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The polyhex/polypent topological paradigm: regularities in the isomer numbers and topological properties of select subclasses of benzenoid hydrocarbons and related systems

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The informatics on benzenoid hydrocarbons and related systems is reviewed. This informatics involves a collection of algorithms used to discover, process, and analyze patterns in structure/formula data sets. The unique organizational structure that emerges will be useful to chemists with an interest in polycyclic aromatic compounds, environmental chemists, material scientists, and other scientists wishing for a greater understanding of the formation of carbonaceous materials. This *tutorial review* will show that isomer enumeration can lead to significant chemical insights. The isomer number regularities will be shown to have a structural origin referred to as the polyhex/polypent topological paradigm.

Introduction

Polycyclic aromatic hydrocarbons are the most abundant class of molecules in the known universe, occurring in meteorites, carbon stars in interstellar space,[1] and as pyrolytic products in the combustion engine. Isomer enumeration is important for a number of reasons. It impacts on combinatorial chemistry and informatics. It lets one compare those isomers that are known *versus* those that are not yet known and speculate why. Is it stability, importance, or just coincidence that some isomers are known others are not? The prevalence of buckminsterfullerene among 1812 possible C60 isomers which has been a subject of intense investigation is just one example.[2] Chemical literature searching by formula requires a unique inventorying process for isomer sets. Environmental analysis of polycyclic conjugated hydrocarbons frequently requires knowledge of the range of isomers.[3]

A chemical structure is a carrier of chemical information in compact form. The molecular formula of a chemical compound is a universal parameter that vastly delimits the range of structures to isomers in which stability plays a significant role. Given a particular chemical formula, the range of structure types that can correspond to it can, in principle, be deduced. What is usually lacking is a systematic process and set of algorithms by which one can arrive at a complete isomer set. Herein we will present a framework by which this has been largely accomplished for benzenoid hydrocarbons and closely related conjugated systems. Along the way, we will show why all the following PAH types have exactly 4 isomers: $C_{30}H_{14}$, $C_{40}H_{16}$, $C_{45}H_{17}$ (monoradicals), $C_{57}H_{19}$ (monoradicals), $C_{62}H_{20}$ (diradicals), $C_{76}H_{22}$ (diradicals), $C_{48}H_{24}$ (hpc), $C_{60}H_{30}$ (hpc), $C_{54}H_{22}$ (TRSs), $C_{78}H_{26}$ (TRSs), $C_{90}H_{28}$ (TRSs), $C_{120}H_{32}$ (TRSs), $C_{48}H_{24}$ (TRSs), $C_{60}H_{32}$ (TRSs), *etc.*

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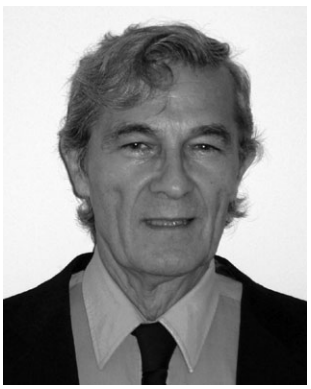

Jerry Ray Dias

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Brief historical background

Acyclic hydrocarbon enumeration. Isomer enumeration of hydrocarbons and its chemical ramifications has a rich history. As early as 1797 Alexander von Humboldt noted that there were compounds with the same overall composition which exhibited different chemical properties.[4] There term "isomer" was introduced in 1830 by Berzelius in recognition of the phenomenon of substances having the same overall molecular formula but different chemical properties.[5] In 1864, Brown attributed isomerism to differences in chemical structure.[6] Subsequently in 1874, Cayley initiated systematic enumeration of alkane isomers.[7] Some time later, this was followed by the alkane enumeration studies of Henze and Blair in 1931.[8] The issue of chirality in alkane enumeration was dealt with by Robinson, Harary, and Balaban in 1976.[9] The special feature of excluded volume due to self-avoiding embedding of alkane trees onto the tetrahedral (diamond) lattice was dealt with by

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Klein;[10] the smallest alkane that cannot be embedded on the diamond lattice is 1,1-di-*tert*-butyl-2-neopentylethane (or 3,3,5-tri-*tert*-butyl-2,2,6,6-tetramethylheptane, $C_{23}H_{48}$). This restriction to being embeddable on the diamond lattice was recently shown to be inadequate as the carbon skeleton of tetra-*tert*-butylmethane (or 3,3-di-*tert*-butyl-2,2,4,4-tetramethylpentane, $C_{17}H_{36}$) can be embedded on the diamond lattice but proved to be extremely crowded and so strained that it could not stably exist;[11] this crowding limitation has implications toward the synthesis of related dendrimers. Ignoring this crowding limitation and chirality, the smallest alkane formula with more realizable isomers than the observed universe has particles is $C_{167}H_{336}$.[12] A formula periodic table for acyclic hydrocarbon isomer classes provided Klein and coworkers with an organized framework to study their averaged properties.[13]

Benzenoid hydrocarbon enumeration. The classic work of Knop, Müller, Szymanski, and Trinajstić involves the computer enumeration and generation of both acyclic hydrocarbons and benzenoid hydrocarbons;[14] this book contains useful depictions of polyhex graphs corresponding to both Kekuléan and non-Kekuléan benzenoid hydrocarbon isomer sets. Earlier efforts in the enumeration of hexagonal animals (the mathematical cell-growth problem) are relevant to enumeration of benzenoid hydrocarbons.[15] A major shift in emphasis of enumeration toward pericondensed benzenoid hydrocarbons was made by Dias.[16] Thereafter, the numerical data on counting non-isomorphic polyhex systems corresponding to benzenoid hydrocarbons which was complete up to 11 hexagonal rings ($r = 11$) became available.[17] This data greatly assisted the evolving benzenoid enumeration studies of Cyvin and coworkers.[18] Our subsequent work led to discoveries that included a new topological paradigm[19] which triggered numerous enumeration/structure studies by the Cyvin group.[20] The issue of chirality emanating from steric twisting of some benzenoids was dealt with by Herndon.[21] The most recent enumeration results are now complete up to $r = 27$ and completely differentiates between Kekuléan and non-Kekuléan (radical) benzenoids.[22] This is just a select sampling of the interesting work on hydrocarbon enumeration and its related chemical ramifications. A major difference in the enumeration of acyclic hydrocarbons compared to benzenoid hydrocarbons is the appearance in the latter of regularities in the isomer numbers of select classes of benzenoids which can be linked to their structures.

Discussion

Some basic terminology

Polyhex is the discrete mathematical equivalent of a benzenoid hydrocarbon. A polyhex is a tessellation (mosaic) of hexagons which corresponds to the molecular graph of a benzenoid. A molecular graph of a benzenoid hydrocarbon (used interchangeably with the term "benzenoid") is the equivalent to its σ-bond skeleton. The benzenoid formula notation (C_nH_s) for the total number of carbons (N_c), hydrogens (N_H), and σ-bonds is equivalent to the polyhex (molecular graph) graph-theoretical notation for total number of vertices (n), degree-2 vertices (s), and lines or edges (q), respectively. There are three distinct kinds of benzenoid carbon atoms, the number of which are denoted by N_{pc}, N_{Ic}, and N_H ($N_c = N_{Ic} + N_{pc} + N_H$) where N_{pc} and N_{Ic} correspond to the peripheral (vertex juncture between two hexagons) and internal (vertex juncture between three hexagons) degree-3 molecular graph vertices and N_H to the degree-2 vertices. The subscripts i or I and p denote internal and peripheral, respectively. The number of hexagonal rings is denoted by r. A benzenoid is strained if it has two or more adjacent bay regions. Thus, benzo[*c*]phenanthrene with two adjacent bay regions is strained but chrysene and triphenylene with nonadjacent bay regions are essentially strain-free. Strained benzenoids cannot be circumscribed and leapfrog benzenoids are strain-free total resonant sextet (TRS) benzenoids. The distinction between ordinary benzenoids and total-resonant-sextet (TRS) benzenoids is the latter can be totally covered by disjoint Clar sextets and represent the most stable subset of benzenoids.[23] Herein we restrict ourselves to fused benzenoid polyhex systems that can be excised out of a perfect graphite polyhex layer. Thus hexahelicene ($C_{26}H_{16}$) and related systems which cannot be excised out of a graphite layer are excluded from this work. The same restriction applies to fluorenoid/fluoranthenoid and indacenoid systems (*vide infra*) which may be regarded as local defects in the graphite layer.

Elementary aufbau units and the aufbau principle

Table 1 summarizes the algorithms and concepts which will be introduced. Atoms, bonds, and functional groups are some standard elementary substructures (or aufbau units) which have broad use in chemistry. In our work, successive circumscribing of coronene and the elementary aufbau units of C_2, C_3H, and C_4H_2 were used both generate the benzenoid isomer sets and in the construction of a periodic table of polycyclic aromatic hydrocarbons (PAHs) comprised of only fused hexagonal rings (PAH6). Scheme 1 illustrates the basic aufbau strategy.

