

Correlations between Topological Ring-Currents, π -Electron Partitions, and Six-Centre Delocalisation Indices in Benzenoid Hydrocarbons

Alexandru T. Balaban^a and Roger B. Mallion^{b,*}

^aTexas A&M University at Galveston, 5007 Avenue U, Galveston, Texas 77551, United States of America

^bSchool of Physical Sciences, University of Kent, Canterbury CT2 7NH, England, United Kingdom

RECEIVED JANUARY 17, 2011; REVISED JUNE 25, 2011; ACCEPTED JULY 14, 2011

Abstract. Comparison is made between three different indices that characterise the individual rings of a wide range of condensed benzenoid hydrocarbons. Two of these (" π -electron partitions" and the six-centre delocalisation-indices that have been called " Δ_6 -values") have been introduced only recently as potential indicators of what might be called "local aromaticity", whilst the third ("topological π -electron ring-currents") was suggested as a possible discriminator in this regard nearly fifty years ago. Whilst linear correlations between ring currents and π -electron partitions within certain restricted classes of ring types are good (with correlation coefficients of up to 0.998), agreement between the two indices over all classes of ring types is poor. Predictions arising from a consideration of π -electron partitions and Δ_6 -values seem, on the other hand, to be in somewhat better accord. It is therefore concluded that, despite its superficially intuitive appeal, the ring-current index is out of step both with π -electron partitions and Δ_6 -values as a general indicator of so-called "local aromaticity". (doi: [10.5562/cca1846](https://doi.org/10.5562/cca1846))

Keywords: topological ring-current, π -electron partitions, delocalisation indices, benzenoid hydrocarbons, local aromaticity

INTRODUCTION

Polycyclic condensed benzenoid hydrocarbons (henceforth frequently referred to simply as benzenoids) have been intensely studied, largely because they are amongst the most stable hydrocarbons. Of the characteristic properties associated with conjugated systems, diamagnetic susceptibilities arising from π -electron ring-currents^{1–4} have been considered as one of the main diagnostics of aromaticity^{5–7} – albeit a controversial one.^{8–11} However, because of the so-called multi-dimensional character of aromaticity,^{12–19} a quantitative measure requires the presence of several attributes, and this complicates quantitative assessments of the concept. One should note, however, that this multi-dimensional character has been discussed mostly for conjugated heterocycles,^{20–22} whilst the present paper is about benzenoid hydrocarbons. Furthermore, in addition to the *global* diamagnetic anisotropy, *local* π -electron ring-current intensities can be determined for *each ring*^{1–4,8} of a conjugated network – in our case, a benzenoid system. In addition to the long-established criteria for aromaticity of continuous conjugation –

stabilising resonance-energy, and a tendency towards bond-length equalisation in planar molecules – three-dimensional aromaticity has also been established.^{23,24} In the present paper, however, we shall consider only benzenoids that are planar – or almost planar^{25,26} – in the geometrical sense, being formed from hexagonal rings that share carbon-carbon bonds; the molecular graphs that represent these structures are also planar in the graph-theoretical sense.

For a general condensed benzenoid hydrocarbon with h benzenoid rings and n carbon atoms, of which a carbon atoms are internal ones – that is, adjacent to three other carbon atoms – the molecular formula is $C_{4h+2-a}H_{2h+4-a}$. We shall examine only two types of benzenoids: catafusenes (with no internal carbon atoms, $a = 0$), and perifusenes (with $a > 0$); moreover, we shall restrict the discussion to Kekuléan benzenoid structures²⁷ for which both n and a are even numbers and there are no odd electrons in their ground-state configurations built up by means of the *Aufbau* process.^{28–32} In most of this paper, we shall confront two indices that characterise the individual rings of such benzenoid systems – namely, π -electron partitions^{33,34} and topolog-

* Author to whom correspondence should be addressed. (E-mail: R.B.Mallion@kent.ac.uk)

ical π -electron ring-currents³⁵ – seeking possible correlations between them. Later, we shall also consider the recently defined³⁶ six-centre delocalisation-indices, Δ_6 .

π -ELECTRON PARTITIONS, TOPOLOGICAL π -ELECTRON RING-CURRENTS, AND SIX-CENTRE DELOCALISATION-INDICES

In several recent papers,^{33,34,37–43} an analysis of how π -electrons are shared amongst adjacent rings has led to material conclusions about what have been called " π -electron partitions" or " π -electron content", based on the following conventions:^{33,34}

- (i) in each resonance-structure of the benzenoid ring in question, a shared double-bond is considered to contribute one π -electron to each of the rings that share it;
- (ii) a double bond that is not shared contributes both its π -electrons to the benzenoid ring in which it is situated;
- (iii) all resonance structures are taken to have equal weights in the global partition of the n π -electrons of a given benzenoid-molecule.

It should be noted that benzene itself is the benzenoid structure having associated with it the highest-possible value (6) that a π -electron partition may assume, because the six π -electrons in benzene are not shared with any adjacent ring. We should, however, emphasise the following very important quantitative difference between the possible numerical values of π -electron partitions and the values that (topological) π -electron ring-currents may themselves take on. Topological π -electron ring-currents are, by their very definition,³⁵ expressed as a *ratio* to the ring-current intensity calculated, by the same method, for benzene. This difference in the numerical values of partitions and ring-currents is thus as follows: π -electron partitions lie between 0 and 6 (with the value 6 occurring *solely* in the case of benzene); on the other hand, ring-current intensities, expressed as a ratio to the similarly-calculated benzene-value, are pure, dimensionless numbers that can be (and frequently are)³⁵ greater than 1 – *i.e.*, are *greater than* the ring-current intensity calculated, by the same method, for benzene. From the data presented by Mandado *et al.*,³⁶ the six-centre delocalisation-index Δ_6 appears – like the π -electron partitions discussed above – to be a maximum in the case of benzene; $\Delta_6 = 0.0484$ for benzene and the index takes on values in the range 0.0037–0.0358 for the 81 symmetrically non-equivalent rings in the other 26 benzenoids studied by those authors.³⁶ Because these are small numbers, we shall find it convenient, in our tables and discussion in this paper, to deal with the Δ_6 -indices that have been arbitrarily multiplied by 100.

