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# Benzenoid Series Having a Constant Number of Isomers. 2. Topological Characteristics of Strictly Peri-Condensed 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 forms a pairwise topologically equivalent class. An extention to our previous algorithm which led to these additional results is presented. Circulenes, benzenoid-related molecular systems having holes, have no constant-isomer series.

## INTRODUCTION

It is well known that as the number of carbons in alkanes increases so does the number of isomers.[1] However, we previously demonstrated that there exist special benzenoid series in which the number of isomers remain constant as the number of carbons increase.[2] The recent availability of the benzenoid isomer table of Stojmenović and co-workers has allowed us to extend these results.[3]

## RESULTS AND DISCUSSION

**Conceptual Tools.** Using the formula periodic table for benzenoids (Table PAH6 = Table 1 in ref 4) and the excised internal structure concept, several new strictly peri-condensed benzenoid series possessing an identical number of isomers have been identified.[5] Strictly peri-condensed benzenoids have all their internal carbon vertices mutually connected and collectively make up their excised internal structures. 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 they are strictly peri-condensed benzenoids that are members of the one-isomer series found in Tables I and II. 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] that allows us to identify this subset of benzenoids that cannot 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 Figure 1 of refs 4 and 5.

**Constant-Isomer Series of Strictly Peri-Condensed Benzenoids.** Tables I and II 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 alternates between singlet and

**Table I.** Constant-Isomer Series of Even Strictly Peri-Condensed Benzenoids

| series | no. of isomers | series | no. of isomers |
|---|---|---|---|
| $(C_6H_6)$ | | $C_{76}H_{22}$ | 12(4) |
| $C_{24}H_{12}$ | 1 | $C_{126}H_{28}$ | |
| $C_{54}H_{18}$ | | $C_{188}H_{34}$ | |
| $C_{96}H_{24}$ | | ... | |
| ... | | $C_{90}H_{24}$ | 27(12) |
| $C_{10}H_8$ | 1 | $C_{144}H_{30}$ | |
| $C_{32}H_{14}$ | | $C_{210}H_{36}$ | |
| $C_{66}H_{20}$ | | ... | |
| $C_{112}H_{26}$ | | $C_{106}H_{26}$ | 38(19) |
| $C_{170}H_{32}$ | | $C_{164}H_{32}$ | |
| ... | | $C_{234}H_{38}$ | |
| $C_{16}H_{10}$ | 1 | ... | |
| $C_{42}H_{16}$ | | $C_{124}H_{28}$ | 38(19) |
| $C_{80}H_{22}$ | | $C_{186}H_{34}$ | |
| $C_{130}H_{28}$ | | $C_{260}H_{40}$ | |
| ... | | ... | |
| $C_{22}H_{12}$ | 2(1)[a] | $C_{142}H_{30}$ | <u>133</u>[b] |
| $C_{52}H_{18}$ | | $C_{208}H_{36}$ | |
| $C_{94}H_{24}$ | | $C_{286}H_{42}$ | |
| $C_{148}H_{30}$ | | ... | |
| ... | | $C_{162}H_{32}$ | <u>199</u> |
| $C_{30}H_{14}$ | 3(1) | $C_{232}H_{38}$ | |
| $C_{64}H_{20}$ | | $C_{314}H_{44}$ | |
| $C_{110}H_{26}$ | | ... | |
| $C_{168}H_{32}$ | | $C_{184}H_{34}$ | <u>199</u> |
| ... | | $C_{258}H_{40}$ | |
| $C_{40}H_{16}$ | 3(1) | $C_{344}H_{46}$ | |
| $C_{78}H_{22}$ | | ... | |
| $C_{128}H_{28}$ | | $C_{206}H_{36}$ | <u>428</u> |
| ... | | $C_{284}H_{42}$ | |
| $C_{50}H_{18}$ | 7(2) | ... | |
| $C_{92}H_{24}$ | | $C_{230}H_{38}$ | <u>616</u> |
| $C_{146}H_{30}$ | | $C_{312}H_{44}$ | |
| ... | | ... | |
| $C_{62}H_{20}$ | 12(4) | $C_{256}H_{40}$ | <u>616</u> |
| $C_{108}H_{26}$ | | $C_{342}H_{46}$ | |
| $C_{166}H_{32}$ | | ... | |
| $C_{236}H_{38}$ | | $C_{282}H_{42}$ | <u>1265</u> |
| ... | | $C_{372}H_{48}$ | |
| | | ... | |

[a] Number of less stable diradical isomers are given in parentheses. [b] Sum of diradical and nonradical isomers are underlined.

