Isomer enumeration of practical benzenoids

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Abstract   Recent development of the leapfrog operation in enumeration and understanding the chemical properties of benzenoid isomer sets having at least one synthesized representative is stressed. Some new enumeration results and correlations of the periodic table for the more stable total resonant sextet (TRS) benzenoid hydrocarbon subset [Table PAH6(sextet)] are presented.

Keywords Benzenoid · Kekulé structure · Enumeration · Clar sextet

1 Introduction

Some years ago we espoused the status of benzenoid hydrocarbon enumeration and its importance in information processing, molecular modeling of their chemical properties, and use in evaluation environmental analytical results [1]. A fundamental theme of our work on information modeling of benzenoid hydrocarbons has been to survey and compare those benzenoids known within a unified framework, and then extrapolate this topological information to benzenoids that are not yet known. In this way, one can gain an epistemology of this class of molecules. We look at those PAHs within an isomer set and then study the interrelationships between the isomer sets. This article continues these themes. Also this prior paper [1] presented a spectacular topological paradigm that occurs among and between the constant-isomer series belonging to ordinary even carbon benzenoid, radical benzenoid, and total resonant sextet (TRS) benzenoid series. Subsequently to the appearance of our article [1], Cyvin and coworkers published a follow-up paper [2] which some critical remarks seem to be warranted.

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

$$(N_C = 3 N_H - 14 - 2 d_S)$$

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

The information given in Table 10 of [1] will be improved due to recent results. Along the way a few comments will be made in connection with the Cyvin et al. paper [2].

Polyhex graphs are the mathematical equivalent to benzenoid hydrocarbons. The primary emphasis of early enumerations of benzenoid hydrocarbons (polyhexes) was on the number of rings or focused on catacondensed benzenoids [3]. However, since a given number of rings can correspond to several benzenoid isomer sets of different formulas, e.g., $C_{24}H_{12}, C_{25}H_{13}, C_{26}H_{14}, C_{27}H_{15}, C_{28}H_{16}, C_{29}H_{17}$, and $C_{30}H_{18}$ benzenoid isomer sets all have $r = 7$, our work has emphasized chemical formulas via a formula periodic table for benzenoid polycyclic aromatic hydrocarbons (Table 1 = Table PAH6) with particular emphasis on pericondensed benzenoids in which the excised internal structure plays a pivotal role [4]. Our work on the algorithmic generation of the corresponding formula periodic table for benzenoid hydrocarbons (Table PAH6) which relied in part on the one-isomer series has some interesting relationships relevant to the analytical approach based on a spiral construction by Harary and Harborth for extremal hexagonal animals [5]. Herein, we will present some significant new enumeration results with particular emphasis on strain-free total resonant sextet (TRS) benzenoid hydrocarbons.

2 Results and discussion

2.1 Definitions

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 which is simply connected and geometrically planar (can be excised from the graphite infinite lattice). A molecular graph of a benzenoid hydrocarbon (used interchangeably with the term "benzenoid") is its C–C σ-bond skeleton with all the carbons, hydrogens, and π-bonds omitted. The benzenoid notation for the total number of carbons (N_c), hydrogens (N_H), and C–C σ-bonds is equivalent to the polyhex (molecular graph) notation for total number of vertices (n), degree-2 vertices (s), and lines or edges (q), respectively. There are three distinct kinds of benzenoid carbons, the number of which are denoted by N_{pc}, N_{Ic}, and N_H ($N_c = N_{Ic} + N_{pc} + N_H$ and $N_{pc} = N_H - 6$) where N_{pc} and N_{Ic} correspond to the peripheral (n_p) and internal (n_i) 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. Internal degree-3 polyhex vertices are at the intersection of 3 hexagons whereas peripheral degree-3 vertices occur on the outer polyhex boundary at the juncture of two hexagons.

In the present article only planar nonradical benzenoids are taken into account as non-planar helicene related benzenoids have never been detected from any pyrolytic origin. It is regarded that planar benzenoids can be excised out from the graphite motif, but helicenes cannot; hexahelicene, the helicene prototype, has four adjacent bay regions. Polyhexes are classified into catacondensed ($n_i = 0$) and pericondensed ($n_i > 0$) where $n_i = n - 2s + 6$. Strictly pericondensed systems have no catacondensed appendages or disconnected internal degree-3 vertices. Accordingly catabenzenoids and catahelicenes (together referred to as catafusenes) will be distinguished from peribenzenoids and perihelicenes (together referred to as perifusenes). For recent enumeration results on fusenes, the reader is referred to the work of Brinkmann et al. [6]. These enumerations do not address the complexity associated with that of stereoisomerism due to formation of enantiomers and diastereomers [7]. Members of our constant-isomer benzenoid series being devoid of adjacent bay regions are always essentially planar.