Integrally related to the circumscribing algorithm is the elementary aufbau unit of the excised internal structure which may be a base structure (first generation member) of a constant-isomer series or forms a base member upon (repetitive) circumscribing.

Benzenoid hydrocarbon periodic table

The formula periodic table for polycyclic benzenoid hydrocarbons (Table PAH6) forms the organized framework which allows us to connect the structures of benzenoid isomer sets.[24] Like the periodic table of elements, it is a 2-dimensional array that complies with the triad principle and has a smallest member (Table 2). This leads to hierarchical ordering and exhibits edge effects (elements on the boundary of Table PAH6

Table 1 Algorithms/concepts

(1) Elementary substructures
(2) Aufbau principle
(3) Periodic table sets
(4) Circumscribing algorithm and constant-isomer series
(5) Leapfrog algorithm
(6) Hexagonal-to-pentagonal ring contraction algorithm

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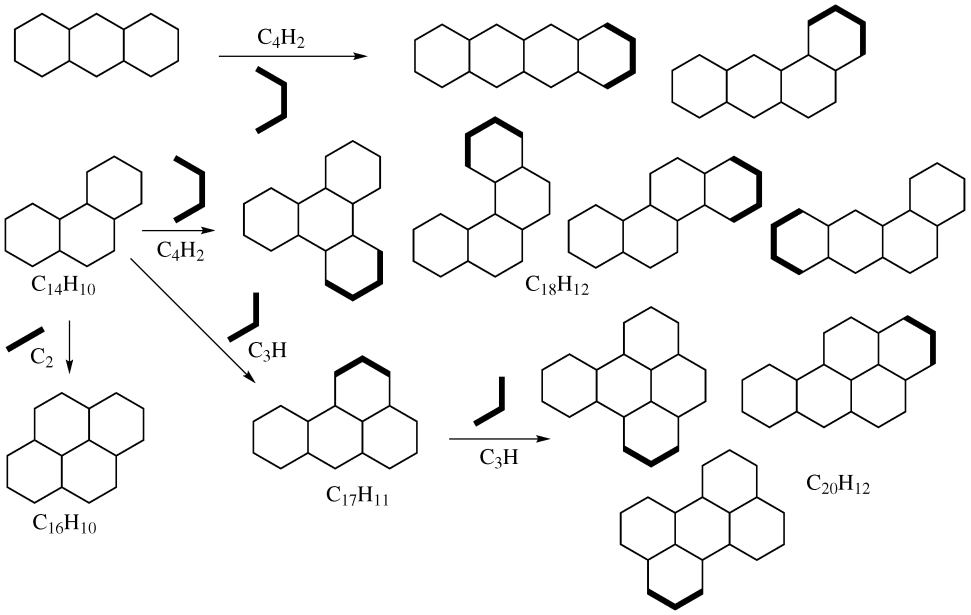

Scheme 1 The aufbau construction of all $C_{16}H_{10}$, $C_{17}H_{11}$, $C_{18}H_{12}$, and $C_{20}H_{12}$ benzenoid isomers using the elementary aufbau units of ethenetetrayl (C_2), 1,3-butadienetetrayl (C_4H_2), and allyltetrayl (C_3H).

Table 2 Periodic table set

Criteria
• Partially ordered set—obeys reflexivity, antisymmetry, and transitivity
• 2-Dimensionality of infinite extent
• Compliance to the triad principle—any central element has a metric property that is the arithmetic mean of two oppositely adjacent elements
• Has a least element (well ordered)
Properties
• Hierarchical ordering
• Edge effects—elements on the 2-dimensional boundary edge are more unusual
• Periodicity of at least one invariant
• The least element is the most unusual

are the most unique). Also, like the octet rule for the periodic table of elements, it will emerge that the formula periodic table for polycyclic benzenoid hydrocarbons (Table PAH6) has a sextet rule which is embodied in a formula periodic table for total resonant sextet benzenoid hydrocarbons [Table PAH6(sextet)]. Thus it is important to understand the structure of Table PAH6 (Table 3). Successive members of this table are generated by elementary aufbau units (C_2, C_3H, and C_4H_2). Starting with naphthalene ($C_{10}H_8$) and successively attaching the C_4H_2 aufbau unit in all combinatorial ways generates all isomers of $C_{14}H_{10}$, $C_{18}H_{12}$, $C_{22}H_{14}$, ... for catacondensed benzenoid formulas going from left to right in the first row of Table PAH6 (Table 3).

Similarly, starting with pyrene ($C_{16}H_{10}$) and successively attaching in all combinatorial ways the C_4H_2 aufbau generates $C_{20}H_{12}$, $C_{24}H_{14}$, $C_{28}H_{16}$, ...for the pericondensed benzenoid formulas in the third row of Table PAH6 (Table 3) as illustrated in Scheme 1. The polyhex molecular graphs to all the catacondensed benzenoids are devoid of degree-3 internal vertices (vertices at the intersection of three hexagons), *i.e.*, catacondensed benzenoids have $N_{Ic} = 0$. The polyhex molecular graphs to all the second row pericondensed benzenoids have one degree-3 internal vertex, *i.e.*, these pericondensed benzenoids have $N_{Ic} = 1$. While all the benzenoid isomers in the $N_{Ic} = 1$ row of Table PAH6 are pericondensed only phenalenyl monoradical is *strictly* pericondensed. Strictly pericondensed benzenoids have no catacondensed appendages or disconnected internal degree-3 vertices. Similarly, pyrene ($C_{16}H_{10}$) is strictly pericondensed but the $C_{20}H_{12}$ benzenoid isomers of benzo[*a*]pyrene and perylene in the $N_{Ic} = 2$ row are not strictly pericondensed because the former has a benzo appendage and the latter has disconnected internal degree-3 vertices.

Every other row of Table PAH6 can collectively be removed to form two other tables, one with only even carbon formulas [Table PAH6(even)] and the other with only odd carbon formulas [Table PAH6(odd)]. This sorts the more stable even carbon benzenoids from the less stable odd carbon benzenoids, the latter of which are all radical species. Table PAH6(sextet) is subset of Table PAH6(even) which sorts out the most stable benzenoid isomers that occur in every third column having their carbon number divisible by six—these total resonant sextet (TRS) benzenoid hydrocarbons are compliant to Clar's sextet rule being fully covered by disjoint sextet rings.[23]

Table 3 Table PAH6 formula periodic table for benzenoid polycyclic aromatic hydrocarbons (PAH6)

