

# What Do We Know about C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> Benzenoid Hydrocarbons and Their Evolution to Related Polymer Strips?<sup>†</sup>

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While critically reviewing the current status of what is known about C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> benzenoid isomers, which are ubiquitous pyrolytic constituents, some new insights will be presented. Representative isomers belonging to these benzenoid hydrocarbons are at the crossroads to homologous series that extend to infinite polymer strips that have been the object of numerous molecular modeling studies. The goal of these studies is to understand their potential electronic properties for material science applications. Along the way, some prior numerical results are supplemented.

## INTRODUCTION

Benzenoid hydrocarbon isomers having formulas of C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> can be regarded as being at the onset of high molecular-weight polycyclic aromatic hydrocarbons (PAHs).<sup>1</sup> As such, they represent important pollutant reference molecules in environmental analysis.<sup>2</sup> Also, in the study of methane<sup>3</sup> and benzene<sup>4</sup> flames using time-of-flight mass spectroscopy, prominent mass spectral peaks corresponding to C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> were observed in the analysis of constant hydrogen sequences. The benzenoid isomers of C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> were first enumerated in 1983 by Dias using his excised internal structure/circumscribing algorithm.<sup>5</sup> Unfortunately, reference standards for all these isomers are not available, and because of this, various other analytical strategies have been investigated for their isomer pollutant identification. Herein, we will summarize the experimental and computed properties of these isomers with the goal of understanding further how enumeration and molecular modeling within the framework of our Formula Periodic Table for Benzenoids (Table PAH6) can aid in the identification of PAH pyrolytic pollutants.<sup>6</sup>

The known and predicted electronic, molecular, physical, spectroscopic, and thermodynamic properties of all the C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> benzenoids will be presented. Many of these results are reported herein for the first time. Also, these benzenoids are members of extensively studied infinite homologous series of polyacene and polyphenanthrene strips of width 3 and 4, which can serve as models for fullerene tubes constructed with the zigzag and armchair hexagon arrangements, respectively.<sup>7</sup> The extrapolation of some of these properties for these series of molecules related by a common aufbau (monomeric) unit will be discussed.

## PRELIMINARIES

Let a molecular graph be a vertex-line depiction which consists of fused hexagons that correspond to the  $\sigma$ -bond skeleton of a benzenoid hydrocarbon. To generate the corresponding benzenoid structure from its molecular graph,

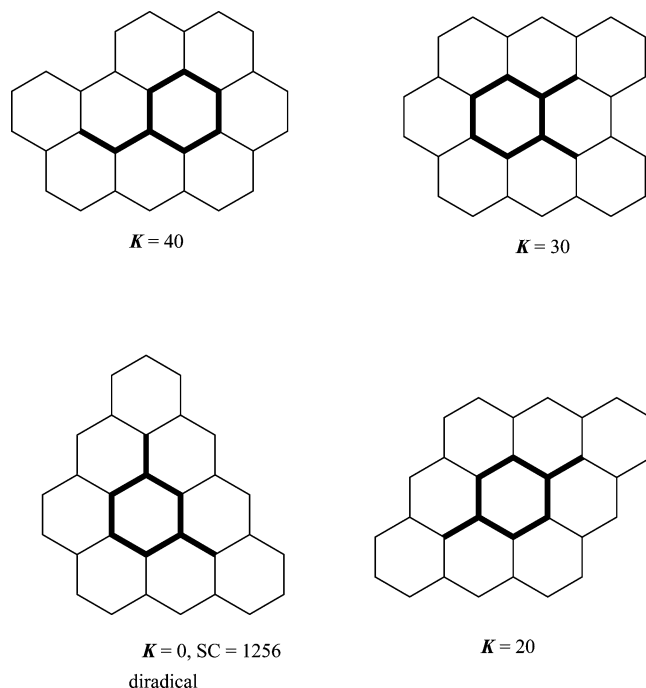
one would have to place a carbon at each vertex, place a line joining the hydrogen at each degree-2 carbon vertex, and fill in the p  $\pi$  bonds in such a way as to complete the valence of four for each carbon; this latter step is always possible for Kekulean but not non-Kekulean (non-Kekulé or radical system) benzenoid hydrocarbons. The benzenoid (C<sub>n</sub>H<sub>s</sub>) polyhex molecular graph consists of only degree-2 ( $s = N_H$ ) and degree-3 ( $N_{Ic} + N_{pc}$ ) vertices, where  $n = N_c = N_H + N_{Ic} + N_{pc}$ . An internal degree-3 molecular graph vertex is common to three hexagons, the number of which is denoted by  $N_{Ic}$ . The number of peripheral degree-3 vertices ( $N_{pc}$ ) is given by  $N_{pc} = N_H - 6$ . A benzenoid hydrocarbon is a PAH composed of only fused hexagonal rings and is denoted by PAH6.

Strictly pericondensed benzenoids (PAH6s) have molecular graphs with all their internal degree-3 vertices mutually connected and have no catacondensed appendages. All the C<sub>30</sub>H<sub>14</sub> PAH6 isomers (Figure 1) are strictly pericondensed, whereas one of the C<sub>28</sub>H<sub>14</sub> PAH6 isomers, benzo[*a*]coronene, is not because it has the benzo catacondensed appendage. All inclusive strictly pericondensed PAH6 isomer sets have formulas on the extreme left-hand edge of Table PAH6 and can be fully enumerated by determining all their excised internal structures.<sup>8</sup>

Consider the four C<sub>8</sub>H<sub>8</sub> conjugated polyene isomers—styrene, *o*-quinodimethane (*o*-xylylene), *m*-quinodimethane (*m*-xylylene), and *p*-quinodimethane (*p*-xylylene)—in Figure 1. To circumscribe them with hexagonal rings, one detaches the eight hydrogens on each and reconnects the dangling bonds formed to an encircling C<sub>22</sub>H<sub>6</sub> polyene octayl in such a way as to give a successor C<sub>30</sub>H<sub>14</sub> benzenoid ( $r = 9$ ,  $N_{Ic} = 8$ ). Since these four precursors are the only hexagonal-ring-related C<sub>8</sub>H<sub>8</sub> conjugated polyene isomers, the C<sub>30</sub>H<sub>14</sub> successors are the only four benzenoid isomers possible where the carbons in the C<sub>8</sub>H<sub>8</sub> excised internal structures become the internal degree-3 vertices ( $N_{Ic} = 8$ ). If this process is repeated indefinitely (C<sub>n</sub>H<sub>s</sub>  $\rightarrow$  C<sub>n+2s+6</sub>H<sub>s+6</sub>), then C<sub>30</sub>H<sub>14</sub>  $\rightarrow$  C<sub>64</sub>H<sub>20</sub>  $\rightarrow$  C<sub>90</sub>H<sub>26</sub>  $\rightarrow$  ... represents a constant-isomer (specifically, four-isomer) series where all the formulas fall on the left-hand staircase borderline of Table PAH6. Since *m*-quinodimethane is a nondisjoint diradical, then so is its dibenzo[*bc,hi*]coronene successor and, likewise, all of its successors; this means that all these systems are triplets.<sup>9</sup>

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<sup>†</sup> Dedicated to Professor Haruo Hosoya on the occasion of his 70th birthday.

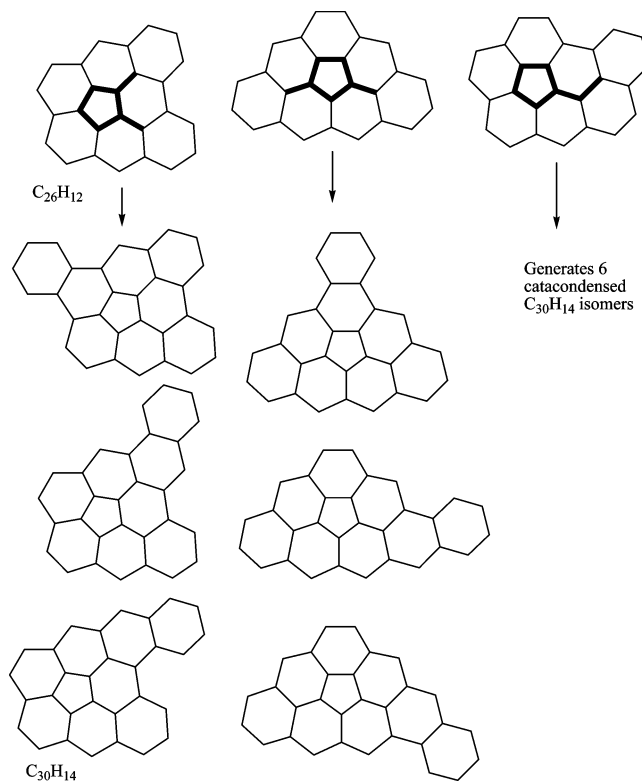


**Figure 1.** Circumscribing the only hexagonal ring-related C<sub>8</sub>H<sub>8</sub> excised internal structures (styrene and quinodimethane isomers shown in bold) gives the only possible C<sub>30</sub>H<sub>14</sub> benzenoid hydrocarbons. Successive circumscribing gives the constant 4-isomer series having formulas given by the recursion equations of  $N_c' = N_c + 2N_H + 6$  and  $N_H' = N_H + 6$ .

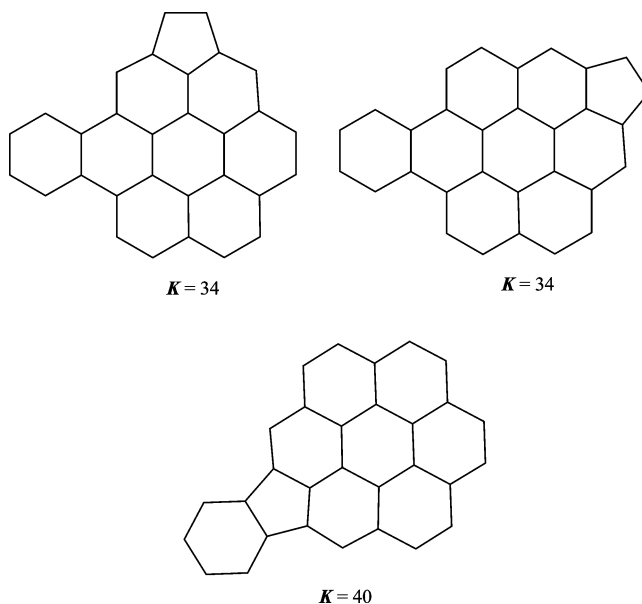
The C<sub>30</sub>H<sub>14</sub> benzenoids are the first-generation members, and the C<sub>8</sub>H<sub>8</sub> isomers are the ultimate excised internal structures of this four-isomer series.

