PAPER

NJC
www.rsc.org/njc

Partitioning of π-electrons in rings of polycyclic conjugated hydrocarbons.

Part 3.† Perifusenes

Alexandru T. Balaban*[a] and Milan Randić‡[b]

[a] *Texas A&M University at Galveston, Department of Marine Sciences, Galveston, TX 77551, USA. E-mail: balabana@tamug.edu; Fax: +1-409-740-4787; Tel: 1-409-741-4313*
[b] *National Institute of Chemistry, Ljubljana, Slovenia*

Received (in Montpellier. France) 7th January 2004, Accepted 24th February 2004
First published as an Advance Article on the web 9th June 2004

For all Kekuléan perifusenes with 4, 5, and 6 benzenoid rings the partitions of π-electrons in each ring have been calculated. Trends in the partitions are discussed in connection with Clar's structures. Partition values are useful for discerning similarity/dissimilarity among benzenoids independently of visual overlapping of formulas and for comparing local features of benzenoids such as bay or cove regions.

Introduction

On inscribing in the center of each benzenoid ring a vertex and on linking vertices corresponding to rings that share an edge, that is rings that are condensed, one obtains the dualist (or inner dual) graph. Unlike normal graphs where bond lengths and angles do not matter, they do matter in dualist graphs.[1,2] Benzenoid polycyclic aromatic hydrocarbons are classified into three structural classes according to the way condensed rings are linked among themselves: (i) catafusenes (catacondensed) in which no carbon atom is common to more than two rings, or when the dualist graph is acyclic; (ii) perifusenes (peri-condensed) when there are carbon atoms common to three rings, or the dualist graph contains three-membered rings; and (iii) coronafusenes (corona-condensed or coronoids) when the dualist graph has larger rings.

The total number K of Kekulé structures can be obtained from the adjacency matrix (also called the Hückel matrix) of the benzenoid, by finding its characteristic polynomial, since the absolute value of the free term of this polynomial is K^2.

The first paper in the present series examined catacondensed benzenoids,[3] the second part dealt with coronoids,[4] and in the present paper we report results for the partition of π-electrons in perifusenes. As indicated in previous papers,[3,4,5] whenever a double bond in a Kekulé structure is shared by two rings, each ring is ascribed one π-electron. By averaging the π-electron count for all Kekulé structures in each ring of the benzenoid, one obtains the partition of π-electrons.

As in previous parts of this series,[3,4] the number of Kekulé structures will be denoted by K and the number of benzenoid rings by R. Starting with triangulene there are many perifusenes that are free radicals with $K = 0$. Only structures of Kekuléan perifusenes (*i.e.*, compounds that have at least one Kekulé structure: $K \geq 1$) will be discussed in the present paper.

Methodology

The Kekulé structures for most of the smaller perifusenes can easily be drawn by hand. For larger perifusenes, the number K of Kekulé structures can be found by simple Hückel Molecular Orbital (HMO) calculations from the characteristic polynomial whose free term is K^2. Also, Pauling bond orders may be easily calculated.[6]

Results and discussion

Partitioning of π-electrons

Pyrene, **1** with $R = 4$, is the smallest perifusene with nonzero K. There are three perifusenes with $R = 5$ and nonzero K (**2**–**4**), one of which is perylene, **2**. In perylene and all its derivatives with extra benzenoid rings attached to the two naphthalene moieties, the bond orders of the two bonds between these moieties are 1.00. There are 15 perifusenes with $R = 6$ and nonzero K (**5**–**19**). Two of these, namely **12** and **13**, are isoarithmic (have the same K and the same partition of π-electrons because they differ only in the direction of the kink of their dualist graph).[7]

In Fig. 1 we present all these perifusenes, denoting by capital letters A–F the benzenoid rings that differ in their symmetry and therefore may have different partitions of π-electrons. Also included is a perifusene (**20**) with $R = 7$.

Table 1 displays the partitioning of π-electrons in perifusenes **1**–**20**. The values for each type of benzenoid ring were calculated from Pauling bond orders, as indicated in previous parts of this series.[1,4]

Trends in the partition of π-electrons

In all cases, the sum of the values for all rings in perifusenes equals the number of π-electrons indicated in Table 1. It may be seen, in agreement with observations made in earlier parts of this series, that the highest values in Table 1 correspond to marginal rings (the first ring, denoted by A, and the last ring). The smallest values are found to correspond to central rings, especially in perylene derivatives (**2**, **7**, **14**) and in systems related to triphenylene (**10**, **15**, **16**, **18**, **20**). The reason for the first observation is obvious, with the lowest possible bond order for the two central bonds in perylene, as mentioned earlier; when discussing triphenylene in Part 1 of the present series,[4] it was shown that its central ring had a very low value for the partition of π-electrons, in agreement with the Clar structure for this catafusene. Also, as shown earlier in both parts of this series,[1,4] when two or more linearly condensed rings appear in the internal region of a benzenoid they have the same values for their partition of π-electrons (this is the case of rings B and C in compound **20**).