There is a marked parallelism between Clar's theoretical qualitative ideas,²⁷ and the quantitative π -electron partitions of benzenoids^{33,34,37,44} – as is argued in several recent articles.^{45–48} In the present paper, we now examine correlations between π -electron ring-partitions^{33,34,44} and π -electron ring-current intensities calculated by means of the simple Hückel^{49,50}–London⁵¹–Pople⁵²–McWeeny⁵³ model (hereafter denoted "HLPM"). One of us (R. B. M.) has recently published³⁵ an extensive table of such ("topological"³⁵) ring-current intensities for a large number of condensed, benzenoid hydrocarbons, each expressed as a ratio to the ring-current intensity calculated, by the same method, for benzene. *Topological ring-currents* are defined³⁵ as being π -electron ring-current intensities – initially, specifically within the class of the *condensed, benzenoid hydrocarbons* (though this restriction has recently been relaxed⁵⁴) – that:

- (a) are calculated by an application of the HLPM method, and
- (b) are such that all Hückel Coulomb-integrals are assigned the value (α) appropriate for a carbon atom in benzene, and all resonance integrals are likewise set equal to the standard value (β) for a carbon-carbon bond in benzene, and
- (c) are based on a molecular geometry that is assumed to consist of regular hexagons of benzene dimensions, and, finally,
- (d) are expressed as a *ratio* to the corresponding ring-current intensity evaluated, by the same method, for benzene.

Once a particular benzenoid hydrocarbon has been specified, such topological ring-currents are *predetermined* and do not further depend on any subjective (or other) parameters;³⁵ they are, therefore, purely graph-theoretical indices, reliant solely on knowledge of a vertex-adjacency matrix⁵⁵ for the graph representing the connectivity of the carbon atoms in the benzenoid molecule under study.^{56,57} Ring-current intensities calculated and presented in this way are what have been referred to³⁵ as *topological π -electron ring-currents*. All the ring-current intensities reported in Ref. 35, some of which are used here, are consistently of this type.

It may be observed that, in order to be in a position to calculate a topological ring-current,³⁵ it is necessary to have knowledge of a well-defined, ground-state π -electronic-configuration for the conjugated system in question, such as is obtained from an application of the *Aufbau* Principle. It has been argued^{28–32} that the *Aufbau* process may itself be simulated by means of what may be considered as an entirely topological algorithm.

In order to explore more deeply how ring types affect the local aromaticity we add to our consideration a

third criterion for local aromaticity in polycyclic benzenoids; this is based on the Mulliken approach and the quantum theory of atoms in molecules (QTAIM) and it is expressed by means of the six-centre delocalisation-indices (denoted as Δ_6^{Mull} and Δ_6^{QTAIM} , respectively) recently introduced by Mandado and coworkers.³⁶ The former values, Δ_6^{Mull} – here denoted simply as Δ_6 – were calculated by Mandado *et al.*³⁶ for a more numerous set of benzenoids than were Δ_6^{QTAIM} -values; the Δ_6^{Mull} -indices are, therefore, the ones that we adopt here. The definition of the six-centre delocalisation-indices, Δ_6 , regarded as a measure of "aromaticity" for individual rings, is presented in detail in Ref. 36.

DATA FOR π -ELECTRON PARTITIONS, TOPOLOGICAL π -ELECTRON RING-CURRENTS AND SIX-CENTRE DELOCALISATION INDICES

The numerical values of the π -electron partitions used here are taken from two previous papers by one of us (A. T. B.) and Randić.^{33,34} When there are differences between the π -electron partitions to be found in Refs. 33 and 34 and those presented in the tables that feature in the current paper, these are either (a) due to the correction of misprints in Refs. 33 and 34, and/or (b) arise because those elements of the data from Refs. 33 and 34 that were there quoted to four significant-figures have, for consistency, been rounded to just three significant-figures, here.

Data on topological π -electron ring-currents have been taken from the compilation recently published³⁵ by the second author (R. B. M.). Again, for consistency, all topological ring-currents are here expressed to three significant-figures – regardless of any greater accuracy claimed in connexion with some of the structures listed in Ref. 35 – in order to be in accord with the number of significant figures to which all the π -electron partitions are quoted in the present paper. What we are here calling the six-centre Δ_6 -indices are the corresponding Δ_6^{Mull} -values – likewise expressed to three significant-figures – taken from the paper by Mandado *et al.*³⁶