									$(N_C = 3\,N_H - 14 - 2\,d_S)$				
$d_S = -9$	$d_S = -8$	$d_S = -7$	$d_S = -6$	$d_S = -5$	$d_S = -4$	$d_S = -3$	$d_S = -2$	$d_S = -1$	$d_S = 0$	$d_S = 1$	$d_S = 2$	$d_S = 3$	N_{Ic}
									$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	… 0
									$C_{13}H_9$	$C_{17}H_{11}$	$C_{21}H_{13}$	$C_{25}H_{15}$	… 1
									$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	… 2
FORBIDDEN REGION									$C_{19}H_{11}$	$C_{23}H_{13}$	$C_{27}H_{15}$	$C_{31}H_{17}$	… 3
					$(N_C/N_H) < 2$				$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{34}H_{18}$	… 4
									$C_{25}H_{13}$	$C_{29}H_{15}$	$C_{33}H_{17}$	$C_{37}H_{19}$	… 5
		$C_{00}H_{00}$						$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$	$C_{36}H_{18}$	$C_{40}H_{20}$	… 6
								$C_{27}H_{13}$	$C_{31}H_{15}$	$C_{35}H_{17}$	$C_{39}H_{19}$	$C_{43}H_{21}$	… 7
				$2 < (N_C/N_H) < 3$				$C_{30}H_{14}$	$C_{34}H_{16}$	$C_{38}H_{18}$	$C_{42}H_{20}$	$C_{46}H_{22}$	… 8
								$C_{33}H_{15}$	$C_{37}H_{17}$	$C_{41}H_{19}$	$C_{45}H_{21}$	$C_{49}H_{23}$	… 9
							$C_{32}H_{14}$	$C_{36}H_{16}$	$C_{40}H_{18}$	$C_{44}H_{20}$	$C_{48}H_{22}$	$C_{52}H_{24}$	…10
							$C_{35}H_{15}$	$C_{39}H_{17}$	$C_{43}H_{19}$	$C_{47}H_{21}$	$C_{51}H_{23}$	$C_{55}H_{25}$	…11
							$C_{38}H_{16}$	$C_{42}H_{18}$	$C_{46}H_{20}$	$C_{50}H_{22}$	$C_{54}H_{24}$	$C_{58}H_{26}$	…12
						$C_{37}H_{15}$	$C_{41}H_{17}$	$C_{45}H_{19}$	$C_{49}H_{21}$	$C_{53}H_{23}$	$C_{57}H_{25}$	$C_{61}H_{27}$	…13
						$C_{40}H_{16}$	$C_{44}H_{18}$	$C_{48}H_{20}$	$C_{52}H_{22}$	$C_{56}H_{24}$	$C_{60}H_{26}$	$C_{64}H_{28}$	…14
						$C_{43}H_{17}$	$C_{47}H_{19}$	$C_{51}H_{21}$	$C_{55}H_{23}$	$C_{59}H_{25}$	$C_{63}H_{27}$	$C_{67}H_{29}$	…15
	$(N_C/N_H) > 3$				$C_{42}H_{16}$	$C_{46}H_{18}$	$C_{50}H_{20}$	$C_{54}H_{22}$	$C_{58}H_{24}$	$C_{62}H_{26}$	$C_{66}H_{28}$	…	
					$C_{45}H_{17}$	$C_{49}H_{19}$	$C_{53}H_{21}$	$C_{57}H_{23}$	$C_{61}H_{25}$	$C_{65}H_{27}$	$C_{69}H_{29}$	…	
					$C_{48}H_{18}$	$C_{52}H_{20}$	$C_{56}H_{22}$	$C_{60}H_{24}$	$C_{64}H_{26}$	$C_{68}H_{28}$	…		
				$C_{47}H_{17}$	$C_{51}H_{19}$	$C_{55}H_{21}$	$C_{59}H_{23}$	$C_{63}H_{25}$	$C_{67}H_{27}$	$C_{71}H_{29}$	…		
				$C_{50}H_{18}$	$C_{54}H_{20}$	$C_{58}H_{22}$	…						
				$C_{53}H_{19}$	$C_{57}H_{21}$	$C_{61}H_{23}$	…						
			$C_{52}H_{18}$	$C_{56}H_{20}$	$C_{60}H_{22}$	…							
			$C_{55}H_{19}$	$C_{59}H_{21}$	$C_{63}H_{23}$	…							
		$C_{54}H_{18}$	$C_{58}H_{20}$	$C_{62}H_{22}$	…								
		$C_{57}H_{19}$	$C_{61}H_{21}$	$C_{65}H_{23}$	…								
		$C_{60}H_{20}$	$C_{64}H_{22}$	…									
	$C_{59}H_{19}$	$C_{63}H_{21}$	$C_{67}H_{23}$	…									
	$C_{62}H_{20}$	$C_{66}H_{22}$	…										
	$C_{65}H_{21}$	$C_{69}H_{23}$	…										
$C_{64}H_{20}$	$C_{68}H_{22}$	…							$r = d_S + N_{Ic} + 2 = ½(N_C - N_H + 2)$				
$C_{67}H_{21}$	$C_{71}H_{23}$	…											
$C_{70}H_{22}$	…												

Circumscribing algorithm and constant-isomer series

The benzenoid constant-isomer series have formulas that occur on the left-hand staircase boundary edge of Table PAH6 and are generated by successive circumscribing. Encircling a conjugated polyene by a perimeter of carbon atoms and incremented by an additional six hydrogens in such a way as to form hexagonal rings is called circumscribing. If this process is reversed, then one obtains the original conjugated polyene called the excised internal structure of the polycyclic hydrocarbon. The excised internal structure of any benzenoid or related polycyclic system is composed of the internal degree-vertices. Coronene is generated by circumscribing the benzene (C_6H_6) hexagon with a rim of 6 hexagons ($C_{18}H_6$). Since benzene is the only possible C_6H_6 hexagonal isomer, coronene is the only possible $C_{24}H_{12}$ isomer composed of strictly hexagonal rings. Benzene is the excised internal structure of coronene. Circumscribing coronene ($C_{24}H_{12}$) gives circumcoronene ($C_{54}H_{18}$). Repeating this process leads to the $\boldsymbol{D}_{6h}$ one-isomer series which has formulas on the staircase boundary edge of Table PAH6 (Table 3). In a similar manner naphthalene ($C_{10}H_8$) and pyrene ($C_{16}H_{10}$) can be successively circumscribed by hexagonal rings to give the two $\boldsymbol{D}_{2h}$ one-isomer series as shown in Fig. 1; the members of these two series have a one-to-one matching in their topology, *i.e.*, symmetry, absence of bay regions, and the presence of selective lineations (lines) corresponding to HMO eigenvalues of ± 1. The general recursion equations for each step of this circumscribing process are $N_c' = N_c + 2N_H + 6$, $N_H' = N_H + 6$, and $r' = r + N_H$. Benzene, naphthalene, and pyrene are the ultimate excised internal structures of these one-isomer series, *i.e.*, the end excised internal structures resulting from repetitive decircumscribing any of the members of these series.

In circumscribing even or odd carbon benzenoids, the outer carbon perimeter that is attached consists of an aromatic $4n + 2$ aromatic or $4n$ antiaromatic macrocyclic ring, respectively. If the ultimate excised internal structure is a nondisjoint or disjoint diradical, the successor benzenoid becomes non-Kekuléan or Kekuléan, respectively.[25] Successively circumscribing a $4n$ antiaromatic annulene leads to graphenes with hole defects in which the macrocyclic antiaromatic contributions have been accentuated.[26] Relaxing the hexagonal ring constraint, the circumscribing algorithm has been used to construct the planar graphs (Schlegel diagrams) of fullerenes by incorporating a total of 12 pentagonal rings along the way.[27] In this process, a base polycyclic polyene structure is successively circumscribed with a perimeter of pentagonal and hexagonal rings until it can no longer be circumscribed because it has adjacent bay regions; this end point can be a fullerene or can be capped to give a fullerene. As will be seen if only one or two pentagonal rings is allowed in the first generation member (base member) being circumscribed, we generate fluorene/fluorantheoid and indacenoid polycyclic hydrocarbon constant-isomer series, respectively. Constant-isomer series have the same number of isomers and corresponding membership topology at each stage of circumscribing process.

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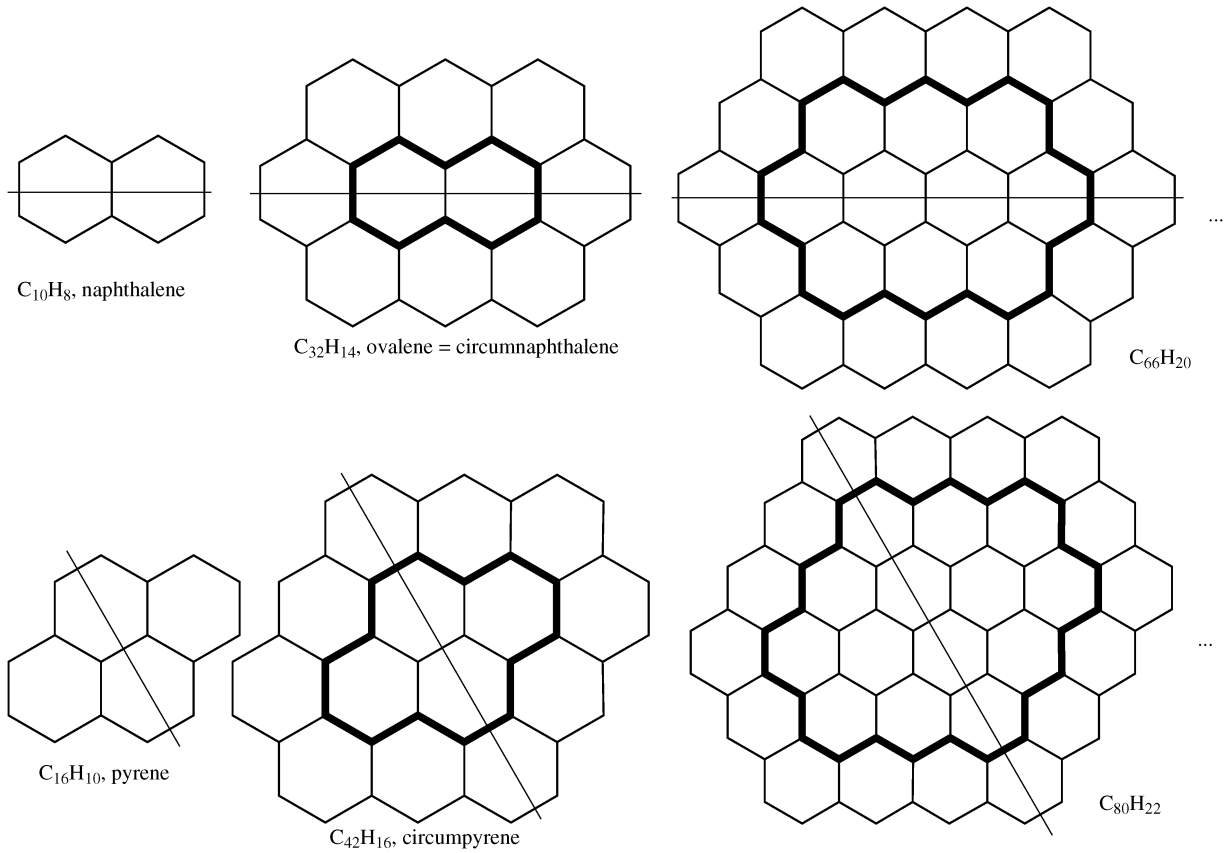

Fig. 1 Circumscribing naphthalene and pyrene gives circumnaphthalene and circumpyrene, respectively. Successively repeating this process leads to the two $\boldsymbol{D}_{2h}$ one-isomer series; the members of these two series have a one-to-one matching in their topology.