† For Part 2 see ref. 4.
‡ Permanent address: 3225 Kingman Rd., Ames, IA 50014 USA. Fax: +1 (515) 292-8629.

DOI: 10.1039/b400253a

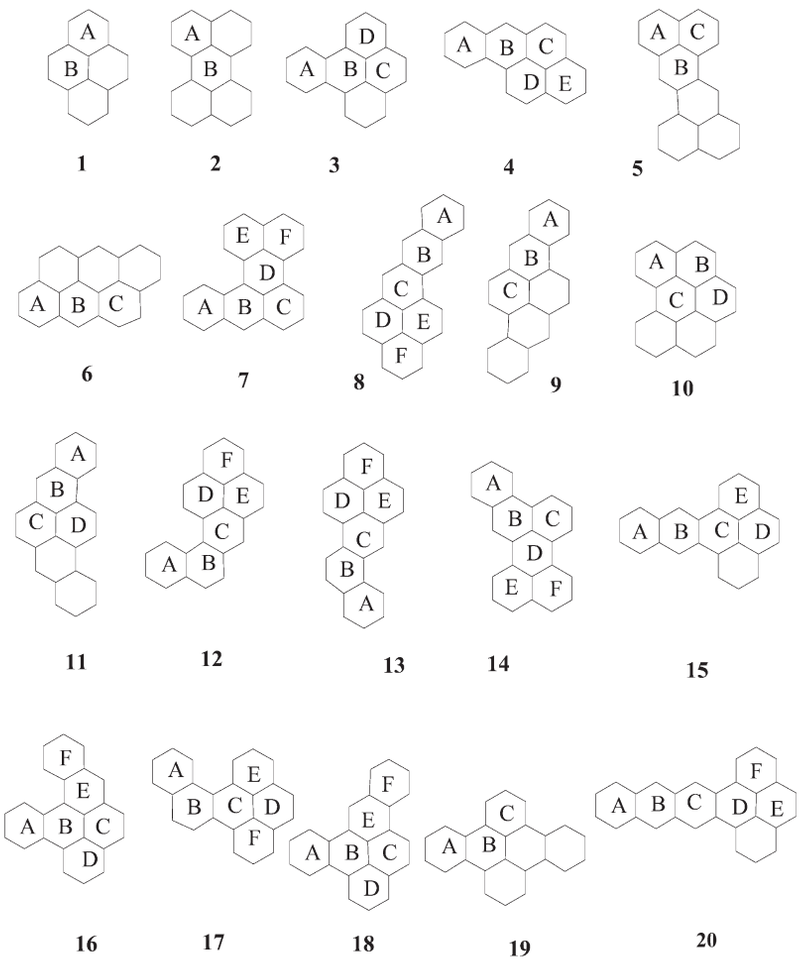

Fig. 1 Structures of perifusenes **1**–**20** discussed in the text. Only one letter was used for symmetry-equivalent rings

A closer look at π-electron partitions in rings of perifusenes

After a closer look at the relative magnitudes of the π-electron ring partitions [for which we will use the symbol $R(\pi)$] in Table 1, a number of interesting observations can be made.

Table 1 Partitioning of π-electrons in rings A–F of perifusenes **1**–**20**

Compound	R	K	No. of π-electrons	Ring A	B	C	D	E	F
1	4	6	16	4.67	3.33				
2	5	9	20	4.67	1.33				
3	5	11	20	5.36	1.82	3.36	4.73		
4	5	9	20	5.00	3.67	3.11	3.56	4.67	
5	6	9	24	4.67	2.67	4.67			
6	6	10	22	4.60	3.30	3.10			
7	6	12	24	4.75	4.00	4.50	1.42	4.67	4.67
8	6	12	24	4.75	4.50	3.42	3.00	3.67	4.67
9	6	13	24	4.92	3.77	3.31			
10	6	14	22	4.79	3.36	1.64	4.07		
11	6	14	24	5.14	3.50	2.79	3.93		
12	6	15	24	5.20	3.60	3.87	3.47	3.20	4.67
13	6	15	24	5.20	3.60	3.87	3.47	3.20	4.67
14	6	15	24	5.20	3.40	4.80	1.27	4.67	4.67
15	6	16	24	4.94	4.63	1.56	3.38	4.75	
16	6	16	24	5.31	2.06	3.13	4.75	3.81	4.94
17	6	17	24	5.06	4.12	2.06	3.35	4.71	4.71
18	6	17	24	5.41	1.59	3.59	4.71	3.65	5.06
19	6	20	24	5.35	1.85	4.80			
20	7	21	28	4.71	4.48	4.48	1.43	3.38	4.76

The first is the identical ring partition for the peripheral rings in pyrene (**1**) and perylene (**2**). This result had not been expected as there is no apparent reason for this coincidence. However, a look at the Pauling bond orders (shown in Table 2) for both pyrene and perylene (for bond labels see the top part of Fig. 2) shows that the corresponding sums for the peripheral rings are identical: 14/6 and 21/9, respectively, which when multiplied by 2 (there being two π-electrons in each CC double bond), gives 14/3 or 4.6667. The same partition is also observed in the benzenoid rings specified in the following parentheses, annulated at ring A of pyrene (ring E in **4**; F in **12**/**13**) or perylene (rings AC in **5** and EF in **7** and **14**).