NOMENCLATURE FOR STRUCTURES AND CLASSIFICATION OF RINGS

As already mentioned, when dealing with the condensed, benzenoid hydrocarbons it is often the convention to divide them into what are called "cata" structures (such as, for example, naphthalene), which possess only peripheral carbon-atoms, and "peri" structures (such as, for example, pyrene), which contain one or more internal carbon-atoms – see, for example, Refs. 27 and 58. An equivalent and more powerful classification is based on a diagram called the "dualist" (or "characteristic

graph").⁵⁹ This is a depiction that consists of points ("vertices") and lines ("edges") in which the vertices are placed at the centres of a given structure's constituent benzenoid-rings, and the edges of the dualist diagram connect those vertices of the dualist diagram that correspond to adjacent rings (that is, rings sharing at least one bond) in the conjugated system under study. Cata-condensed benzenoids have acyclic dualist diagrams, peri-condensed benzenoids have dualist diagrams with triangles, and the dualist diagrams of corona-condensed benzenoids possess larger rings. We adopt this categorisation here. The dualist diagram ("characteristic graph"⁵⁹) is *not* actually a *graph* as such, in the normal graph-theoretical sense, for – in contradistinction to what is the case with genuine graphs – the angles between the lines representing the edges of dualist diagrams *do* matter. These angles are material to the information about the associated conjugated structure that the dualist diagram conveys. In a sense, therefore, the dualist diagram – originally (mis)named as the "characteristic graph"⁵⁹ of a conjugated system – is essentially what, in graph theory, would be called the "inner dual"⁶⁰ of the molecular graph representing the structure in question, but with the further imposition of pre-specified *angles* between the edges of the inner dual.

As is clear from Figure 1, the anthracene and phenanthrene molecular-graphs have *different* dualist diagrams (Figures 1a and 1b, respectively) but the *same* inner dual (Figure 1c). The vertex degrees of dualist diagrams (that is, the number of edges incident on each vertex of the given dualist in question) have a particular significance for ring types, as will now be indicated.

We shall find that it is also convenient to classify individual *rings* according to the local geometrical environment in which they are situated within the given condensed benzenoid hydrocarbon under consideration.

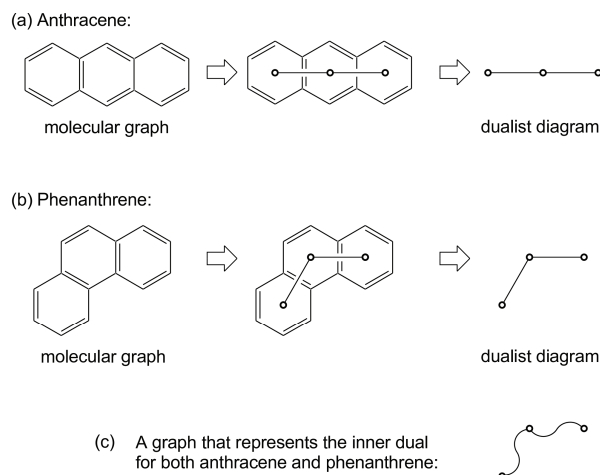


Figure 1. The Dualist Diagram for anthracene (a) and phenanthrene (b), together with the Inner Dual of both (c).

A six-membered ring in such a structure can have anything from one to six adjacent rings and, according to the mutual positions of these rings, various *ring types* can be distinguished; even once- or twice-removed rings (*i.e.*, rings that are not adjacent but are separated by one or two intervening rings) exert a certain influence. The several ring-types are denoted by letters (and, for once- or twice-removed non-adjacent rings, by primed or double-primed letters). Rings are thus categorised and labelled as *a, a', a'', b, c, d, d', d'', e, f, g, h, i, j, k, and l*. The twelve ring types in question (with *a* and *d* having two sub-types each) are defined (as the *unshaded* ring, in each case) in Figure 2. It should be noted that, of the molecules that we are dealing with here, rings of types *a, a', c, d, d'*, and *g* may occur in both cata- and peri-structures; those of types *a'', b, e, f, h, i, j, k, and l* can arise only in peri-structures; and rings of type *d''* and *g* will be found only in cata-structures. If, however, we had dealt with benzenoid hydrocarbons having more than seven rings, those rings categorised as being of types *d''* and *g* could occur in peri-structures as well as cata ones.

It is expected that a benzenoid ring will be influenced by the number and position of the rings adjacent to it; it will be seen that, for two exceptional types, *a* and *d*, the influence of rings next to immediately-adjacent ones is also felt. In order better to delineate various types, several identical sub-types are displayed in Figure 2, with the corresponding letter enclosed in square brackets.

Figure 2 shows what we are calling the twelve "types" of benzenoid rings, denoted by letters *a* to *l*, and four "sub-types", denoted by prime and double-prime symbols (sixteen, therefore, in all) that will be seen to be revealed by a comparison between topological π -electron ring-currents and π -electron partitions. The types are discriminated by the degree of the vertex in the dualist diagram⁵⁹ corresponding to a given ring (the *unshaded* ring in each part of Figure 2), whereas sub-types occur in two cases (for types *a* and *d*). Descriptions of each of these ring types are listed in Table 1, which should be studied in conjunction with Figure 2.