Constant-isomer benzenoid series are generated by successive circumscribing and have successive formulas per the operator of $\boldsymbol{P}(C_nH_s) \rightarrow \boldsymbol{C}(C_{n+2s+6}H_{s+6})$ where $\boldsymbol{P}$ is the precursor parent and $\boldsymbol{C}$ is the circumscribed successor. For the Kekuléan (nonradical) benzenoids, the number of successive nonradical isomers beginning with the (first generation) formulas listed below will have the respective values given in parentheses. Note the a, b, b, ... repetitive isomer number pattern. For all those sets below having the same isomer number there is a one-to-one matching in topology among the members between the two sets.

Kekuléan benzenoids

C_6H_6 (1), $C_{10}H_8$ (1), $C_{16}H_{10}$ (1),
$C_{22}H_{12}$ (2), $C_{30}H_{14}$ (3), $C_{40}H_{16}$ (3),
$C_{50}H_{18}$ (7), $C_{62}H_{20}$ (12), $C_{76}H_{22}$ (12),
$C_{90}H_{24}$ (27), $C_{106}H_{26}$ (38), $C_{124}H_{28}$ (38),
$C_{142}H_{30}$ (86), $C_{162}H_{32}$ (128), $C_{184}H_{34}$ (128),
$C_{206}H_{36}$ (264), $C_{230}H_{38}$ (373), $C_{256}H_{40}$ (373),
$C_{282}H_{42}$ (749), $C_{310}H_{44}$ (1055), $C_{340}H_{46}$ (1055),
$C_{370}H_{48}$ (2022), $C_{402}H_{50}$ (2765), $C_{436}H_{52}$ (2765)

The number of successive radical isomers beginning with the formulas listed below will have the respective values given in parentheses. These isomer numbers are identical for all the constant-isomer series of monoradical, diradical, triradical, tetraradical, pentaradical, *etc.*; only the monoradical and diradical isomer numbers are shown below as an illustration. Also note the a, b, b, ... repetitive isomer number pattern and that the even carbon radical formulas are subsets to the Kekuléan (nonradical) benzenoids above.

Benzenoid monoradicals

$C_{13}H_9$ (1), $C_{19}H_{11}$ (1), $C_{27}H_{13}$ (1),
$C_{35}H_{15}$ (2), $C_{45}H_{17}$ (4), $C_{57}H_{19}$ (4),
$C_{69}H_{21}$ (12), $C_{83}H_{23}$ (19), $C_{99}H_{25}$ (19),
$C_{115}H_{27}$ (46), $C_{133}H_{29}$ (70), $C_{153}H_{31}$ (70),
$C_{173}H_{33}$ (162), $C_{195}H_{35}$ (239), $C_{219}H_{37}$ (239),
$C_{243}H_{39}$ (504), $C_{269}H_{41}$ (726), $C_{297}H_{43}$ (726),
$C_{325}H_{45}$ (1471), $C_{355}H_{47}$ (2062), $C_{387}H_{49}$ (2062).

Benzenoid diradicals

$C_{22}H_{12}$ (1), $C_{30}H_{14}$ (1), $C_{40}H_{16}$ (1),
$C_{50}H_{18}$ (2), $C_{62}H_{20}$ (4), $C_{76}H_{22}$ (4),
$C_{90}H_{24}$ (12), $C_{106}H_{26}$ (19), $C_{124}H_{28}$ (19),
$C_{142}H_{30}$ (46), $C_{162}H_{32}$ (70), $C_{184}H_{34}$ (70),
$C_{206}H_{36}$ (162), $C_{230}H_{38}$ (239), $C_{256}H_{40}$ (239),
$C_{282}H_{42}$ (504), $C_{310}H_{44}$ (726), $C_{340}H_{46}$ (726),
$C_{370}H_{48}$ (1471), $C_{402}H_{50}$ (2062), $C_{436}H_{52}$ (2062).

Constant-isomer fluoranthenoid/fluorenoid series (one pentagonal ring among otherwise hexagonal ones) are generated by successive circumscribing and have successive

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formulas per the operator of $\boldsymbol{P}(C_nH_s) \rightarrow \boldsymbol{C}(C_{n+2s+5}H_{s+5})$. Note the a, a, b, c, b, ... repetitive isomer number pattern.

[C_5H_5 (1)],
C_9H_7 (1), $C_{12}H_8$ (1), $C_{15}H_9$ (2), $C_{18}H_{10}$ (3), $C_{23}H_{11}$ (2), $C_{26}H_{12}$ (7), $C_{31}H_{13}$ (7), $C_{36}H_{14}$ (9), $C_{41}H_{15}$ (17), $C_{48}H_{16}$ (9), $C_{53}H_{17}$ (31), $C_{60}H_{18}$ (31), $C_{67}H_{19}$ (41), $C_{74}H_{20}$ (72), $C_{83}H_{21}$ (41), $C_{90}H_{22}$ (120), $C_{99}H_{23}$(120), $C_{108}H_{24}$(...), $C_{117}H_{25}$(...), $C_{128}H_{26}$ (...)

Constant-isomer indacenoid series (two pentagonal rings among otherwise hexagonal ones) are generated by successive circumscribing and have successive formulas per the operator of $\boldsymbol{P}(C_nH_s) \rightarrow \boldsymbol{C}(C_{n+2s+4}H_{s+4})$. Note the a, b, a, c, ... repetitive isomer number pattern.

[C_5H_5 (1)], C_8H_6 (1), $C_{11}H_7$ (1), $C_{14}H_8$ (3), $C_{17}H_9$ (6), $C_{22}H_{10}$ (7), $C_{27}H_{11}$ (6), $C_{32}H_{12}$ (12), $C_{37}H_{13}$ (28), $C_{44}H_{14}$ (26), $C_{51}H_{15}$ (28), $C_{58}H_{16}$ (51), $C_{65}H_{17}$ (...), $C_{74}H_{18}$ (...), $C_{83}H_{19}$ (...), $C_{92}H_{20}$ (...),

The hollow primitive coronoid (hpc) isomer number sequence will be shown to have the repetitive pattern of a, b, c, a, ... where every number occurs exactly twice.

Perimeter topology

Circumscribing is a perimeter process which preserves the number of bay regions (η_o), selective lineations, and molecular symmetry. Also, the odd carbon (radical) benzenoids have $4n = N_{pc} + N_H = q_p$ perimeters and the more stable even carbon benzenoids have $4n + 2 = q_p$ perimeters ($n = 1, 2, 3, \ldots$). Most reactions of benzenoids occur at their perimeter where solo positions are usually the most reactive. The number of solo positions (η_1) increases with increasing circumscription. Thus, the perimeter topology of benzenoids manifests itself in a variety of ways requiring its thorough understanding.[28]

Let the chemical formula of a benzenoid be denoted by $C_nH_s \equiv (n;s)$. Its polyhex molecular graph has only degree-2 and degree-3 vertices interconnected by lines (or edges). Let $e(i,j)$ equal the number of edges with end points (vertices) of degree-i and degree-j, then a polyhex molecular graph has only $e(2,2)$, $e(2,3)$, and $e(3,3)$ types of edges where $e(2,2)$ occurs only on the perimeter, $e(3,3)$ occurs internally or on bay regions, and $e(2,3)$ occurs in between the other two types of edges. The total number of carbons atoms ($N_c = n$), hydrogen atoms ($N_H = s$), and C–C σ-bonds [$q = \frac{1}{2}(3N_c - N_H)$] in a benzenoid hydrocarbon (C_nH_s) is the total number of vertices (n), degree-2 vertices (s), and interconnecting lines (edges), respectively, in the corresponding polyhex molecular graph. Thus, of special importance in regard to the benzenoid perimeter topology are the invariants of C (No. of coves = two proximate bay regions), F (No. of fjords = three proximate bay regions), f (fissures = 1,3-parallel CH units), $e(2,2)$ = No. of free edges, N_H = No. of hydrogens, N_{pc} = No. of perimeter degree-3 molecular graph vertices, and q_p = No. of perimeter molecular graph edges which will be defined more completely in the following sections.

