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REVIEW COMMENTARY

THE CURRENT STATUS OF ISOMER ENUMERATION OF USEFUL BENZENOIDS AND A NEW TOPOLOGICAL PARADIGM

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The enumeration and development of conceptual tools for understanding the chemical properties of practical benzenoid hydrocarbons is stressed. Currently known isomer numbers for benzenoids having up to 60 carbons are summarized. Although there are well over 2 *million* isomers in this range, only approximately 500 benzenoid hydrocarbons have been characterized.

INTRODUCTION

Knowing which benzenoid isomers are absent and present in the environment should provide novel insights and will allow one to speculate the reasons. Herein, the current status of the enumeration of practical benzenoids and the concepts that evolved from these studies are reviewed. The successful enumeration of non-branched benzenoids was achieved by the classical paper of Balaban and Harary.[1] A computerized approach for enumeration of general benzenoids was first accomplished by Knop *et al.*[2] and with its depictions remains a major resource for many useful benzenoids. Although numerous benzenoid computer enumerations have subsequently appeared, they are less useful to practising chemists because the numerical data are in a form which does not allow one to identify the isomer groups easily.[3] It is well known that the number of alkane isomers increases as the number of carbon atoms increases.[4] In contrast, our formula periodic table for benzenoid hydrocarbons (Table 1 or Table PAH6; see the Glossary of Terms) led us to identify special benzenoid series whose number of isomers remains constant as the number of carbons increases.[5] These constant-isomer benzenoid series constitute a phenomenon that we call an edge effect of Table PAH6 that is intricately related to the topology of the benzenoid members. Constant-isomer benzenoid series have formulas found on the left-hand staircase edge (boundary) of Table PAH6. Thus, we claim to have identified a new paradigm that may have universal topological implications since the polyhex structure is fundamental to nature.[6]

A FORMULA PERIODIC TABLE FOR BENZENOID HYDROCARBONS (TABLE PAH6)

Previously, we presented a formal definition of a periodic table set.[7] Key features of this definition are hierarchal ordering, two-dimensionality and edge effects. Both Table PAH6 and the Periodic Table of elements possess these features.

Since our enumeration studies have focused principally on the more stable even-carbon benzenoids of practical importance,[8] odd-carbon benzenoids which are always radical species will only be discussed when it enhances our understanding of even-carbon compounds through intercomparison of their relationships.

The formula periodic table for even-carbon benzenoids will be designated Table PAH6 and for odd-carbon benzenoids Table PAH6(odd). Throughout this paper the carbon and hydrogen atoms and the pπ 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.

The formulas for all benzenoids are given in Table PAH6 which has x, y-coordinates of (d_s, N_{IC}). Recursive construction of this table was accomplished using the aufbau principle.[9] Table PAH6 complies with a sextet rule analogous to the octet rule for the Periodic

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Table 1. Table PAH6: formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6)

$d_s = -9$	$d_s = -8$	$d_s = -7$	$d_s = -6$	$d_s = -5$	$d_s = -4$	$d_s = -3$	$d_s = -2$	$d_s = -1$	$d_s = 0$	$d_s = 1$	$d_s = 2$	$d_s = 3$		N_{IC}
	Forbidden Region						Most Reactive		$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	…	0
									$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	…	2
					$N_C/N_H < 2$				$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$	…	4
		$C_{00}H_{00}$						$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$	…	6
					$2 < \frac{N_C}{N_H} < 3$			$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	…	8
							$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	…	10
	$\frac{N_C}{N_H} > 3$						$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	…	12
						$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	…	14
					$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	…		
					$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	…			
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	…	…	…	…				
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	…								
Least Reactive		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	…									
		$C_{60}H_{20}$	$C_{64}H_{22}$	…				Intermediate Reactive						
	$C_{62}H_{20}$	$C_{66}H_{22}$	…											
$C_{64}H_{20}$	$C_{68}H_{22}$	…												
$C_{70}H_{22}$	…													
…														

Table of elements, and $d_s = r - 2 - N_{IC}$ is analogous to the outer-shell electronic configuration and N_{IC} is analogous to the principal quantum number associated with the Periodic Table of elements. Thus, Table PAH6 can be considered to be 'Mendeleevian.'[2]

Table PAH6 represents a partially ordered set which sorts benzenoid hydrocarbons into isomer groups and delineates their graph-derived properties. These absolute group properties are fixed and are useful in studying differences among isomer groups. For example, the average electronic pπ energy between isomer groups is principally determined by N_C and q.[9] To study differences among PAH6 isomers, one needs graphical invariants that change from one isomer to another. The members of a benzenoid isomer set have the same values for the invariants of d_s, N_C, N_H, N_{IC}, q and r (see Glossary of Terms). Table 2 presents a summary of the properties associated with Table PAH6.

In Table PAH6 every compound in a particular column has the same d_s value, and every compound in the same row has the same N_{IC} value. Member compounds in the same column with the same d_s value belong to the same column series ($N_C = 3N_H - 14 - 2d_s$, where d_s is specified), and member compounds in the same row with the same N_{IC} value belong to the same row series ($N_C = 2N_H - 6 + N_{IC}$, N_{IC} is specified). For example, all PAH6 isomers of the formulas $C_{16}H_{10}$ and $C_{20}H_{12}$ have the same value of $N_{IC} = 2$ and, similarly, all PAH6 isomers of the formulas $C_{20}H_{12}$ and $C_{26}H_{14}$ have the same value of $d_S = 1$. Table PAH6 extends infinitely in three directions: horizontally to the right, vertically to the bottom and in a slanting direction to the left. The top of this table contains the *cata*-condensed benzenoids ($N_{IC} = 0$) of progressively larger size as one goes from left to right.

The criteria for a periodic table set is that it is a partially ordered set (poset) forming a two-dimensional array complying with reflexivity, antisymmetry, and transitivity, and Dobereiner's triad principle where the middle member (element) has a metric property which is the arithmetic mean of the other two surrounding members.[7] This constitutes a formal definition of a periodic table set.

The recognition of the attributes that define a periodic table set began with Dobereiner's principle of triads, which was subsequently expanded into a Mendeleevian two-dimensional partial ordering. We now propose that every such set possesses a boundary (edge) which exhibits special characteristics. The members of a periodic table set found on the edge (boundary) possess unique properties. For example, the Periodic Table of elements is bounded by three edges or boundaries. The upper edge consists of First and Second Period elements which are the most unique elements of the family because of their small size and absence of d subshells. On the left edge the alkali metals are the most reactive of all metals and on the right edge the noble gases are the least reactive of all elements. Similarly, the formula periodic table for benzenoids (Table PAH6) has two edges. The upper horizontal edge consists of *cata*-condensed benzenoids with characteristically

Table 2. Hierarchical two-dimensional ordering of benzenoid isomer groups by Table PAH6

1. Properties
   - A. Molecular weight
   - B. Average $E\pi$
2. Topological characteristics
   - A. *Strictly peri-condensed* benzenoids are sorted toward the left-hand staircase edge and highly branched benzenoids toward the right-hand horizontal edge. Constant-isomer benzenoids occur on the staircase edge.
   - B. *Row series*
     - a. Sorts benzenoids with the same N_{IC} values into the same row
     - b. Sorts *cata*-condensed benzenoids into $N_{IC} = 0$ row
     - c. Sorts pyrene/perylene/zethrene benzenoids into the $N_{IC} = 2$ row
     - d. Sorts benzenoids with $N_C/N_H = 2$ into the $N_{IC} = 6$ row
     - e. Sorts benzenoids having spanning subgraphs with an odd number of K_2 and C_{4n+2} components into the $N_{IC} \equiv \mathbf{0}$ (mod 4) rows
     - f. Benzenoids with Hamiltonian circuits are only found in the $N_{IC} \equiv \mathbf{0}$ (mod 4) rows
   - C. *Column series*
     - a. Sorts benzenoids with the same d_s value into the same column
     - b. Sorts non-radical threefold, sixfold and total resonant sextet benzenoids into the $N_{IC} \equiv 0$ (mod 6) columns
     - c. Sorts benzenoids with an odd number of rings into every other column
     - d. Sorts benzenoids with $N_C/N_H = 3$ into the $d_s = -7$ column
   - D. *Other series*
     - a. Sorts benzenoids of the same perimeter (N_H) into positive sloping alignments with shift coordinates ($\Delta d_s, \Delta N_{IC}/2$) of (1, 1)
     - b. Sorts benzenoids of the same N_C according to shift coordinates of (3, 2) and of the same r according to (2, 1)
     - c. Sorts benzenoids of the same q_1 according to shift coordinates of (4, 1)

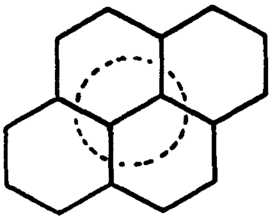
unique properties and the sloping left-hand staircase edge which consists of strictly *peri*-condensed benzenoids having unique properties that have been the subject of our work. This edge effect is characteristic of all two-dimensional posets.

Through a vector addition analog method, we previously showed that the total pπ energy (E_π^L) of a large benzenoid hydrocarbon can be estimated from the known E_π values of smaller hydrocarbons.[9] Thus, when the number of carbon (N_C^L) and hydrogen (N_H^L) atoms of a large benzenoid hydrocarbon is related by $(N_C^L, N_H^L) = (N_C, N_H) + (N_C', N_H') = (N_C + N_C', N_H + N_H')$ to the number of carbon and hydrogen atoms of smaller benzenoid hydrocarbons, then $E_\pi^L = E_\pi + E_\pi'$.