In Table 2 we also show the Pauling bond orders for peropyrene **21** and terrylene **22**. In the case of terrylene, because the three naphthalene moieties are connected with essentially single bonds all three naphthalene units have the same bond orders. Again we see the same regularity, which is that the terminal rings of peropyrene and all "naphthalene moieties" of terrylene have the same ring partition of 14/3. This time, by summing the Pauling bond orders in the peripheral rings (and taking only half of the bond order for the CC bond that belongs to two rings) we obtain 42/18 and 63/27, which when multiplied by two give for the π-electron ring partitions a value of 4.6667.

That for terrylene one finds $R(\pi) = 1.3333$ in the "connecting" rings, that is the same value as in perylene, is not surprising and follows from the nature of the essentially single CC bonds. It is more interesting to find that the two central rings of pyrene have the same ring partition, $R(\pi) = 3.3333$, as in the four corresponding rings of peropyrene. Moreover, we see from Fig. 2 that the single central ring of peropyrene also has the same $R(\pi)$. These observations suggest that the same

Table 2 Bond orders for pyrene (**1**), peropyrene (**21**), perylene (**2**) and terrylene (**22**)

	Bond								
Compound	a	b	c	d	e	f	g	h	i
1	3/6	3/6	2/6	2/6					
21	9/18	9/18	6/18	6/18	3/18	15/18	3/18	6/18	9/18
2	3/9	6/9	3/9	6/9	3/9	3/9	0		
22	3/9	6/9	3/9	6/9	3/9	3/9	0		

may hold also for higher analogs of peropyrene, shown in Fig. 3. We verified this to be true. Indeed, all rings in these "extended" peropyrenes, except for the terminal rings, have an identical π-electron partition. This results in a uniform partition of π-electrons to all interior rings, which makes these structures potential models of one-dimensional graphite.[8]

The occurrence of $R(\pi) = 2.67$ in zethrene (**5**) can be traced to the same presence of essentially single bonds. The CC bonds in zethrene connecting the two terminal naphthalene moieties, being either single CC bonds or double CC bonds in all Kekulé valence structures, necessarily give for the Pauling bond order zero and one, respectively. In this respect, compounds **7** and **14** are also interesting, both having essentially CC bonds of zero bond order, a fact that may result in $R(\pi)$ values that will also occur in other pyrene derivatives. Thus, the occurrence of $R(\pi) = 4.80$ in **14** and **19** suggests, in analogy with pyrene and peropyrene, that benzenoids **23** and **24**, shown in Fig. 4, would have same $R(\pi)$ values as dibenzopyrene (**19**), except for the central ring (which does not appear in **19**). That indeed this is the case can be verified using the Pauling bond orders listed in Table 2. The identity for ring A with $R(\pi) = 4.75$ in **7** and **8**, or $R(\pi) = 5.20$ in **12**/**13** and **14** is also due to the same Pauling bond orders in benzenoids having the same K values and number of π-electrons. Also, $R(\pi) = 5.06$ both for ring A in **17** and ring F in **18**; $R(\pi) = 4.71$ for rings EF in **17** and ring D in **18** for the same reasons.

Similarity of benzenoids having $n = 24$ π-electrons

We will now consider the use of the ring partition of π-electrons to discern the most similar and the least similar benzenoids. We will confine the comparison only to benzenoids having the same number of π-electrons and have selected benzenoids in Table 1

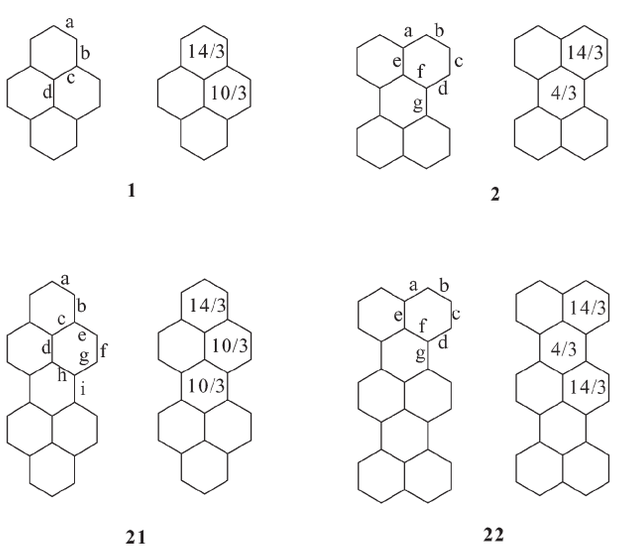

Fig. 2 Pyrene (**1**), perylene (**2**) and the similar perifusenes, peropyrene (**21**) and terrylene (**22**), with their bond types and partitions of π-electrons.

