a 30-carbon-atom perimeter followed by incrementation with 6 hydrogens, one obtains the only three benzenoid isomers possible for $C_{52}H_{18}$. Because trimethylenemethane is a diradical, triangulene and its $C_{52}H_{18}$ successor are also diradicals.⁴

In using excised internal structures for benzenoid enumeration, one must make sure that the perimeter of the excised internal structures has no less than two-carbon gaps.⁴ For example, *s-cis*-1,3-butadiene in Figure 1 has a two-carbon-gap

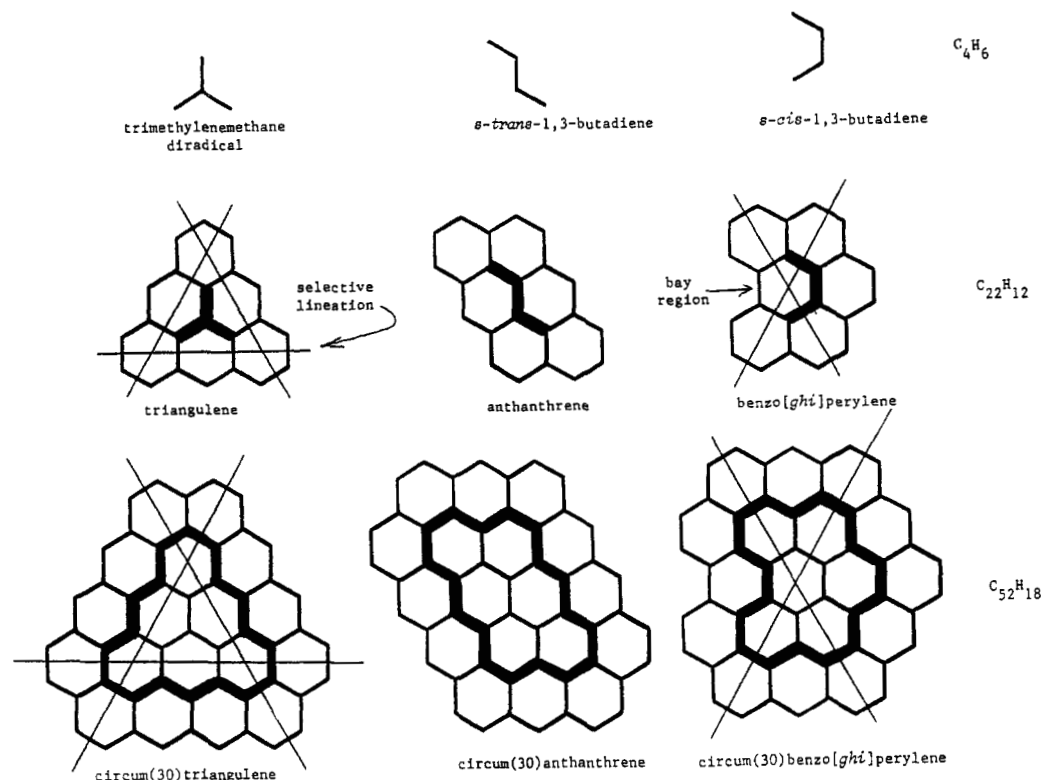
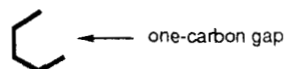


Figure 1. Illustration of the excised internal structure concept in enumeration of all the benzenoid isomers of $C_{22}H_{12}$, $C_{52}H_{18}$, $C_{94}H_{24}$,

between its terminal methylene groups but pentadienyl does not.



Thus, benzo[c]phenanthrene and helicenes cannot be excised internal structures.

Formula Periodic Table for Benzenoids. Tables PAH6 and PAH6(odd) were algorithmically constructed by using our aufbau principle.^{4,6,7} Table PAH6 has x,y coordinates of (d_s, N_{ic}) , where d_s is the net number of disconnections among the internal edges (analogous to the number of outer shell electrons in an element) and N_{ic} is the number of internal carbon vertices (analogous to the outer shell number of an element). Isomers are analogous to atomic isotopes, and Table PAH6 complies with the sextet rule, analogous to the octet rule for the periodic table of elements.