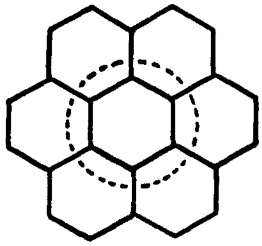
STRICTLY *PERI*-CONDENSED BENZENOIDS AND THEIR EXCIZED INTERNAL STRUCTURES

In this paper only the σ-bond molecular graph (polyhex graph) will be shown for all benzenoids. The number of carbon atom vertices will be denoted by N_C, the number of internal carbon vertices bounded by three hexagonal rings by N_{IC} and the net number of disconnections (positive values) and/or rings (negative values) among the internal edges (edges bounded by two rings) by 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 *peri*-condensed benzenoid hydrocarbon has all its internal third-degree vertices mutually connected ($d_s = 0, -1, -2, \ldots$) and has no *cata*-condensed appendages. An excized internal structure is the set of connected internal vertices usually associated with a strictly *peri*-condensed benzenoid which has a formula found at the extreme left-hand boundary of the formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6s).[5] For example, the excized internal structure of pyrene is ethene and of coronene is benzene as shown below by the dotted line. Even carbon strictly *peri*-condensed benzenoids have no proximate triplet of bay regions and on a per carbon basis have the fewest number of bay regions and are among the benzenoids with the highest pπ electronic energy.[5,8]

Strictly *peri*-condensed benzenoids have many distinctive properties that uniquely characterize them. As the ratio N_C/N_H increases, a benzenoid becomes more *peri*-condensed, which is of crucial importance in determining whether a β-packing crystal structure (graphite rhombohedral) is adopted or not.[10] A higher N_C/N_H ratio favors the β-packing over the non-β (herringbone) packing because of the differing relative importance of C–C and C–H interactions in these two situations. Higher fused ring benzenoids become increasingly graphitic and tend toward the ultimate β-packing where the crystal stabilization is exclusively through C–C interactions. Thus, all *cata*-condensed benzenoids having their peripheral H atoms exposed adopt a herringbone crystal packing structure, and strictly *peri*-condensed benzenoids with $N_C/N_H > 2{\cdot}3$ are expected to adopt a β-graphite-like crystal packing.



Pyrene (ethene)



Coronene (benzene)

BENZENOID ENUMERATION VIA THEIR EXCIZED INTERNAL STRUCTURES

Strictly *peri*-condensed benzenoid isomers can be generated by enumeration of their excized internal structures.[9] This method has led to the identification of strictly *peri*-condensed benzenoid series having a constant number of isomers (Tables 3 and 4). For example, the excized internal structures of pyrene ($C_{16}H_{10}$), coronene ($C_{24}H_{12}$) and ovalene ($C_{32}H_{14}$) are ethene, benzene and naphthalene, respectively, which have no other isomers composed exclusively of hexagonal rings. By successively circumscribing a carbon-atom perimeter around each of these strictly *peri*-condensed benzenoids of pyrene, coronene and ovalene, the one-isomer series presented in Table 3 are obtained. Note that each time a benzenoid is circumscribed it must be incremented with six hydrogens. One must clearly distinguish between a base excized structure belonging to a constant-isomer series and the ultimate excized internal structure. A base excized internal structure is the first strictly *peri*-condensed benzenoid (first generation) of a constant-isomer series. For example, pyrene, coronene and ovalene are base excized internal structures for the one-isomer series summarized in Table 3, whereas ethene, benzene and naphthalene are their respective ultimate excized internal structures.

Pyrene is a strictly *peri*-condensed benzenoid with an ethene excized internal structure.[5,6] Since ethene is incapable of having isomers, pyrene has no other

Table 3. Constant isomer series of even-carbon strictly *peri*-condensed benzenoids

Series	No. of isomers[a]	Series	No. of isomers[a]
(C_6H_6)		$C_{124}H_{28}$	38(19)
$C_{24}H_{12}$	1	$C_{186}H_{34}$	
$C_{54}H_{18}$		$C_{260}H_{40}$	
$C_{96}H_{24}$		⋮	
⋮		$C_{142}H_{30}$	86(47)
($C_{10}H_8$)	1	$C_{208}H_{36}$	
$C_{32}H_{14}$		$C_{286}H_{42}$	
$C_{66}H_{20}$		⋮	
$C_{112}H_{26}$		$C_{162}H_{32}$	128(71)
$C_{170}H_{32}$		$C_{232}H_{38}$	
⋮		$C_{314}H_{44}$	
$C_{16}H_{10}$	1	⋮	
$C_{42}H_{16}$		$C_{184}H_{34}$	128(71)
$C_{80}H_{22}$		$C_{258}H_{40}$	
$C_{130}H_{28}$		$C_{344}H_{46}$	
⋮		⋮	
$C_{22}H_{12}$	2(1)	$C_{206}H_{36}$	264(164)
$C_{52}H_{18}$		$C_{284}H_{42}$	
$C_{94}H_{24}$		$C_{374}H_{48}$	
$C_{148}H_{30}$		⋮	
⋮		$C_{230}H_{38}$	373(243)
$C_{30}H_{14}$	3(1)	$C_{312}H_{44}$	
$C_{64}H_{20}$		$C_{406}H_{50}$	
$C_{110}H_{26}$		⋮	
$C_{168}H_{32}$		$C_{256}H_{40}$	373(243)
⋮		$C_{342}H_{46}$	
$C_{40}H_{16}$	3(1)	$C_{440}H_{52}$	
$C_{78}H_{22}$		⋮	
$C_{128}H_{28}$		$C_{282}H_{42}$	749(516)
⋮		$C_{372}H_{48}$	
$C_{50}H_{18}$	7(2)	$C_{474}H_{54}$	
$C_{92}H_{24}$		⋮	
$C_{146}H_{30}$		$C_{310}H_{44}$	~1055(745)
⋮		$C_{404}H_{50}$	
$C_{62}H_{20}$	12(4)	⋮	
$C_{108}H_{26}$		$C_{340}H_{46}$	~1055(745)
$C_{166}H_{32}$		$C_{438}H_{52}$	
$C_{236}H_{38}$		⋮	
⋮			
$C_{76}H_{22}$	12(4)		
$C_{126}H_{28}$			
$C_{188}H_{34}$			
⋮			
$C_{90}H_{24}$	27(12)		
$C_{144}H_{30}$			
$C_{210}H_{36}$			
⋮			
$C_{106}H_{26}$	38(19)		
$C_{164}H_{32}$			
$C_{234}H_{38}$			

[a] The number of less stable radical isomers is given in parentheses.

benzenoid isomer since it has only one arrangement of its internal third-degree vertices. There are three isomers of the formula C_4H_6 (Figure 1): *s-cis*-buta-1,3-diene, *s-trans*-buta-1,3-diene and trimethylenemethane diradical. If an 18-carbon-atom perimeter is circumscribed about each of these C_4H_6 isomers with the resulting species being incremented with six hydrogens, one obtains the only three $C_{22}H_{12}$ benzenoid isomers possible for this formula, i.e. benzo[*ghi*]perylene, anthanthrene and triangulene. If these three latter strictly *peri*-condensed benzenoids are circumscribed by a 30-carbon-atom perimeter followed by incrementa-

Table 4. Constant isomer series of odd-carbon strictly *peri*-condensed benzenoids