Another classification distinguishes between Kekuléan ($K > 0$) and non-Kekuléan ($K = 0$) polyhex systems where the latter represent radical benzenoids of varying structure count (SC). Some analytical expressions for SC of radical benzenoids are now available [8]. There exists two types of even radical benzenoid systems. The obvious even radical systems will exhibit a difference in their peak-to-valley count which will be an even number. The concealed even radical benzenoid systems will exhibit a peak-to-valley difference of zero [9]. It has been shown that the former will have triplet electronic ground states while the latter will have low stability singlet electronic ground states even though both have $K = 0$ [10]. Even carbon diradical benzenoids, like triangulene ($C_{22}H_{12}$), are triplet diradicals, in compliance with Hund's rule [11]. While in principle catafusenes are invariably Kekuléan, heptacene and larger acenes have very small HOMO/LUMO gaps and are very reactive. Thus heptacene and longer (linear) acenes might be regarded as singlet diradicals. Even carbon/hydrogen benzenoid

systems are either Kekuléan or even radical systems while odd carbon/hydrogen benz-
enoids must be odd-degree radical systems. First and second generation free-radical
members of our benzenoid constant-isomer series have been detected by time-of-flight
mass spectrometry [12]. Also, free radical benzenoid hydrocarbons and their ionized
carbocation analogs are speculated interstellar species [13]. On the other extreme, all
members of the TRS benzenoid subgroup are Kekuléan with maximum K values and
HOMO–LUMO bandgaps. Leapfrogging radical benzenoid hydrocarbons generates
TRS benzenoids which are always Kekuléan.

2.2 Benzenoid chemical formulae

Table 1 presents the Formula Periodic Table for Benzenoid Hydrocarbons (Table
PAH6). The range of benzenoid hydrocarbon formulae C_nH_s can be deduced by
inequalities from the Harary and Harborth paper [5]. Starting with Eq. 37 of their
paper, we go through the following transformations

$$n + 1 - \lceil \tfrac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil \geq r \geq \lceil \tfrac{1}{4}(n - 2) \rceil$$

Using $r = \tfrac{1}{2}(n - s + 2)$ and multiplying throughout by 2 gives

$$2n + 2 - 2\lceil \tfrac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil \geq n - s + 2 \geq 2\lceil \tfrac{1}{4}(n - 2) \rceil$$

Subtracting $n + 2$ throughout this inequality gives

$$n - 2\lceil \tfrac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil \geq -s \geq -n - 2 + 2\lceil \tfrac{1}{4}(n - 2) \rceil$$

Multiplying this inequality by minus throughout reverses the inequality signs to give

$$2\lceil \tfrac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil - n \leq s \leq n + 2 - 2\lceil \tfrac{1}{4}(n - 2) \rceil \tag{1}$$

where $\lceil x \rceil$ is the ceiling function and corresponds to the smallest integer not smaller
than x. The left-hand side of Eq. 1 corresponds to pericondensed systems and the
right-hand side to catacondensed systems. Equation 1 gives the range for the number
of hydrogens (s) for a given number of carbons (n) found in benzenoid formulae; note
that $n = 6, 10, 13, 14$ and $n \geq 16$ for $s = 6, 8, 9, 10, 11, 12, 13, 14, \ldots$ and n and
s must be either both odd or even numbers. Starting with Eq. 36 of the Harary and
Harborth paper [5] and using $n = n_i + n_p + s$, $n_p = s - 6$, and $n_i = 4r + 2 - n$, we
can go through the following sequence of transformations

$$2r + 1 + \lceil (12r - 3)^{\frac{1}{2}} \rceil \leq n \leq 4r + 2$$
$$2\lceil (12r - 3)^{\frac{1}{2}} \rceil \leq n - n_i = n_p + s = 2s - 6 \leq 4r + 2$$
$$\lceil (12r - 3)^{\frac{1}{2}} \rceil + 3 \leq s \leq 2r + 4$$