If the poyhex requirement is relaxed and a single pentagonal ring among otherwise hexagonal ones is allowed, then these PAHs are called fluoranthenoid (even carbon)/fluorenoïd (odd carbon) hydrocarbons.<sup>8</sup> If one allows two pentagonal rings among otherwise hexagonal ones, then these PAHs are called indacenoid hydrocarbons; the term “indacenoid” is used even when the two pentagonal rings are adjacent. In general, for a given PAH6 formula,  $r_5 + N_{lc}(\text{PAH}) = N_{lc}(\text{PAH6})$ , where  $r_5$  is the number of pentagonal rings among otherwise hexagonal ones. Our hexagonal-to-pentagonal ring-contraction algorithm ( $C_nH_s \rightarrow C_{n-1}H_{s-1}$ ) allows one to enumerate all fluoranthenoid/fluorenoïd hydrocarbons ( $C_{n-1}H_{s-1}$ ) with  $N_{lc} < 5$  from known isomer sets of benzenoids ( $C_nH_s$ ) and indacenoids with  $N_{lc} < 5$  from known isomer sets of fluoranthenoids/fluorenoïds. To enumerate fluoranthenoid/fluorenoïd and indacenoid hydrocarbons with  $N_{lc} \geq 5$ , one has to additionally include circumscription of all pentagonal-ring-related excised internal structures.

To enumerate all of the C<sub>30</sub>H<sub>14</sub> fluoranthenoids ( $r = 9$ ,  $N_{lc} = 7$ ), take all the unique hexagonal-to-pentagonal ring contractions of all 15 C<sub>31</sub>H<sub>15</sub> benzenoids ( $r = 9$ ,  $N_{lc} = 7$ ) listed in the Knop et al. book.<sup>10</sup> This gives 94 to which we must add 12 more catacondensed fluoranthenoid isomers derived by circumscribing the three C<sub>7</sub>H<sub>7</sub> dimethylenylcyclopentadienyl excised internal structures listed in bold in Figure 2 and subsequently attaching C<sub>4</sub>H<sub>2</sub> aufbau units in all distinct ways. This gives a grand total of 106 C<sub>30</sub>H<sub>14</sub> fluoranthenoids. Figure 3 lists the three most stable and pyrolytically probable C<sub>30</sub>H<sub>14</sub> fluoranthenoids.



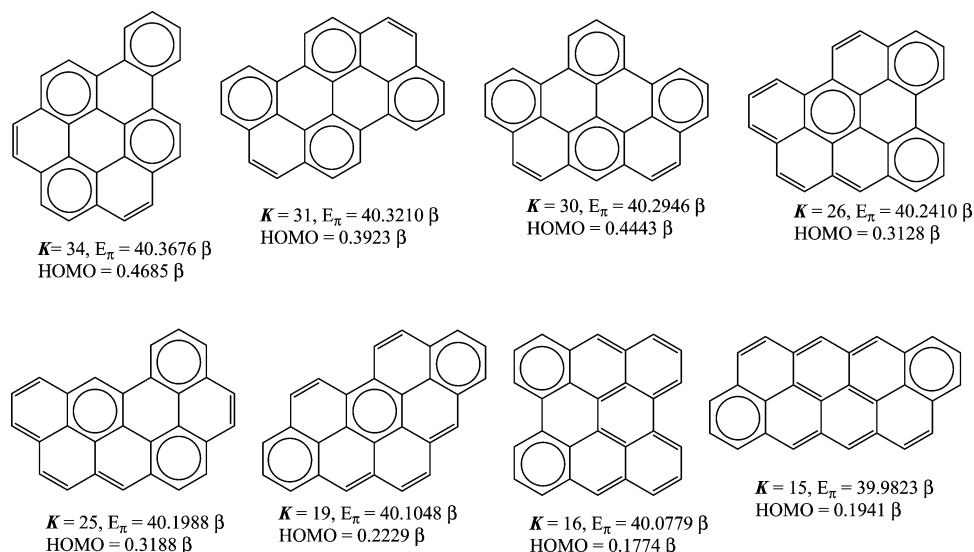
**Figure 2.** Circumscribing the three C<sub>7</sub>H<sub>7</sub> dimethylenylcyclopentadienyl isomers shown in bold gives three C<sub>26</sub>H<sub>12</sub> fluoranthenoid successors from which 12 catacondensed C<sub>30</sub>H<sub>14</sub> fluoranthenoid isomers can be generated.



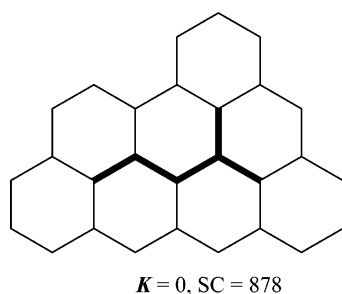
**Figure 3.** The three most stable and pyrolytically probable C<sub>30</sub>H<sub>14</sub> fluoranthenoid hydrocarbons.

#### PAH ISOMERS OF C<sub>28</sub>H<sub>14</sub>

The enumeration of the C<sub>28</sub>H<sub>14</sub> benzenoid isomers ( $r = 8$ ,  $N_{lc} = 6$ ) is more involved since this isomer group has a member that is not strictly pericondensed, namely, benzo-[a]coronene (first Clar structure in Figure 4). Note that this formula does not lie on the borderline of Table PAH6 because the formula for coronene (C<sub>24</sub>H<sub>12</sub>) precedes it. The full algorithm can be found in our prior work.<sup>8</sup> The eight nonradical C<sub>28</sub>H<sub>14</sub> benzenoid isomers are listed in Figure 4 and the diradical isomer in Figure 5. Unlike the C<sub>30</sub>H<sub>14</sub>



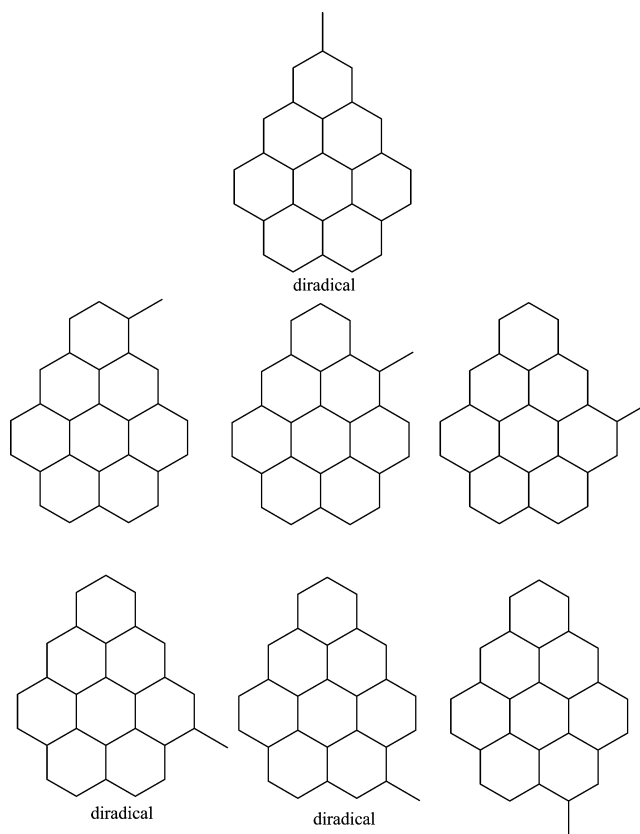
**Figure 4.** Maximum Clar structures for all the  $\text{C}_{28}\text{H}_{14}$  Kekulean benzenoid isomers.



**Figure 5.** The  $\text{C}_{28}\text{H}_{14}$  diradical benzenoid hydrocarbon. Note that the excised internal structure shown in bold is a nondisjoint diradical and its circumscribed successor must also be a triplet diradical.

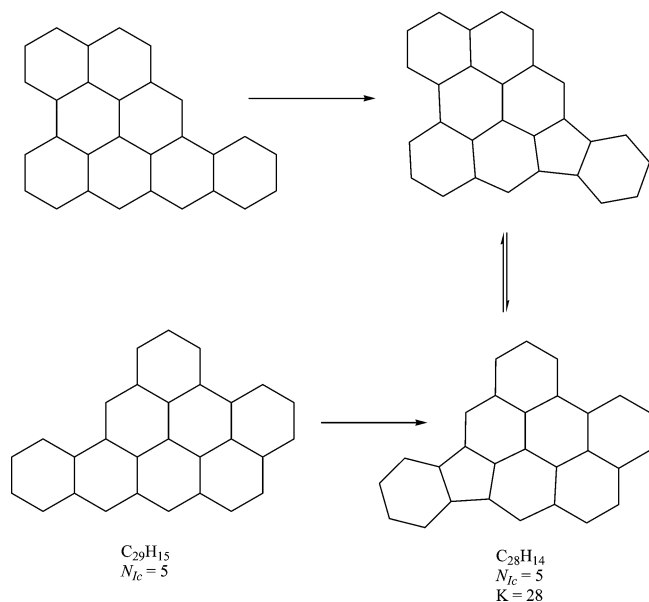
benzenoid isomers, these nine  $\text{C}_{28}\text{H}_{14}$  benzenoid isomers are not first-generation members of the constant-isomer series because there is a  $\text{C}_{27}\text{H}_{13}$  benzenoid that has seven methylenyl-substituted isomers, shown in Figure 6, which, when circumscribed along with the nine  $\text{C}_{28}\text{H}_{14}$  benzenoid isomers in Figures 4–5, gives a total of 12 nonradical and 4 diradical  $\text{C}_{62}\text{H}_{20}$  benzenoid isomers that belong to one of the first-generation 16-constant-isomer series.