ISOARITHMIC STRUCTURES

By virtue of the arithmetically rather simple, virtually "pencil-and-paper", definition of π -electron partitions,^{33,34,37,38} there exist families of structures amongst the condensed benzenoid hydrocarbons which, though distinct conjugated systems, have identical π -electron-partition values for their corresponding constituent-rings.^{33,34} We call such structures "isoarithmic".^{61,62}

The topological π -electron ring-current intensity is, by contrast, a somewhat more-sophisticated index. It is dependent, in a rather subtle and intricate way,^{35,49-54,56,57} on the eigenvalues and eigenvectors of an adjacency matrix⁵⁵ of the graph representing the carbon-atom connectivity of the condensed, benzenoid hydrocarbon under study (as well as on a knowledge of the

Table 1. Classification of Ring Types. (Please study in conjunction with Figure 2)

Types	Description of vertex degree and the corresponding context in the dualist diagram
Type <i>a</i>	degree 1 acenic (linear condensation – 180° angle in the dualist diagram)
Type <i>a'</i>	degree 1 phenanthrenic, triphenylenic or pyrenic (kinked – 120° angle in the dualist diagram)
Type <i>a''</i>	degree 1 pyrenic on the symmetry axis
Type <i>b</i>	degree 2 vicinal (a vertex of a triangle in a perifusene dualist diagram)
Type <i>c</i>	degree 2 phenanthrenic
Type <i>d</i>	degree 2 anthracenic (doubly-kinked at both anthracenic end-rings)
Type <i>d'</i>	degree 2 anthracenic (singly-kinked at one of the anthracenic end-rings)
Type <i>d''</i>	degree 2 acenic (tetracenic or acenic in general)
Type <i>e</i>	degree 3 vicinal (a vertex of two condensed triangles in a perifusene dualist diagram)
Type <i>f</i>	degree 3 (by means of degree 2 and degree 1)
Type <i>g</i>	degree 3 triphenylenic (the central ring in a triphenylenic sub-diagram within the dualist diagram)
Type <i>h</i>	degree 4 vicinal (a vertex of 3 condensed triangles in a perifusene dualist diagram)
Type <i>i</i>	degree 4 non-vicinal (by means of degree 3 and degree 1)
Type <i>j</i>	degree 4 non-vicinal (by means of degree 2 and degree 2)
Type <i>k</i>	degree 5
Type <i>l</i>	degree 6

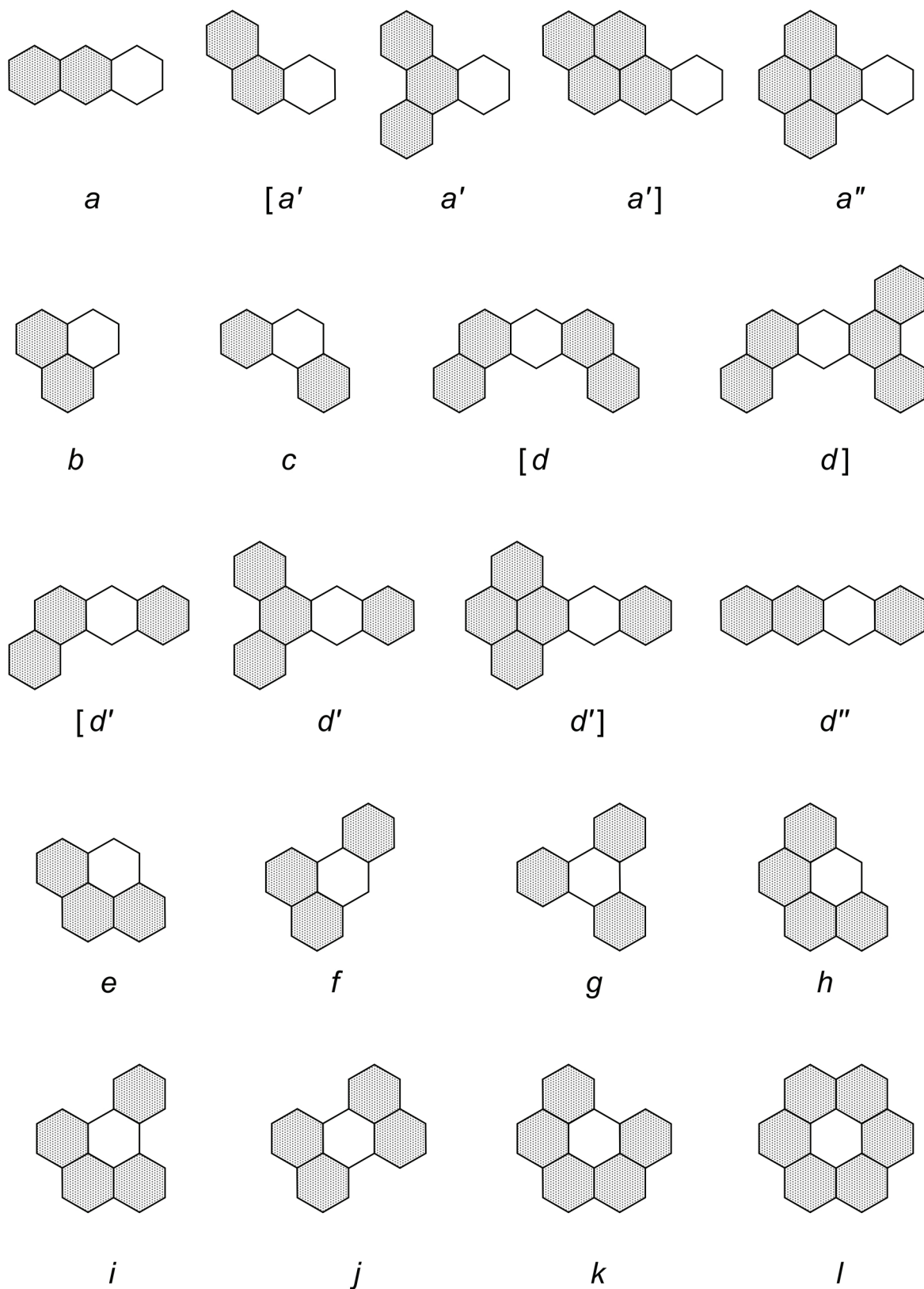


Figure 2. Ring types (denoted by letters) and sub-types (denoted by prime or double prime symbols). In each case, the unshaded ring is the ring being categorised.

ground-state π -electronic-configuration for the system).^{28–32} Because of this (on grounds of differences in symmetry, for one thing), the corresponding rings of isoarithmic structures are by no means guaranteed to have associated with them identically the *same* topological π -electron ring-currents. That said, however, it is a remarkable fact that, in practice, the topological π -electron ring-currents in the respective rings of isoarithmic structures seem frequently to differ only in the third decimal-place.