The left-hand side of this latter equation pertains to highly condensed extremal benzenoids found on the left-hand side staircase edge of Table PAH6 and the right-hand pertains to the catacondensed benzenoids for even n and s and to the benzenoids with one internal degree-3 for odd n and s. Thus, we may write the following transformations

$$
\begin{aligned}
\lceil (12r - 3)^{\frac{1}{2}} \rceil + 3 &\leq s \\
(s - 3)^2 &\geq \lceil 12r - 3 \rceil \\
s^2 - 6s + 12 &\geq \lceil 12r \rceil \\
\tfrac{1}{12}(s^2 - 6s + 12) &\geq \lceil r \rceil \\
\lfloor \tfrac{1}{12}(s^2 - 6s + 12) \rfloor &\geq r = \tfrac{1}{2}(n + 2 - s) \\
\lfloor \tfrac{1}{12}(s^2 - 6s) \rfloor + 1 &\geq \tfrac{1}{2}(n + 2 - s) \\
2\lfloor \tfrac{1}{12}(s^2 - 6s) \rfloor + s &\geq n
\end{aligned}
$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x.

The left-hand side of this last inequality corresponds to the highly condensed extremal benzenoids found on the left-hand side staircase edge of Table PAH6. To obtain the relationship to last inequality which must correspond to catacondensed benzenoids for even n and s $(n = 2s - 6)$ and to the benzenoids with one internal degree-3 for odd n and s $(n = 2s - 5)$, we may capture both these equalities by $n = s - 6 + 2\lceil s/2 \rceil$. Thus, the last inequality becomes

$$
2\lfloor \tfrac{1}{12}(s^2 - 6s) \rfloor + s \geq n \geq s - 6 + 2\lceil s/2 \rceil \tag{2}
$$

which gives the upper and lower bound for the number of hydrogens ($s = 6$ and $s \geq 8$) for a given number of benzenoid carbons. The left-hand side of Eq. 2 corresponds to pericondensed systems and the right-hand side to catacondensed systems. By means of Eqs. 1 and 2, it can be decided whether a formula $C_n H_s$ is compatible with a benzenoid hydrocarbon (i.e., belong to Table PAH6). For most chemical applications Table PAH6 is conceptually more useful. For more on the Harary and Harborth equations the reader should consult the recent work of Dias [14].
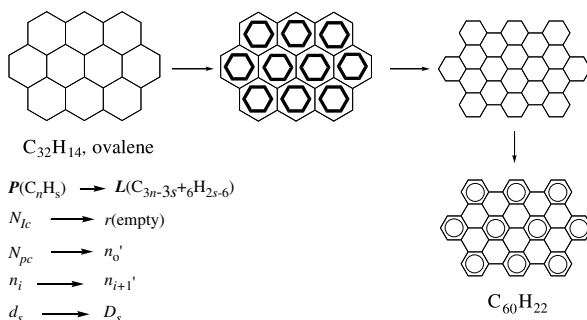
2.3 Constant-isomer series and total resonant sextet benzenoid systems

Much of the content in the prior paper [1] deals with the constant-isomer benzenoid series. This topic has been further advanced [15,16]. Among these works one will find the following general formula ($C_n H_s$) which gives the first generation formula to every constant-isomer benzenoid series:

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

Using $s = 6$ and $s \geq 8$ in Eq. 3 generates all 39 formulae in Tables 6 and 7 of [1] and beyond. Both Eqs. 2 and 3 herein correct Eqs. 2 and 3 in [2] given by Cyvin et al. [2].