Five of the eight nonradical  $\text{C}_{28}\text{H}_{14}$  benzenoid isomers (Figure 4) have been either synthesized or analytically identified in the environment. Phenanthro[1,10,9,8-*opqrs*]perylene (bisanthrene;  $K = 16$ , where  $K$  is the Kekulé number) was synthesized by Scholl and Meyer in 1934 by Zn dust reduction of bisanthenequinone<sup>11</sup> and subsequently verified by X-ray crystallography of its benzo[*cde*]bisanthrene ( $\text{C}_{30}\text{H}_{14}$ ; second molecular graph in Figure 1) derivative made from it via maleic anhydride addition.<sup>12</sup> It is probably the most readily available isomer, has been used in numerous studies, and has not been observed in the analysis of environmental samples probably because it readily forms the corresponding quinone (7,14-dione) as a result of pyrolytic oxidation of its reactive solo positions. The two most stable isomers, benzo[*a*]coronene ( $K = 34$ ) and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ), were synthesized by Clar and co-workers<sup>13</sup> and subsequently identified in soot extracts from coal-burning stoves.<sup>14</sup> These two isomers and benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene ( $K = 26$ ) were identified as being present in the extracts of carbon black.<sup>15</sup> Phenanthro[5,4,3,2-*efghi*]perylene ( $K = 30$ ), benzo[*a*]coro-



**Figure 6.** All  $\text{C}_{28}\text{H}_{14}$  methylenyl isomers of the only  $\text{C}_{27}\text{H}_{13}$  benzenoid, which, when circumscribed with hexagonal rings, give the remaining  $\text{C}_{62}\text{H}_{20}$  first-generation members of the 16-constant-isomer series.

nene ( $K = 34$ ), and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ) were identified in coal tar pitch by Fetzer and co-workers and correlated in harbor Zebra mussels, air particulate, and coal tar from Hamilton, Canada, by Marvin and co-workers.<sup>16</sup> Thus, the four most stable  $\text{C}_{28}\text{H}_{14}$  benzenoids in Figure 4 have been identified as pyrolytic constituents, and only benzo[*a*]coronene ( $K = 34$ ), benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ), and phenanthro[1,10,9,8-*opqrs*]perylene ( $K = 16$ ) appear to be commercially available.



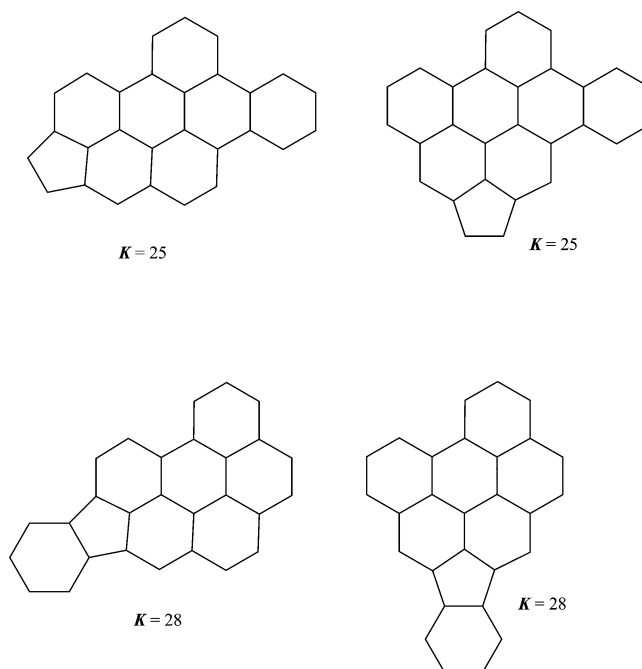
**Figure 7.** Hexagonal-to-pentagonal ring contraction of two different C<sub>29</sub>H<sub>15</sub> benzenoids give the same C<sub>28</sub>H<sub>14</sub> fluoranthenoid successor.

In the seminal paper of Simmonsick and Hite,<sup>2</sup> only Clar's two most stable isomers, benzo[*a*]coronene ( $K = 34$ ) and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ), were available as reference standards in their analysis of extracts from carbon black, which gave nine capillary GC/MS peaks corresponding to  $m/z = 350$  mass units (C<sub>28</sub>H<sub>14</sub>). The first eluting peak was assigned at a 90% confidence to the indacenoid, diindeno[1,2,3-*cd*:1',2',3'-*jk*]pyrene ( $K = 24$ ), which was previously synthesized by pyrolysis of a mixture of benzene and pyrene in a pipe bomb.<sup>17</sup> As it will be shown, this represents a spectacular assignment. While there were eight more later-eluting GC/MS peaks of  $m/z = 350$  mass units, only two of them could be assigned to the available Clar standards. At this juncture, the reader might be tempted to surmise that the remaining six peaks belong to the remaining six unassigned C<sub>28</sub>H<sub>14</sub> benzenoid isomers (Figure 4). However, it will become apparent below that things are more complicated than this.

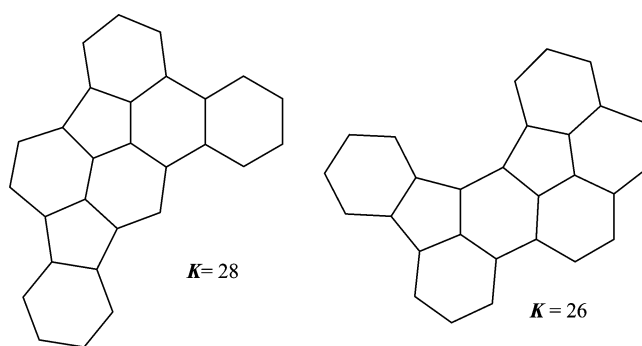
Using our hexagonal-to-pentagonal ring-contraction algorithm on the 21 depicted C<sub>29</sub>H<sub>15</sub> ( $r = 8$ ,  $N_{lc} = 5$ ) benzenoid isomers<sup>10</sup> gives 141 C<sub>28</sub>H<sub>14</sub> fluoranthenoid combinations from which six duplicates of the type illustrated in Figure 7 must be subtracted. Adding the two dibenzocorannulene isomers<sup>18</sup> gives a grand total of 137 C<sub>28</sub>H<sub>14</sub> fluoranthenoid isomers. Figure 8 depicts four of the most stable C<sub>28</sub>H<sub>14</sub> fluoranthenoid isomers. The number of C<sub>28</sub>H<sub>14</sub> indacenoid isomers ( $r = 8$ ,  $N_{lc} = 4$ ) is estimated to be approximately 670. Figure 9 gives two examples of recently synthesized C<sub>28</sub>H<sub>14</sub> indacenoids predicted to be more stable than the above diindeno[1,2,3-*cd*:1',2',3'-*jk*]pyrene ( $K = 24$ ).<sup>19</sup> No phenyl-substituted C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> benzenoids are structurally possible.<sup>6,8</sup>

#### SYNTHESIS OF C<sub>28</sub>H<sub>14</sub> AND C<sub>30</sub>H<sub>14</sub> PAHS

The synthesis of benzo[*a*]coronene ( $K = 34$ ) was accomplished by double Diels–Alder addition of maleic anhydride to dibenzo[*b,l*]pyrene in the presence of chloaniol followed by decarboxylation in aqueous KOH at 350 °C under pressure.<sup>20</sup> Naphtho[8,1,2-*bcd*]perylene made by the



**Figure 8.** The more stable C<sub>28</sub>H<sub>14</sub> fluoranthenoid isomers.



**Figure 9.** Example C<sub>28</sub>H<sub>14</sub> indacenoids recently synthesized.

reaction of 1-bromonaphthalene, pyrene, and AlCl<sub>3</sub> condenses with boiling maleic anhydride in the presence of chloaniol to give a product that is decarboxylated by boiling quinoline and Cu powder to give benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ).<sup>21</sup> This same reaction sequence should have also given some benzo[*ghi*]naphtho[8,1,2-*bcd*]perylene ( $K = 25$ ) as a coproduct, but none has yet been identified. Benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene (naphtho[8,1,2-*efg*]anthanthrene;  $K = 26$ ) was synthesized by the dehydrogenation of 1-(1-naphthyl)-benzo[*a*]anthracene.<sup>22</sup>

Fetzer and Biggs synthesized three C<sub>28</sub>H<sub>14</sub> benzenoid isomers—benzo[*a*]coronene ( $K = 34$ ), benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene ( $K = 31$ ), and phenanthro[5,4,3,2-*efghi*]perylene ( $K = 30$ )—in one reaction.<sup>23</sup> They reacted dibenzo[*e,ghi*]perylene with maleic anhydride in the presence of chloranil followed by decarboxylation in boiling quinoline containing Cu powder.<sup>23</sup> All three of these C<sub>28</sub>H<sub>14</sub> PAHs can be further reacted with maleic anhydride and chloranil followed by treatment with boiling quinoline and Cu powder to give naphtho[8,1,2-*abc*]coronene (C<sub>30</sub>H<sub>14</sub>;  $K = 40$ ).<sup>24</sup>

Dibenzo[*bc,ef*]coronene (benzo[*cde*]bisanthrene;  $K = 30$ ) is made by decarboxylation of the adduct formed by reacting bisanthrene with maleic anhydride<sup>25</sup> or Zn dust distillation from hypericin.<sup>26</sup> Dibenzo[*bc,kl*]coronene (dibenzoperopyrene;  $K = 20$ ) is made by reacting *o*-tolylmagnesium bromide