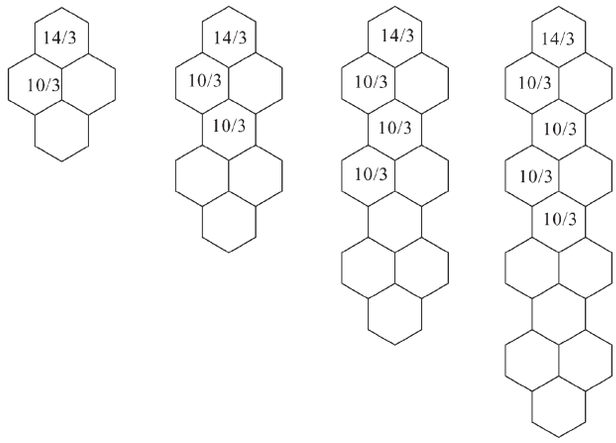

Fig. 3 Partitions of π-electrons in pyrene and its "homologs".

having $n = 24$ π-electrons, there being thirteen such compounds. The two structures **12** and **13** are iso-Kekuléan (isoarithmic) compounds, having a 1:1 correspondence in Pauling bond orders between their Kekulé valence structures.

The first problem we face is of a mathematical nature. The $R(\pi)$ values of Table 1 constitute a set of descriptors for each benzenoid, yet we need a vector representation of benzenoids, not a set theoretical one. In other words, if we are to compare benzenoids, then we have a problem of "alignment," that is, which ring in one benzenoid corresponds to which ring in another. While for some benzenoids such an alignment is simple, if not trivial, for others it is an almost impossible or arbitrary problem. For example, it is not difficult to align rings in **15** and **17**, or **16** and **18**, but it is almost impossible to do the same for **7** and **19**, for instance. In view of this difficulty we decided to order all $R(\pi)$ values relative to their magnitude, regardless from which ring they come from. In this way we obtain an ordered set (that is, a sequence, or a vector) even though in some cases such an ordering may not parallel the natural alignment of rings, for which such an alignment seems obvious. For example, such an ordering does not match ring D in **16** with ring D in **18**. Nevertheless, we felt that by this procedure the benefits outweigh by far any disadvantages that would occur due to doubtful alignment of rings where such is not at all clear. We show in Table 3 the corresponding vectors for twelve compounds, which will form the basis for evaluation of similarities among the compounds considered.

In Table 4 we show the 12×12 similarity/dissimilarity matrix obtained by viewing the components of Table 3 as coordinates in a 6-dimensional vector space and the similarity given by the Euclidean distance between the end points of vectors. Using this approach we find as the most similar the pair (**14**, **15**) and the least similar the pair (**12**/**13**, **19**), with minimum/maximum values, respectively. In Fig. 5 we illustrate a

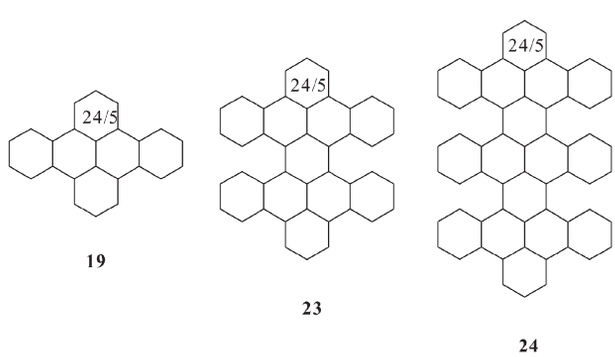

Fig. 4 A series of perifusenes combining pyrene and perylene scaffolds.

Table 3 $R(\pi)$ ordered by decreasing value for benzenoids having six rings and $n = 24$ π-electrons

Compound	$R(\pi)$					
5	4.67	4.67	4.67	4.67	2.67	2.67
7	4.75	4.67	4.67	4.50	4.00	1.42
8	4.75	4.67	4.50	3.67	3.42	3.00
9	4.92	4.92	3.77	3.77	3.31	3.31
11	5.14	5.14	3.93	3.50	3.50	2.79
12,**13**	5.20	4.67	3.87	3.60	3.47	3.20
14	5.20	4.80	4.67	4.67	3.40	1.27
15	4.94	4.75	4.75	4.63	3.38	1.56
16	5.31	4.94	4.75	3.81	3.13	2.06
17	5.06	4.71	4.71	4.12	3.35	2.06
18	5.41	5.06	4.71	3.65	3.59	1.59
19	5.35	5.35	4.80	4.80	1.85	1.85

few of the most similar perifusenes in order to help one visualize the apparent similarities among the compounds shown. That the most similar pair turns out to be the pair (**14**, **15**) may be an artifact due to the afore-mentioned coincidence in $R(\pi)$ values among pyrene and perylene. The remaining three cases shown in Fig. 5 (where we used **13** to represent the pair of iso-Kekuléan (isoarithmic) structures **12**/**13**) appear to agree with expectations, giving some credibility to the approach. The transitivity of similarity is revealed by the fact that the similarity values are 0.4664 for **9** *vs.* **12**/**13** (2nd place in Table 4), 0.6380 for **11** *vs.* **12**/**13** (4th place) and 0.7083 for **9** *vs.* **11** (7th place).