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

$C_{32}H_{14}$, ovalene

$P(C_nH_s) \longrightarrow L(C_{3n-3s+6}H_{2s-6})$

$N_{Ic} \longrightarrow r(\text{empty})$

$N_{pc} \longrightarrow n_o'$

$n_i \longrightarrow n_{i+1}'$

$d_s \longrightarrow D_s$

$C_{60}H_{22}$

Total resonant sextet (TRS) benzenoids (sexy) represent a subgroup of benzenoid hydrocarbons and correspond to what Clar called fully benzenoid hydrocarbons [17]. TRS benzenoid hydrocarbons are molecules whose the number of carbons is divisible by six and can be represented by a polyhex covered by disjoint resonant sextet rings indicated by circles within hexagons. According to Clar's evidence TRS benzenoids are the more stable benzenoid species [17]. Constant-isomer series for TRS benzenoids were first reported by Dias [18]. This topic has been recently advanced [19,20]. Figure 1 illustrates the leapfrog operation [19] on the only $C_{32}H_{14}$ benzenoid, ovalene, to generate the only TRS benzenoid out 3775 $C_{60}H_{22}$ Kekuléan benzenoid isomers without needing to know what the remainder of the isomers look like. The procedure begins by using the retroleapfrog relationships [$N_c = \frac{1}{3} N_c(\text{TRS}) + \frac{1}{2} N_H(\text{TRS}) + 1$ and $N_H = \frac{1}{2} N_H(\text{TRS}) + 3$] to identify the formula of the precursor benzenoid set upon which the leapfrog will generate the required TRS benzenoid isomer set. The structures for all the precursor benzenoids, both radical and Kekuléan, need to be known. In each structure one draws a smaller hexagon rotated 30° relative to each hexagon within the polyhex structure, joins all the new hexagons by lines passing perpendicularly through the edges of the surrounding hexagons of the polyhex, and then discarding or peeling away the original polyhex. Covering the new polyhex with disjoint circles gives the TRS sextet benzenoid depiction.

Using the leapfrog algorithm, the derivation of the following equation for the first generation formula of the all the TRS constant-isomer series can be easily derived from Eq. 3:

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

Using $s = 6$, (10), 12, 14, 16, etc., Eq. 3 generates all 39 formulae in Tables 8 and 9 of [1], where the parenthesized value (10) corresponds to biphenyl ($C_{12}H_{10}$) which has provisional status in Table PAH6(sextet).

Another inequality given by Harary and Harborth [5] is $n - 1 + \lceil \frac{1}{4}(n-2) \rceil \le q \le 2n - \lceil \frac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil$ which when combined with Eq. 1 gives

$$n + \lceil \tfrac{1}{2}(n + 6^{\frac{1}{2}}n^{\frac{1}{2}}) \rceil \le q + s \le 2n + 1 - \lceil \tfrac{1}{4}(n-2) \rceil \tag{5}$$

The left-hand side of Eq. 5 corresponds to pericondensed systems and the right-hand side to catacondensed systems. The quantity $q + s$ in Eq. 5 can be used to arrange benzenoid isomer sets having specific n, q, and s values in relative order of increasing average heats of atomization. For example, consider $n = 22$ [$C_{22}H_{12}$ and $C_{22}H_{14}$, $\Delta(q + s) = 4.785$ eV]. Equation 5 gives $39 \leq q + s \leq 40$ for which the average heat of atomization is $187 \leq 191$ eV [21].

2.4 Selection of formulae

As in the prior paper [1], the criterion for selecting a formula for Table 2 is at least one benzenoid isomer with that formula is chemically known.

2.4.1 Catacondensed systems

Not listed are the catacondensed benzenoids ($n_i = 0$) which have known compounds up to and including $C_{54}H_{20}$. If one includes helicenes which are catafusenes, the largest known compound would go to $C_{58}H_{22}$. Large helicenes may lead to insights regarding the screw dislocation defect that occurs in solids, but they have never been observed as forming in pyrolytic processes. The isomer numbers given in Table 2 only include non-radical (Kekuléan) benzenoids and can be found in recently published works [6,22]. The consequence of nonplanarity due to two or more adjacent bay regions which can lead to chiral isomers (enantiomers and diastereomers) has been discussed [7,23]. The isomer numbers in Table 2 do not include stereoisomers when they do occur. In recognition of the possible occurrence of stereoisomers for the catafusenes listed in our Part A book, the isomer numbers were preceded by the mathematical notation for "greater than". Thus the statement by Cyvin and coworkers, "In the data compilation of Dias' book, the number of isomers of the catafusenes $C_{30}H_{18}$ and $C_{34}H_{20}$ are given as >123 and >446, respectively, which is positively wrong." is simply an exaggeration.

2.4.2 Pericondensed systems

The valid synthesis circumanthracene ($C_{40}H_{16}$) has been described [24] and is a first generation member of our 4-isomers series (counting the radical isomer) [16]; there is a one-to-one matching between the members of this constant-isomer series and those of the $C_{30}H_{14}$ benzenoids listed in Table 2. The book of Fetzer [25] should be consulted for an update review of large pericondensed benzenoids of analytical interest. Contrary to statement of Cyvin et al. [2], several known isomers of the formulas $C_{48}H_{20}$ and $C_{58}H_{24}$ can be found on pp. 402–403 of our part B book [26]; also confer with the biomarker catalogue of CHIRON in Trondheim, Norway (http://www.chiron. no). The latter part of Table 2 contains all the largest benzenoids synthesized to date. These turn out to be the highly stable TRS benzenoid hydrocarbons synthesized by the Müllen research group [27].