doublet occurrence. Also, the pattern for the progressive increase in the first member formula of each series should be

**Table II.** Constant-Isomer Series of Odd Strictly Peri-Condensed Benzenoids

| series | no. of isomers | series | no. of isomers |
|---|---|---|---|
| $C_{13}H_9$ | 1 | $C_{115}H_{27}$ | 48 |
| $C_{37}H_{15}$ | | $C_{175}H_{33}$ | |
| $C_{73}H_{21}$ | | $C_{247}H_{39}$ | |
| $C_{121}H_{27}$ | | ... | |
| ... | | $C_{133}H_{29}$ | 74 |
| $C_{19}H_{11}$ | 1 | $C_{197}H_{35}$ | |
| $C_{47}H_{17}$ | | $C_{273}H_{41}$ | |
| $C_{87}H_{23}$ | | ... | |
| $C_{139}H_{29}$ | | $C_{153}H_{31}$ | 74 |
| ... | | $C_{221}H_{37}$ | |
| $C_{27}H_{13}$ | 1 | $C_{301}H_{43}$ | |
| $C_{59}H_{19}$ | | ... | |
| $C_{103}H_{25}$ | | $C_{173}H_{33}$ | 174 |
| $C_{159}H_{31}$ | | $C_{245}H_{39}$ | |
| ... | | $C_{329}H_{45}$ | |
| $C_{35}H_{15}$ | 2 | ... | |
| $C_{71}H_{21}$ | | $C_{195}H_{35}$ | 258 |
| $C_{119}H_{27}$ | | $C_{271}H_{41}$ | |
| $C_{179}H_{33}$ | | $C_{359}H_{47}$ | |
| ... | | ... | |
| $C_{45}H_{17}$ | 4[a] | $C_{219}H_{37}$ | 258 |
| $C_{85}H_{23}$ | | $C_{299}H_{43}$ | |
| $C_{137}H_{29}$ | | $C_{391}H_{49}$ | |
| $C_{201}H_{35}$ | | ... | |
| ... | | $C_{243}H_{39}$ | 550 |
| $C_{57}H_{19}$ | 4 | $C_{327}H_{45}$ | |
| $C_{101}H_{25}$ | | $C_{423}H_{51}$ | |
| $C_{157}H_{31}$ | | ... | |
| $C_{225}H_{37}$ | | $C_{269}H_{41}$ | 796 |
| ... | | $C_{357}H_{47}$ | |
| $C_{69}H_{21}$ | 13[b] | $C_{457}H_{53}$ | |
| $C_{117}H_{27}$ | | ... | |
| $C_{177}H_{33}$ | | $C_{297}H_{43}$ | 796[c] |
| ... | | $C_{389}H_{49}$ | |
| $C_{83}H_{23}$ | 20[b] | $C_{493}H_{55}$ | |
| $C_{135}H_{29}$ | | ... | |
| $C_{199}H_{35}$ | | | |
| ... | | | |
| $C_{99}H_{25}$ | 20 | | |
| $C_{155}H_{31}$ | | | |
| $C_{223}H_{37}$ | | | |
| ... | | | |

[a] In the previous enumeration,[2] one structure was inadvertently overlooked. [b] These two series were published with undetected misprints.[2] [c] Predicted value based on induction.

evident and will allow one to extend these tables even further. Strictly peri-condensed benzenoid hydrocarbons $(N_c', N_H')$ have excised internal structures $(N_c, N_H)$ with a formula six hydrogens less $(N_H = N_H' - 6)$ and the number of carbons given by $N_{Ic}' = N_c = N_c' - 2N_H' + 6$, which is the direct result of an equation previously derived by us.[6,8] Thus, $N_c' = N_c + 2N_H' - 6 = N_c + 2N_H + 6$ and $N_H' = N_H + 6$ are useful recursion relationships for obtaining successive strictly peri-condensed formulas.

**Algorithm for Generating Constant-Isomer Benzenoids.**

1. Systematically enumerate all excised internal structures of $N_{Ic}$ carbon atoms and circumscribe them with a perimeter of $q_P$ carbon atoms incrementing with 6 H's to give strictly peri-condensed benzenoids of the formula $C_{N_c}H_{N_H}$.