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

[a] Predicted value based on induction

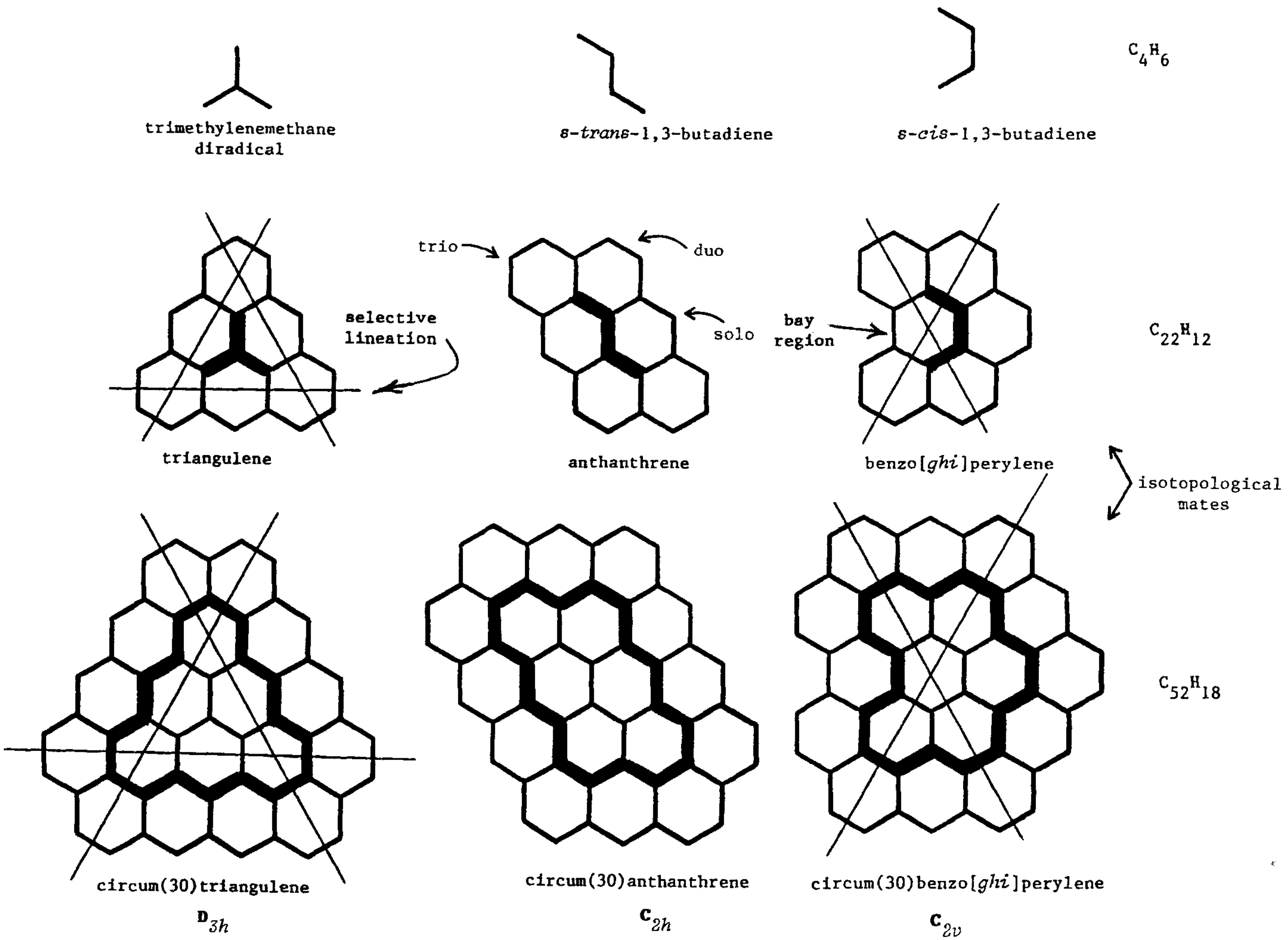


Figure 1. Illustration of the excized internal structure concept in enumeration of all the benzenoid isomers of $C_{22}H_{12}$, $C_{52}H_{18}$, $C_{94}H_{24}$, ...

tion with six Hs, one obtains the only three benzenoid isomers possible for $C_{52}H_{18}$.

Whenever a strictly *peri*-condensed benzenoid has an excized internal structure that can be ultimately pruned to trimethylenemethane diradical, then the corresponding strictly *peri*-condensed benzenoid will also be a diradical. Triangulene is a diradical because its excized internal structure is trimethylenemethane diradical.[5,11] Similarly, dibenzo[*bc*, *hi*]coronene is a diradical because its excized internal structure is *meta*-quinodimethane which can be pruned of buta-1,3-diene to give trimethylenemethane diradical. Since triangulene is a diradical with three selective lineations (shown as lines in Figure 1), by visual inspection we immediately know 8 of its 22 eigenvalues as 0, 0, ±1, ±1 and ±1β. For each unpaired electron in a radical polyene, there will be an HMO eigenvalue (energy level) of zero. Whenever a benzenoid structure can have a succession of parallel edges bisected with a straight line drawn from one side of the molecule to the other with the terminal rings being symmetrically convex relative to this line, then those edges intersected can be embedded with a succession of ethene substructures and the benzenoid structure as a whole will have at least one eigenvalue pair of ±1.

CONSTANT-ISOMER SERIES OF STRICTLY *PERI*-CONDENSED BENZENOIDS

Tables 3 and 4 present all known benzenoid constant-isomer series in which the latter contains odd carbon radical benzenoids.[6] Each table reveals the same distinct pattern in which the number of isomers alternate between single and pairwise 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. As will now be shown, each pair of series with the same isomer number possess a one-to-one topological correspondence between their benzenoid members in the characteristics defined below.

There are three structural or topological properties considered: symmetry and the number of bay regions and selective lineations possessed by the benzenoids. Topology is the study of the way that lines, surfaces, etc. connect themselves; it deals with properties of a geometric figure that do not vary when the figure is distorted without tearing surfaces or breaking edges. One can deform the polyhex structures associated with the constant-isomer benzenoids and the carbon vertex adjacency described by what we refer to as symmetry, bay region and selective lineation will be invariant. When two benzenoids are identical in these parameters, they are said to be isotopological as they are not isomorphic. Within a constant-isomer series the benzenoid members have isotopological mates in going from one isomer set to another. Figure 1 shows an example of a constant-isomer series with a bay region, selective lineations and isotopological mates. It will now be shown that the paired constant-isomer series with the same isomer number (Tables 3 and 4) also have the same topological characteristics.[6]

TOPOLOGICAL CHARACTERISTICS

The one-isomer series (Table 3) beginning with benzene is unique and has corresponding benzenoids with D_{6h} symmetry.[6] Both of 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. 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 non-radical 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.[5] 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 each have D_{2h} symmetry, no bay region and one selective lineation.[5] Figures 2–5 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 4) beginning with phenalenyl ($C_{13}H_9$) is unique and has benzenoids with D_{3h} symmetry.[6] 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 $C_{57}H_{19}$ are shown in Figures 6 and 7, respectively, and form topologically equivalent benzenoid groups. The constant-isomer series starting with $C_{83}H_{23}$ and $C_{99}H_{25}$ each 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.

For the constant-isomer series in Tables 3 and 4, the diradical benzenoids (Table 3) have a one-to-one topological correspondence to the monoradical benzenoids (Table 4).[6] The $C_{22}H_{12}$ diradical (triangulene) and $C_{13}H_9$ monoradical (phenalenyl) both have D_{3h} symmetry, no bay regions and three selective lineations. The $C_{30}H_{14}$ diradical and $C_{19}H_{11}$ monoradical both have C_{2v} symmetry, no bay regions and one selective lineation, as do the $C_{40}H_{16}$ diradical and the $C_{27}H_{18}$ monoradical. The two $C_{50}H_{18}$ diradicals and the two $C_{35}H_{15}$ monoradicals each have C_s symmetry and a

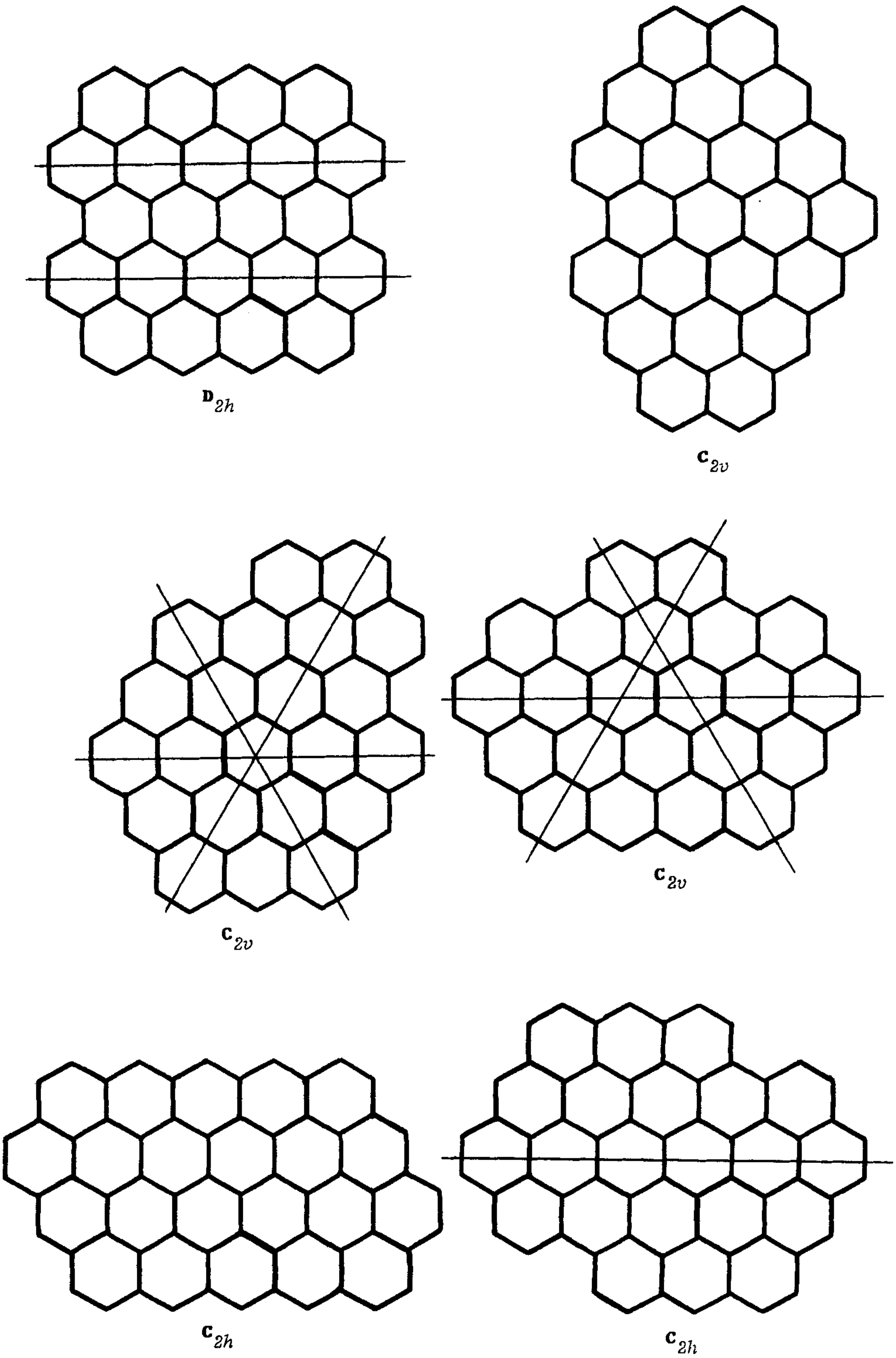
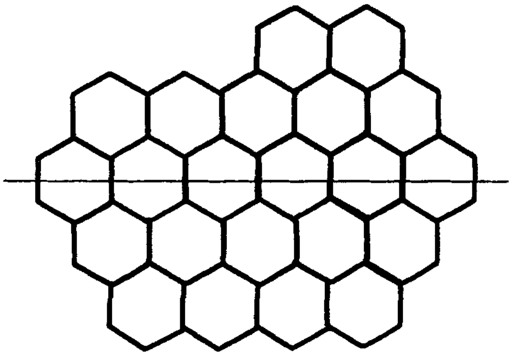
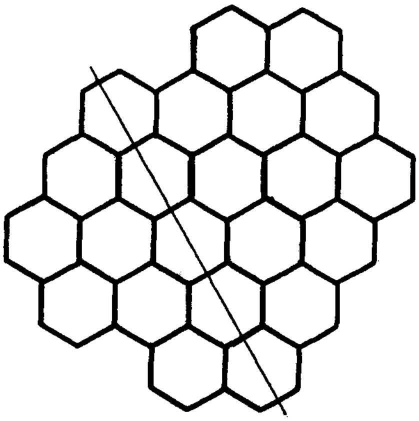