Fig. 6, which shows the least similar cases, also gives plausible results, perhaps those that might have been expected in view that it opposes some of the longest benzenoids to some of the widest.

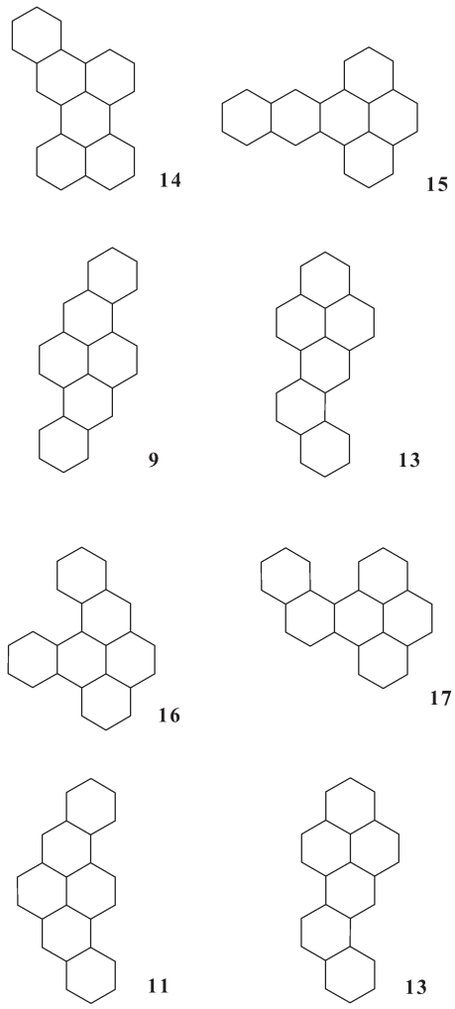

Fig. 5 A few pairs of the most similar perifusenes

Similarity of local molecular features in perifusenes

Let us return to the dilemma of "alignment" of rings and the difficulties involved. By illustrating the similarity/dissimilarity among the 12 benzenoids of Table 3 we are not necessarily advocating use of $R(\pi)$ for similarity/dissimilarity studies, precisely because of the difficulties in mismatching of rings that appear to have similar structural environments. However, we strongly believe that use of $R(\pi)$ may be of considerable value for similarity/dissimilarity studies of *local molecular features* when alignment of rings is straightforward. Thus, for example, this will allow one to characterize different "bay" regions, different "cove" regions and different "fjords," which refer to parts of the peripheries of benzenoids consisting of three, four, or five consecutive CC bonds forming peripheral concave regions. In Table 5 we illustrate similarity measures for bay regions by listing in order the π-electron partitions of the three rings bordering the bay region; when there are several such regions in the same benzenoid, then the three rings are indicated. It should be emphasized that structures **12** and **13**, although isoarithmic and therefore identical in similarity/dissimilarity as measured in Table 4 by *unordered* π-electron partitions, differ in their bay or cove regions and will also require different similarity/dissimilarity measures for their *ordered* π-electron partitions.

A more detailed discussion of this similarity would be too long and will form the object of a separate paper, with implications for the carcinogenicity of benzenoids with bay regions. Briefly, the necessary but insufficient condition for carcinogenicity of a polycyclic benzenoid is to have a bay region with a ring possessing four contiguous CH groups that may be enzymatically oxidized to an epoxy diol, which is the ultimate carcinogen. Its oxiranic three-membered ring-opening affords a carbocationic site stabilized by electronic delocalization around the bay region, leading to electrophilic attack on both strands of DNA.[9] The bay regions that fulfill the above condition of being "carcinogenic suspects" are italicized in Table 5.