Table 2 Number of isomers of Kekuléan pericondensed ($n_i > 0$) planar benzenoid hydrocarbons for formulas having at least one known isomer

n_i	r	Formula	No. isomers
2	4	$C_{16}H_{10}$	1
	5	$C_{20}H_{12}$	3
	6	$C_{24}H_{14}$	13
	7	$C_{28}H_{16}$	62
	8	$C_{32}H_{18}$	287
	9	$C_{36}H_{20}$	1352
	10	$C_{40}H_{22}$	6256
	11	$C_{44}H_{24}$	28737
	12	$C_{48}H_{26}$	130665
4	6	$C_{22}H_{12}$	2
	7	$C_{26}H_{14}$	9
	8	$C_{30}H_{16}$	58
	9	$C_{34}H_{18}$	333
	10	$C_{38}H_{20}$	1907
	11	$C_{42}H_{22}$	10552
	12	$C_{46}H_{24}$	57019
	13	$C_{50}H_{26}$	300833
6	7	$C_{24}H_{12}$	1
	8	$C_{28}H_{14}$	8
	9	$C_{32}H_{16}$	46
	10	$C_{36}H_{18}$	337
	11	$C_{40}H_{20}$	2191
	12	$C_{44}H_{22}$	13805
	13	$C_{48}H_{24}$	83376
8	9	$C_{30}H_{14}$	3
	10	$C_{34}H_{16}$	34
	11	$C_{38}H_{18}$	264
	12	$C_{42}H_{20}$	2085
	13	$C_{46}H_{22}$	14896
	15	$C_{54}H_{26}$	653556[a,b]
10	10	$C_{32}H_{14}$	1
	11	$C_{36}H_{16}$	20
	12	$C_{40}H_{18}$	213
	13	$C_{44}H_{20}$	1836
	14	$C_{48}H_{22}$	14693
12	12	$C_{38}H_{16}$	10
	13	$C_{42}H_{18}$	139
	14	$C_{46}H_{20}$	1471
	15	$C_{50}H_{22}$	13137[a]

Table 2 continued

n_i	r	Formula	No. Isomers
14	13	$C_{40}H_{16}$	3
	14	$C_{44}H_{18}$	89
	15	$C_{48}H_{20}$	1124
16	17	$C_{54}H_{22}$	9188[a,b]
	18	$C_{58}H_{24}$	90154[a]
20	21	$C_{66}H_{26}$	1029521[b]
22	20	$C_{60}H_{22}$	3775[a,b]
24	25	$C_{78}H_{30}$	49375048[a,b]
26	24	$C_{72}H_{26}$	401936[a,b]
32	27	$C_{78}H_{26}$	<319258[b,c]
42	34	$C_{96}H_{30}$	[b]
44	36	$C_{102}H_{32}$	[b]
48	37	$C_{102}H_{30}$	[b]
52	41	$C_{114}H_{34}$	[b]
54	46	$C_{132}H_{42}$	[b]
60	43	$C_{114}H_{30}$	[b]
70	50	$C_{132}H_{34}$	[b]
72	55	$C_{150}H_{42}$	[b]
144	91	$C_{222}H_{42}$	[b]

[a] Brinkmann, G.; Grothaus, C.; Gutman, I. Fusenes and Benzenoids with perfect matchings[22] and private communication
[b] These are TRS benzenoids (except $C_{102}H_{30}$) synthesized by the Müllen research group.[27] The formulas without isomer numbers have an unknown but extremely large number of isomers
[c] Upperbound estimate