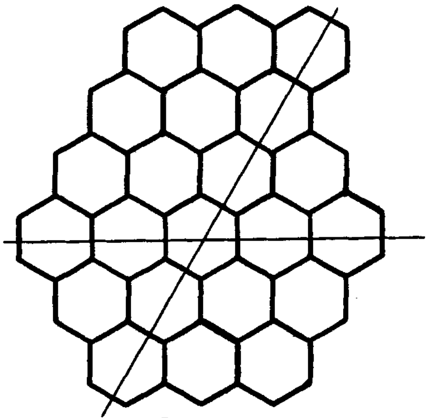
Figure 2. Base members of the $C_{62}H_{20}$ constant-isomer benzenoid series (*continued*)



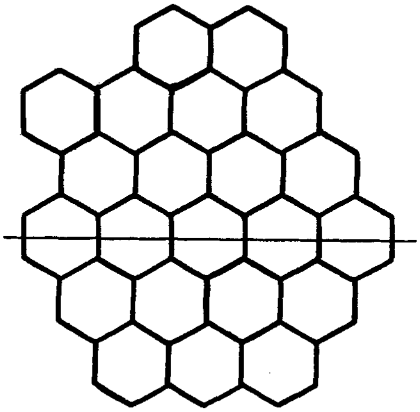
C_s



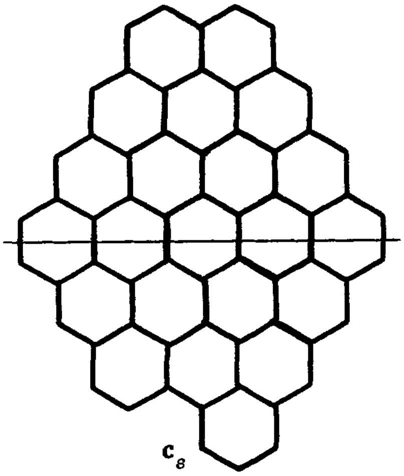
C_s



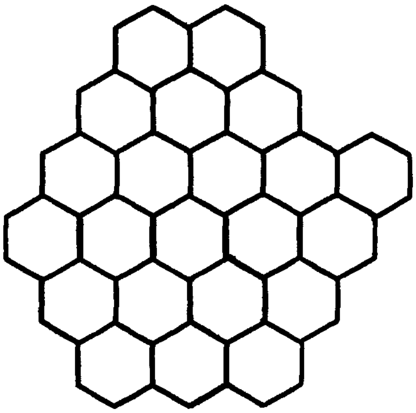
C_s



C_s

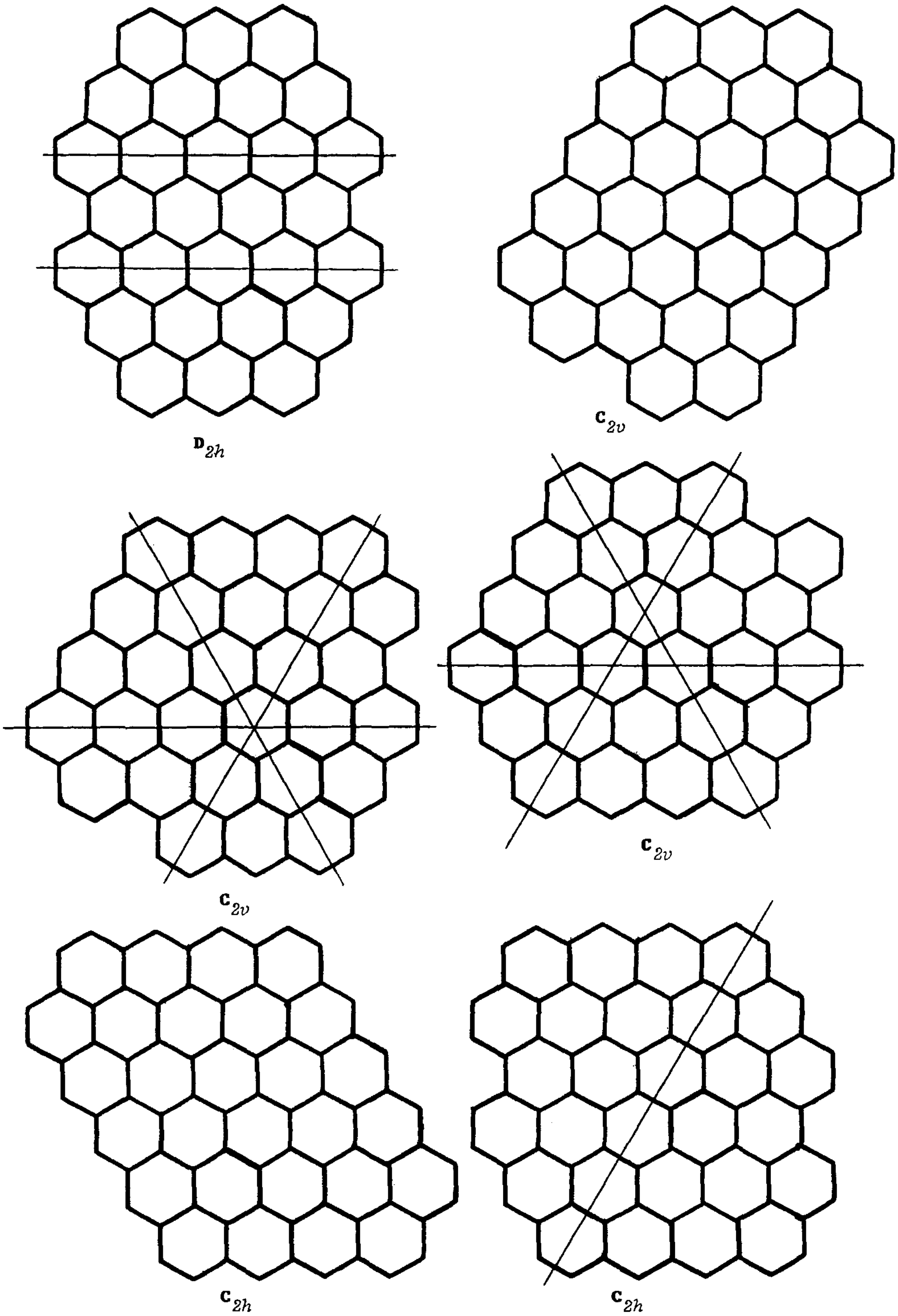


C_s



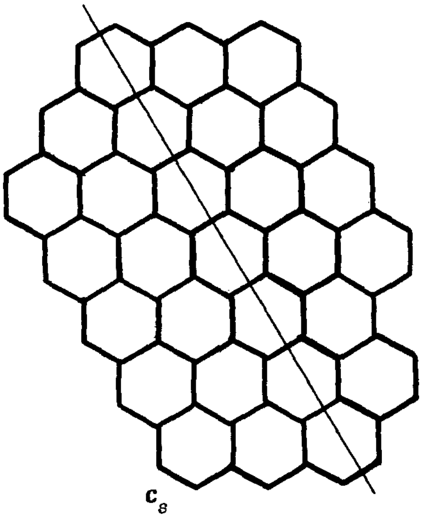
C_s

Figure 2. (*Continued*)