This phenomenon is well illustrated by Figure 3, which depicts the topological ring-currents in three pairs of isoarithmic structures, and one family of greater multiplicity (a triplet). Exceptionally, where they are available in the literature³⁵ to this accuracy, some ring-current values in this Figure are quoted to three decimal-places; this third decimal-place is included in order to show just how fine and sensitive are the differences in topological π -electron ring-current intensities between the corresponding rings of structures that, so far as π -electron *partitions* are concerned, constitute families of isoarithmic systems where π -electron partitions are precisely the same. Because the differences in topological ring-current intensities between the respective corresponding rings of each family of isoarithmic structures are comparatively so small, only *one* of each isoarithmic pair/multiple will be included in the comparative tables and plots that are to follow in this paper.

CONFRONTATION OF π -ELECTRON PARTITIONS AND THE CORRESPONDING TOPOLOGICAL π -ELECTRON RING-CURRENTS

Table 2 illustrates π -electron partitions and the corresponding topological π -electron ring-currents for 103 distinct rings in 27 different non-isoarithmic cata-condensed structures and for 73 distinct rings in 16 different peri-condensed benzenoids with up to seven rings. The partitions data are taken from Refs. 33 and 34, and the ring-current values are from the compilation presented in Ref. 35. It should be noted that (a) compound numberings follow Ref. 33 for the cata-structures and Ref. 34 (where the same numbers are repeated) for the peri ones, and (b) these numbers do not run consecutively within each category of structure. The latter is because not every structure treated in Refs. 33 and 34 has corresponding ring-current data listed for it in Ref. 35 and, naturally, we are dealing here only with those structures for which data are available on both indices. Here, the labellings of the cata- structures will be preceded by the letter "C", and will be written in blue, in bold type; peri-structures will be labelled with a bold number written in red, and preceded by the letter "P". This is merely a convenience as far as the structure labellings are concerned but, in the plots of ring currents vs. electron partitions, presented later, the use of colour

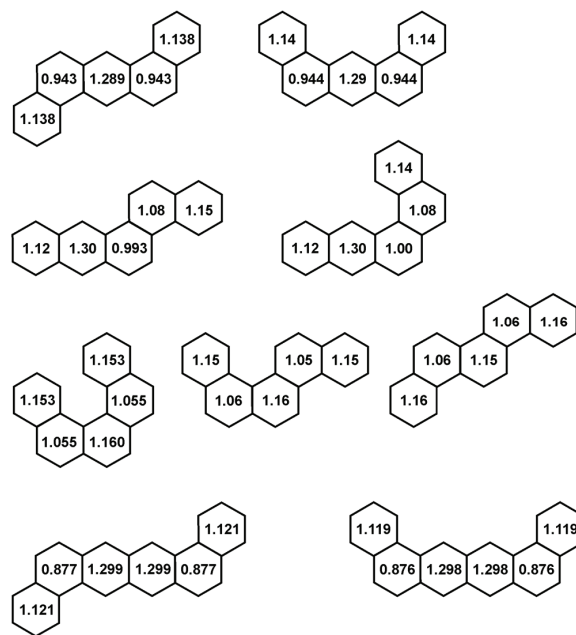


Figure 3. Three pairs and a triplet of isoarithmic benzenoids, together with the intensities of the topological π -electron ring-currents borne by each of their constituent rings (indicated within the respective rings).

will be seen to be essential. The number, K , of resonance (or Kekulé) structures is presented in a separate column in Table 2, because it serves as an ordering criterion for isomeric benzenoids having the same number of rings.

Table 3 presents data for what we are going to refer to as "anomalous" polycyclic benzenoids, which lead to outliers in our plots. The anomalous perifusenes have localised bonds (such as zethrene (**P5**) or its benzologue (**P19**)), essential single-bonds (such as perylene (**P2**) or its benzologs (**P12**) and (**P55**)), and unique environments, such as coronene (**P35**).

"FRAGMENTED" LINEAR-CORRELATIONS OF π -ELECTRON PARTITIONS AND TOPOLOGICAL π -ELECTRON RING-CURRENTS

In Figure 4 we present a plot of topological π -electron ring-currents vs. π -electron partitions using all the data from Table 2. It can be seen that there are several distinct regions of the diagram where there are linear correlations. However, the most striking aspect is that, amongst what we are calling here these "fragmented" linear-correlations (where correlations are limited to being within certain types of ring), some have positive slopes – as expected if the aromaticity due to delocalised π -electrons were "uni-dimensional" – whereas, surprisingly, a few of the others even have *negative* slopes. In Table 4, these fragmented linear-correlations

Table 2. π -Electron partitions and the corresponding topological π -electron ring-currents for 103 distinct rings in 27 different cata-condensed structures and for 73 distinct rings in 16 different peri-condensed benzenoids. The partitions data are taken from Refs. 33 and 34, and the ring-current values are from the compilation presented in Ref. 35