2.5 Total resonant sextet benzenoids and new enumeration results

The structures for all the TRS benzenoid hydrocarbons corresponding to the largest formulas in Tables 2 and 3 are listed in Fig. 2. Under each TRS structure are two numbers separated by a slash. The first number (before the slash) gives the number of the more stable TRS isomers which are a subset of the total number of Kekuléan benzenoids given by the second number (after the slash), if known. In Fig. 2, it is seen that while there are 11 $C_{54}H_{26}$ TRS benzenoid isomers only the one shown has been synthesized [27]; the structures of the remaining unknown TRS isomers can be found listed on pp. 92–93 of our book [26]. Overall there are 947291 possible Kekuléan $C_{54}H_{26}$ benzenoid isomers [22] and only one has been synthesized [27]. Similarly, only the two $C_{54}H_{22}$ TRS benzenoid isomers shown (Fig. 2) out of four have been synthesized [27]; the remaining unknown isomers can be found on pp. 95–96 of our book [26]. Again, these are the only $C_{54}H_{22}$ benzenoid hydrocarbon synthesized out of 13286 possible benzenoid isomers [22]. These $C_{54}H_{22}$ TRS benzenoid isomers are leapfrogs of the $C_{30}H_{14}$ constant-isomers [16,18]. The sole $C_{60}H_{22}$ TRS benzenoid
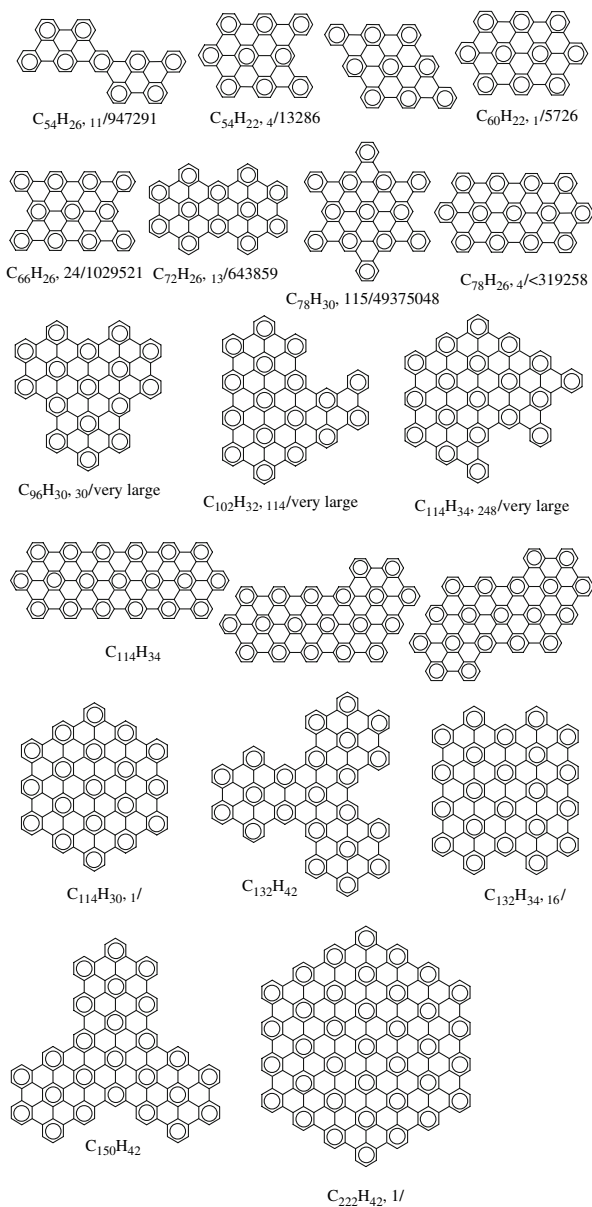
isomer (also cf. with Fig. 1) [18] and the sole $C_{114}H_{30}$ TRS benzenoid isomer (page 46) [26] have been previously depicted. The $D_{2h}C_{78}H_{26}$ TRS benzenoid is the leapfrog of the one of the four $C_{40}H_{16}$ constant-isomers and is a correspondent to the $D_{2h}C_{54}H_{22}$ TRS benzenoid isomer shown in Fig. 2 (3rd structure) [16], and the structures its four TRS benzenoid isomers were previously depicted [28]. The $C_{78}H_{30}$ TRS benzenoid is the leapfrog of the $C_{42}H_{18}$ TRS benzenoid previously depicted [29]. All 13 structures of $C_{72}H_{26}$ TRS benzenoids have been enumerated [30]. The $C_{102}H_{32}$ and first $C_{114}H_{34}$ TRS structures in Fig. 2 cannot be supercircumscribed because they possess a *s-cis-m,m*-quaterphenyl perimeter configuration [18,31]. Supercircumscribing hexabenzo[*bc,ef,hi,kl,no,qr*]coronene ($C_{42}H_{18}$) gives the Fig. 2 $C_{114}H_{30}$ TRS structure and supercircumscribing this structure again gives the $C_{222}H_{42}$ TRS structure which are the second and third generation members of our one-isomer D_{6h} TRS benzenoid series [18]. The $C_{54}H_{22}$ and $C_{78}H_{26}$ TRS structures are first generation members belonging to our corresponding matching four-isomer TRS benzenoid series [16]. The $C_{60}H_{22}$ TRS structure in Fig. 2 is generated by supercircumscribing biphenyl and is the first generation member belonging to our D_{2h} one-isomer TRS benzenoid series [19,31]. The $C_{132}H_{34}$ TRS structure is one member of the first generation belonging to our sixteen-isomer benzenoid series [18,30]. What should be evident to the reader at this point is that Dias predicted these structures and their topological properties [18,26] before they were successfully synthesized by the Müllen research group [27].