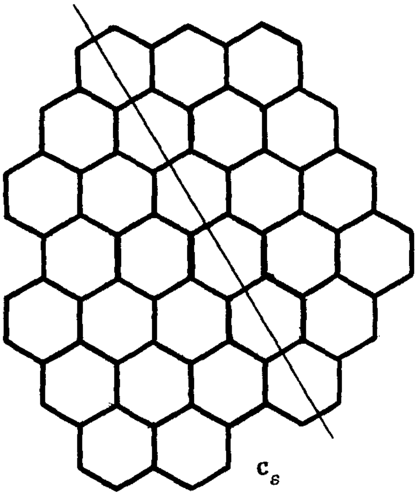


D_{2h} C_{2v} C_{2v} C_{2v} C_{2h} C_{2h}

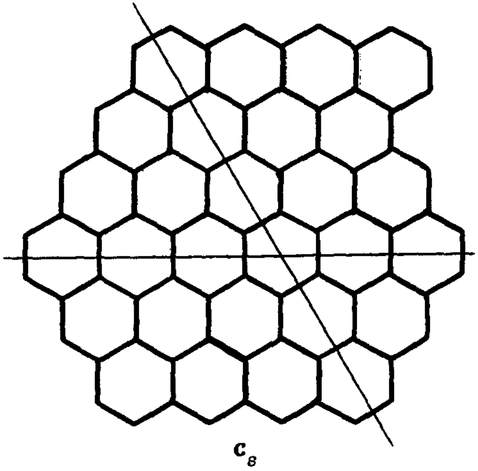
Figure 3. Base members of the $C_{76}H_{22}$ constant-isomer benzenoid series (*continued*)



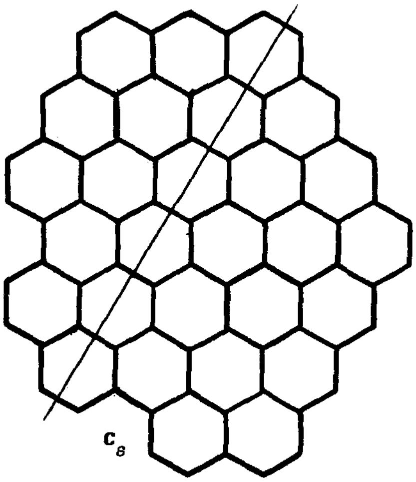
C_s



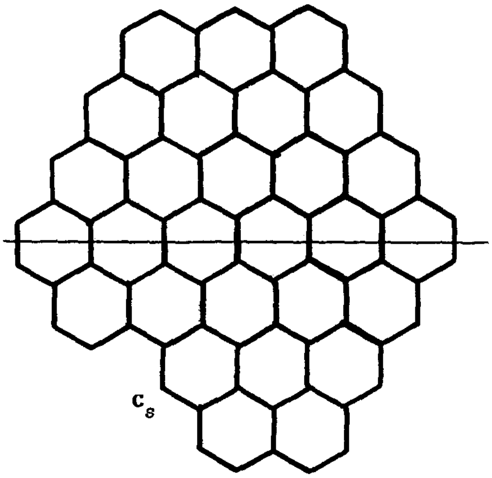
C_s



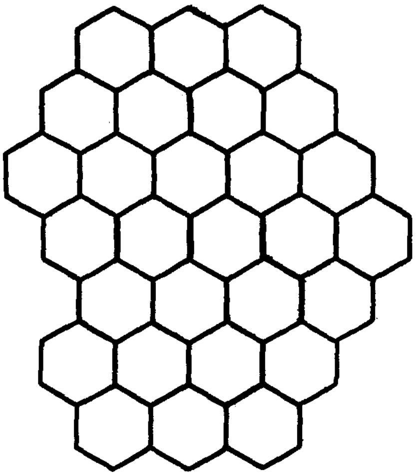
C_s



C_s



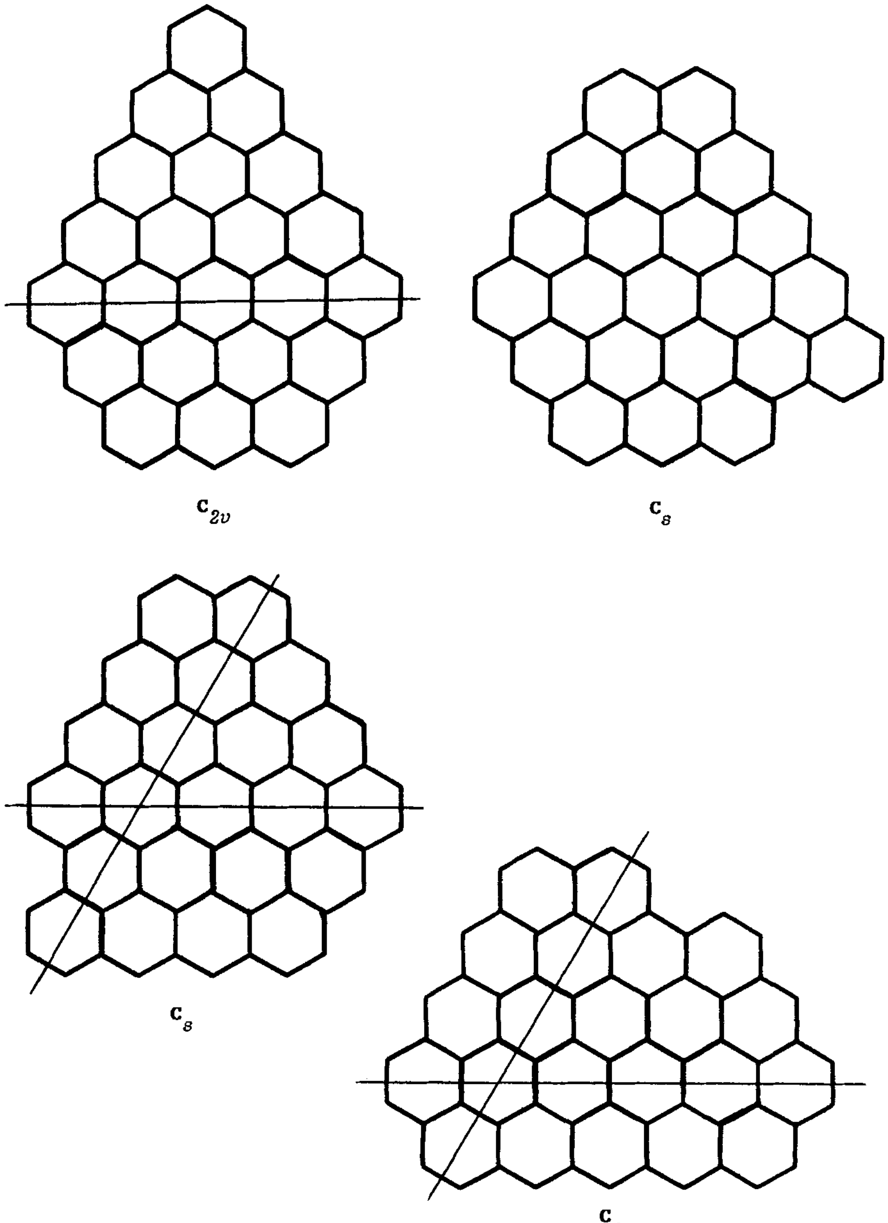
C_s



C_s

Figure 3. (*continued*)

member of each pair has one bay region and two selective lineations while the other has neither. There is a one-to-one topological correspondence between the four diradicals of $C_{62}H_{20}$ and the four monoradicals of $C_{45}H_{17}$, as there is for the four diradicals of $C_{76}H_{22}$ and the four monoradicals of $C_{57}H_{19}$ (Figures 4–7). There is a one-to-one topological correspondence between the 12 diradicals of $C_{90}H_{24}$ and 12 of the monoradicals of $C_{69}H_{21}$. In addition, $C_{69}H_{21}$ possesses a triradical which has no correspondent. With regard to symmetry, number of bay regions and number of selective lineations, there is again a one-to-one correspondence between the 19 ($16C_s + 3C_{2v}$) $C_{106}H_{26}$ and $C_{124}H_{28}$ benzenoid diradicals and the 19 $C_{83}H_{23}$ and $C_{99}H_{25}$