Table 4 Similarity/dissimilarity displayed as a fragmented 12×12 matrix (low/high coefficients, respectively)

Compound	**5**	**7**	**8**	**9**	**11**	**12**,**13**
5	0	1.8349	1.3064	1.6013	1.7497	1.7282
7		0	1.7523	2.3415	2.0118	2.2587
8			0	0.8617	0.8816	0.8042
9				0	0.7083	0.4664
11					0	0.6380
12, **13**						0
	14	**15**	**16**	**17**	**18**	**19**
5	1.6705	1.3504	1.3462	1.1368	2.0185	1.5177
7	0.7942	0.6854	1.4267	1.0372	1.2283	2.3951
8	2.0595	1.7612	1.1985	1.1103	1.6276	2.4447
9	2.4254	2.1900	1.6460	1.6229	2.0480	2.5990
11	2.0871	1.9154	1.2277	1.3189	1.4691	2.0779
12, **13**	2.3519	2.1464	1.5227	1.5600	1.8737	2.6901
14	0	0.4032	1.2144	0.9871	1.1367	1.7600
15		0	1.0761	0.7270	1.1507	1.1276
16			0	0.5114	0.6958	1.3619
17				0	0.8628	1.8051
18					0	2.1245
19						0

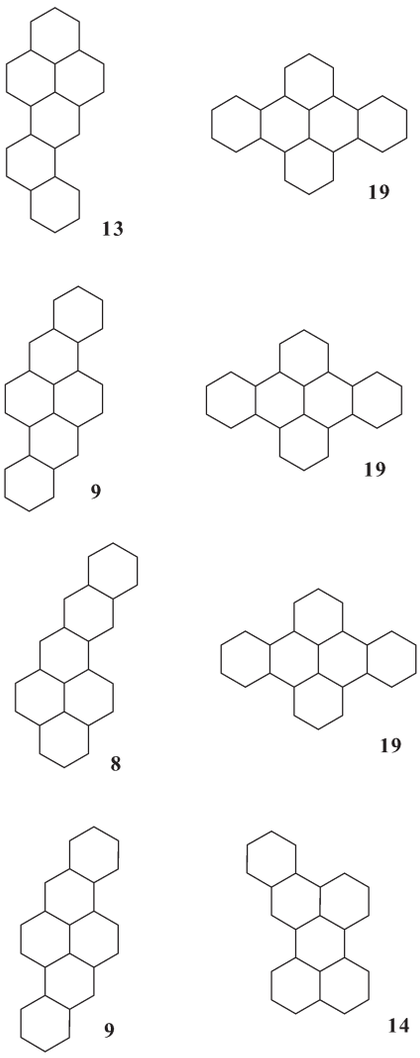

Fig. 6 A few pairs of the most dissimilar perifusenes

Next, consider, for example, the four benzenoid rings forming the "cove" regions in compounds **7**, **12**, **16** and **17** (Fig. 7). Just by viewing molecular diagrams one would expect this region to be the most similar between the last three structures.

Table 5 Similarity among the "bay" regions in benzenoids from Fig. 1, bordered by ordered triplets of rings X,Y, and Z

Ring in pyrene type				Ring in perylene type			
Compound	X	Y	Z	Compound	X	Y	Z
3	*5.36*	*1.82*	*4.73*	**2**	4.67	1.33	4.67
4	*5.00*	*3.67*	*3.56*	**5**	4.67	2.67	2.67
8	4.50	3.42	3.00	**7**	4.67	1.42	4.50
9	*4.92*	*3.77*	*3.31*	**14**EDB	4.67	1.27	3.40
10	4.79	1.64	4.79	**14**CDF	4.80	1.27	4.67
11	*5.14*	*3.50*	*2.79*	**14***ABC*	*5.20*	*3.40*	*4.80*
13*ABC*	*5.20*	*3.60*	*3.87*				
13BCD	3.60	3.87	3.47				
15	4.75	1.56	4.63				
16	*5.31*	*2.06*	*4.75*				
17	4.71	2.06	4.12				
18*ABD*	*5.41*	*1.59*	*4.71*				
18ABE	5.41	1.59	3.65				
18*CEF*	*3.59*	*3.65*	*5.06*				
19	*5.35*	*1.85*	*4.80*				
20	4.76	1.43	4.48				

Table 6 Similarity among the four "fjord" regions in compounds **7**, **12**, **16**, and **17** displayed by a 4×4 matrix

Compound	**7**	**12**	**16**	**17**
7	0	2.7937	0.9484	0.7223
12		0	2.6007	2.2591
16			0	0.6827
17				0

In Fig. 7 we have depicted these four benzenoids with "cove" regions, inserting in each benzenoid ring the corresponding $R(\pi)$ value. In Table 6 we show the "regional" local similarity/dissimilarity for the four cases. As expected, the most similar are indeed the "cove" regions in **16** and **17**.