**Table 1.** Properties of C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> Benzenoid Hydrocarbons<sup>a</sup>

<i>K</i>	mp, °C	<i>E</i> <sub>π</sub> , β	HOMO, β	SHOMO, β	$\Delta H_f^\circ$ kcal/mol	UV, nm $\alpha, p, \beta$	( <i>M</i> + <i>H</i> )/ <i>M</i>	<i>L/B</i>	IP, eV	RE (eV)
C <sub>28</sub> H <sub>14</sub>										
34	292–4, SC = 1668	40.3676	0.4685	0.5842	89.6	432, 376, 320 <sup>b</sup>	0.814 (0.698)	1.215	7.08	
31	396	40.3210	0.3923	0.6874	91.0	420, 406, 322 <sup>c</sup>	0.506 (0.497)	1.331	6.92	4.11
30		40.2946	0.4443	0.4985	91.6	367, 344, 327 <sup>d</sup>	0.792	1.216		
26	318–9	40.2410	0.3128	0.6583	94.4	460, 407, 312	0.421	1.183		
25		40.1988	0.3188	0.6331	96.3		0.465	1.290		
19		40.1048	0.2229	0.6995	101.6		0.257	1.511		
16	SC = 1152	40.0779	0.1774	0.7046	103.9	424, 662.5, 312 <sup>b</sup>	0.197	1.064	6.30	3.20
15	SC = 1038	39.9823	0.1941	0.5685	107.3		0.218	1.599		3.05
0	SC = 878	39.6107	0.0	0.0	159.3 <sup>e</sup>					
C <sub>30</sub> H <sub>14</sub>										
40	345	43.4138	0.3823	0.5836	95.2	–, 410, 342 <sup>f</sup>	0.516 (0.511)	1.212		4.33
30	452	43.3000	0.2539	0.7119	100.8	–, 535.5, 345 <sup>b</sup>	0.285 (0.316)	1.098	6.50	3.97
20	SC = 1565	43.1197	0.1859	0.5389	109.8	–, 524, 362 <sup>g,h</sup>	0.191	1.351	6.42	3.43
0	SC = 1256	42.8350	0.0	0.0	168.5 <sup>e</sup>					
<i>K</i>	Δ <i>K</i> /Δ <i>K</i> (benzene)				conjugated circuit resonance energy parameters					
C <sub>28</sub> H <sub>14</sub>										
34										
31	(7.12)				<sup>1</sup> / <sub>31</sub> (120 <i>R</i> <sub>1</sub> + 76 <i>R</i> <sub>2</sub> + 40 <i>R</i> <sub>3</sub> + 12 <i>R</i> <sub>4</sub> )					
30	(7.17)									
26	(6.94)									
25	(6.97)									
19										
16	4.41 (5.67)				<sup>1</sup> / <sub>16</sub> (48 <i>R</i> <sub>1</sub> + 32 <i>R</i> <sub>2</sub> + 16 <i>R</i> <sub>3</sub> )					
15	(7.14)									
0										
C <sub>30</sub> H <sub>14</sub>										
40					<sup>1</sup> / <sub>40</sub> (158 <i>R</i> <sub>1</sub> + 114 <i>R</i> <sub>2</sub> + 69 <i>R</i> <sub>3</sub> + 18 <i>R</i> <sub>4</sub> + <i>R</i> <sub>5</sub> )					
30	8.20				<sup>1</sup> / <sub>30</sub> (108 <i>R</i> <sub>1</sub> + 78 <i>R</i> <sub>2</sub> + 49 <i>R</i> <sub>3</sub> + 26 <i>R</i> <sub>4</sub> + 9 <i>R</i> <sub>5</sub> )					
20					<sup>1</sup> / <sub>20</sub> (60 <i>R</i> <sub>1</sub> + 48 <i>R</i> <sub>2</sub> + 36 <i>R</i> <sub>3</sub> + 24 <i>R</i> <sub>4</sub> + 12 <i>R</i> <sub>5</sub> )					

<sup>a</sup> The Kekulé (*K*) number in the first column is used to identify the benzenoid in figures. <sup>b</sup> Benzene. <sup>c</sup> Dioxane. <sup>d</sup> Dichloromethane. <sup>e</sup> Value for the diradical isomer based on the assumption that *K* = 1. <sup>f</sup> CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. <sup>g</sup>  $\alpha$ -methyl naphthalene. <sup>h</sup> 362 goes to 340 nm in benzene.

with 9,10-dimethyl anthraquinone, reducing the diol formed with HI in acetic acid, and effecting cyclodehydrogenation by sublimation of the anthracene derivative obtained over Pd/C at 500 °C.<sup>27</sup>

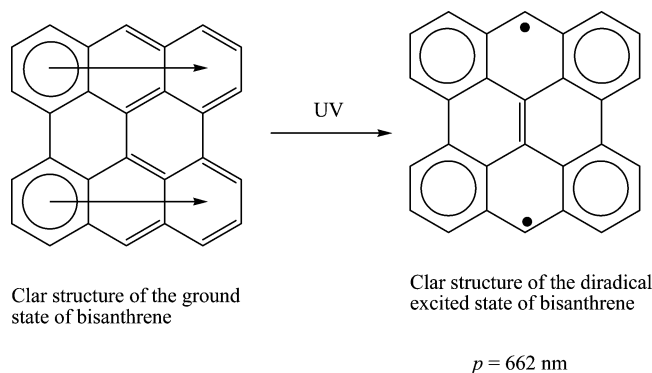
#### PROPERTIES OF C<sub>28</sub>H<sub>14</sub> AND C<sub>30</sub>H<sub>14</sub> BENZENOID HYDROCARBONS

Table 1 summarizes the known properties of C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> benzenoid hydrocarbons. As it should be evident, much of this information is sporadic. Although Fetzner and Biggs<sup>28</sup> identified phenanthro[5,4,3,2-*efghi*]perylene (*K* = 30) on the basis of its synthetic origin as a coproduct with benzo[*a*]coronene (*K* = 34) and benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene (*K* = 31), HPLC retention time, mass spectral analysis, and UV spectrum versus its theoretically predicted one, no melting point (mp) was reported. The melting point of the glass melting point tube occurs before both bisanthrene (phenanthro[1,10,9,8-*opqra*]perylene; *K* = 16) and dibenzo[*bc,kl*]coronene (*K* = 20) melt.<sup>11</sup> Thus, while five of the eight nonradical C<sub>28</sub>H<sub>14</sub> benzenoids and all three of the nonradical C<sub>30</sub>H<sub>14</sub> benzenoids have been synthesized, only five melting points have been determined and recorded in Table 1.

The HMO  $\pi$ -electronic energies ( $E_{\pi}$ ), highest occupied molecular orbital (HOMO) values, and the standard enthalpy of formation ( $\Delta H_f^\circ$ ) were determined by the author. A nine-parameter (for PAH6s) additive method recently published was used to calculate the standard enthalpy of formation

values.<sup>29</sup> This nine-parameter method is also applicable to non-AHs, and the authors compare their results with the previous literature calculations and experimental results.<sup>29</sup> Note that the values of *K*,  $E_{\pi}$ , and  $\Delta H_f^\circ$  measure relative stability of PAH6 isomers and all correlate to each other in Table 1. The  $(M + H)/M$  data are from Simmonsick and Hites;<sup>2</sup> the experimental values are in parentheses. The *L/B* (length-to-breadth) values are from a compilation by Sander and Wise.<sup>30</sup> For PAH6's isomer sets,  $(M + H)/M [(m/z + 1)/(m/z)]$  for the molecular ion in chemical ionization mass spectrometry values increase with increasing HOMO values and GC and HPLC retention times increase with increasing *L/B* values and are useful in determining PAH6 isomers in the GC/MS analysis.<sup>31</sup> The ionization potential energies (IP) were obtained from a compilation by Lias and co-workers.<sup>32</sup>

The UV data in Table 1 are from the various synthesis references already cited. The *p* absorption band is due to polarization along the PAH6 long molecular axis and is strongly red-shifted if the number of Clar sextets can increase in the excited (diradical-like) state.<sup>33</sup> Thus, bisanthrene (C<sub>28</sub>H<sub>14</sub>; *K* = 16) appears strongly red-shifted to 662 nm compared to the remaining known isomers because, in its first excited state, the number of sextets increases by two (Figure 10). For this reason also, dibenzo[*bc,ef*]coronene (C<sub>30</sub>H<sub>14</sub>; *K* = 30) is relatively red-shifted to 535 nm compared to 410 nm for naphtho[8,1,2-*abc*]coronene (*K* = 40) because its first excited state increases by one sextet.



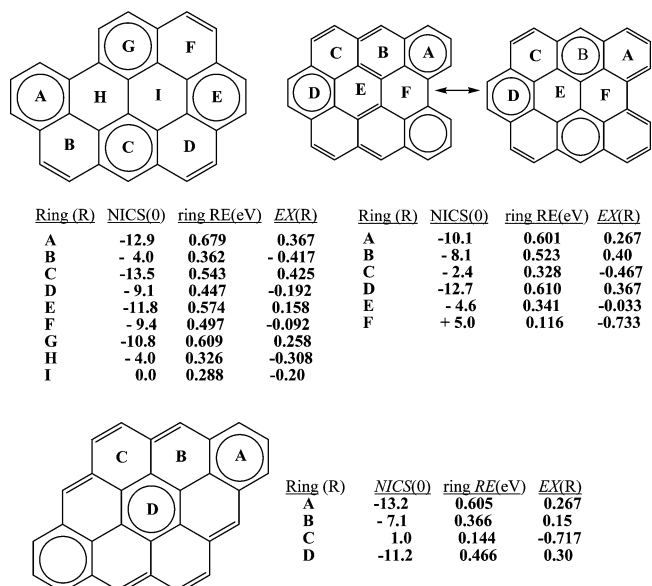
**Figure 10.** First excited state of bisanthrene responsible for the UV  $p$  absorption band.

Also, a benzenoid system becomes strongly red-shifted when the number of sextets remains unchanged between the ground state and the first excited state and the number of pairs' solo positions located on opposite sides of the molecular graph increase. This is why dibenzo[*bc,lm*]coronene (C<sub>30</sub>H<sub>14</sub>;  $K = 20$ ) becomes relatively red-shifted to 524 nm compared to 410 nm for naphtho[8,1,2-*abc*]coronene ( $K = 40$ ). Those isomers that have a maximum number of ground-state sextets are unable to increase their number of excited-state sextets and generally show similar  $p$ -band absorptions in their UV spectra.