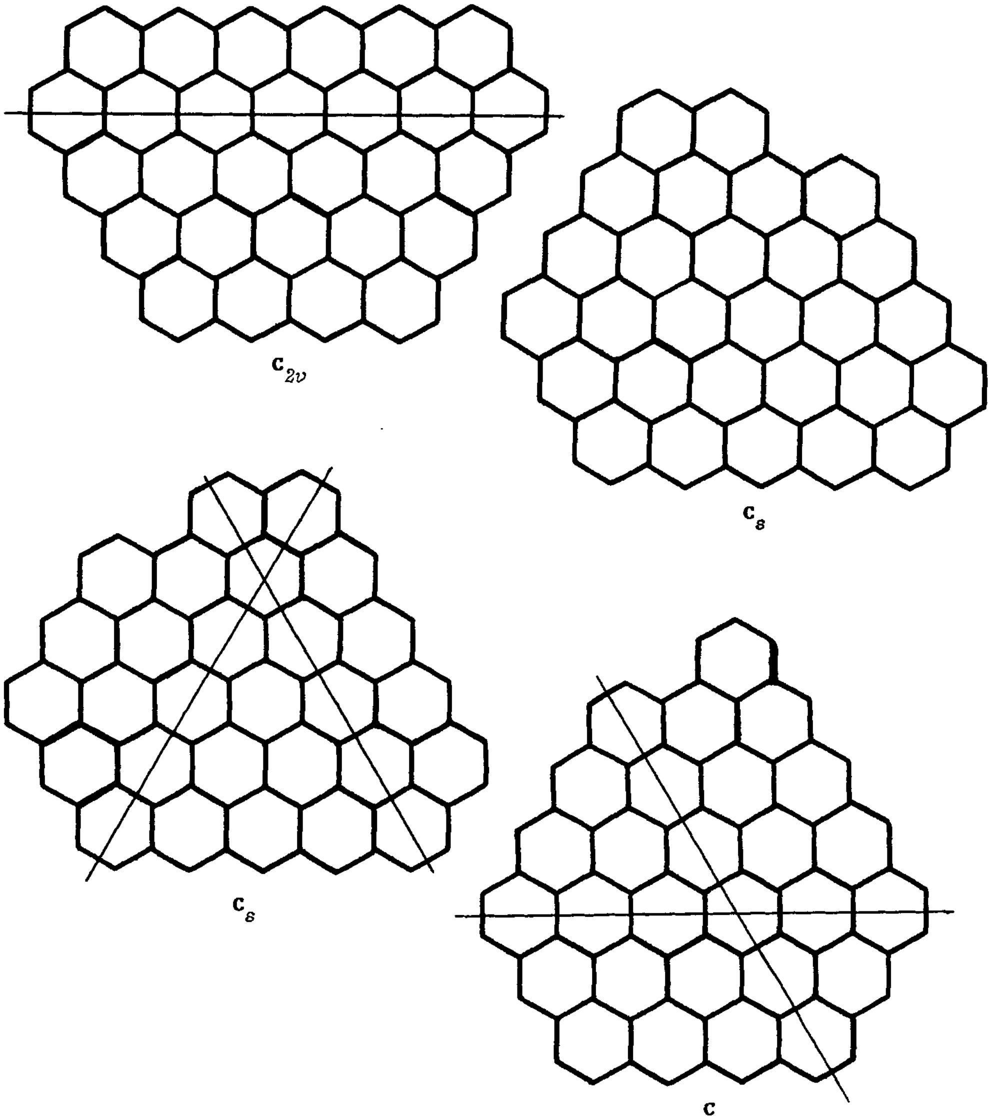

C_{2v} C_s

C_s C_s

Figure 4. Diradical base members of the $C_{62}H_{20}$ constant-isomer benzenoid series

benzenoid monoradicals. The additional triradical benzenoid isomers of $C_{83}H_{23}$ and $C_{99}H_{25}$ have no correspondents. The origin of the topological correspondence between these odd-carbon monoradicals and even-carbon diradical benzenoids belonging to the constant-isomer series appears to arise from the common threefold symmetry of the centralized methyl radical and trimethylenemethane diradical substructures in a polyhex system. This correspondence of benzenoids belonging to the left-hand staircase edge of Table PAH6 appears to be governed by a fundamental topological principle which limits the number of possible arrangements of hexagons. Hence this edge effect of Table PAH6 is intricately related to the topological characteristics of the benzenoid members having the formulas given in Tables 3 and 4.

Previously, we showed that the perimeter topology of benzenoids followed the equation $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6$, where η_0 is the number of bay regions, η_2 is the number of duo groups, η_3 is the number of trio groups and η_4 is the number of quartet groups (*cata*-condensed appendages);[8] the number of



C_{2v}

C_s

C_s

C_s

Figure 5. Diradical base members of the $C_{76}H_{22}$ constant-isomer benzenoid series

solo (η_1) groups is independent of this equation (Figure 1). These perimeter groups have distinct infrared absorption bands due to out-of-plane bending vibrations and distinct nuclear magnetic resonance chemical shifts and splitting patterns. The solo group has the highest IR vibration frequency (900–860 cm^{-1}) and PMR chemical shift value (*ca* 8·3 ppm in the absence of proximate bay regions).[8] 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 $-\eta_0 + \eta_2 = 6$ ($\eta_2 \geqslant 6$). Thus, η_0 and η_2 remain constant while η_1 increases ($\Delta\eta_1 = 6$ for each incrementation) as the number of carbons in a constant-isomer 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 might yield considerable information by determining the ratio η_1 to η_2.

In general, the most reactive sites on a benzenoid hydrocarbon are solo positions and the least reactive are the central trio positions. The second most reactive type of site is the non-central trio position. For example, anthanthrene ($C_{22}H_{12}$) has two each of the solo (positions 6 and 12), duo (positions 4, 5, 10 and 11) and trio (positions 1, 2, 3, 7, 8 and 19) peripheral groups. If electrophilic substitution occurs at position 6, one obtains a carbocation transition intermediate with 58 resonance structures, whereas electrophilic substitution at the central position 2 gives a carbocation transition intermediate with only 24 resonance structures. Similarly, the non-central trio positions 1 and 3 give 54 and 52 cation resonance structures, respectively, and the duo positions 4 and 5 both give 34 cation tran-

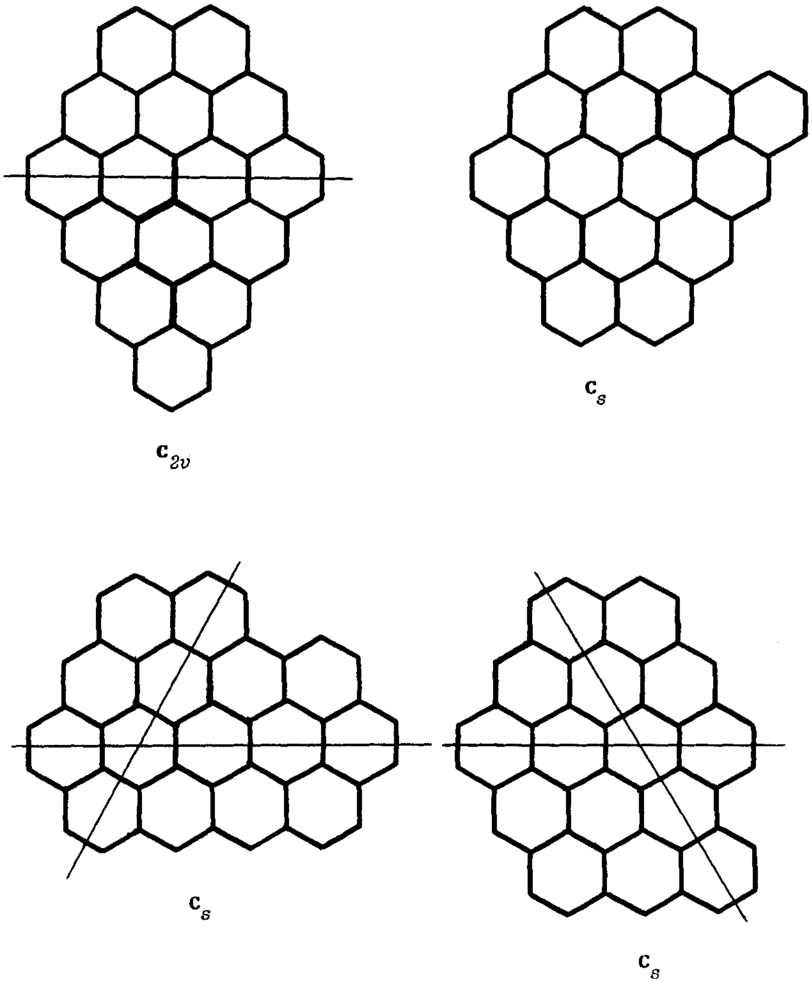
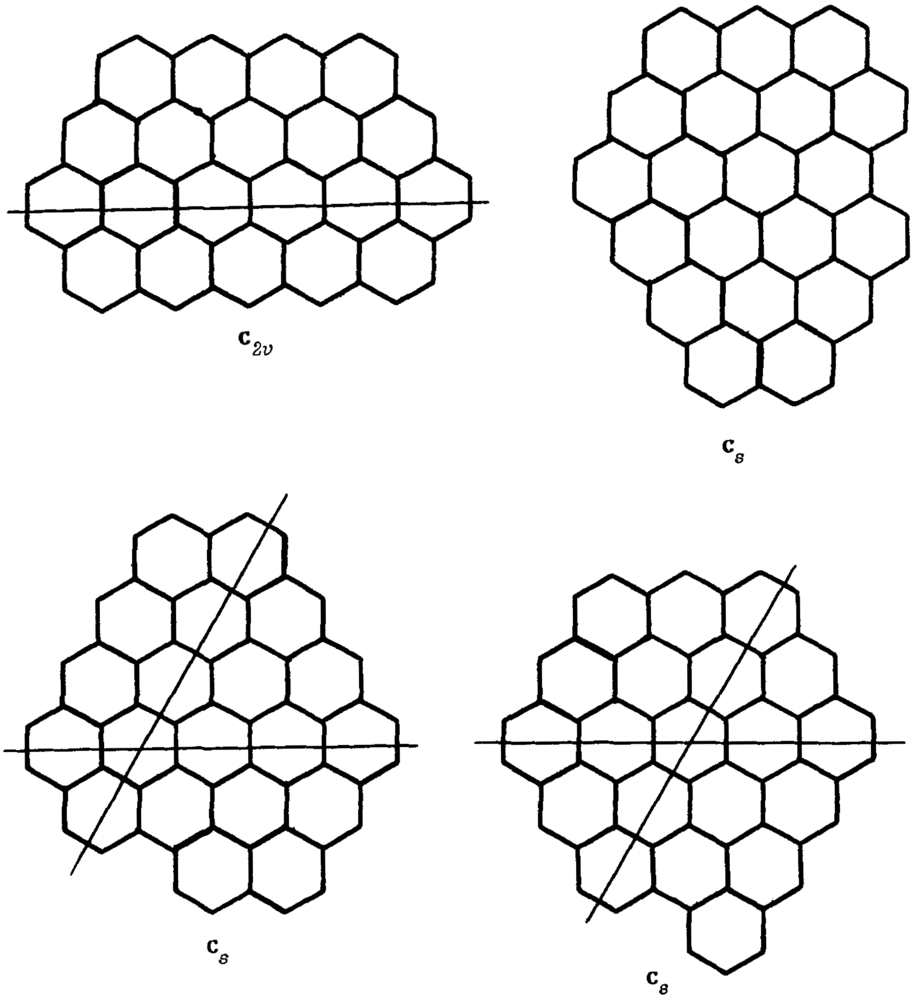