2. If $C_{N_c-4}H_{N_H-2}$ exists on Table PAH6, obtain all combinatorial benzo derivatives.

3. If $C_{N_c-2}H_{N_H-2}$ exists on Table PAH6, obtain all ethenyl and dimethylenyl derivatives.

4. If $C_{N_c-1}H_{N_H-1}$ exists on Table PAH6, obtain all methylenyl derivatives.

5. If $C_{N_c+1}H_{N_H-1}$ exists on Table PAH6, obtain all combinatorial deletions of the solo positions.

6. In doing 2–4 make sure that two-carbon-atom gaps exist everywhere on the perimeters.
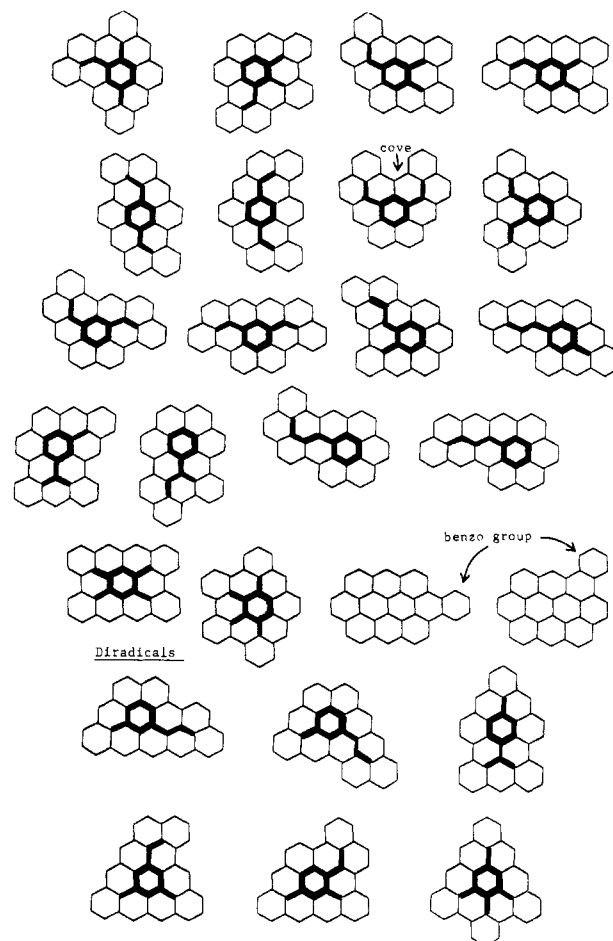


**Figure 1.** The 26 $C_{36}H_{16}$ isomers with their excised internal structures shown in bold.

**Scheme I.** Algorithm for Generating Strictly Peri-Condensed Benzenoid Isomers
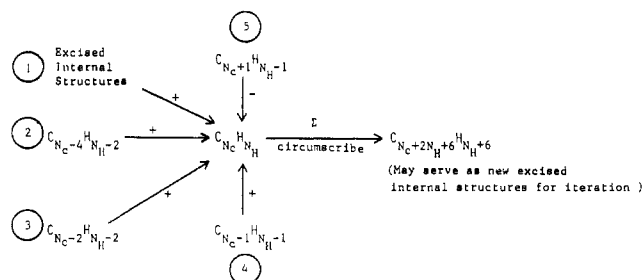


7. Sum 1–4 and substract 5. Circumscribe all these $C_{N_c}H_{N_H}$ isomers with carbon atom perimeters incrementing with 6 Hs to obtain all strictly peri-condensed benzenoids of the formula $C_{N_c+2N_H+6}H_{N_H+6}$.

8. Iterate until 2–5 can not be further performed. The resulting set of strictly peri-condensed benzenoids represent the base members (first generation) of a constant-isomer benzenoid series.

Scheme I summarizes this algorithm which will now be demonstrated.

Figure 1 depicts all 26 of the $C_{36}H_{16}$ benzenoid isomers previously published.[2,6] They were generated by enumerating their excised internal structures shown in bold. Subtracting $C_4H_2$ from $C_{36}H_{16}$ gives $C_{32}H_{14}$, which is the second generation of the one-isomer series given in Table I. Use of our aufbau algorithm on this $C_{32}H_{14}$ benzenoid gives the penultimate $C_{36}H_{16}$ benzobenzenoid isomers (Figure 1) that are not strictly peri-condensed. Only one of these $C_{36}H_{16}$ benzenoids has a cove and cannot serve as an excised internal structure. Subtracting CH from $C_{36}H_{16}$ gives $C_{35}H_{15}$ which corresponds to
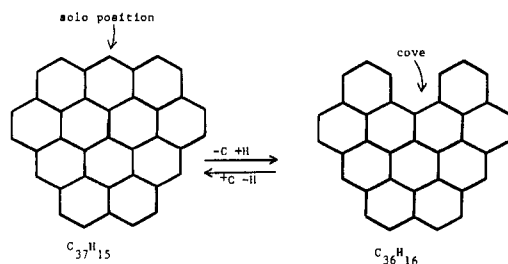
**Figure 2.** Algorithmic determination of strictly peri-condensed benzenoid isomers having doublet bay regions (coves).