The perimeter topology of a benzenoid contains plenty of useful information. The number of peripheral degree-3 vertices, N_{pc}, on the perimeter of a benzenoid (polyhex) molecular graph is $N_{pc} = N_H - 6$. There can be 0, 1, 2, 3, and 4 successive degree-2 vertices between any two nearest peripheral degree-3 vertices designated as bay, solo, duo, trio, and quarto regions, respectively. η_0, η_1, η_2, η_3, and η_4 designate the number of bay, solo, duo, trio, and quarto peripheral regions on a given benzenoid molecular graph.[28] The perimeter topology of any benzenoid molecular graph is described by the eqn (1),

$$-\eta_0 + 0\eta_1 + \eta_2 + 2\eta_3 + 3\eta_4 = 6 \qquad (1)$$

which is independent of the number of solo regions (η_1); also $N_H = 0\eta_0 + \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4$; we include here the $0\eta_1$ (*i.e.*, zero solos) in eqn (1) and $0\eta_0$ to make the numeric pattern more obvious to the reader. The molecular graph of a strictly pericondensed benzenoid hydrocarbon has all its internal edges (edges between two adjoined hexagons) and internal degree-3 vertices (N_{Ic}) mutually connected and a perimeter topology that is defined by $-\eta_0 + \eta_2 + 2\eta_3 = 6$ where $\eta_4 = 0$. All second generation and higher members of our constant-isomer series have the perimeter topology of $-\eta_0 + \eta_2 = 6$. The molecular graph of a catacondensed benzenoid has $\eta_3 = 0$, every internal edge disconnected from any other internal edge, and a perimeter topology defined by $-\eta_0 + \eta_2 + 3\eta_4 = 6$. We derived eqn (1) in 1984 by subtracting $N_{pc} = \eta_0 + \eta_1 + \eta_2 + \eta_3 + \eta_4$ from $N_H = \eta_1 + 2\eta_2 + 3\eta_3 + 4\eta_4$ and noting $6 = N_H - N_{pc}$. Alternatively, the perimeter circumference length (q_p) was obtained by adding these two equations to give $\eta_0 + 2\eta_1 + 3\eta_2 + 4\eta_3 + 5\eta_4 = N_H + N_{pc} = q_p$ where q_p equals $4n$ ($n = 1, 2, 3, \ldots$) for odd carbon and $4n + 2$ for even carbon benzenoids.[28,29]

All constant-isomer benzenoids are a subclass of extremal benzenoids; extremal benzenoids are those which have molecular graphs with a maximum number of internal vertices (N_{Ic}) for a given number of rings (r). A constant-isomer benzenoid has the following properties. For a given number of hexagon rings (r), it has a minimum perimeter length [$\min(q_p)_r$], a maximum number of internal vertices [$\max(N_{Ic})_r$], and a minimum number of vertices [$\min(N_c)_r$], edges [$\min(q)_r$], and degree-2 vertices [$\min(N_H)_r$].

In general, the more bay regions (η_0) a benzenoid has the more stable it is. Total resonant sextet (TRS) benzenoid isomers have a maximum number of bay regions. Among other things, TRS benzenoids have N_c divisible by six, are devoid of coves and fissures, and have a maximum number of bay regions given by $\eta_o(\text{TRS}) = \frac{1}{2}N_H - 3$.

Supercircumscribing and TRS constant-isomer series

The TRS constant-isomer series have formulas that occur on the left-hand staircase boundary edge of Table PAH6(sextet) which is a subset of Table PAH6.[30] They are generated by successive supercircumscribing (augmented circumscribing). Encircling a TRS benzenoid by a polyphenylene necklace and incremented by 12 additional hydrogens in such a way as to form only hexagonal rings is called supercircumscribing. Supercircumscribing biphenyl ($C_{12}H_{10}$) gives the $C_{60}H_{22}$ TRS shown in Fig. 2. Successively repeating this process generates the $\boldsymbol{D}_{2h}$ TRS one-isomer series having formulas occurring on the left-hand staircase edge of Table PAH6(sextet). This series is an exact

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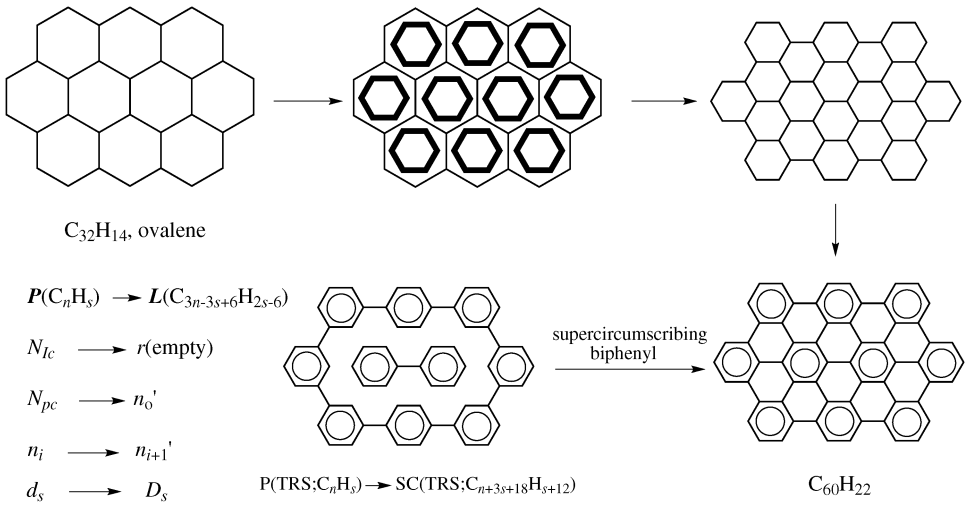

Fig. 2 Illustration of the leapfrog operation on ovalene to generate the only TRS benzenoid out of 3775 Kekulean (nonradical) $C_{60}H_{22}$ benzenoid isomers. The retroleapfrog is given by $L[C_nH_s] \rightarrow P[C_{(1/3)n+(1/2)s+1}H_{(1/2)s+3}]$. The leapfrog of naphthalene is biphenyl and supercircumscribing biphenyl also gives the $C_{60}H_{22}$ TRS benzenoid.

analog to the $\boldsymbol{D_{2h}}$ one-isomer series starting with naphthalene in Fig. 1 which has formulas occurring on the left-hand staircase edge of Table PAH6. In fact, all the constant-isomer series generated by successive circumscribing of ordinary benzenoids and all the TRS constant-isomer series generated by successive supercircumscribing have a one-to-one agreement in isomer numbers and topology. The leapfrog algorithm described in the next section proves this one-to-one isomorphism between ordinary benzenoids and TRS benzenoids. This isomorphism is part of the polyhex/polypent paradigm (*vide infra*).

Leapfrog algorithm

Fowler defined the leapfrog transformation for any polyhedron $\boldsymbol{P}$ as capping all faces of $\boldsymbol{P}$ and switching to the dual of the result.[31] Our adaptation of Fowler's leapfrog transformation on planar polyhex benzenoid hydrocarbons proves the isomorphism that exists between all benzenoids and the TRS subset.[32] To carry out the leapfrog operation on a given fused benzenoid, draw a smaller inscribed hexagon rotated 30 degree within each hexagon of a polyhex, connect each of the new hexagons to its nearest neighbors, and finally discard the original polyhex; for clarity or emphasis, one can then inscribe a maximum number of disjoint circles to represent the sextets. The leapfrog of ovalene, the only $C_{32}H_{14}$ benzenoid, gives the only $C_{60}H_{28}$ TRS benzenoid out of 3775 Kekuléan benzenoids and is illustrated in Fig. 2. If one wishes to identify the more stable TRS benzenoids belonging to an isomer set having their carbon number divisible by six without knowing what the remaining isomers look like, one should use the following retroleapfrog equations to obtain the formula of the benzenoids upon which the leapfrog operation will generate the target TRS benzenoids as done in this example.

$$N_c = \tfrac{1}{3}N_c(\mathrm{TRS}) + \tfrac{1}{2}N_H(\mathrm{TRS}) + 1$$

$$N_H = \tfrac{1}{2}N_H(\mathrm{TRS}) + 3$$

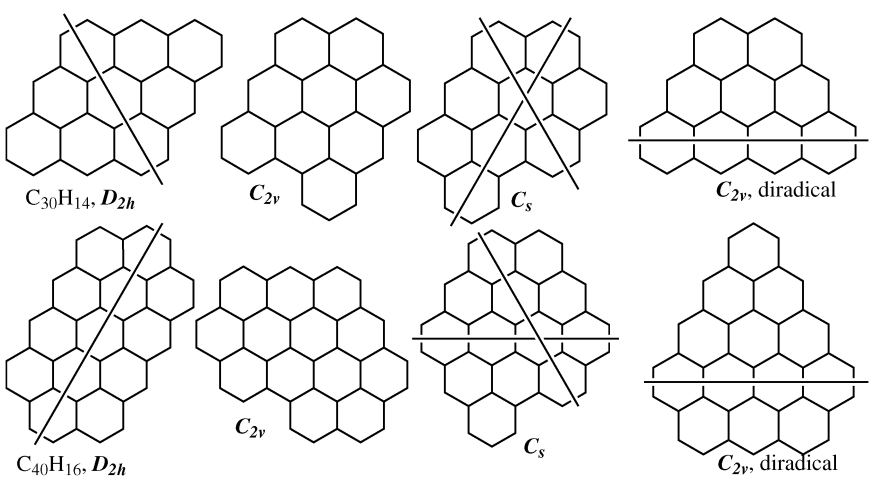

Fig. 3 The first generation strictly pericondensed benzenoid members belonging to the two corresponding four-isomer series arranged in parallel order according to their matching topological characteristics.