Figure 6. Base members of the $C_{45}H_{17}$ constant-isomer benzenoid series



C_{2v} C_s C_s C_s

Figure 7. Base members of the $C_{57}H_{19}$ constant-isomer benzenoid series

sition resonance structures. These results are in agreement with the magnitude of the HMO coefficients for the HOMO $= 0{\cdot}291\beta$: $C_6 = 0{\cdot}371$, $C_2 = -0{\cdot}056$, $C_1 = -0{\cdot}328$, $C_3 = 0{\cdot}311$ $C_4 = -0{\cdot}209$ and $C_5 = -0{\cdot}208$.

The efficient two-dimensional packing of equal-sized spheres in such a way as to minimize void space is a useful model for studying the underlying geometrical principles that play a role in cellular agglomeration and growth. It turns out that this model is isomorphic to the arrangements of polyhex systems where each sphere is replaced by a hexagon. Thus, from Tables 3 and 4 using $r = \frac{1}{2}(N_c + 2 - N_H)$ one can determine the number of compact arrangements of equal-sized spheres. For example, from the series $C_{90}H_{24}$, $C_{144}H_{30}$, $C_{210}H_{36}, \ldots$, one can determine that 34, 58, 88, 124,... spheres have only 39 compact arrangements.

ENUMERATION OF PRACTICAL BENZENOID HYDROCARBONS

No benzenoid with more than 58 carbons has yet been characterized and reported in the literature.[8] Table 5 summarizes the known information on formulas for the benzenoids having up to 60 carbon atoms together with their theoretical number of non-radical (Kekulean) constitutional isomers. These results were taken from several sources and represent what the author believes to be most reliable values.[2,3,12] These numbers need to be carefully interpreted because helicenic isomers which also exhibit stereoisomeric forms have been excluded, even though the largest *cata*-condensed benzenoid synthesized to date was [14]helicene ($C_{58}H_{32}$). In spite of their strain, it may well be that helicenic benzenoids are among the more stable isomers.[13] Also helicenes can

Table 5. Number of constitutional isomers of benzenoid hydrocarbons with up to 60 carbons

N_{IC}	No. of isomers	N_{IC}	No. of isomers
$N_{\text{IC}} = 0$		$N_{\text{IC}} = 10$	
$C_{10}H_8$	1	$C_{32}H_{14}$	3
$C_{14}H_{10}$	2	$C_{36}H_{16}$	20
$C_{18}H_{12}$	5	$C_{40}H_{18}$	$< 279^{c}$
$C_{22}H_{14}$	12	$C_{44}H_{18}$	< 2459
$C_{26}H_{16}$	37	$C_{48}H_{22}$	< 20321
$C_{30}H_{18}$	123	$C_{52}H_{24}$	$\sim 155656^{d}$
$C_{34}H_{20}$	$> 411^{a}$	$C_{56}H_{26}$	$\sim 1132642^{d}$
$C_{38}H_{22}$	> 1489		
$C_{42}H_{24}$	> 5572	$N_{\text{IC}} = 12$	
$C_{46}H_{26}$	> 21115		
$C_{50}H_{28}$	> 81121	$C_{38}H_{16}$	10
$C_{54}H_{30}$	> 311408	$C_{42}H_{18}$	$< 187^{c}$
$C_{58}H_{32}$	> 1212066	$C_{46}H_{20}$	$< 2001^{d}$
		$C_{50}H_{22}$	< 18396
$N_{\text{IC}} = 2$		$C_{54}H_{24}$	$\sim 156434^{d}$
		$C_{58}H_{26}$	$\sim 1236839^{d}$
$C_{16}H_{10}$	1		
$C_{20}H_{12}$	3	$N_{\text{IC}} = 14$	
$C_{24}H_{14}$	13		
$C_{28}H_{16}$	62	$C_{40}H_{16}$	3^{d}
$C_{32}H_{18}$	$> 287^{a}$	$C_{44}H_{18}$	$< 120^{c,d}$
$C_{36}H_{20}$	> 1352	$C_{48}H_{20}$	< 1570
$C_{40}H_{22}$	> 6256	$C_{52}H_{22}$	$< 16234^{d}$
$C_{44}H_{24}$	$\sim 36109^{b}$	$C_{56}H_{24}$	$\sim 148430^{b,d}$
$C_{48}H_{26}$	~ 168318	$C_{60}H_{26}$	$\sim 1262442^{d}$
$N_{\text{IC}} = 4$		$N_{\text{IC}} = 16$	
$C_{22}H_{12}$	2	$C_{42}H_{16}$	1^{d}
$C_{26}H_{14}$	9	$C_{46}H_{18}$	49^{d}
$C_{30}H_{16}$	58	$C_{50}H_{20}$	$< 1121^{c,d}$
$C_{34}H_{18}$	$> 333^{a}$	$C_{54}H_{22}$	$< 13286^{d}$
$C_{38}H_{20}$	> 1907	$C_{58}H_{24}$	$\sim 133713^{b}$
$C_{42}H_{22}$	$\sim 13415^{b}$		
$C_{46}H_{24}$	~ 74985	$N_{\text{IC}} = 18$	
$C_{50}H_{26}$	~ 408785		
		$C_{48}H_{18}$	22^{d}
		$C_{52}H_{20}$	$< 763^{c,d}$
		$C_{56}H_{22}$	$< 10587^{d}$
		$C_{60}H_{24}$	$\sim 116648^{b,d}$
$N_{\text{IC}} = 6$		$N_{\text{IC}} = 20$	
$C_{24}H_{12}$	1	$C_{50}H_{18}$	7^{d}
$C_{28}H_{14}$	8	$C_{54}H_{20}$	$< 461^{c,d}$
$C_{32}H_{16}$	46	$C_{58}H_{22}$	$< 7885^{d}$
$C_{36}H_{18}$	337		
$C_{40}H_{20}$	$\sim 2811^{b}$	$N_{\text{IC}} = 22$	
$C_{44}H_{22}$	~ 18306		
$C_{48}H_{24}$	~ 114326	$C_{52}H_{18}$	2^{d}
$C_{52}H_{26}$	$\sim 691933^{d}$	$C_{56}H_{20}$	$< 256^{c,d}$
		$C_{60}H_{22}$	$< 5726^{d}$
$N_{\text{IC}} = 8$		$N_{\text{IC}} = 24$	
$C_{30}H_{14}$	3		
$C_{34}H_{16}$	34	$C_{54}H_{18}$	1^{d}
$C_{38}H_{18}$	$< 333^{c}$	$C_{58}H_{20}$	85^{d}
$C_{42}H_{20}$	< 2713		
$C_{46}H_{22}$	$\sim 20119^{b}$	$N_{\text{IC}} = 26$	
$C_{50}H_{24}$	$\sim 141268^{d}$		
$C_{54}H_{26}$	$\sim 947291^{d}$	$C_{60}H_{20}$	32^{d}

[a] Helicenic benzenoid hydrocarbons have not been counted.
[b] Includes radicaloid benzenoids but excludes helicenic benzenoids.
[c] Includes radicaloid benzenoid isomers.
[d] This formula has no known hydrocarbon.

serve as models for study of screw dislocations.[8] Table 4 includes benzenoid formulas for which at least one isomer has been reported in the literature and those regarded by the author as being potentially tractable because of the advent of supercritical fluid extraction and chromatography.[14]

Out of over 2 million analytically tractable benzenoids, only approximately 500 benzenoids have been characterized.[8] Thus, part of our work has been directed toward sorting out those isomers not yet synthesized that are among the more stable ones believed to have a greater likelihood of occurring in thermal processes.[15] These are predicted to be strictly *peri*-condensed, essentially strain-free (devoid of coves) total resonant sextet, and threefold and sixfold symmetrical benzenoids.[15] Hence these are the benzenoids that should be the first targets for future synthetic efforts.

Given the volume of papers on the enumeration of *cata*-condensed benzenoid hydrocarbons that do not include helicenic isomers, it is ironic that this very class is one of the most synthesized groups for the *cata*-condensed formulas of $C_{38}H_{22}$ to $C_{58}H_{32}$. Further, for the $N_{\text{IC}} = 2$ series, the isomer numbers in Table 5 for $C_{44}H_{26}$ include radical benzenoids and exclude helicenic benzenoids, and similarly the $N_{\text{IC}} = 4$, 6, 8, 10, 12 and 16 series have formulas that also include radical benzenoids but exclude helicenic benzenoids. Hence these latter isomer numbers are almost meaningless, from a practical point of view.