It is of interest to note that bisanthrene (C<sub>28</sub>H<sub>14</sub>;  $K = 16$ ) has a total of 1152 excited diradical states ( $SC = 1152$ ) and the Clar structure in Figure 10 only represents 16 of these states, but these 16 states are relatively more important because the electrons have a higher probability of being located at solo positions for the HOMO and LUMO energy levels involved in the ground state to first excited-state transition. Another important feature that should be noted here is that, for the eight C<sub>28</sub>H<sub>14</sub> and three C<sub>30</sub>H<sub>14</sub> benzenoids, the SC for the first excited-state diradicals are all larger than their valence-bond diradical isomers. For example, the least stable Kekulean (nonradical) C<sub>28</sub>H<sub>14</sub> ( $K = 15$ ) and C<sub>30</sub>H<sub>14</sub> ( $K = 20$ ) structures have  $SC = 1038$  and  $1565$  compared to their valence-bond diradical isomers with  $SC = 878$  and  $1256$  (Figure 5 and third structure in Figure 1), respectively.

## ELECTRONIC/DIAMAGNETIC PROPERTIES

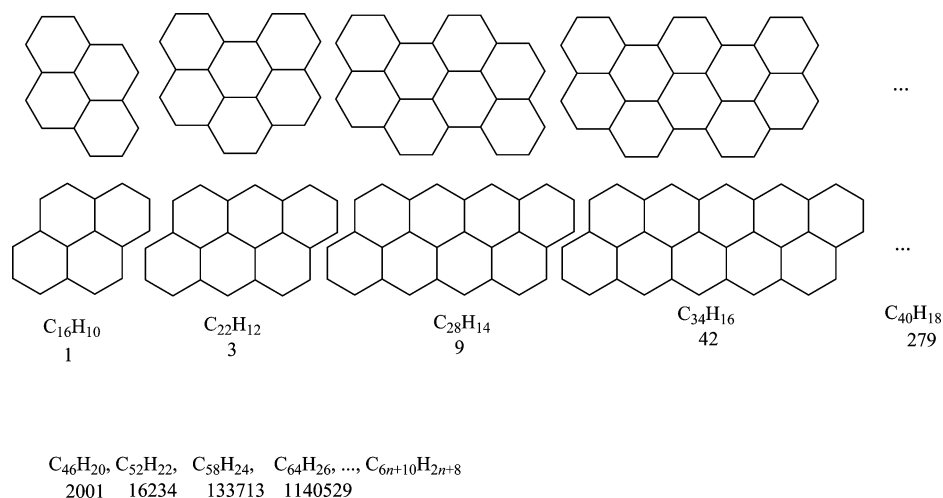
Figure 11 gives the Clar structures for the three C<sub>30</sub>H<sub>14</sub> benzenoid isomers.<sup>33</sup> A benzenoid Clar structure has a maximum number of sextets (hexagon benzene rings) having three mutually permutable  $p \pi$  bonds denoted by inscribed circles and involves completing the remaining carbon valences with double bonds. While both naphtho[2,1,8-*abc*]coronene and dibenzo[*bc,kl*]coronene have a single Clar structure, dibenzo[*bc,ef*]coronene has two, as shown in Figure 11. Figure 11 also summarizes the respective ring electronic distributions computed by three different methods—the Schleyer nucleus-independent chemical shift [NICS(0)] method,<sup>34</sup> the Randić local conjugated circuit method,<sup>35</sup> and the Gutman ring electron excess [EX(R)] method.<sup>36</sup> The NICS(0) values were calculated by Ruiz-Morales.<sup>37</sup> An external magnetic field induces local and delocalized magnetic fields in closed-shell species, the latter which can be used to distinguish between aromatic and antiaromatic polycyclic conjugated hydrocarbons by diatropic and para-



**Figure 11.** NICS(0), ring RE(eV), and electron excess [EX(R)] for ring R for the C<sub>30</sub>H<sub>14</sub> benzenoid isomers. Note that, for benzene, NICS(0) = -9.9 and ring resonance energies  $R_1 = 0.869$ ,  $R_2 = 0.247$ ,  $R_3 = 0.100$ ,  $R_4 = 0.041$ , and  $R_5 = 0$  eV.

tropic ring currents, respectively. Hence, in an external magnetic field, aromatic and antiaromatic ring centers are shielded and deshielded, respectively. Schleyer introduced NICS(0) as a criterion for aromaticity, whereby shieldings are computed in the molecular plane. Their magnitudes are compared to that of benzene, which has NICS(0) = -9.6.<sup>34</sup> The distribution of aromatic sextet centers in the C<sub>30</sub>H<sub>14</sub> benzenoids in Figure 11 by all methods is in full agreement with Clar's sextet rule.

While area practitioners are usually able to quickly identify the Clar structure with a maximum number of sextet rings of any benzenoid by identifying its array of polyphenylene substructures, several systematic methods for accomplishing this objective have appeared in print. Watson and co-workers used oxidative cyclodehydrogenation of specifically synthesized polyphenylenes to generate superlarge total resonant sextet (TRS) benzenoids (benzenoids having formula carbons divisible by six and the maximum number of sextet rings).<sup>38</sup> Hansen and Zheng gave the following rules for obtaining a Clar structure: (a) circles are never adjacent, (b) the generalized benzenoid system obtained by deleting the vertices of all hexagons containing a circle must have a perfect matching (i.e., a Kekulé structure), and (c) the number of circles is a maximum subject to a and b. Their full method for obtaining the maximum number of sextets in any benzenoid has been detailed in terms of theorems with illustrations.<sup>39</sup> This method applies to all benzenoid-related systems including polyphenylenes and systems with holes. Randić and Hosoya presented a nine-step algorithm for determining Clar structures.<sup>40</sup> Their algorithm gives all the Clar structures belonging to any benzenoid, even those having multiple Clar structures. The method of Ruiz-Morales involves simply drawing in the maximum number of sextet rings (circles) so as to cover all the internal third-degree vertices (i.e., the excited internal structure) and then finishing by placing double bonds so as to complete the Clar structure while maintaining a valence of four for all the carbons.<sup>37</sup> The latter method only applies to pericondensed benzenoids.



**Figure 12.** Two isomeric series and their increasing isomer numbers with size.

Identifying the polyphenylene substructures in a given benzenoid as done by Watson and co-workers<sup>38</sup> probably represents the simplest method to determine its TRS Clar structure.

#### TWO DIFFERENT STRATEGIES FOR STUDYING RELATED MOLECULES

There are two different strategies for studying related molecules, the study of homologous series and the study of isomer sets. The first strategy allows one to investigate trends resulting from a uniform incremental increase in size, and the second allows one to discern how structure variation causes changes in the properties of molecules independently of size. Unfortunately, very few studies of the  $C_{28}H_{14}$  and  $C_{30}H_{14}$  benzenoids have employed either of these strategies. This has resulted in incomplete data on these benzenoids, which will now be addressed. Among the few studies that did include all isomers belonging to a given PAH6 formula were those of Simmonsick and Hite,<sup>2</sup> Alberty and co-workers,<sup>41</sup> Knopp et al.,<sup>10</sup> and Sander and Wise.<sup>30</sup> Studies involving incomplete isomer sets include those of Randić,<sup>35</sup> Ruiz-Morales,<sup>37</sup> and Kataoka.<sup>42</sup> The calculated magnetic anisotropies [ $\Delta K/\Delta K(\text{benzene})$ ] by Kataoka and conjugated circuit resonance energies (RE) by Randić are unfortunately sparse in Table 1 for the  $C_{28}H_{14}$  and  $C_{30}H_{14}$  PAH6 isomer sets.

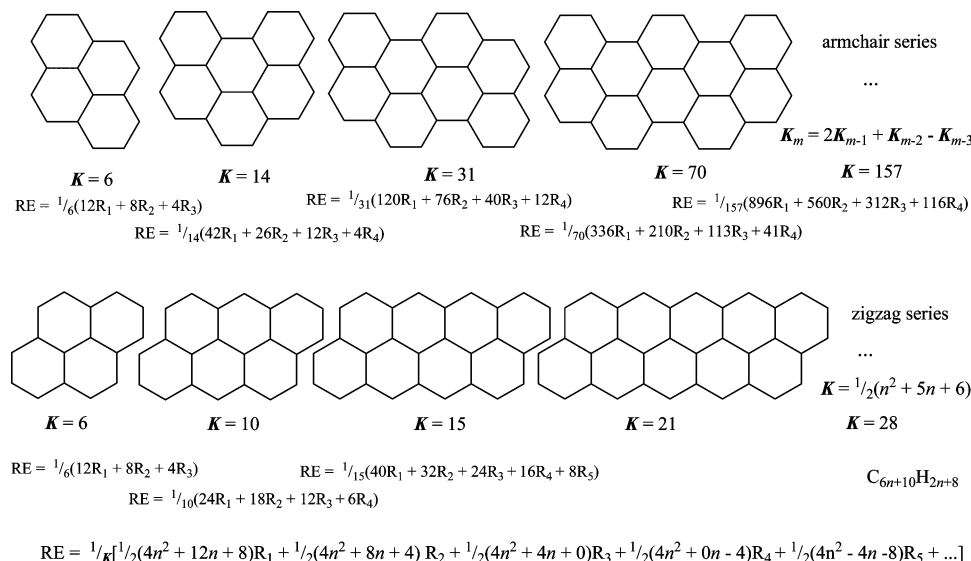
Table 1 shows that Kataoka's statement,<sup>42</sup> "Although phenanthro[1,10,9,8-*opqra*]perylene (bisanthrene,  $K = 16$ ) and benzo[*cd*]naphtho[3,2,1,8-*pqra*]perylene ( $K = 26$ ) have been synthesized, neither their magnetic susceptibilities nor their  $^1\text{H}$  NMR spectra have been reported", is incorrect. The magnetic susceptibility of phenanthro[1,10,9,8-*opqra*]perylene has been reported by Akamatu and Matsunaga.<sup>43</sup> While computed NICS values for only four of the eight  $C_{28}H_{14}$  benzenoid isomers were performed, Ruiz-Morales did compute NICS values for all three of the  $C_{30}H_{14}$  benzenoid isomers.<sup>37</sup> Figure 11 shows that these NICS values correlate to ring RE values computed by the method of Randić.<sup>44</sup> Gutman's ring (R) electron excess  $\text{EX}(\text{R})$ <sup>45</sup> values are also given in Figure 11. While all three methods clearly corroborate the corresponding Clar structures, they disagree in the relative importance of the sextets.