two benzenoid isomers.[2,6] All combinatorial attachments of CH methylenyl units (done by replacing a hydrogen with CH and placing this H onto the CH) in these two isomers avoiding less than two-carbon-atom gaps that occur at the edge of bay regions generate 28 methylenylbenzenoid isomers of $C_{36}H_{16}$. Circumscribing a 38-carbon-atom perimeter around these 53 $C_{36}H_{16}$ isomers and incrementing with 6 H's gives 53 $C_{74}H_{22}$ benzenoid isomers. $C_{70}H_{20}$ is not found in Table PAH6 and, therefore, does correspond to a benzenoid. This means there are no benzo isomers of the formula $C_{74}H_{22}$. Subtracting CH from $C_{74}H_{22}$ gives $C_{73}H_{21}$, which corresponds to the third formula of the one-isomer series commencing with phenalenyl. All combinatorial attachments of a CH methylenyl unit to this dicircumphenalenyl give four $C_{74}H_{22}$ methylenylbenzenoid isomers. Circumscribing a 50-carbon-atom perimeter around these 53 + 4 = 57 isomers and incrementing with 6 H's gives the base members of the constant-isomer series beginning with $C_{124}H_{28}$. Subtracting CH from $C_{124}H_{28}$ gives $C_{123}H_{27}$, which is not found in Table PAH6. Thus, there are only 57 strictly peri-condensed benzenoid isomers of the formula $C_{124}H_{28}$ that serve as base members for the relevant constant-isomer series. Suppose one did not have the 26 $C_{36}H_{16}$ benzenoid depictions. How would one know how many benzenoids possessed coves and could not serve 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 $C_{36}H_{16}$ to get $C_{37}H_{15}$, which is circumphenalenyl as shown in Figure 2. If any of the three equivalent solo positions are deleted, one obtains the $C_{36}H_{16}$ structure having a cove (Figures 1 and 2).

Let's now apply this algorithm to the data provided by Stojmenović and co-workers.[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 II that has four different solo positions,[5] the deletion of which gives four $C_{58}H_{20}$ 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 members of the second four-isomer series in Table II. These four $C_{57}H_{19}$ (Figure 6) 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 H's gives 186 $C_{104}H_{26}$ benzenoid isomers. This derived isomer number of 186 for $C_{104}H_{26}$ agrees with the one given by the data of Stojmenović and co-workers[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 II 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-atom perimeter and incrementing with 6 H's gives 199

**Scheme II.** Algorithmic Determination of the Number of Isomers of $C_{162}H_{32}$ and $C_{184}H_{34}$
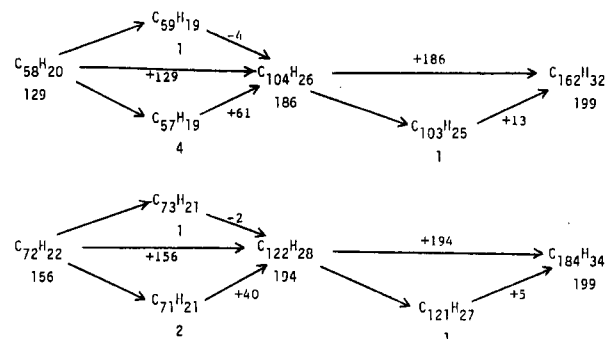


**Table III.** Formula Subset of Table PAH6 Corresponding to Monocirculenes

| $N_c$ | even $N_H$[a,b] | $N_c$ | odd $N_H$[a,b] |
|---|---|---|---|
| 32 | →16 | 35 | →17 |
| 36 | 18 | 37 | →17 |
| 38 | →18 | 39 | 19 |
| 40 | →18-20 | 41 | 19 |
| 42 | →18-20 | 43 | →19-21 |
| 44 | 20-22 | 45 | →19-21 |
| 46 | 20-22 | 47 | →19-23 |
| 48 | →20-24 | 49 | 21-23 |
| 50 | →20-24 | 51 | 21-25 |
| 52 | →20-26 | 53 | →21-25 |
| 54 | →20-26 | 55 | →21-27 |
| 56 | 22-28 | 57 | →21-27 |
| 58 | 22-28 | 59 | →21-29 |
| 60 | →22-30 | 61 | 23-29 |
| 62 | →22-30 | 63 | 23-31 |
| 64 | →22-32 | 65 | →23-31 |
| 66 | →22-32 | 67 | →23-33 |
| 68 | 24-34 | 69 | →23-33 |
| 70 | 24-34 | 71 | →23-35 |
| 72 | →24-36 | 73 | →23-35 |
| 74 | →24-36 | 75 | 25-37 |
| 76 | →24-38 | 77 | 25-37 |
| 78 | →24-38 | 79 | →25-39 |
| 80 | →24-40 | 81 | →25-39 |
| 82 | 26-40 | 83 | →25-41 |
| 84 | 26-42 | 85 | →25-41 |
| 86 | →26-42 | 87 | →25-43 |
| 88 | →26-44 | 89 | 27-43 |
| 90 | →26-44 | 91 | 27-45 |
| 92 | →26-46 | 93 | →27-45 |
| 94 | →26-46 | 95 | →27-47 |
| 96 | →26-48 | | |