A recent communication has appeared which provides limited numerical data for helicenic and other related stereoisomeric forms of benzenoids.[16] Not only do helicenic (hexahelicenic) components lead to steroisomers, but non-planarity and stereoisomers are engendered by structural features associated with substructural components corresponding to benzo[*c*]phenanthrene, having a 1–5 H–H or cove steric interaction, and dibenzo[*c*, *g*]phenanthrene, having a 1–6 H–H or fjord steric interaction.

In addition to helicenic benzenoid isomers, some researchers would like to include benzenoids with benzenoid-shaped holes containing hydrogens,[17] such as kekulene.[18] However, as there are only two known compounds of this type, they are of limited importance. Since strictly *peri*-condensed benzenoids are incapable of having either of these benzenoid types, the isomer numbers given Tables 3 and 4 are totally unambiguous. Further, it is believed that these strictly *peri*-condensed benzenoids are ultimate pyrolytic products, since carbonization processes tend toward more condensed benzenoids with larger N_C/N_H ratios.

Should an environmental analytical chemist determine via gas chromatography–mass spectrometry (GC–MS) that a sample contained a molecular ion peak corresponding to a benzenoid of formula $C_{42}H_{22}$, from Table 5 they would surmise that this corresponds to approximately 10 000 isomers and that they would have no chance whatsoever of specifying its precise identity. From Table PAH6 however, they could surmise some general properties, such as general structural features including the number of internal carbon atoms ($N_{IC} = 4$), rings ($r = 11$) and average electronic pπ energy ($E_\pi = 60 \cdot 2\beta$) Now suppose in the same GC–MS spectrum for this same environmental sample a molecular ion peak is observed six mass units lower corresponding to a benzenoid with the formula of $C_{42}H_{16}$. Since this formula corresponds to only one benzenoid isomer (Tables 3 and 5), the analyst can obtain total information concerning the precise identity of the benzenoid structure corresponding to this latter ion peak. Clearly, this review and Table PAH6 are a mediator between the chemistry and the epistemology for the field of benzenoid hydrocarbons.

Total resonant sextet benzenoid isomers (e.g. Figure 8) are found only in the $N_C \equiv 0 \pmod 6$ columns of Table PAH6 (i.e. N_C must be divisible by 6). These benzenoids are predicted to be among the more stable isomers and should resist quinone formation via aerobic processes in the environment. Essentially strain-free total resonant sextet isomers have no proximate bay regions and are incapable of undergoing further oxidative intracondensation ($C_nH_S + [O] \rightarrow C_nH_{S-2} + H_2$).[15]

Our work has enumerated essentially strain-free (devoid of fjords = triplet of bay regions) total resonant sextet benzenoid isomers (e.g. Figure 8) of exceptional stability.[8,15] Since there are only two $C_{42}H_{22}$ essentially strain-free total resonant sextet benzenoid isomers ($E_\pi = 60 \cdot 33\beta$) and given the difficulty associated with characterization of approximately 10 000 $C_{42}H_{22}$ isomers, these two benzenoids should be worthy candidates for targeted synthesis and investigation. In fact, one of these two essentially strain-free total resonant sextet isomers is among the nine known $C_{42}H_{22}$ benzenoid isomers.[8] Although the previous paragraph suggested that approximately 10 000 $C_{42}H_{22}$ isomers represented a nearly intractable analytical GC–MS situation, nevertheless, if a polluting source was generating a preponderance of the two predicted more stable $C_{42}H_{22}$ benzenoid isomers, then classical chemical characterization of these species is within our capability.

The isomer numbers given in Table 5 can be used to establish lower bounds for formulas in Table PAH6 for which the number of isomers is unknown. This determination takes advantage of the fact that the number of isomers increase on going from left to right in a particular row series and on going down in a column series. For example, the formula of $C_{56}H_{28}$ in the $N_{IC} = 6$ row series and $d_s = -7$ column series is to the right of $C_{52}H_{26}$ with approximately 600 000 isomers and below $C_{50}H_{26}$ with approximately 400 000 isomers. Thus, $C_{56}H_{28}$ corresponds to approximately 500 000 benzenoid isomers.

Hence the average properties of large isomer sets become the only meaningful way to describe these systems, and one cannot even to begin to consider the possibility of generally characterizing individual benzenoids having much more than 60 carbons, except for some of the strictly *peri*-condensed benzenoids with small isomer numbers.[19]

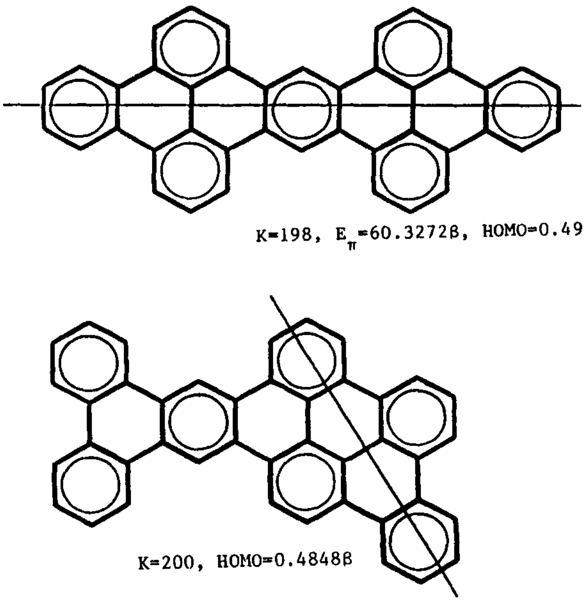


Figure 8. The two $C_{42}H_{22}$ essentially strain-free total resonant sextet isomers out of >13 415 predicted to be the most stable

ISOMER COUNTING EQUATIONS FOR SUBSTITUTED ISOSKELETAL ANALOGS AND NON-RADICAL MONOQUINONES OF BENZENOID HYDROCARBONS

For a given polyhex skeleton without any axis of symmetry, the number of poly-homosubstituted isomers is given by the binomial generating function.[8,20] If the given polyhex skeleton has a single twofold axis of rotation, the isomer counting generating function is given by $Z(1+x, C_2) \geqslant \frac{1}{2}[(1+x)^n + (1+x^2)^{n/2}]$, where $n = N_H$ for the precursor benzenoid; the 'greater than' situation occurs only for an odd number of substituents in some C_{2v} benzenoid precursors. For example, the number of triaza isomers having the twofold chrysene ($C_{18}H_{12}$) skeleton is $\frac{1}{2}[12!/3!9! + 0] = 110$ compared with the 220 triaza isomers of the benzo[*a*]anthracene ($C_{18}H_{12}$) skeleton. Similarly, the number of trimethylchrysene isomers is 110 and the number of isomers of trimethylbenzo[*a*]anthracene is 220.

For a given polyhex skeleton having no symmetry axis of rotation, the number of monoquinone isomers is estimated by $n^2/4$. For a given twofold polyhex skeleton, the number of monoquinone isomers is estimated by $\geqslant n^2/8$. Thus, benzo[*a*]anthracene has 36 monoquinone isomeric derivatives and chrysene has 18 monoquinone isomers. The four relationships above cover about two thirds of all possible cases for benzenoid-related molecular systems. For exact counting equations for benzenoids of various symmetries, the reader should consult a recently published paper.[20] One should expect that environmental samples will only contain the more stable benzenoid quinones and, thus, these isomer-counting equations only define upper bounds for the expected number of monoquinone constituents.

CONCLUSION

The aufbau principle, excized internal structure concept, strictly *peri*-condensed classification and formula periodic table (Table PAH6) are powerful conceptualization tools for enumerating and understanding the general properties of benzenoid hydrocarbons of practical interest to chemists. The strictly *peri*-condensed benzenoid series with a constant number of isomers is particularly illustrative. The above has been instrumental in organizing both experimental and theoretical properties of known benzenoids into a two-volume monograph.[8]

Tables 3 and 4 greatly extend the isomer numbers found in previous work on benzenoid hydrocarbons. As has been demonstrated here, 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 non-identical invariants of N_C, N_{IC}, q and r. This work again demonstrates the power of Table PAH6 in sorting benzenoid formulas into a hierarchal order, forming series with unique characteristics. This edge effect of Table PAH6 constitutes what the author believes is a new topological paradigm that will have implications in other systems. Our enumeration work and Table PAH6 define the epistemology of the field of benzenoid hydrocarbons. In the limit of formulas corresponding to large isomer numbers, average (global) properties organized in hierarchal form in Table PAH6 is all that can be hoped for, and the largest potentially characterizable benzenoids will probably have formulas in Table 3. Hence this review shows how Table PAH6 can help us define the limits of what we can do and can know about benzenoids to graphite.

GLOSSARY OF TERMS

d_s	net tree disconnections of internal graph edges (positive values) or connections (negative values are called negative disconnection)
N_C	total number of carbon atoms in a PAH
N_H	total number of hydrogen atoms in a PAH
N_{IC}	number of internal carbon atoms in a PAH having a degree of 3
N_{PC}	number of peripheral carbon atoms in a PAH having a degree of 3
PAH6	polycyclic aromatic hydrocarbon containing exclusively fused hexagonal rings; also referred to as benzenoid and polyhex.
$\lvert P \rvert = p = N_C$	total number of graph points
$\lvert Q \rvert = q$	number of graph edges (lines or C—C bonds)
q_I	number of internal graph edges
q_P	number of peripheral graph edges
r	number of rings

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