Strictly pericondensed benzenoid hydrocarbons have all their internal edges mutually connected ($d_s \leq 0$) and have formulas found at the extreme left-hand diagonal edge of Table PAH6. Strictly pericondensed benzenoids have no catacondensed appendages (i.e., $n_4 = 0$) and may contain a maximum number of internal carbon vertices. Formulas at the extreme left-hand diagonal edge of Table PAH6 will correspond to benzenoid hydrocarbons having only strictly pericondensed isomers, and formulas just adjacent to these will correspond to benzenoid hydrocarbons having both strictly pericondensed and non-strictly pericondensed isomers. For example, $C_{28}H_{14}$ has eight nonradical benzenoid isomers, seven that are strictly pericondensed and benzo[a]coronene, which is not. Strictly pericondensed benzenoid hydrocarbons have no adjacent bay regions; i.e., their perimeters have no coves (two proximate bay regions) or fjords (three proximate bay regions). For a given number of carbon atoms, strictly pericondensed benzenoid hydrocarbons are among the more stable benzenoids, have a maximum number of internal carbon atoms, and possess a minimum number of bay regions.

Tables PAH6 and PAH6(odd) have been published before and are not repeated here.⁴ However, another version of these

Table I. All Possible Formulas for Benzenoid Polycyclic Aromatic Hydrocarbons (PAH6')

N_c	N_H^a	N_c	N_H^a
10	8	70	22- 38 ^b
14	10	72	→22-38
16	→10	74	→22-40
18	12	76	→22-40
20	12	78	→22-42
22	→22,14	80	→22-42
24	→12,14	82	24-44
26	14,16	84	24-44
28	14,16	86	→24-46
30	→14,16,18	88	→24-46
32	→14,16,18	90	→24-48
34	16,18,20	92	→24-48
36	16,18,20	94	→24-50
38	→16,18,20,22	96	→24-50
40	→16,18,20,22	98	26-52
42	→16,18,20,22,24	100	26-52
44	18,20,22,24	102	→26-54
46	18,20,22,24,26	104	→26-54
48	→18,20,22,24,26	106	→26-56
50	→18,20,22,24,26,28	108	→26-56
52	→18,20,22,24,26,28	110	→26-58
54	→18,20,22,24,26,28,30	112	→26-58
56	20,22,24,26,28,30	114	28-60
58	20,22,24,26,28,30,32	116	28-60
60	→20,22,24,26,28,30,32	118	→28-62
62	→20,22,24,26,28,30,32,34	120	→28-62
64	→20,22,24,26,28,30,32,34	122	→28-64
66	→20,22,24,26,28,30,32,34,36	124	→28-64
68	22,24,26,28,30,32,34,36	126	→28-66
		128	→28-66
		130	→28-68
	

^a Catacondensed benzenoid formulas are boldfaced and boundary strictly pericondensed formulas are marked at the left with an arrow.

^b Range of successive even numbers.

tables arranged in *index order* rather than in *hierarchical order* is presented.¹ When Table PAH6 is arranged in the index order format, it is referred to as Table PAH6' (Table I). Similarly, when Table PAH(odd) is arranged in the index order format, it is referred to as Table PAH6'(odd) (Table

Table II. All Possible Formulas for Radical Odd-Carbon Benzenoid Hydrocarbons [PAH6'(odd)]

N_c	N_H^a	N_c	N_H^a
13	9	79	→23-41
17	11	81	→23-43
19	→11	83	→23-43
21	13	85	→23-45
23	13	87	→23-45
25	→13-15 ^b	89	25-47
27	→13-15	91	25-47
29	15-17	93	→25-49
31	15-17	95	→25-49
33	→15-19	97	→25-51
35	→15-19	99	→25-51
37	→15-21	101	→25-53
39	17-21	103	→25-53
41	17-23	105	27-55
43	→17-23	107	27-55
45	→17-25	109	→27-57
47	→17-25	111	→27-57
49	19-27	113	→27-59
51	19-27	115	→27-59
53	→19-29	117	→27-61
55	→19-29	119	→27-61
57	→19-31	121	→27-63
59	→19-31	123	29-63
61	21-33	125	29-65
63	21-33	127	→29-65
65	→21-35	129	→29-67
67	→21-35	131	→29-67
69	→21-37	133	→29-69
71	→21-37	135	→29-69
73	→21-39	137	→29-71
75	23-39	139	→29-71
77	23-41

^a Benzenoid formulas with $N_{lc} = 1$ are boldfaced and boundary strictly pericondensed formulas are marked at the left with an arrow.