[a] Range of even numbers. [b] Formulas found on the left-hand staircase edge are marked at the left with an arrow.

$C_{162}H_{32}$ 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 II 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 I–III 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 co-workers,[3] we have been able to deduce isomer numbers that were heretofore unknown.
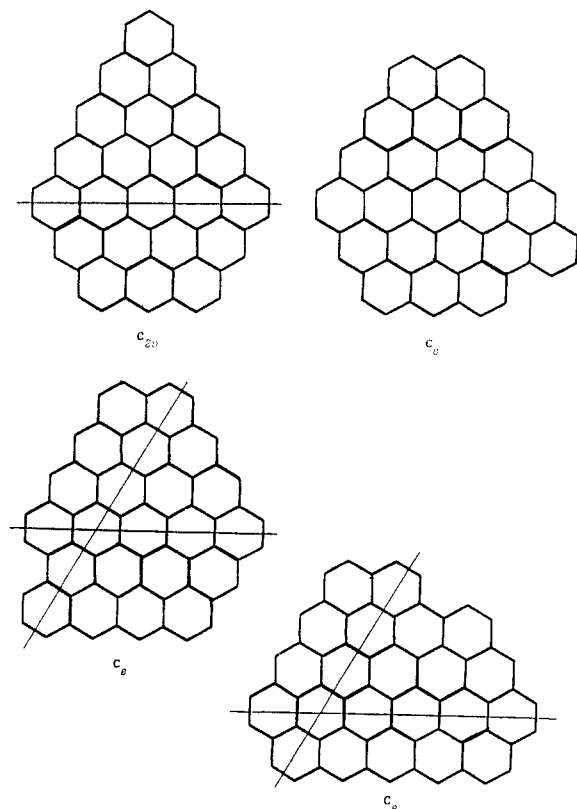
**Figure 3.** Diradical base members of the $C_{62}H_{20}$ constant-isomer benzenoid series.



**Figure 4.** Diradical base members of $C_{76}H_{22}$ constant-isomer benzenoid series.

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. with Figure 1 in ref 5). It has been shown that there is a one-to-one topological correspondence between the member benzenoids of constant-isomer series with the same isomer number when one compares their symmetry and number of bay regions and selective lineations.[7]