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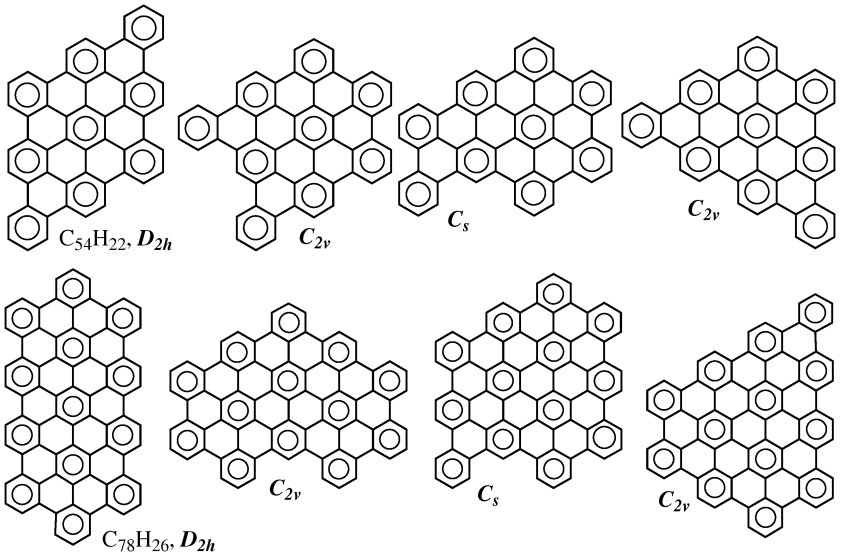

Fig. 4 The first generation total resonant sextet benzenoid members of the two corresponding four-isomer series arranged in parallel order according to their matching topological characteristics. Leapfrogging the four-isomer series in Fig. 3 will generate the four-isomer series in Fig. 4.

To illustrate further the isomorphism that exists between ordinary benzenoids and the TRS subset, consider the first generation members of the matching two constant isomer series of $C_{30}H_{14}$ and $C_{40}H_{16}$ shown in Fig. 3. Leapfrogging these ordinary benzenoids gives the corresponding and only $C_{54}H_{22}$ and $C_{78}H_{26}$ TRS benzenoids shown in Fig. 4 that exist among the total number of 13286 $C_{54}H_{22}$ and <319258 $C_{78}H_{26}$ benzenoid isomers, respectively.[22,33] Several items need to be observed here in Fig. 2–4. First, leapfrogging both nonradical and radical benzenoids always gives Kekuléan (nonradical) even carbon successor TRS benzenoids. Second, symmetry is preserved and the number of empty rings (rings without circles) corresponds to the number of internal degree-3 vertices and the number of Clar sextet rings (rings with circles) to the number of rings in the benzenoid precursor. Third, several of the benzenoids in Fig. 2–4 have been synthesized.[29,33,34]

Table PAH6 (sextet). Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons

…	$d_S = -13$	$d_S = -10$	$d_S = -7$	$d_S = -4$	$d_S = -1$	$d_S = 2$	$d_S = 5$	$d_S = 8$	$d_S = 11$	$d_S = 14$	$d_S = 17$	$d_S = 20$	N_{Ic}
						$C_{18}H_{12}$ (1)	$C_{30}H_{18}$ (1)	$C_{42}H_{24}$ (1)	$C_{54}H_{30}$ (3)	$C_{66}H_{36}$ (3)	$C_{78}H_{42}$ (8)	$C_{90}H_{48}$ (12)	… 0
						$C_{24}H_{14}$ (1)	$C_{36}H_{20}$ (1)	$C_{48}H_{26}$ (2)	$C_{60}H_{32}$ (4)	$C_{72}H_{38}$ (11)	$C_{84}H_{44}$ (25)	$C_{96}H_{50}$ (63)	… 2
						$C_{30}H_{16}$ (1)	$C_{42}H_{22}$ (2)	$C_{54}H_{28}$ (5)	$C_{66}H_{34}$ (13)	$C_{78}H_{40}$ (35)	$C_{90}H_{46}$ (100)	$C_{102}H_{52}$ (257)…	4
						$C_{36}H_{18}$ (3)	$C_{48}H_{24}$ (4)	$C_{60}H_{30}$ (13)	$C_{72}H_{36}$ (36)	$C_{84}H_{42}$ (112) …			… 6
						$C_{42}H_{20}$ (3)	$C_{54}H_{26}$ (11)	$C_{66}H_{32}$ (35)	$C_{78}H_{38}$ (112)	…			… 8
						$C_{48}H_{22}$ (8)	$C_{60}H_{28}$ (25)	$C_{72}H_{34}$ (100)					…10
					$C_{42}H_{18}$ (1)	$C_{54}H_{24}$ (12)	$C_{66}H_{30}$ (63)	$C_{78}H_{36}$ (257)	…				…12
					$C_{48}H_{20}$ (1)	$C_{60}H_{26}$ (26)	$C_{72}H_{32}$ (144)	....					
					$C_{54}H_{22}$ (4)	$C_{66}H_{28}$ (48)	…						
					$C_{60}H_{24}$ (9)	$C_{72}H_{30}$ (114)							
					$C_{66}H_{26}$ (24)	…							
				$C_{60}H_{22}$ (1)	$C_{72}H_{28}$ (48)								
				$C_{66}H_{24}$ (2)	$C_{78}H_{30}$ (115)…								
				$C_{72}H_{26}$ (13)	$C_{84}H_{32}$ (260)…								
				$C_{78}H_{28}$ (34)	$C_{90}H_{34}$ …								
			$C_{72}H_{24}$ (1)	$C_{84}H_{30}$ (104)									
			$C_{78}H_{26}$ (4)	$C_{90}H_{32}$ (244)…									
			$C_{84}H_{28}$ (16)	$C_{96}H_{34}$ …									
			$C_{90}H_{30}$ (68)										
		$C_{84}H_{26}$ (1)	$C_{96}H_{32}$ (199)										
		$C_{90}H_{28}$ (4)	$C_{102}H_{34}$ (575)…										
		$C_{96}H_{30}$ (30)											
		$C_{102}H_{32}$ (114)											
	$C_{96}H_{28}$ (1)	$C_{108}H_{34}$ (419)…											
	$C_{102}H_{30}$ (9)												
	$C_{108}H_{32}$ (53)…												
	$C_{114}H_{34}$ (248)…												
	…												
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Constant-isomer TRS benzenoid series are generated by successive supercircumscribing with a polyphenylene necklace and have successive formulas per the operation of $\boldsymbol{P}(\mathrm{TRS};\mathrm{C}_n\mathrm{H}_s) \rightarrow \boldsymbol{SC}(\mathrm{TRS};\mathrm{C}_{n+3s+18}\mathrm{H}_{s+12})$ where ***SC*** is the supercircumscribed TRS successor. TRS benzenoids are composed of the most stable subset of benzenoids and can also be generated from ordinary benzenoids by the leapfrog algorithm.

TRS benzenoid leapfrogs of even carbon benzenoids which are the sum of the even carbon Kekuléan, diradical, *etc*. from the above constant-isomer series.

[C_6H_6 (1), $C_{12}H_{10}$ (1)], $C_{24}H_{14}$ (1),
$C_{36}H_{18}$ (3), $C_{54}H_{22}$ (4), $C_{78}H_{26}$ (4),
$C_{102}H_{30}$ (9), $C_{132}H_{34}$ (16), $C_{168}H_{38}$ (16),
$C_{204}H_{42}$ (39), $C_{246}H_{46}$ (57), $C_{294}H_{50}$ (57),
$C_{342}H_{54}$ (133), $C_{396}H_{58}$ (199), $C_{456}H_{62}$ (199),
$C_{516}H_{66}$ (428), $C_{582}H_{70}$ (616), $C_{654}H_{74}$ (616),
$C_{726}H_{78}$ (1265), $C_{804}H_{82}$ (1800), $C_{888}H_{86}$ (1800)

TRS benzenoid leapfrogs of odd carbon benzenoids which are the sum of the odd carbon monoradical, triradical, pentaradical, *etc*. constant-isomer series.