Miscellaneous pericondensed benzenoids

In Table 7 we have collected the π-electron ring partitions for several pericondensed benzenoids illustrated in Fig. 8. There are similarities and dissimilarities between various rings and various molecules. If we refer to rings with $R(\pi) > 5$ as "π-electron rich" and those with $R(\pi) < 2$ as "π-electron poor", then we may say that there are not many benzenoids with rings that are π-electrons rich. Among the compounds of Fig. 8 this is only the case for Clar's fully benzenoid hydrocarbons **30**, **34** and **35**. Even the fully benzenoid "giant" benzene (one of the two isomers of symmetrical hexabenzocoronene, **33**) does not qualify, although its peripheral ring A has a rather high $R(\pi)$ value. One should recall that benzene itself has an $R(\pi)$ value of 6.0000, which is the limit that any ring can attain. On the other hand, the presence of $R(\pi) < 2$ is rather common, even though there are many benzenoids without π-electron poor rings. This is the case of **26**, **28**, and **29**. Of these three compounds, **26** seems rather special in that it shows a rather small range of $R(\pi)$ values. Except for the terminal ring D the partitions of π-electrons for the "interior" rings vary very little and thus to a degree this parallels the situation found in peropyrene and its higher homologs. A close look at various "intermediate" rings, those with $R(\pi)$ around 3.00, shows that such rings correspond to "migrating" rings in Clar's model of benzenoid hydrocarbons. Observe, for example, that such "neither poor nor rich" π-electron rings do not occur in fully benzenoid hydrocarbons, like **30** and **33**, but the occurrence of $R(\pi)$ values close to 3.00 does not necessarily imply "migrating" sextets, as is illustrated by **29** with $R(\pi) = 3.15$, which has but a single Clar structure and no migrating sextets.

The smallest value of $R(\pi)$ found among compounds **25**–**35** is that of the central ring C in the second symmetrical hexabenzocoronene (**34**). This is interesting, because this ring, occurring in only 16 out of 432 Kekulé valence structures, has a benzenoid ring Kekulé structure with three double and three single CC bonds. Many Kekulé structures of this compound show the central ring C as "empty" ring with six exocyclic CC double bonds.

In the second part of this series,[4] it was shown that the present ring partition of π-electrons was compatible with other measures of local aromaticity[10–13] but different from them. Schleyer *et al.*'s nucleus-independent chemical shift (NICS) values,[14] computed at various distances from the molecular plane, provide rich information on ring currents. The benzenoid character discussed in ref. 15 (the fraction of resonance structures in which a ring has three double bonds) does not discriminate among the central and marginal rings in anthracene, but the "Clar index", introduced in the same publication, does. It appears, therefore, that the presently discussed ring partition of π-electrons is most similar to the Clar index, because they are derived from considering all resonance structures viewed both from an algebraic and a graph theoretical viewpoint.

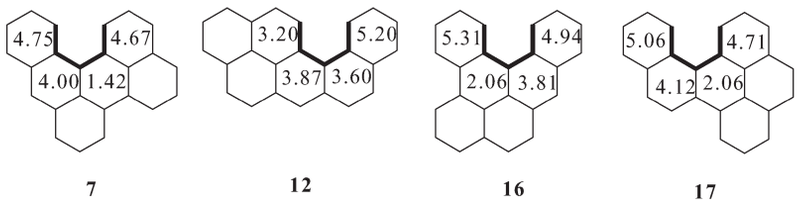

Fig. 7 Partitions of π-electrons in rings surrounding cove regions in all possible isomers of Kekuléan perifusenes with six benzenoid rings.

Conclusions

The 140 years of Kekulé valence structures have unexpectedly provided one more "surprise"—the $R(\pi)$ ring indices that signify the partition of π-electrons to individual benzene rings as governed by individual Kekulé valence structures when two π-electrons are assigned to CC double bonds within each ring if not shared by other rings, and one π-electron if shared. Not so long ago the "innate degree of freedom" of Kekulé valence structures was discovered[16] and before that the "conjugated circuits"[17] within each of the Kekulé valence structures have been recognized as important structural constituents. All this came from looking at Kekulé structures as mathematical objects of combinatorial and topological content—a view that has advanced with the growth and development of applications of graph theory to chemistry. It turns out that conjugated circuits not only discriminate among aromatic and antiaromatic compounds in a more general way than the Hückel $4n+2$ rule but also lead to expressions for the molecular resonance energy. On the other hand, the "innate degree of freedom," or simply the "degree of freedom" first appeared to be at best a curiosity, but very recently—ten years after being "discovered"—was found to lead to the solution of the "Inverse Clar Problem." As known, it is straightforward for any Clar structure to determine the set of Kekulé valence structures, which when superimposed, produce the Clar structure. The inverse, namely to find in advance which subset of Kekulé structures will produce Clar structures, was unsolved—until it was realized that a Clar structure is given by a superposition of all Kekulé valence structures of the maximal degree of freedom.[5,16]

Where else—besides in identifying local similarity in polycyclic conjugated hydrocarbons—can $R(\pi)$ be of use? It is perhaps too early to speculate, but if it remains in use only for

Table 7 Ring partitions of π-electrons in miscellaneous benzenoids

Compound	Ring A	B	C	D	E	*K*
25	3.70	1.50				20
26	3.00	3.13	3.33	4.53		15
27	3.42	4.71	4.03	1.84		31
28	4.68	3.34	2.29			35
29	4.60	3.15	2.95	2.30		20
30	5.30	2.13	4.01	1.67		104
31	3.40	3.40	3.90	1.90		50
32	3.69	3.75	1.74	2.38		136
33	4.80	1.80	2.40			250
34	5.17	2.59	1.22			432
35	5.33	1.93	3.57	4.12	1.78	520