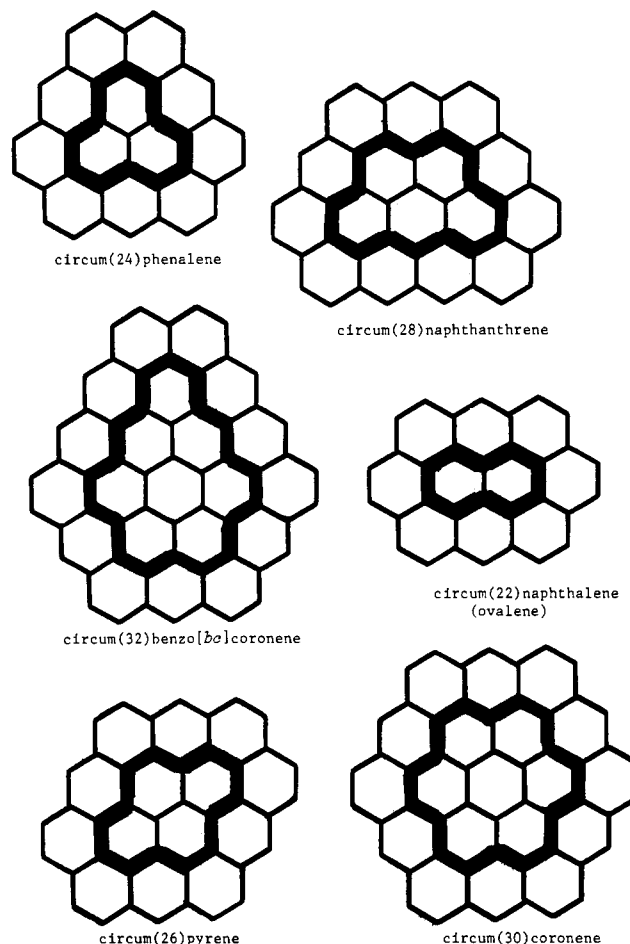
^b Range of successive odd numbers.

II). The advantage to the index order versions is that they facilitate chemical literature searching since they order the formulas according to the Hill system. Also, upon examination of Tables PAH6' and PAH6'(odd), the recursion pattern will become apparent, and one may extrapolate to even higher formulas if it is so desired.

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 smaller 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. It has been speculated that the strictly pericondensed benzenoids along this edge are potentially among the more important ones since carbonization processes tend to increase the carbon-to-hydrogen ratio.^{5,7}

Isomer Enumeration of Strictly Pericondensed Benzenoids.

Previously, we presented several one-isomer series⁴ summarized in Tables III and IV. Figure 2 gives the base excised internal structure (bold) for these one-isomer series. By circumscribing a carbon-atom perimeter about each of these base structures and incrementing with six hydrogens, one obtains the next member of the series which is shown. Successively repeating this process generates the series summarized in Tables III and IV. Here, one must distinguish between base excised internal structure, which is benzenoid shown in bold, and ultimate excised internal structure. Naphthalene is both a base and ultimate excised internal structure, whereas methyl, allyl, and benzyl are the ultimate excised internal structures of phenalene ($C_{13}H_9$), naphthanthrene ($C_{19}H_{11}$), and benzo[bc]coronene ($C_{27}H_{13}$), respectively; ethene and benzene are the ultimate excised internal structures of pyrene and coronene, respectively. Similarly, the strictly pericondensed constant isomer series

**Figure 2.** Base excised internal structures (bold) and the first circum members of the one-isomer series.**Table III.** Constant-Isomer Series of Odd Strictly Pericondensed Benzenoids