Table 3 presents the Formula Periodic Table for Total Resonant Sextet Benzenoid Hydrocarbons [Table PAH6(sextet)] with the corresponding strain-free TRS isomer numbers indicated in parentheses [31]. As one goes from left to right along any row of Table 3 the formulas increase successively by $C_{12}H_6$ and as one goes down the formulas increase by C_6H_2 which correspond to the relevant sextet aufbau units. Much of the TRS benzenoid isomer numbers listed toward the left-hand staircase edge is new: $C_{72}H_{28}$ (48), $C_{78}H_{30}$ (115), $C_{84}H_{32}$ (260), $C_{84}H_{30}$ (104), $C_{90}H_{32}$ (244), $C_{90}H_{30}$ (68), $C_{96}H_{32}$ (199), $C_{102}H_{34}$ (575), $C_{108}H_{34}$ (420), $C_{108}H_{32}$ (53), and $C_{114}H_{34}$ (248). These numbers were generated by an algorithm which we will now detail [30]. To illustrate consider the $C_{84}H_{32}$ and $C_{114}H_{34}$ TRS benzenoid isomers listed in Table 3. Application of the retroleapfrog equations [$N_c = \frac{1}{3}N_c$(sextet) + $\frac{1}{2}N_H$(sextet) + 1; $N_H = \frac{1}{2}N_H$(sextet) + 3] give the precursor formulas of $C_{45}H_{19}$ and $C_{56}H_{20}$, respectively, which can be found in Table 1 (Table PAH6). Subtracting the C_4H_2 aufbau unit from each of the latter formulas gives $C_{41}H_{17}$ and $C_{52}H_{18}$ found to the left of these formulas in Table 1 (Table PAH6). From the depictions of $C_{41}H_{17}$, the number of benzoPAH and dibenzoPAH isomers corresponding to $C_{45}H_{19}$ is determined to be 265 and 8 (includes 3 naphtho isomers), respectively [32]. These 273 benzoPAH isomers must be subtracted from the total number of 533 $C_{45}H_{19}$ benzenoid isomers ($r = 14$) given in the work of Stojmenović, Tosić, Doroslavacki [33]. Performing the leapfrog operation on the remaining $C_{45}H_{19}$ benzenoid isomers gives 260 $C_{84}H_{32}$ TRS benzenoid isomers. The isomers of $C_{52}H_{18}$ are present in Fig. 3 of [1], and the number of benzoP-AHs of $C_{52}H_{18}$ can be determined by inspection to be 8. Subtracting this number from 256 isomers of $C_{56}H_{20}$ given by Caporossi and Hansen gives 248 [34]. Performing the leapfrog operation on these $C_{52}H_{18}$ benzenoids that are devoid of benzoPAHs gives 248 $C_{114}H_{34}$ TRS benzenoid hydrocarbon isomers.