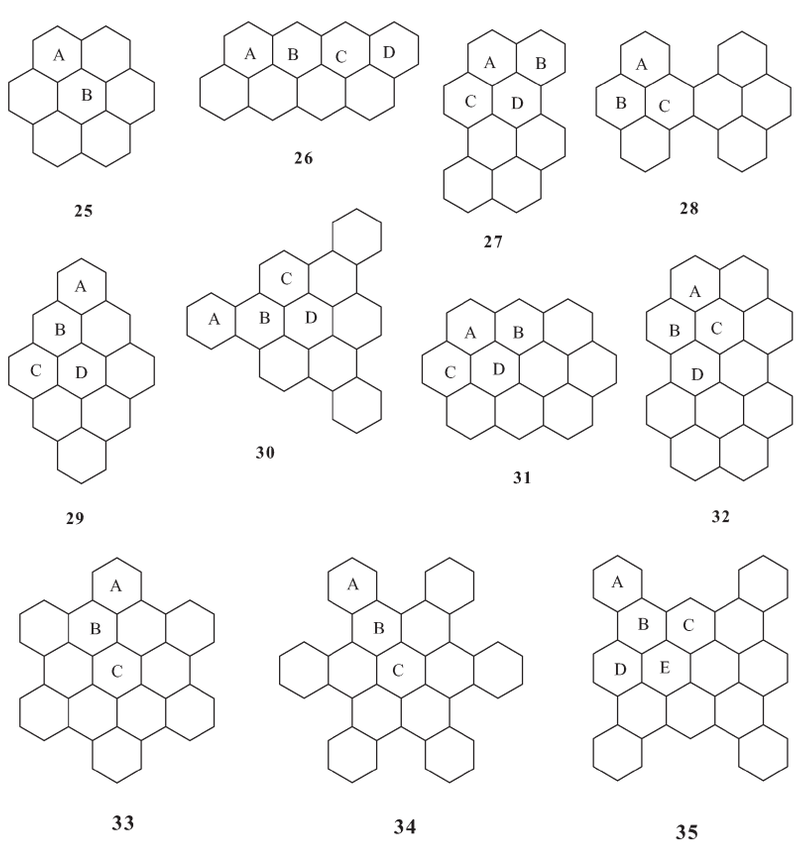

Fig. 8 Miscellaneous perifusenes **25**–**35** discussed in the text. Only one letter was used for symmetry-equivalent rings.

quantifying the degree of similarity of local regions in benzenoids it would already justify its "existence."

In a forthcoming paper, a comparison will be made between partitions of π-electrons and other measures of local aromaticities in polycyclic benzenoids and nonalternant conjugated hydrocarbons with cata-/peri-/corona-condensation.

References

1 A. T. Balaban and F. Harary, *Tetrahedron*, 1968, **24**, 2505.
2 A. T. Balaban, *Tetrahedron*, 1969, **25**, 2949.
3 Part 1, M. Randić and A. T. Balaban, *Polycyclic Aromat. Compd.*, in press.
4 Part 2, A. T. Balaban and M. Randić, *J. Chem. Inf. Comput. Sci.*, 2004, **44**, 50.
5 M. Randić, *Chem. Rev.*, 2003, **103**, 3449.
6 I. Gutman and S. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989, p. 38–39.
7 A. T. Balaban and I. Tomescu, *MATCH Commun. Math. Comput. Chem*, 1983, **14**, 155.
8 Part 4, D. Vukicević, M. Randić, and A. T. Balaban, *J. Math. Chem.*, in press.
9 R. G. Harvey, *Polycyclic Hydrocarbons and Carcinogenesis*, ACS Symposium. Monograph 283, ACS, Washington, DC, 1985; R. G. Harvey, *Polycyclic Aromatic Hydrocarbons and Carcinogenicity*, Cambridge University Press, Cambridge, UK, 1991; R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, New York, 1997.
10 O. Polansky and G. Derflinger, *Int. J. Quantum Chem.*, 1967, **1**, 379.
11 M. Randić, *Tetrahedron*, 1974, **30**, 2067.
12 T. M. Krygowski and M. Cyranski, *Tetrahedron*, 1996, **52**, 1713.
13 J. Aihara, *Chem. Phys. Lett.*, 2002, **365**, 34.
14 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. V. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.
15 M. Randić, D. Plavšić and N. Trinajstić, *Gazz. Chim. Ital.*, 1988, **118**, 441.
16 D. J. Klein and M. Randić, *J. Comput. Chem.*, 1987, **8**, 516.
17 M. Randić, *Chem. Phys. Lett.*, 1976, **38**, 68; M. Randić, *J. Am. Chem. Soc.*, 1977, **99**, 444; M. Randić, *Tetrahedron*, 1977, **33**, 1905.