$C_{18}H_{12}$ (1), $C_{30}H_{16}$ (1), $C_{48}H_{20}$ (1),
$C_{66}H_{24}$ (2), $C_{90}H_{28}$ (4), $C_{120}H_{32}$ (4),
$C_{150}H_{36}$ (13), $C_{186}H_{40}$ (20), $C_{228}H_{44}$ (20),
$C_{270}H_{48}$ (48), $C_{318}H_{52}$ (74), $C_{372}H_{56}$ (74),
$C_{426}H_{60}$ (174), $C_{486}H_{64}$ (258), $C_{552}H_{68}$ (258),
$C_{618}H_{72}$ (550), $C_{690}H_{76}$ (796), $C_{768}H_{80}$ (796)

In the table above [Table PAH6(sextet)] note that the isomer numbers (in parentheses) for strain-free TRS benzenoids (the most stable benzenoid isomer subsets) for the columns going to the right of the $d_s = -1$ column are identical with the isomer numbers for the respective rows.

This triangular correlation for the isomer numbers in Table PAH6(sextet)[35] has been structurally explained by the correlation of the empty ring configuration (antisextet dualist graphs)[36] which coincides with the excised internal structure of the retro-leapfrog.[37] To illustrate consider the TRS isomer numbers for $C_{30}H_{16}$, $C_{36}H_{20}$, and $C_{42}H_{24}$ all having r(empty) = 3 in Fig. 5. Leapfrogging the bottom benzenoids gives the only fused TRS benzenoids shown on top.

Excised internal structure

As the above demonstrated the excised internal structure is an important elementary substructure associated with circumscribing and with generating TRS benzenoids. In discrete mathematics the dual of a polycyclic graph is generated by placing a point within every region and connecting the nearest neighbors with a line, the inner dual graph results also by this process but leaves out a point from the infinite outer region, and the dualist graph is the same as the inner dual graph but retains the precise angles between the lines connecting nearest neighbor points.[37] Hall showed that the inner dual of the inner dual is the excised internal structure of a benzenoid if it exists.[38] It has been proven that when a connected excised internal structure has a perfect matching (is nonradical) then the successor benzenoid is nonradical.[39] If the excised internal structure is a nondisjoint or disjoint even carbon radical system, then the successor benzenoid is a nondisjoint even carbon radical or nonradical (Kekuléan) system, respectively.[25]

Structural invariants and similarities

The members of any given benzenoid isomer set have the same structural invariants of formula, rings (r), internal degree-3 vertices (N_{Ic}), edges (q), net disconnections (d_s) among the internal edges, the fourth coefficient to the characteristic polynomial (a_4), and $a_6 + \eta_o + 2r$ where a_6 is the sixth coefficient to the characteristic polynomial.[40] Leapfrogs have the additional invariants of D_s, η_o, r(empty), and r(sextet) which have the same values for every member of a given set of strain-free TRS isomers; D_s is the net disconnection

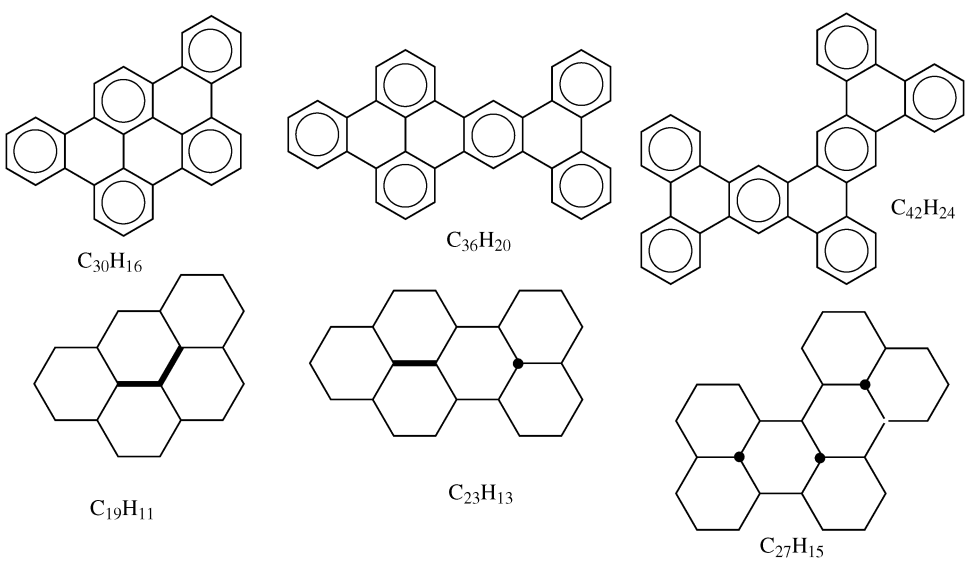

Fig. 5 Leapfrogging the bottom benzenoids gives the only fused TRS benzenoids shown on top.

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of empty rings. Thus, we expect that the members of a fused strain-free TRS isomer set to be more similar than members belonging to an ordinary benzenoid isomer set. This should be particularly true for members of any TRS constant-isomer set.[41] In general, strain-free TRS benzenoids not only have the largest number of Kekulé structures (***K***) but also smallest range in values among their isomers (confer with pages 85–97 in ref. 29). The more independent invariants that a set of molecular graphs have in common, then the corresponding set of molecules will have more similar chemical properties.

Coronoid hydrocarbons

A single coronoid (one hole benzenoid-related system) is obtained from a benzenoid by deleting some internal vertices and/or edge(s) so that a hole with the size of at least two hexagons emerges and is completely surrounded by hexagons.[42] Single coronoids with one hole surrounded by a single shell of hexagons are called primitive coronoids. A hollow coronoid has exactly six sides and belongs to a subclass of the primitive coronoids which in turn is a subclass of catacondensed coronoids.[43] A hexagon of a primitive coronoid is either linearly or angularly annelated. The angularly annelated hexagons of a primitive coronoid are called corners. They may be protruding on the coronoid outer perimeter or intruding within its inner perimeter associated with the hole. A hollow coronoid is a primitive coronoid with no intruding corners or corresponding bay regions on its perimeter. Kekulene ($C_{48}H_{24}$),[44] which has a hole shaped like coronene, is one of four hollow coronoids. Hollow coronoids have a repetitive isomer number pattern of … a, b, c, a, … which is interlaced so that every number occurs only twice.[45] Fig. 6 and 7 illustrates the structural origin of this duplication of isomer number for hollow coronoids. The C_4H_2 aufbau is spliced into every other side of the C_nH_s coronoid isomer set so as to generate the $C_{n+12}H_{s+6}$ coronoid isomer set of the same number of isomers.

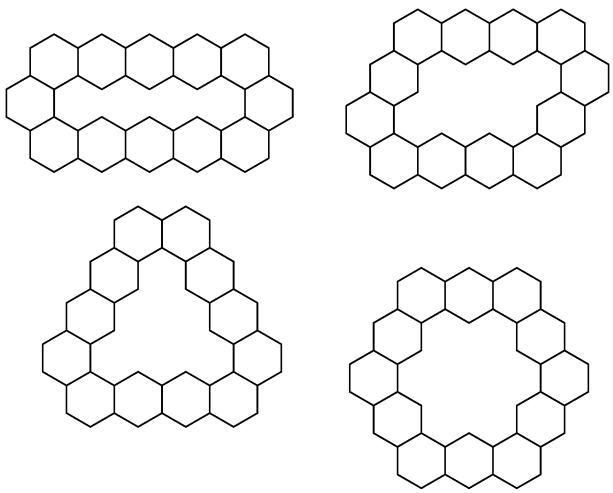

Fig. 6 The only 4 $C_{48}H_{24}$ hollow primitive coronoids.

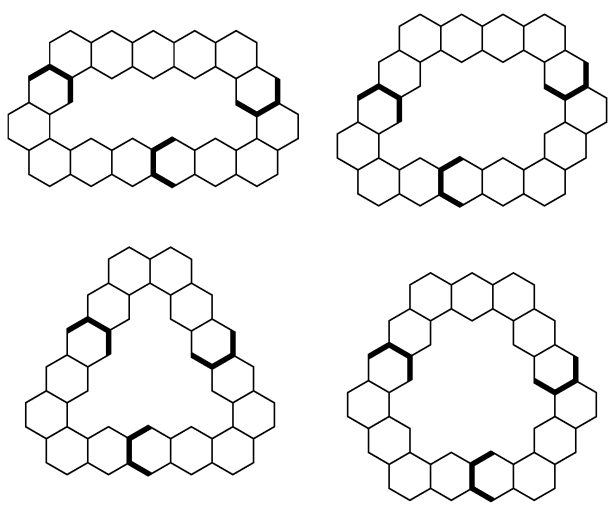

Fig. 7 The 4 matching $C_{60}H_{30}$ hollow coronoids are generated from the 4 $C_{48}H_{24}$ hollow coronoids shown in Fig. 6 by insertion of the C_4H_2 aufbau unit shown in bold on every other side.