Compound	K	Ring	Partition	Ring Current	Ring Type	Structure
C1	3	AA	5.00	1.09	a	
C2	4	AA	4.75	1.09	a	
		B	4.50	1.28	d''	
C3	5	AA	5.20	1.13	a'	
		B	3.60	0.975	c	
C4	5	AA	4.60	1.07	a	
		BB	4.40	1.31	d''	
C5	7	A	4.86	1.12	a	
		B	4.57	1.27	d'	
		C	3.29	0.891	c	
		D	5.29	1.12	a'	
C6	8	AA	5.13	1.15	a'	
		BB	3.88	1.07	c	
C7	9	AAA	5.33	1.11	a'	
		B	2.00	0.747	g	
C8	6	AA	4.50	1.06	a	
		BB	4.33	1.30	d''	
		C	4.33	1.35	d''	
C9	9	A	4.67	1.09	a	
		B	4.44	1.32	d''	
		C	4.44	1.35	d''	
		D	3.11	0.847	c	
		E	5.33	1.11	a'	
C10	10	AA	4.90	1.11	a	
		BB	4.60	1.23	d'	
		C	3.00	0.784	c	
C11	11	A	4.82	1.12	a	
		B	4.55	1.30	d'	
		C	3.55	0.993	c	
		D	4.00	1.08	c	
		E	5.09	1.15	a'	
C12	12	AA	5.25	1.14	a'	
		BB	3.42	0.944	c	
		C	4.67	1.29	d	
C13	13	AA	5.15	1.16	a'	
		BB	3.77	1.06	c	
		C	4.15	1.15	c	
C14	13	A	4.92	1.12	a	
		B	4.62	1.21	d'	
		C	1.69	0.648	g	
		DD	5.39	1.08	a	
C15	14	A	5.07	1.10	a'	
		B	4.07	1.09	c	
		C	2.29	0.853	g	
		D	5.29	1.14	a'	
		E	5.29	1.13	a'	

Table 2. Continued

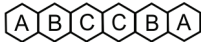
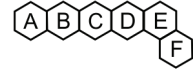
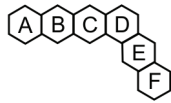
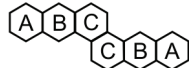
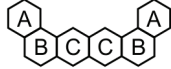
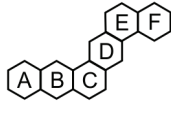

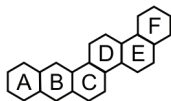
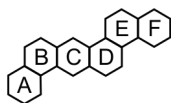
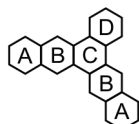
Compound	<i>K</i>	Ring	Partition	Ring Current	Ring Type	Structure
C16	7	AA	4.43	1.05	<i>a</i>	
		BB	4.29	1.29	<i>d''</i>	
		CC	4.29	1.35	<i>d''</i>	
C17	11	A	4.55	1.07	<i>a</i>	
		B	4.36	1.32	<i>d''</i>	
		C	4.36	1.36	<i>d''</i>	
		D	4.36	1.24	<i>d''</i>	
		E	3.00	0.825	<i>c</i>	
		F	5.36	1.10	<i>a'</i>	
C18	13	A	4.69	1.09	<i>a</i>	
		B	4.46	1.31	<i>d''</i>	
		C	4.46	1.22	<i>d''</i>	
		D	2.85	0.732	<i>c</i>	
		E	4.62	1.21	<i>d'</i>	
		F	4.92	1.11	<i>a</i>	
C20	15	AA	4.80	1.12	<i>a</i>	
		BB	4.53	1.31	<i>d'</i>	
		CC	3.67	1.01	<i>c</i>	
C21	16	AA	5.31	1.12	<i>a'</i>	
		BB	3.19	0.876	<i>c</i>	
		CC	4.50	1.30	<i>d''</i>	
C22	17	A	4.88	1.12	<i>a</i>	
		B	4.59	1.26	<i>d'</i>	
		C	3.12	0.839	<i>c</i>	
		D	4.71	1.26	<i>d</i>	
		E	3.47	0.951	<i>c</i>	
		F	5.24	1.14	<i>a</i>	
C23	17	A	4.71	1.09	<i>a</i>	
		B	4.47	1.31	<i>d''</i>	
		C	4.47	1.19	<i>d''</i>	
		D	1.53	0.603	<i>g</i>	
		EE	5.41	1.06	<i>a'</i>	
C24	18	A	4.83	1.13	<i>a</i>	
		B	4.56	1.30	<i>d'</i>	
		C	3.44	0.973	<i>c</i>	
		D	4.28	1.15	<i>c</i>	
		E	3.72	1.04	<i>c</i>	
		F	5.17	1.15	<i>a'</i>	
C25	19	A	5.26	1.14	<i>a'</i>	
		B	3.37	0.936	<i>c</i>	
		C	4.63	1.31	<i>d</i>	
		D	3.68	1.05	<i>c</i>	
		E	3.95	1.08	<i>c</i>	
		F	5.11	1.15	<i>a'</i>	
C27	19	AA	4.95	1.10	<i>a</i>	
		BB	4.63	1.17	<i>d'</i>	
		C	1.42	0.548	<i>g</i>	
		D	5.42	1.04	<i>a'</i>	