series	no. of isomers	series	no. of isomers
$C_{13}H_9$	1	$C_{157}H_{31}$	4
$C_{37}H_{15}$		$C_{225}H_{37}$	
$C_{73}H_{21}$...	
$C_{121}H_{27}$		$C_{69}H_{21}$	13 ^b
...		$C_{117}H_{27}$	
$C_{19}H_{11}$	1	$C_{177}H_{33}$	
$C_{47}H_{17}$...	
$C_{87}H_{23}$		$C_{83}H_{23}$	20 ^b
$C_{139}H_{29}$		$C_{135}H_{29}$	
...		$C_{199}H_{35}$	
$C_{27}H_{13}$	1	...	
$C_{59}H_{19}$		$C_{99}H_{25}$	20
$C_{103}H_{25}$		$C_{155}H_{31}$	
$C_{159}H_{31}$		$C_{223}H_{37}$	
...		...	
$C_{35}H_{15}$	2	$C_{115}H_{27}$	48
$C_{71}H_{21}$		$C_{175}H_{33}$	
$C_{119}H_{27}$		$C_{247}H_{39}$	
$C_{179}H_{33}$...	
...		$C_{133}H_{29}$	74
$C_{45}H_{17}$	4 ^a	$C_{197}H_{35}$	
$C_{85}H_{23}$		$C_{273}H_{41}$	
$C_{137}H_{29}$...	
$C_{201}H_{35}$		$C_{153}H_{31}$	74
...		$C_{221}H_{37}$	
$C_{57}H_{19}$	4	$C_{301}H_{43}$	
$C_{101}H_{25}$...	

^a In the previous enumeration,⁷ one structure was inadvertently overlooked. ^b These two series were published with undetected misprints.⁷

starting with $C_{35}H_{15}$ (two isomers), $C_{45}H_{17}$ (four isomers), $C_{57}H_{19}$ (four isomers), $C_{22}H_{12}$ (two Kekuléan and one non-

Table IV. Constant-Isomer Series of Even Strictly Pericondensed Benzenoids

series	no. of isomers ^a	series	no. of isomers ^a
C ₁₀ H ₈	1	C ₄₀ H ₁₆	3 (1)
C ₃₂ H ₁₄		C ₇₈ H ₂₂	
C ₆₆ H ₂₀		C ₁₂₈ H ₂₈	
C ₁₁₂ H ₂₆		...	
C ₁₇₀ H ₃₂		C ₅₀ H ₁₈	7 (2)
...		C ₉₂ H ₂₄	
C ₁₆ H ₁₀	1	C ₁₄₆ H ₃₀	
C ₄₂ H ₁₆		...	
C ₈₀ H ₂₂		C ₆₂ H ₂₀	12 (4)
C ₁₃₀ H ₂₈		C ₁₀₈ H ₂₆	
...		C ₁₆₆ H ₃₂	
C ₂₂ H ₁₂	2 (1)	C ₂₃₆ H ₃₈	
C ₅₂ H ₁₈		...	
C ₉₄ H ₂₄		C ₇₆ H ₂₂	12 (4)
C ₁₄₈ H ₃₀		C ₁₂₆ H ₂₈	
...		C ₁₈₈ H ₃₄	
C ₂₄ H ₁₂	1	...	
C ₅₄ H ₁₈		C ₉₀ H ₂₄	27 (12)
C ₉₆ H ₂₄		C ₁₄₄ H ₃₀	
C ₁₅₀ H ₃₀		C ₂₁₀ H ₃₆	
...		...	
C ₃₀ H ₁₄	3 (1)	C ₁₀₆ H ₂₆	38 (19)
C ₆₄ H ₂₀		C ₁₆₄ H ₃₂	
C ₁₁₀ H ₂₆		C ₂₃₄ H ₃₈	
C ₁₆₈ H ₃₂		...	
...			

^a The number of less stable diradical isomers is given in parentheses.

Kekuléan in Figure 1), C₃₀H₁₄ (three Kekuléan and one non-Kekuléan), C₄₀H₁₆ (three Kekuléan and one non-Kekuléan), and C₅₀H₁₈ (seven Kekuléan and two non-Kekuléan) have been given.⁴

We now illustrate how to derive the remaining constant isomer series given in Tables III and IV. Consider the three benzenoid isomers of C₂₅H₁₃ given in bold in Figure 3. In Table PAH6' (Table I) a formula C₂₄H₁₂ (coronene) is found from which a methylene isomer (Figure 3) can be generated, giving in all four C₂₅H₁₃ isomers. Circumscribing a 32-carbon-atom perimeter about these isomers and incrementing with 6 hydrogens give all the isomers of C₅₇H₁₉ (Figure 3) which serve as the base excised internal structures for the relevant series given in Table III. A check of Table PAH6' (Table I) verifies that no C₅₆H₁₈ formula exists. Thus, base excised internal structures must all be strictly pericondensed benzenoids.