Fluoranthenoid/fluorenoid and indacenoid hydrocarbons and their constant-isomer series

Polycyclic hydrocarbons related to fluoranthenes/fluorenes (one pentagonal ring among otherwise hexagonal ones) and indacenes (two pentagonal rings among otherwise hexagonal ones) represent important subgroups of polycyclic pyrolytic pollutants.[46] As of yet, no pyrolytic pollutants having other rings sizes, like tetragonal or octagonal rings, have been analytically identified in the environment. Early on those fluoranthenoid/fluorenoid and indacenoid hydrocarbons isomeric to benzenoid hydrocarbons were comprehensively listed.[47] Numerous new representatives have since been synthesized by flash vacuum pyrolysis by the research group of Scott.[48] The first enumerations of fluoranthenoid/fluorenoid and indacenoid hydrocarbons isomers were reported by Dias[49,50] and subsequently pursued by the research group of Cyvin.[51] These results exploited the circumscribing algorithm and the hexagonal-to-pentagonal ring contraction algorithm. The latter took the known structures of a benzenoid isomer group having $N_{Ic} < 6$ and performed all combinatorial hexagonal-to-pentagonal ring contractions of the benzenoid structures and deleted all duplicates thus generated. Constant-isomer fluoranthenoid/fluorenoid series have a repetitive isomer number pattern of a, a, b, c, b, … and constant-isomer indacenoid series have a repetitive isomer number pattern of a, b, a, c, … in which those series with the same isomer number have a one-to-one matching in topology among their membership.

Some analytical expressions for deriving the first generation formulas of constant-isomer series

According to Harary and Harborth [their eqn (36) and eqn (39)],[52] benzenoid hydrocarbons (which they called hexagonal animals) exist if and only if n (number of vertices), and r (number of rings) are integers within the ranges of

$$2r + 1 + \lceil (12r - 3)^{1/2} \rceil \leq n \leq 4r + 2 \qquad (1)$$

$$\lceil 1/4(n - 2) \rceil \leq r \leq n + 1 - \lceil \tfrac{1}{2}(n + 6^{1/2}n^{1/2}) \rceil \qquad (2)$$

where $\lceil x \rceil$ is the ceiling function and corresponds to the smallest integer not smaller than x. The two sides of these

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equations define the extreme values (upper and lower bounds) for n and r for polyhexes. The right-hand of eqn (1) corresponds to the catacondensed benzenoids located on the right-hand horizontal edge of Table PAH6, and the left-hand of eqn (1) corresponds to benzenoids having formulas on the extreme left-hand staircase edge of Table PAH6.

From the equations of Harary and Harborth, eqn (3) can be derived[41,53] which determines the first generation formula for any given benzenoid constant-isomer series:

$$n = s + 2\lfloor {}^{1}/_{12}(s^2 - 8s + 19)\rfloor \quad (3)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x. To use eqn (3) successively input the number of benzenoid hydrogens possible (s = 6, 8, 9, 10, 11, 12, ...). For example, $s = 11$ gives $n = 11 + 2\lfloor 4.333 \rfloor = 11 + 2 \times 4 = 19$ which gives $C_{19}H_{11}$ as the first generation formula for the $\boldsymbol{C}_{2v}$ one-isomer monoradical benzenoid series. As another example, $s = 14$ & 16 gives $n = 14 + 2\lfloor 8.58 \rfloor = 14 + 2 \times 8 = 30$ & $n = 16 + 2\lfloor 12.25 \rfloor = 16 + 2 \times 12 = 40$ which gives $C_{30}H_{14}$ & $C_{40}H_{16}$ (Fig. 3), respectively, as the first generation formulas for the matching pair of 4-isomer series. In this way eqn (3) generates all 39 formulas (C_6H_6, $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, $C_{27}H_{13}$, ...) in ref. 19. In a similar way, the first-generation formula for strain-free total resonant sextet (TRS) benzenoid constant-isomer series is given by eqn (4):

$$n = 6\lfloor {}^{1}/_{48}(s^2 - 4s + 64)\rfloor \quad (4)$$

Unlike the prior equations only even numbers of hydrogens are permissible, *i.e.*, s = (6, 10) 12, 14, 16, 18, 20, ... where the first two numbers pertain to benzene and biphenyl which only have provisional status in Table PAH6(sextet) because they are not fused benzenoids. To illustrate the use of eqn (4) consider $s = 12$. Application of eqn (4) gives $n = 6\lfloor {}^{1}/_{48}(12^2 - 4 \times 12 + 64)\rfloor = 6\lfloor {}^{1}/_{48}(144 - 48 + 64)\rfloor = 6\lfloor 3.33 \rfloor = 6 \times 3 = 18$ which corresponds to triphenylene $C_{18}H_{12}$, the first generation member of the $\boldsymbol{D}_{3h}$ one-isomer total resonant sextet series. In a like manner, eqn (4) generates the 39 pertinent formulas (C_6H_6, $C_{12}H_{10}$, $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, $C_{36}H_{18}$, $C_{48}H_{20}$, ...) found in ref. 30 and 32.

Thus, in general, the C_nH_s formula numerical subscripts for the first generation members (n;s) of the benzenoid constant-isomer series is given by

$$(n;s) = (s + 2\lfloor {}^{1}/_{12}(s^2 - 8s + 19)\rfloor;s)$$

and for the first generation members of the TRS constant-isomer series by

$$(n;s) = (6\lfloor {}^{1}/_{48}(s^2 - 4s + 64)\rfloor;s).$$

Similarly, the formula numerical subscripts for the first generation members (n;s) of the fluorenoid/fluoranthenoid constant-isomer series derived by the Cyvin group[51] is given by

$$(n;s) = (s + 2 + 2\lfloor {}^{1}/_{10}(s^2 - 7s + 6)\rfloor;s)$$

where s = 5, 7, 8, 9, 10, ..., 23, ... gives all the first generation members (C_5H_5, C_9H_7, $C_{12}H_8$, $C_{15}H_9$, $C_{18}H_{10}$, ..., $C_{99}H_{23}$, ...) listed by Dias.[49] The formula numerical subscripts for the first generation members of the indacenoid constant-isomer series derived by the Cyvin group[51] are given by

$$(n;s) = (s - 4 + 2\lfloor {}^{1}/_{8}(s^2 - 6s + 25)\rfloor;s)$$

where s = 5, 6, 7, 8, 9, ..., 16, ... duplicates the formulas to all the first generation members (C_5H_5, C_8H_6, $C_{11}H_7$, $C_{14}H_8$, $C_{17}H_9$, ..., $C_{58}H_{16}$, ...) listed by Dias.[50] All the constant-isomer series have formulas on the staircase edge of the corresponding periodic table and the above equations can be used to used by systematic application to generate the corresponding table.

The polyhex/polypent paradigm

The polyhex/polypent topological paradigm[54,55] consists of the following elements:

(1) A corresponding formula periodic table with $(x,y) = (d_s,N_{Ic})$ coordinates contains formulas on the left-hand staircase-like edge of a 2-dimensional array that belong to constant-isomer series generated by successive circumscribing (or supercircumscribing for TRS benzenoids).

(2) As the formula of the first generation members to each successive constant-isomer series increases so does the corresponding number of isomers.

(3) The number of isomers increases according to a regular pattern where some of the isomer numbers repeat.

(4) In those constant-isomer series having the same number of isomers, there is a one-to-one matching of the topology between the structures of the two sets.

(5) The topological invariants in this one-to-one matching of structures include symmetry, characteristics of 1-factorability and 2-factorability, number of bay regions, number of selective lineations and the associated ±1 eigenvalues, and the adjacency/nonadjacency of pentagonal rings (for the indacenoid constant-isomer series).

(6) The formula periodic tables and constant-isomer series for strictly pericondensed monoradical, diradical, triradical, tetraradical, *etc.* benzenoids are totally isomorphic. The formula periodic tables and constant-isomer series for strictly pericondensed and strain-free TRS benzenoids are totally isomorphic where the leapfrog algorithm associates any given benzenoid with its symmetry equivalent TRS isomorph.

Summary

This review provides an overview of the organized framework thus far established for the field of polycyclic hydrocarbons. The results summarized in this review are expected to eventually lead to a better understanding of how, why, and what polycyclic aromatic hydrocarbons are formed in various pyrolytic processes. Graphenes which are being intensely investigated for application to microelectronics are extended polycyclic aromatic hydrocarbons. This understanding may even have relevance to global warming, for if we could favor combustion processes which result in charring that leads to retention of solid carbon rather than form gaseous CO_2, this would be revolutionary technology.

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