Table 2. Continued







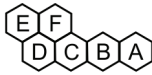

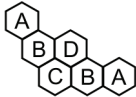


Compound	<i>K</i>	Ring	Partition	Ring Current	Ring Type	Structure
C29	21	AA	5.14	1.16	<i>a'</i>	
		BB	3.81	1.07	<i>c</i>	
		CC	4.05	1.15	<i>c</i>	
C30	22	A	5.23	1.14	<i>a'</i>	
		B	3.50	0.962	<i>c</i>	
		C	4.73	1.25	<i>d</i>	
		D	1.82	0.698	<i>g</i>	
		E	5.36	1.09	<i>a'</i>	
		F	5.36	1.10	<i>a'</i>	
P1	6	AA	4.67	1.33	<i>b</i>	
		BB	3.33	0.964	<i>e</i>	
P3	9	A	5.00	1.21	<i>a'</i>	
		B	3.67	1.29	<i>f</i>	
		C	3.11	0.848	<i>e</i>	
		D	4.67	1.30	<i>b</i>	
		E	3.56	1.08	<i>e</i>	
P4	11	A	5.36	1.10	<i>a''</i>	
		B	1.82	0.719	<i>i</i>	
		CC	4.73	1.29	<i>b</i>	
		D	3.36	0.987	<i>e</i>	
P6	10	AA	4.60	1.34	<i>b</i>	
		BB	3.30	1.30	<i>h</i>	
		CC	3.10	0.854	<i>e</i>	
P8	12	A	4.75	1.14	<i>a</i>	
		B	4.50	1.37	<i>d'</i>	
		C	3.42	1.21	<i>f</i>	
		D	3.00	0.790	<i>e</i>	
		E	4.67	1.27	<i>b</i>	
		F	3.67	1.09	<i>e</i>	
P9	13	AA	4.92	1.20	<i>a'</i>	
		BB	3.77	1.31	<i>f</i>	
		CC	3.31	0.979	<i>e</i>	
P10	14	AA	5.07	1.19	<i>a'</i>	
		BB	3.57	1.21	<i>f</i>	
		C	2.93	0.725	<i>e</i>	
		D	3.79	1.18	<i>e</i>	
P11	14	AA	4.71	1.29	<i>b</i>	
		BB	3.50	1.08	<i>e</i>	
		C	3.86	1.38	<i>e</i>	
		D	1.71	0.684	<i>k</i>	
P14	16	A	4.94	1.20	<i>a'</i>	
		B	3.81	1.33	<i>f</i>	
		C	3.13	0.888	<i>e</i>	
		D	4.75	1.30	<i>b</i>	
		E	2.06	0.843	<i>i</i>	
		F	5.31	1.13	<i>a''</i>	

Table 2. Continued

Compound	<i>K</i>	Ring	Partition	Ring Current	Ring Type	Structure
P15	16	A	4.94	1.11	<i>a</i>	
		B	4.63	1.19	<i>d'</i>	
		C	1.56	0.614	<i>i</i>	
		D	3.38	0.989	<i>e</i>	
		EE	4.75	1.26	<i>b</i>	
P17	17	A	5.06	1.20	<i>a'</i>	
		B	3.65	1.23	<i>f</i>	
		C	3.59	1.09	<i>e</i>	
		D	4.71	1.26	<i>b</i>	
		E	1.59	0.606	<i>i</i>	
		F	5.41	1.06	<i>a'</i>	
P18	20	AA	5.35	1.11	<i>a'</i>	
		BB	1.85	0.745	<i>i</i>	
		CC	4.80	1.27	<i>b</i>	
P29	18	AA	4.67	1.33	<i>b</i>	
		BBBB	3.33	1.03	<i>e</i>	
		C	3.33	1.45	<i>j</i>	
P40	21	A	5.29	1.14	<i>a'</i>	
		B	3.29	0.932	<i>c</i>	
		C	4.57	1.37	<i>d</i>	
		D	3.52	1.26	<i>f</i>	
		E	3.05	0.824	<i>e</i>	
		F	4.67	1.29	<i>b</i>	
		G	3.62	1.09	<i>e</i>	
P46	23	A	4.78	1.14	<i>a</i>	
		B	4.52	1.36	<i>d'</i>	
		C	3.39	1.14	<i>f</i>	
		D	3.70	1.10	<i>e</i>	
		E	4.70	1.23	<i>b</i>	
		F	1.48	0.559	<i>i</i>	
		G	5.44	1.04	<i>a</i>	
P60	27	AA	5.11	1.18	<i>a'</i>	
		BB	3.56	1.16	<i>f</i>	
		C	3.82	1.18	<i>e</i>	
		D	1.41	0.508	<i>i</i>	
		E	5.44	1.02	<i>a'</i>	

are presented separately for some of the positive slopes and for all of the negative ones. In Figure 5, we illustrate the first three correlations of Table 4 that have positive slopes, which appear in the lower left ("South-West") part of Figure 4.

It can be seen from the part of Table 4 concerned with positive slopes that both the π -electron partitions and the topological π -electron ring-currents ascribe distinctly lower values to rings of types *g*, *i*, and *k* (so-called "empty rings" in Clar's theory),^{27,58} as shown by Figures 2 and 4. Terminal rings with degree 1 in acenic portions of catafusenes (type *a*) are, by contrast, assigned high values both by the topological π -electron

ring-currents and the π -electron partitions.