Benz[de]lanthryl is the only benzenoid isomer of the formula C₁₇H₁₁ in Table PAH6(odd). In Table PAH6, an edge formula of C₁₆H₁₀ (pyrene) is found that gives three methylene isomers of the formula C₁₇H₁₁. Circumscribing a 22-carbon-atom perimeter around these four C₁₇H₁₁ isomers and incrementing with 6 hydrogens give the C₄₅H₁₇ base excised internal structures for the four-isomer series in Table III. A check of Table PAH6 verifies that no C₄₄H₁₆ formula exists. Thus, the one-isomer series plays a pivotal role in generating methylene-substituted benzenoid isomers from which base excised internal structures are ultimately derived for higher constant isomer series.

Consider the eight Kekuléan (nonradical) and one non-Kekuléan (radical) C₂₈H₁₄ benzenoid hydrocarbons previously enumerated.⁴ In Table PAH6'(odd) (Table II) a formula C₂₇H₁₃ is found that corresponds to the base excised internal of the circumbenzo[bc]coronene one-isomer series (Figure 2). Three diradical and 4 nonradical methylenebenzo[bc]coronene isomers can be generated from this C₂₇H₁₃ structure, giving 12 nonradical and 4 diradical C₂₈H₁₄ isomers. Circumscribing these C₂₈H₁₄ isomers by a 34-carbon-atom perimeter and augmenting with 6 hydrogens give all the C₆₂H₂₀ isomers that can serve as base excised internal structures for the series given

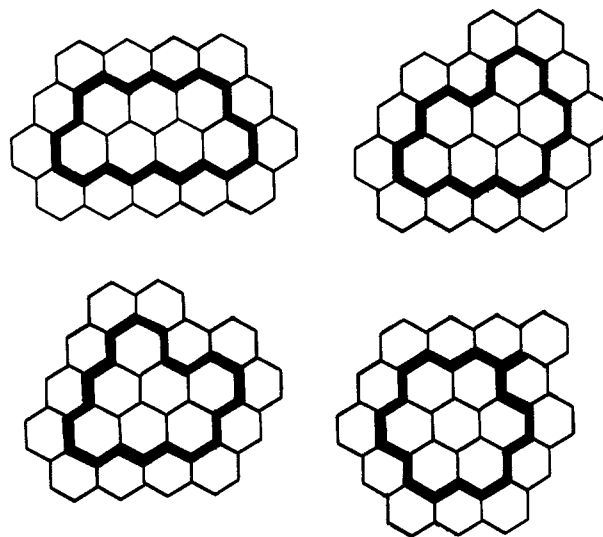


Figure 3. Base excised internal structures of the C₅₇H₁₉ series and their precursors shown in bold.

in Table IV since Table PAH6'(odd) (Table II) contains no C₆₁H₁₉ formula.

It should now be apparent that whenever a staircase edge formula in either Table PAH6 or Table PAH6(odd) corresponds to a complete set of strictly pericondensed benzenoids with no methylene isomers (as determined by checking the complementary table for staircase formulas with one less CH), then these benzenoids represent the base excised internal structures for a strictly pericondensed constant isomer series. To extend the constant isomer series given in Tables III and IV, the following recursion³ is useful

$$C_{N_c'}H_{N_H'} = C_{N_c+2N_H+6}H_{N_H+6}$$

where N_c' is the number of carbons and N_H' is the number of hydrogens of the next larger series member.

SUMMARY

Table PAH6 and the excised internal structure concept have been instrumental in providing the conceptual basis for enumerating strictly pericondensed benzenoid hydrocarbons. Unlike the enumeration of alkanes in which the number of isomers increases as the number of carbons increases, we see that there exist special benzenoid families in which the number of isomers is constant as the number of carbons increases. While manual enumeration of small benzenoid isomers is relatively straightforward, it is nevertheless prone to inadvertent omissions. What is stressed here is the conceptual approach. Since it has been shown^{1,7} that the largest reported benzenoids are of the order of C₆₀, the extension of Tables III and IV to larger benzenoids is more academic and less of practical utility. Also, the more stable even-carbon benzenoids are relatively more important than the odd-carbon ones which are radicals.

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