The inclusion of all isomers in a computational study, particularly in those sets having a small number of isomers, should be a general practice, as this would make the corresponding results more definitive. In the next section, we will study homologous series that start with the most and least stable pair of  $C_{28}H_{14}$  and  $C_{30}H_{14}$  isomers.

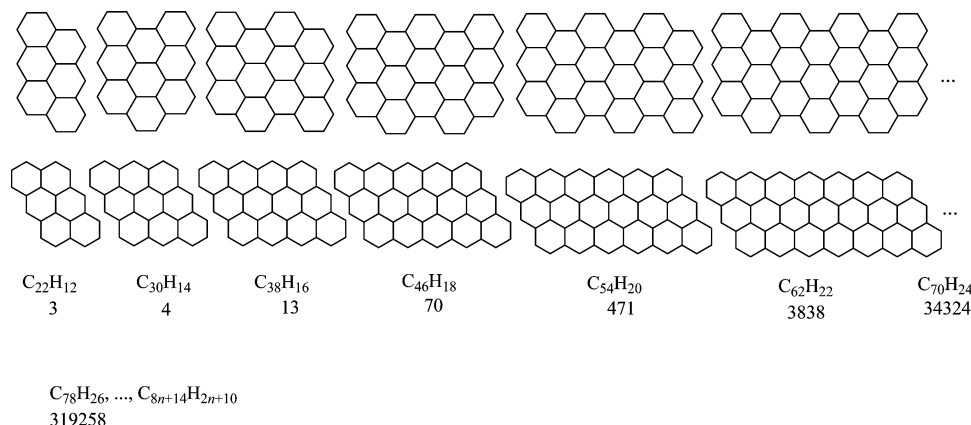
#### EXTRAPOLATIONS FROM $C_{28}H_{14}$ AND $C_{30}H_{14}$ TO INFINITE BENZENOID STRIPS

Connecting a specific aufbau unit on a given unique core structure of two different orientations will generate the most and least stable, strictly pericondensed isomeric members of the  $C_{28}H_{14}$  benzenoids. Successively repeating this process generates an isomeric pair of series of indefinite extent. Four series have been investigated in regard to the closeness of the properties of finite-size members for modeling the corresponding infinite polymeric strips. How these series approach infinity, how large a finite structure must be to adequately approximate an infinite system, and which properties are convergent and which are divergent in magnitude are some of the questions that will be discussed. Numerous studies including these infinite polymers have been reported, but none with an isomeric pairwise comparison as done herein.<sup>7,46</sup>

Connecting a 1,3,5-hexatrienehexayl ( $C_6H_2$  aufbau unit) to naphthalene ( $C_{10}H_8$ ) gives pyrene ( $C_{16}H_{10}$ ). Orienting pyrene two different ways and appropriately connecting a  $C_6H_2$  aufbau unit gives benzo[*ghi*]perylene and anthanthrene ( $C_{22}H_{12}$ ), as shown in Figure 12. While there is only one  $C_{10}H_8$  and one  $C_{16}H_{10}$  benzenoid isomer, there are three  $C_{22}H_{12}$  benzenoid isomers. Benzo[*ghi*]perylene is the most stable and anthanthrene the least stable Kekulean  $C_{22}H_{12}$  benzenoid; the third  $C_{22}H_{12}$  benzenoid isomer is triangulene, which is a diradical. Repeating this aufbau construction on benzo[*ghi*]perylene and anthanthrene gives the two  $C_{28}H_{14}$  benzenoids shown in Figure 12, where benzo[*pqr*]naphtho[8,1,2-*bcd*]perylene is derived from benzo[*ghi*]perylene (upper row in Figure 12) and dibenzo[*cd,lm*]anthanthrene is derived from anthanthrene (lower row in Figure 12). Continuing this aufbau construction successively generates the two series of Figure 12. The infinite member (polymer strip) of the upper series, in the absence of the lower one, has been extensively studied by Klein and co-workers.<sup>46</sup>



**Figure 13.** Resonance energies ( $R_1 = 0.869$ ,  $R_2 = 0.247$ ,  $R_3 = 0.100$ ,  $R_4 = 0.041$ , and  $R_5 = 0$  eV) and number of resonance structures.



**Figure 14.** Two series and their increasing isomer numbers with size.

Studies of both polymer strips belonging to the series in Figure 12 were reported by Bonchev and co-workers<sup>47</sup> and Hosoya and co-workers.<sup>48</sup> The polymer strip belonging to the lower series was investigated in a separate study by the Klein and co-workers.<sup>49</sup> The infinite member of the upper series belongs to the poly(polyphenanthrene) family of polymer strips of different widths in which *cis*-polyacetylene has a width  $w = 1$  and polyacene has a width  $w = 2$ . The polymer strips ( $w = 3$ ) corresponding to the upper and lower series in Figure 12 were called polyphenanthrephenanthrene and poly(polyacene), respectively.<sup>46,49</sup>

Listed in Figure 12 is the increasing number of benzenoid isomers for each formula,<sup>50</sup> in which the upper member is the most stable Kekulean representative and the lower member is the least stable one. While the numbers of isomers rapidly escalate, the corresponding members of the isomeric pair of series in Figure 12 bracket all the remaining isomers in stability. Clar has synthesized the benzenoids shown in the upper series up to the C<sub>40</sub>H<sub>18</sub>, but only pyrene and anthanthrene in the lower series have been synthesized.<sup>51</sup> For each, the number of Kekulé structures and the conjugated circuit resonance energy (RE) expressions are listed in Figure 13. The RE expressions for the upper series were from the work of Randić,<sup>37,44</sup> but the general RE expression for the lower series was derived by the present author. The analytical expression for the recursion of the number of Kekulé

structures ( $K_n$ ) for the upper series of Figure 13 is given by

$$K_n = 0.033136(0.55496)^n + 0.22463(-0.80194)^n + 2.74224(2.24698)^n$$

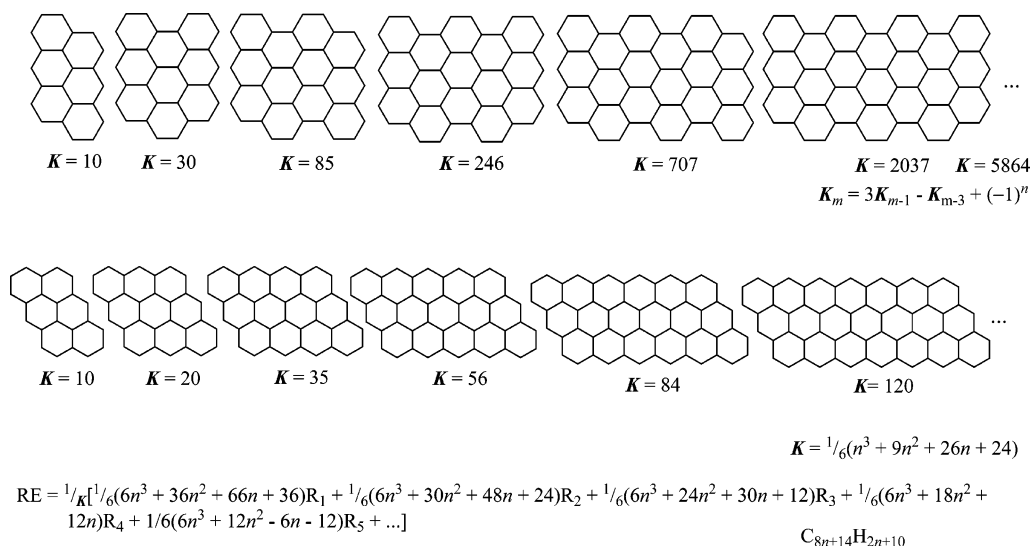
where  $n$  is the generation number (e.g.,  $n = 1$  for pyrene) and  $K_n$  is rounded off to the nearest integer.

Starting with differently oriented anthanthrene core structures and using a C<sub>8</sub>H<sub>2</sub> aufbau unit, we can generate the two series in Figure 14. Listed in Figure 14 is the increasing number of benzenoid isomers for each formula,<sup>50</sup> where the corresponding members of the lower of series is the least stable isomer of each isomer set. An interesting feature of these series is that every third formula (C<sub>30</sub>H<sub>14</sub>, C<sub>54</sub>H<sub>20</sub>, C<sub>78</sub>H<sub>26</sub>, ..., C<sub>24m+6</sub>H<sub>6m+8</sub>;  $m = 1, 2, 3, \dots$ ) has carbon numbers divisible by six ( $N/6$ ) but no TRS isomers. The infinite limit member for each of these two isomeric series are polymer strips of width  $w = 4$ . For each, the number of Kekulé structures and the general RE expression for the lower series derived by the author are listed in Figure 15.