Table 3 [Table PAH6 (sexet)]. 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}
$C_{96}H_{28}(1)$	$C_{84}H_{26}(1)$	$C_{72}H_{24}(1)$	$C_{60}H_{22}(1)$	$C_{42}H_{18}(1)$	$C_{18}H_{12}(1)$	$C_{30}H_{18}(1)$	$C_{42}H_{24}(1)$	$C_{54}H_{30}(3)$	$C_{66}H_{36}(3)$	$C_{78}H_{42}(8)$	$C_{90}H_{48}(12)$	... 0
$C_{102}H_{30}(9)$	$C_{90}H_{28}(4)$	$C_{78}H_{26}(4)$	$C_{66}H_{24}(2)$	$C_{48}H_{20}(1)$	$C_{24}H_{14}(1)$	$C_{36}H_{20}(1)$	$C_{48}H_{26}(2)$	$C_{60}H_{32}(4)$	$C_{72}H_{38}(11)$	$C_{84}H_{44}(25)$	$C_{96}H_{50}(63)$	... 2
$C_{108}H_{32}(53)...$	$C_{96}H_{30}(30)$	$C_{84}H_{28}(16)$	$C_{72}H_{26}(13)$	$C_{54}H_{22}(4)$	$C_{30}H_{16}(1)$	$C_{42}H_{22}(2)$	$C_{54}H_{28}(5)$	$C_{66}H_{34}(13)$	$C_{78}H_{40}(35)$	$C_{90}H_{46}(100)$	$C_{102}H_{52}(257)...$	... 4
$C_{114}H_{34}(248)...$	$C_{102}H_{32}(114)$	$C_{90}H_{30}(68)$	$C_{78}H_{28}(34)$	$C_{60}H_{24}(9)$	$C_{36}H_{18}(3)$	$C_{48}H_{24}(4)$	$C_{60}H_{30}(13)$	$C_{72}H_{36}(36)$	$C_{84}H_{42}(112)...$			... 6
$......$	$C_{108}H_{34}(420)...$	$C_{96}H_{32}(199)$	$C_{84}H_{30}(104)$	$C_{66}H_{26}(24)$	$C_{42}H_{20}(3)$	$C_{54}H_{26}(11)$	$C_{66}H_{32}(35)$	$C_{78}H_{38}(112)...$				... 8
		$C_{102}H_{34}(575)...$	$C_{90}H_{32}(244)...$	$C_{72}H_{28}(48)$	$C_{48}H_{22}(8)$	$C_{60}H_{28}(25)$	$C_{72}H_{34}(100)$					... 10
			$C_{96}H_{34}...$	$C_{78}H_{30}(115)...$	$C_{54}H_{24}(12)$	$C_{66}H_{30}(63)$	$C_{78}H_{36}(257)...$					... 12
				$C_{84}H_{32}(260)...$	$C_{60}H_{26}(26)$	$C_{72}H_{32}(144)...$						
				$C_{90}H_{34}...$	$C_{66}H_{28}(48)$							
					$C_{72}H_{30}(114)...$							

Fig. 2 TRS benzenoid hydrocarbons recently synthesized by the Müllen research group and their isomer numbers (TRS isomers/total number of Kekuléan isomers)

$C_{54}H_{26}$, 11/947291 $C_{54}H_{22}$, 4/13286 $C_{60}H_{22}$, 1/5726

$C_{66}H_{26}$, 24/1029521 $C_{72}H_{26}$, 13/643859 $C_{78}H_{26}$, 4/<319258

$C_{78}H_{30}$, 115/49375048

$C_{96}H_{30}$, 30/very large $C_{102}H_{32}$, 114/very large $C_{114}H_{34}$, 248/very large

$C_{114}H_{34}$

$C_{114}H_{30}$, 1/ $C_{132}H_{42}$ $C_{132}H_{34}$, 16/

$C_{150}H_{42}$

$C_{222}H_{42}$, 1/

Some trends in the isomer numbers in Table 3 should be apparent. Beginning at the $d_s = 2$ column, the magnitude and sequence of isomer numbers for the $d_s = 2, 5, 8, 11, 14, \ldots$ columns are identical to those in the $N_{Ic} = 0, 2, 4, 6, 8, \ldots$ row, respectively [31]. In addition to this regularity, The isomer numbers progressively increase in every column and row. Thus for formulas like $C_{90}H_{34}$ the largest isomer

number is usually located above and defines a lower bound for those yet unknown
isomer numbers proximate formulas.

3 Conclusion

The formula periodic tables are conceptually useful in that they reveal numerous regu-
larities and trends in the corresponding structures [4,16,31]. Recent enumeration and
synthetic work has resulted in improved data on the number of chemically plausible
benzenoid hydrocarbons [6,22,27,34]. The fact that the largest synthesized benzenoid
hydrocarbons to date are TRS benzenoids testifies to the utility and validity of Clar's
sextet principle [17]. The leapfrog algorithm leads to the precisely the same results
previously obtained heuristically and corroborates the topological paradigm that exists
between all the benzenoids (Table PAH6) and the TRS subset [Table PAH6(sextet)]
[18,19,30,31].

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