**Topological Characteristics.** The one-isomer series (Table I) beginning with benzene is unique and has corresponding benzenoids with $D_{6h}$ symmetry. Both 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. Even carbon strictly peri-condensed benzenoids up to $C_{46}H_{18}$ can only possess nonradical and diradical 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 ($C_{40}H_{14}$) 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 and 4 show only the diradical 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 II) 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
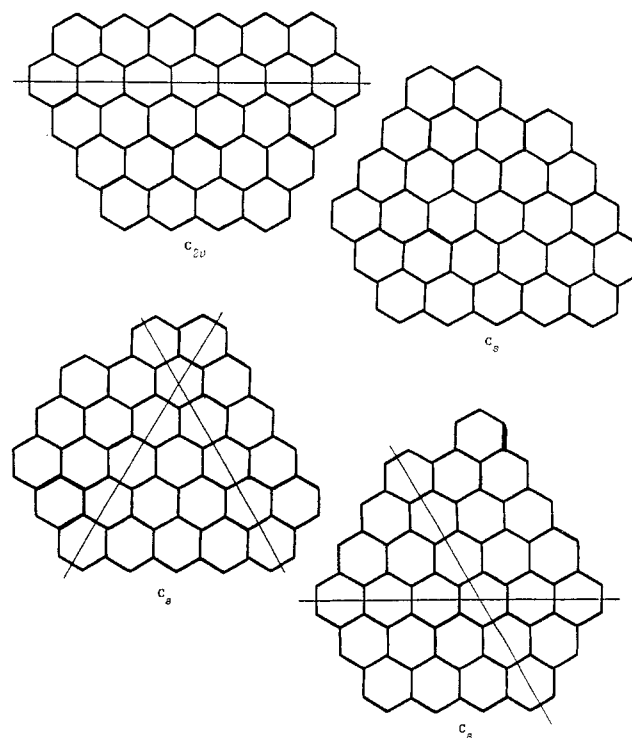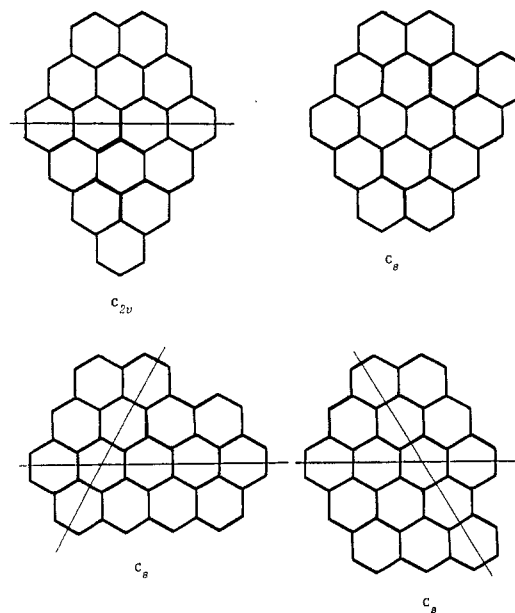


**Figure 5.** Base members of the $C_{45}H_{17}$ constant-isomer benzenoid series.

$C_{57}H_{19}$ are shown in Figures 5 and 6, respectively, and 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. Also, the diradical benzenoids (Table I) have a one-to-one topological correspondence to the mononoradical benzenoids (Table II) which can be seen by comparing Figures 3–6.

Previously,[6] we showed that the perimeter topology of benzenoids followed the equation of $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6$ where $\eta_0$ is the number of bay regions, $\eta_2$ is the number of duo groups, $\eta_3$ is the number of trio groups, and $\eta_4$ is the number of quartet groups (cata-condensed appendages); the number of solo ($\eta_1$) groups is independent of this equation. These perimeter groups have distinct infrared absorption bands due to out-of-plane bending vibrations and distinct nuclear
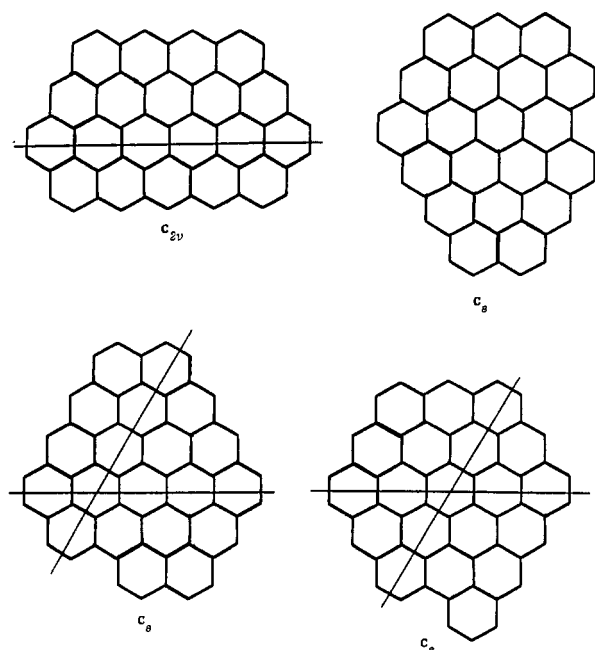
**Figure 6.** Base members of the $C_{57}H_{19}$ constant-isomer benzenoid series.