#### HMO BAND GAP OF THE DENSITY OF STATES

Expressions for 77 infinite polymer networks have been published by Hosoya and co-workers which include three of the polymer strips in Figures 12–15.<sup>52</sup> The method used





**Figure 15.** Resonance energies ( $R_1 = 0.869$ ,  $R_2 = 0.247$ ,  $R_3 = 0.100$ ,  $R_4 = 0.041$ , and  $R_5 = 0$  eV) and number of resonance structures.

assumed cyclic boundary conditions since the density of states of any given polymer is independent of its boundary conditions.<sup>53</sup> A key observation made by Hosoya was that a zero HOMO–LUMO band gap in certain classes of conjugated polymer networks coincided with the existence of a nonbonding MO in their hypothetical cyclic monomer or dimer. The characteristic polynomial for the cyclic unit of the polymer strip belonging to the upper series in Figure 13 is

$$P(\text{PP};X) = X^6 - (8 + 2 \cos k\theta)X^4 + (19 + 6 \cos k\theta - 8 \cos^2 k\theta)X^2 - (13 + 8 \cos k\theta - 12 \cos^2 k\theta - 8 \cos^3 k\theta) \quad (1)$$

where  $k\theta = 2k\pi/n$  ( $k = 0, 1, 2, \dots, n-1$ ) and  $n$  is the number of units in the cyclic system. For the lower series, it is

$$P(\text{PA};X) = X^6 - (8 + 6 \cos k\theta)X^4 + (17 + 28 \cos k\theta + 12 \cos^2 k\theta)X^2 - 8(1 + \cos k\theta)^3 \quad (2)$$

For the cyclic dimer ( $n = 2$ ), eq 1 gives  $X = \pm 0.2470$ ,  $\pm 0.5550$ ,  $\pm 0.8019$ ,  $\pm 1.4450$ ,  $\pm 2.2470$ , and  $\pm 2.8019$  as eigenvalues for  $P(\text{PP};X) = 0$  ( $k = 0, 1$ ;  $\cos k\theta = 1, -1$ ), which correspond to the points of singularity of the density of states of the corresponding infinite polymer strip. This result shows that the polymer strip in Figure 13 belonging to the upper series has a nonzero band gap. Repeating this procedure with eq 2 gives  $X = 0, 0, \pm 1, \pm 1, \pm 1.3633$ ,  $\pm 2.1249$ , and  $\pm 2.7616$ , which means that the polymer strip corresponding to the lower series has a zero band gap.

The characteristic polynomial for the cyclic unit of the polymer strip belonging to the lower series in Figure 15 is

$$P(\text{PAA};X) = X^8 - (11 + 8 \cos k\theta)X^6 + (39 + 60 \cos k\theta + 24 \cos^2 k\theta)X^4 - (49 + 124 \cos k\theta + 108 \cos^2 k\theta + 32 \cos^3 k\theta)X^2 + 16(1 + \cos k\theta)^4 \quad (3)$$

The solution of eq 3 for the cyclic dimer gives eigenvalues of  $X = 0, 0, \pm 1, \pm 1, \pm 1, \pm 1.2555$ ,  $\pm 1.8372$ ,  $\pm 2.4329$ , and  $\pm 2.8512$ , corresponding to the points of singularity

for the density of states, which shows that the infinite polymer strip belonging to this lower series has a zero band gap.

Analytical solutions to the  $\pi$ -electron bands of the infinite polymer strips belonging to the upper series of Figures 12–15 have been given by Klein.<sup>54</sup> Both these polymeric strips belong to the same topological class (Class I). The polymeric strip belonging to the upper series ( $w = 3$ ) in Figures 12 and 13 is a TRS benzenoid system and has a nonzero band gap, and the polymeric strip belonging to the upper series ( $w = 4$ ) in Figures 14 and 15 has a zero band gap.

#### RESONANCE ENERGY PER P $\Pi$ -ELECTRON OF INFINITE BENZENOID STRIPS

The general expression for the conjugated circuit resonance energy (RE) for the lower series in Figure 13 is

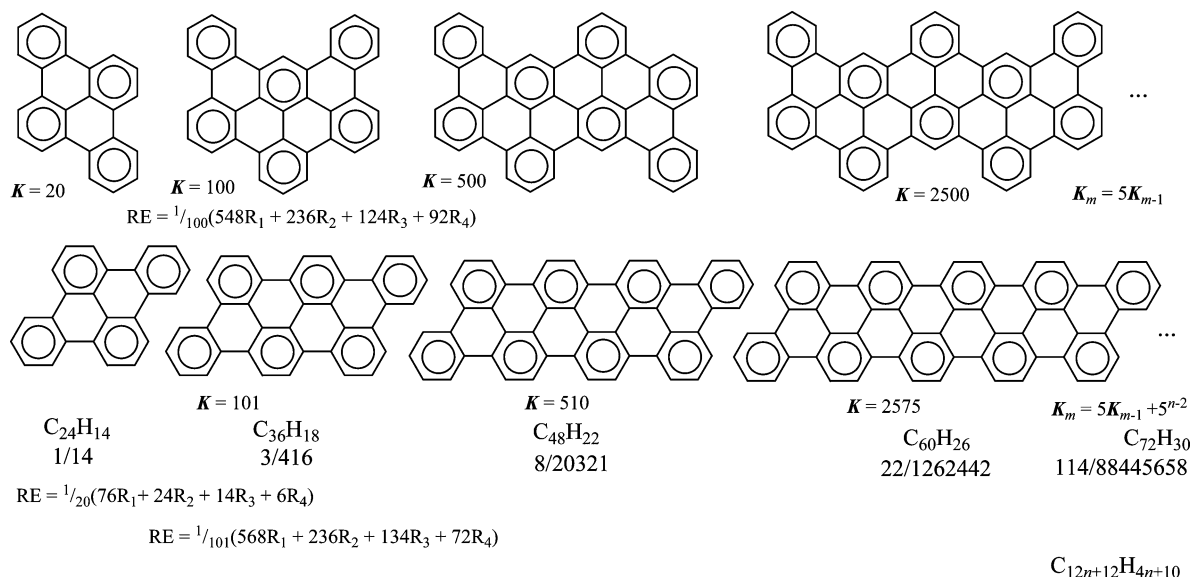
$$\text{RE}(\text{PA}) = (1/K)[(2n^2 + 6n + 4)R_1 + (2n^2 + 4n + 2)R_2 + (2n^2 + 2n)R_3 + (2n^2 - 2)R_4 + (2n^2 - 2n - 4)R_5 + \dots] \quad (4)$$

where  $n = 1, 2, 3, \dots$  is the membership number;  $C_{6n+10}H_{2n+8}$  is the formula;  $K = 1/2(n^2 + 5n + 6)$ ; and  $R_1 = 0.869$ ,  $R_2 = 0.247$ ,  $R_3 = 0.100$ ,  $R_4 = 0.041$ , and  $R_5 = 0$  eV are the Randić conjugated circuit parameters.<sup>35,44</sup> The general expression for resonance energy per electron (REPE) for infinitely large  $n$  is, thus, given by

$$\lim_{n \rightarrow \infty} \text{REPE}(\text{PA}) = \lim_{n \rightarrow \infty} \text{RE}(\text{PA})/(6n + 10) = 0 \quad (5)$$

The general expression for RE for the lower series in Figure 15 is

$$\text{RE}(\text{PAA}) = (1/K)[(n^3 + 6n^2 + 11n + 6)R_1 + (n^3 + 5n^2 + 8n + 4)R_2 + (n^3 + 4n^2 + 5n + 2)R_3 + (n^3 + 3n^2 + 2n)R_4 + (n^3 + 2n^2 - n - 2)R_5 + \dots] \quad (6)$$



**Figure 16.** Two isomeric TRS benzenoid series and their increasing isomer numbers with size. These TRS benzenoids are corresponding leapfrogs to those in Figures 12 and 13.

where  $K = (1/6)(n^3 + 9n^2 + 26n + 24)$  and C<sub>8n+14</sub>H<sub>2n+10</sub>. Thus, the REPE is

$$\lim_{n \rightarrow \infty} \text{REPE(PAA)} = \lim_{n \rightarrow \infty} \text{RE(PA)} / (8n + 14) = 0 \quad (7)$$

The results of eqs 5 and 7 are in full agreement with the recent work of Lukovits on parallelogram-shaped graphite sheets which only included  $R_1$  and  $R_2$  conjugated circuits and the prior work of Zhu and Klein, who also obtained REPE(PP) = 0.1553 eV for the polymer strip corresponding to the upper series in Figure 13.<sup>55,56</sup> From the RE expressions in Figures 13 and 15, it should be evident that the number and magnitudes of  $R_1$ - and  $R_2$ -conjugated circuits dominate over the number and magnitudes of  $R_3$ -,  $R_4$ -, and  $R_5$ -conjugated circuits, so one should expect that the convergence to zero should not be altered by their inclusion as done herein in eqs 4 and 6.

#### LEAPFROG-RELATED POLYMERIC STRIPS

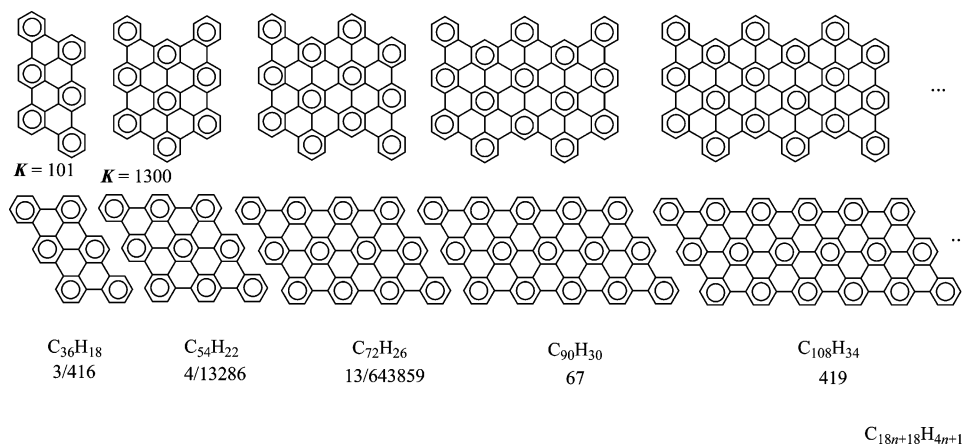
Leapfrogging fullerenes or benzenoid hydrocarbons is used to identify the more stable isomers without the need to generate all the isomers.<sup>57,58</sup> Leapfrogging the two series in Figure 12 (or Figure 13) gives the two series presented in Figure 16. The first two members of both series were synthesized by Clar.<sup>61</sup> Klein and co-workers<sup>7,54</sup> and Guo and co-workers<sup>52,60</sup> have extensively studied the infinite polymer strips corresponding to these series.

The number of strain-free TRS benzenoid isomers/total number of benzenoid isomers<sup>50</sup> are given below the corresponding formulas in Figure 16. The number of TRS benzenoid isomers was obtained from our prior work.<sup>51,58</sup> The RE expressions for the first two members are also given in Figure 16. Using the numerical assignments for the resonance energy parameters derived by Randić for the second pair of TRS benzenoids in Figure 16, we get RE = 5.51 eV for the upper TRS and RE = 5.63 eV for the lower one. For comparison with an isomer that is not a TRS benzenoid, teropyrene (C<sub>36</sub>H<sub>18</sub>) is computed to have a RE = 4.65 eV, which is substantially lower. Another interesting

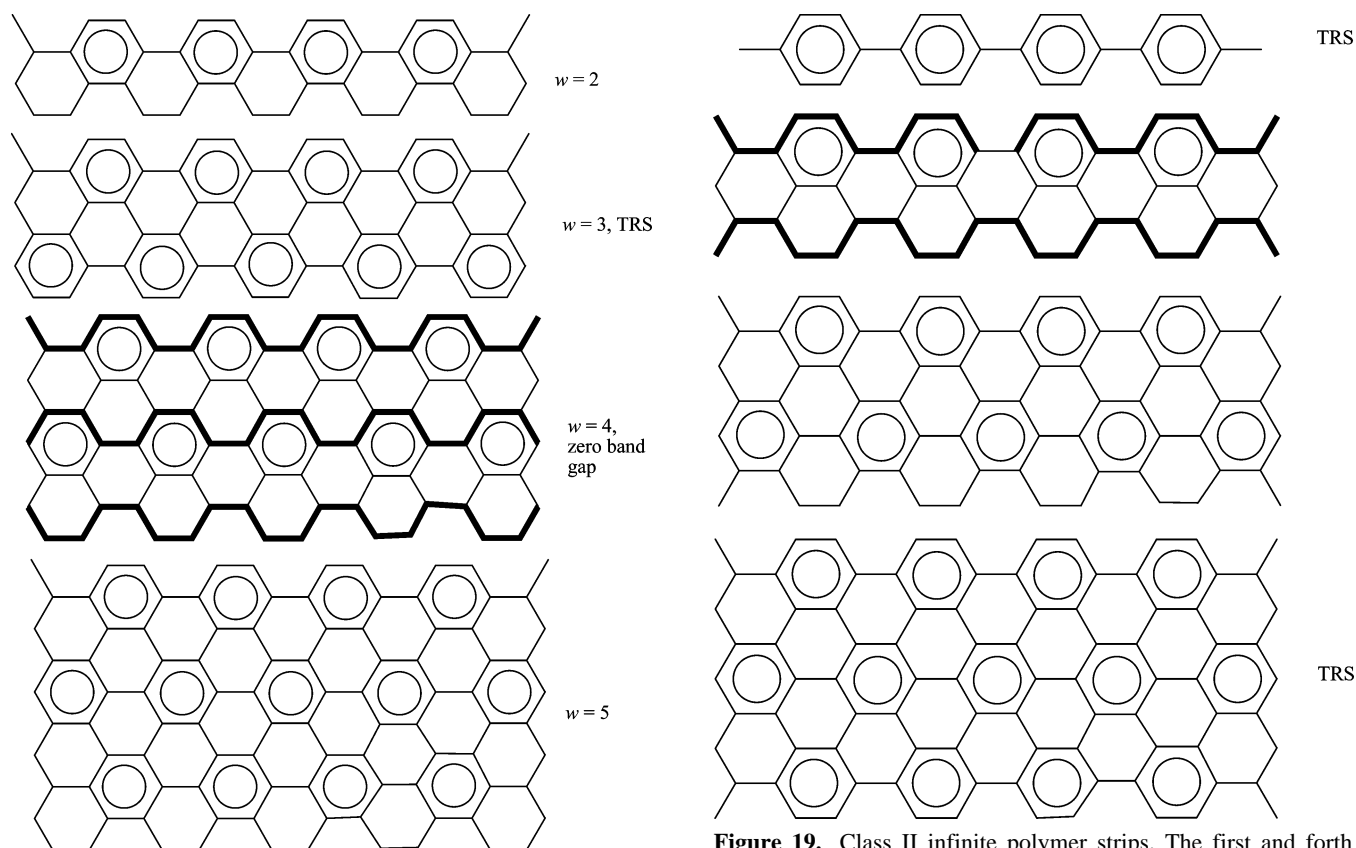
correlation is that the infinite polymer strip belonging to the lower TRS series of Figure 16 is identical to that belonging to the upper series in Figure 13 (or Figure 12). This is a result of the fact that the density of states of infinite polymer strips is independent of the end groups. We now see that the infinite strip associated with the upper series in Figures 12 and 13 is a TRS polymer strip. Recall that the infinite strip corresponding to both series in Figures 12 and 13 has a width  $w = 3$ . While the infinite strip belonging to the lower series in Figure 16 likewise has a width  $w = 3$  (Class I), the infinite polymer strip corresponding to the upper series cannot be characterized as having a width (Class II).

Leapfrogging the pair of series in Figure 14 (or Figure 15) gives the pair of TRS benzenoid series in Figure 17. The first two TRS benzenoids in both series have been synthesized by the Clar and Müllen research groups, respectively.<sup>1,51,61–62</sup> The number of strain-free TRS benzenoid isomers/total number of benzenoid isomers are given below the respective formulas in Figure 17. The infinite strip belonging to the two series in Figures 14 and 15 has a width  $w = 4$ . But the TRS infinite strips in Figure 17 have infinite polymer strips that cannot be characterized as having a width (Class II). In this case, the infinite TRS polymer strips belonging to the upper series in Figures 14 and 15 and the lower series in Figure 17 are not identical, as this correlation only holds for polymer strips of the type in Figures 12 and 13 having a width  $w = 3m + 3$ , where  $m = 0, 1, 2, 3, \dots$ . The TRS benzenoids in the upper series of Figure 16 and both of those in Figure 17 belong to Class II systems.

To explain this further, consider the infinite polymer strips in Figures 18 and 19. The infinite polymer strips in Figure 18 belong to Class I and those in Figure 19 to Class II. Class I systems can be characterized by a given width, whereas those belonging to Class II cannot.<sup>54</sup> The first member belonging to Class I is polyacetylene (not shown in Figure 18) and the first member belonging to Class II is polyphenylene (first structure in Figure 19). Polyacetylene ( $w = 1$ ) has a zero band gap and can be embedded on the fourth member of Class I, as shown in bold in Figure 18 (third structure,  $w = 4$ ) per Hall's rules.<sup>63</sup> Thus, every third member



**Figure 17.** Two isomeric TRS benzenoid series and their increasing isomer numbers with size. These TRS benzenoids are corresponding leapfrogs to those in Figures 14 and 15.



**Figure 18.** Class I infinite polymer strips that can be characterized by width ( $w$ ). The first member, polyacetylene ( $w = 1$ ), is not shown and has a zero band gap. Every third member ( $w = 3m + 1$ ;  $m = 0, 1, 2, \dots$ ) can be embedded by polyacetylene as illustrated in bold for  $w = 4$  and, therefore, have zero band gaps. The third member of Class I (second structure from top) is a total resonant sextet (TRS) system and has a distinct band gap. Every third member thereafter ( $w = 3m + 3$ ) is also a TRS system with a distinct band gap. Sextet rings are indicated by inscribed circles.

( $w = 3m + 1$ ;  $m = 0, 1, 2, 3, \dots$ ) of Class I has a zero band gap. Every third member of Class I is a TRS system ( $w = 3m + 3$ ) with a distinct band gap.

Polyphenylene (first member) and the fourth structure shown in Figure 19 are TRS systems with HMO nonzero band gaps. In general, every third member ( $3m + 1$ ;  $m = 0, 1, 2, 3, \dots$ ) of Class II is a TRS polymer system with nonzero band gaps. Polyacetylene can be embedded on the polyteropyrene (second structure, Figure 19), meaning that polymer

**Figure 19.** Class II infinite polymer strips. The first and fourth structures and every third structure thereafter ( $3m + 1$ ;  $m = 0, 1, 2, \dots$ ) are TRS polymers with distinct band gaps. The second structure from the top and every third structure thereafter ( $3m + 2$ ) can be embedded by polyacetylene (shown in bold) and, therefore, have zero band gaps.

system has a HMO zero band gap. In general, every third polymer member ( $3m + 2$ ) thereafter also has a zero band gap. We have arrived at the same results as those of Klein but in a different way.<sup>54</sup>

## CONCLUSION

Starting with pyrene, the only  $C_{16}H_{10}$  benzenoid, oriented differently and using a  $C_6H_2$  aufbau, we generate two series of benzenoid hydrocarbons (Figures 12 and 13). These series pass through the most and least stable strictly pericondensed  $C_{28}H_{14}$  benzenoids and, at the infinite limit, evolve to the most and least stable benzenoid polymer strips of width  $w$

= 3. While the number of other benzenoid isomers progressively increases at each aufbau step, the members of these two series bracket the other isomers in relative stability. Leapfrogging the members of the least stable (lower) series generates a TRS series ( $w = 3$ ) having the same infinite limit member (TRS benzenoid polymer strip) as the more stable (upper) series.

Because the C<sub>28</sub>H<sub>14</sub> and C<sub>30</sub>H<sub>14</sub> isomers are at the onset of high molecular-weight benzenoid hydrocarbons, they play a pivotal role in numerous environmental and theoretical studies. Thus, a full understanding of their properties is essential for extrapolations to higher congeners and the advancement of the relevant science of combustion formation processes and related environmental pollution and material sciences. While supplementing some of the prior numerical results, we uniquely integrate and show the hidden relationship that exists among widely different studies involving the environmental analysis and molecular modeling of potential materials.

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