**Figure 7.** Monocirculenes derived from ovalene and circumovalene.

**Table IV.** Monocirculenes (Coronoids) of Strictly Peri-Condensed Benzenoids

| even series | no. of isomers | odd series | no. of isomers |
|---|---|---|---|
| $(C_{24}H_{12})$ | (1) | $C_{37}H_{17}$ | 1 |
| $C_{54}H_{20}$ | 2 | $C_{73}H_{23}$ | 5 |
| $C_{96}H_{26}$ | 5 | $C_{121}H_{29}$ | 12 |
| $C_{150}H_{32}$ | 10 | $C_{181}H_{35}$ | 22 |
| $C_{216}H_{38}$ | 16 | $C_{253}H_{41}$ | 35 |
| $C_{294}H_{44}$ | 24 | ... | |
| ... | | | |
| $C_{32}H_{16}$ | 1 | $C_{47}H_{19}$ | 4 |
| $C_{66}H_{22}$ | 6 | $C_{87}H_{25}$ | 18 |
| $C_{112}H_{28}$ | 16 | $C_{139}H_{31}$ | 41 |
| $C_{170}H_{34}$ | 30 | $C_{203}H_{37}$ | 73 |
| $C_{240}H_{40}$ | 49 | ... | |
| ... | | | |
| $C_{42}H_{18}$ | 2 | $C_{59}H_{21}$ | 8 |
| $C_{80}H_{24}$ | 8 | $C_{103}H_{27}$ | 25 |
| $C_{130}H_{30}$ | 19 | $C_{159}H_{33}$ | 51 |
| $C_{192}H_{36}$ | 35 | $C_{227}H_{39}$ | 86 |
| $C_{266}H_{42}$ | 55 | ... | |
| ... | | | |

magnetic resonance chemical shifts and spin–spin coupling interactions. The solo group has the highest IR vibration frequency (900–860 cm$^{-1}$) and PMR chemical shift value ($\sim 8.3$ ppm in the absence of proximate bay regions). For the base (first generation) members of the constant-isomer series the above equation becomes $-\eta_0 + \eta_2 + 2\eta_3 = 6$, and for the second generation it becomes $-\eta_0 + \eta_2 = 6$ ($\eta_2 \geq 6$). Thus, $\eta_0$ and $\eta_2$ remain constant while $\eta_1$ increases ($\Delta\eta_1 = 6$) as the number of carbons in a constant-isomers series successively increases starting from the second generation isomer set. This means that magic-angle NMR of benzenoid solids composed of constituents of these strictly peri-condensed benzenoids should yield considerable information by determining the ratio $\eta_1$ to $\eta_2$. For these constant-isomer series $\eta_0 = 6$ for the first time for the series starting with $C_{282}H_{42}$.

Tables I and II greatly extend the isomer numbers found in previous work of benzenoid hydrocarbons.[2-6] As it 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 $N_c$, $N_{Ic}$, $q$, and $r$. This work again demonstrates the power of Table PAH6 to sort benzenoid formulas into a hierarchal order forming series with unique characteristics.

**Circulenes (Coronoids).** Enumerations of class I monocirculenes (benzenoid-related systems with a single hole) have been investigated.[8-9] Only two synthetic representatives of this class of compounds have been reported.[10-11] Although this class of compounds appears to be of limited practical importance, our brief investigation[8] of these systems was done as background to contribute to our total understanding of all benzenoid hydrocarbons, real or potential. The formulas of this class of compounds is a subset of Table PAH6 whose tabular boundary can be identified by incrementing the formulas of strictly peri-condensed benzenoids by two hydrogens starting with ovalene ($C_{32}H_{14}$). No formula above the $N_{Ic} = 6$ row series in Table PAH6 can correspond to monocirculenes. In this way Table III was generated, which is presented in the index order format. One should note that the pattern of Table III mirrors that of Tables I and II in ref 5. What is important about Table III is that the number of monocirculene isomers for the lower members having formulas on the left-hand
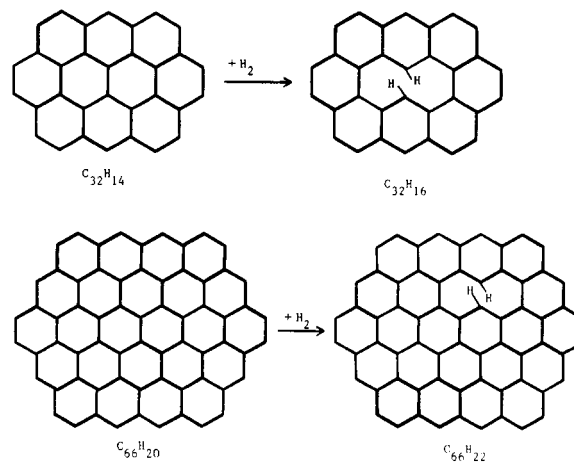
staircase boundary of Table III can be readily enumerated by hand from our prior results.

Consider the one-isomer series. Ovalene is illustrative of our approach. Figure 7 shows that hydrogen can be added (in formal sense) to ovalene to generate a naphthalene-shaped hole. Similarly, addition of $H_2$ to circumovalene ($C_{66}H_{20}$) gives a benzenoid-like successor ($C_{66}H_{22}$) having a naphthalene-shaped hole, and this can be done in six distinct ways giving six isomers. Are there any precursor benzenoids to which $2H_2$ can be added to give another $C_{66}H_{22}$ isomer with a hole shaped like anthracene or phananthrene? No, because $C_{66}H_{18}$ does not correspond to benzenoid formula (i.e., is not on Table PAH6). Are there any precursor benzenoids from which two adjacent internal carbon atoms can be removed and four hydrogens added to the four dangling bonds thus created to give a $C_{66}H_{22}$ isomer with a pyrene-shaped hole? Again the answer is no, since $C_{68}H_{18}$ is not a benzenoid formula. Finally, are there any odd carbon benzenoids from which a single internal carbon atom can be removed and three hydrogens attached to the three dangling bonds thus created to give a $C_{66}H_{22}$ isomer with a phenalenyl-shaped hole? No, because $C_{67}H_{19}$ is not a benzenoid formula [not found on Table PAH6(odd)]. Thus, it must be concluded that there are only six $C_{66}H_{22}$ benzenoid-like isomers with a single hole. Via this algorithm all the monocirculene isomer numbers given in Table IV were enumerated using the one-isomer series in Tables I and II as antecedents. From Table IV it can be seen that the alternating singlet/doublet isomer number occurrence (and the associated topological correspondence) does not appear in this class of

compounds which was the motivation of this investigation.

## SUMMARY

Our conceptual tools of the excised internal structure, strictly peri-condensed, and formula periodic table for benzenoids has led to our recognition of these constant-isomer series and their topological properties. Given that strictly peri-condensed benzenoids cannot 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.[4,6,7] 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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# The Knowledge-Based Organic Physical Property Data System (KB-OPDS)

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The purpose of this paper is to report on a new and comprehensive computer program called the Knowledge-Based Organic Physical Property Data System (KB-OPDS), which was developed at the Institute of Chemical Metallurgy, Academia Sinica. This computer system is an effective integration of five functional software packages—Organic Physical Property Database, Prediction Package, Generalized Package of Automation of Group Additive Methods, Organic Structure Information Processing, and Systematic Qualification of Data and Models. The design principles, program functions, and software structure of KB-OPDS are discussed in detail.

Reliable physical property data are essential to many areas of chemistry and chemical engineering including process design, energy conversion, environmental engineering, organic synthesis, semiconductors, and ceramics processing. The development of computerized databases for chemicals and the computer manipulation of predictive methods have grown significantly in recent years. Chemical engineering databases in various forms have been designed by experienced scientists and engineers at many organizations in the world. These include the Physical Property Data Service (PPDS),[1] the DIPPR Pure Component Data Complication,[2] the Engineering Chemistry Data Bases (ECDB),[3] the DECHEMA[4] Thermophysical Property Databank,[5] and the TRC[6] Vapor Pressure Database.[5]

As a result of examining the chemical literature on databases and expert systems, we find that a need still exists for the development of mature data prediction systems. Such systems should evolve from a systematic and continuous effort. To meet the requirements of industry and academia, additional efforts must be made in accurate property prediction, data evaluation, and the linkage of databases to artificial intelligence (AI). The following sections of this paper will discuss two examples of the computerized database systems, the current evolution of combining AI technology with databases, and database developments in China.

## DATABASE SYSTEMS AND DATABASE SYSTEM DEVELOPMENTS

**Two Successful Database Systems.** The hallmark of a database system is the combination of its reliability and prac-

ticality. One system of this type is PPDS. A widely used software system, it is a joint effort of the National Engineering Laboratory and the Institution of Chemical Engineers (U.K.). It is designed to provide reliable data for engineers involved in the chemical, petrochemical, and process industries. The system contains (a) a pure component database of thermal physical properties for 870 compounds and a program that calculates 18 constant properties and 20 variable properties for mixtures of up to 20 components, (b) a package for certain special purposes of calculating thermal physical data on liquid-phase salts and acid solutions, and (c) a user interface dealing with the direct entry of the user's data, regression of phase equilibrium data, and property prediction; this can help users obtain useful data even if their compound is not in the PPDS database. A feature of the PPDS system is that it offers engineers more than one predictive model for each property. It also permits manual or automatic selection of an appropriate model.

Another important database is the Pure Component Data Compilation under the sponsorship of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers (AIChE). The DIPPR database now provides 26 constant properties and 13 temperature-dependent properties of the 1023 compounds. One major feature of this project is quality control of data in the database. In the DIPPR Data Compilation, two quality codes are used to designate the quality level of data. One is for each property, while the other is for the correlation coefficient. This is of considerable assistance to users because it provides them with an effective method for selecting data from the database and