Whilst linear correlations between ring currents and π -electron partitions within certain restricted classes of ring types displayed in Figure 5 are good (with correlation coefficients of up to 0.996), correlation coefficients for cata-rings *a* (0.854) and for peri-rings *f* (0.706) are decidedly weak. Correlation coefficients for the correlations that have negative slopes range from -0.996 for cata- and peri-rings-types *d* down to -0.868 for the correlation attempted for ring types *a'* in the cata- and peri-structures combined. It can also be seen from Table 4 that the negative slope characterises terminal rings of degree 1 (types *a'* or *a''*) adjacent to a

Table 3. "Anomalous" polycyclic benzenoids

Compound	K	Ring	Partition	Ring Current	Ring Type	Structure
P2	9	AAAA	4.67	0.970	<i>b</i>	
		B	1.33	0.239	<i>j</i>	
P5	9	AA	4.67	0.922	<i>b</i>	
		BB	4.67	0.865	<i>b</i>	
		CC	2.67	0.365	<i>f</i>	
P12	15	A	5.20	1.08	<i>a</i>	
		B	3.40	0.875	<i>f</i>	
		C	4.80	1.04	<i>b</i>	
		D	1.26	0.236	<i>j</i>	
		E	4.68	0.973	<i>b</i>	
		F	4.68	0.974	<i>b</i>	
P19	9	AA	4.67	0.905	<i>b</i>	
		BB	4.67	0.820	<i>b</i>	
		CC	2.67	0.410	<i>f</i>	
		D	4.00	0.577	<i>d</i>	
P35	20	AAAAAA	3.70	1.46	<i>e</i>	
		B	1.80	1.04	<i>l</i>	
P55	25	AA	5.20	1.08	<i>a</i>	
		BB	3.40	0.876	<i>f</i>	
		CC	4.80	1.04	<i>b</i>	
		D	1.20	0.233	<i>j</i>	

benzenoid ring followed by a "kink" in catafusenes or perifusenes, as well as middle rings of degree 2 (type *d'*). All these ring-types appear in the "North-East" part of Figure 4, characterised by the higher values of both topological π -electron ring-currents and π -electron partitions.

It has been established⁶³ that, in terms (a) of energy criteria, (b) of chemical reactivity manifested by additions of hydrogen or halogens, and (c) of π -electron partitions, the aromaticity of the *central* ring in

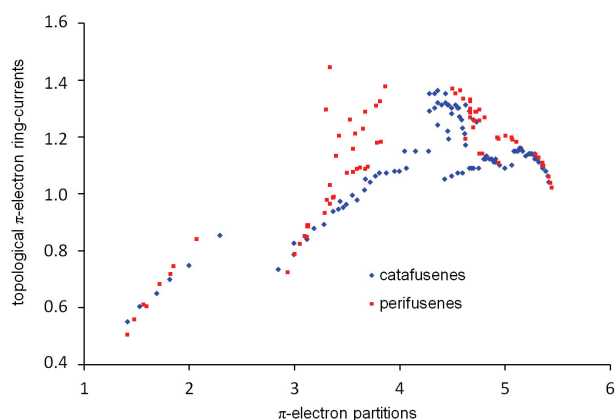


Figure 4. Plot of topological π -electron ring-currents (on the vertical axis) vs. π -electron partitions (along the horizontal axis) for catafusenes (blue points) and perifusenes (red points).

anthracene or phenanthrene is lower than that of the *terminal* rings. However, as far as the topological π -electron ring-currents are concerned – if, indeed, one *can* properly take such quantities to be some sort of indication of "aromaticity"^{8,11} – the opposite is true for anthracene (and other linear acenes),⁶⁴ as can be seen from the data in Table 1, or from a comparison of the NICS values calculated by Schleyer and co-workers.^{65–67} The present authors are inclined to view this observation as essentially another manifestation of the so-called "multi-dimensional" character of "aromaticity"¹¹ – but see Ref. 15 for an alternative view.

A THIRD KIND OF CORRELATION INVOLVING QUANTUM-CHEMICAL CRITERIA

Ring currents calculated for polycyclic benzenoids by various methods frequently seem to provide results that are in conflict with intuitive representations of local aromaticity.^{8,11} Thus, as just mentioned, NICS values,^{65–67} or the topological π -electron ring-current intensities discussed in previous sections of the present study, indicate higher delocalisation for the central rings of anthracene and phenanthrene than for the marginal ones. However, bond distances and chemical reactivities show that the central rings are prone to 1,4- and 1,2-additions, respectively, revealing their dienic or alkenic character,

Table 4. "Fragmented" linear-correlations^{(a),(b)} of topological π -electron ring-currents³⁵ (as the dependent variable) vs. π -electron partitions^{33,34} (as the independent variable), according to ring type (as in Table 1 and Figure 4)

Structure Type	Ring Type ^(c)	Place on Map of Figure 4 ^(e)	No. of Points	R^2 ^(d)	Slope s	Intercept t
Positive Slopes						
Cata	<i>g</i>	South-West	6	0.996	0.341	0.072
Peri	<i>i,k</i>	South-West	8	0.992	0.498	-0.179
Cata + Peri	<i>g,i,k</i>	South-West	14	0.951	0.395	-0.015
Peri	<i>e</i>	Centre	20	0.924	0.522	-0.769
Cata	<i>c</i>	Centre	25	0.968	0.293	-0.065
Peri	<i>f</i>	Centre	9	0.706	0.382	-0.135
Cata	<i>a</i>	Centre	18	0.854	0.139	0.439
Negative Slopes						
Peri	<i>a'</i>	North-East	6	0.979	-0.804	5.408
Cata + Peri	<i>a'</i>	North-East	30	0.868	-0.274	2.568
Cata + Peri	<i>d'</i>	North-East	11	0.978	-1.441	7.858
Cata + Peri	<i>d</i>	North-East	5	0.996	-0.753	4.805

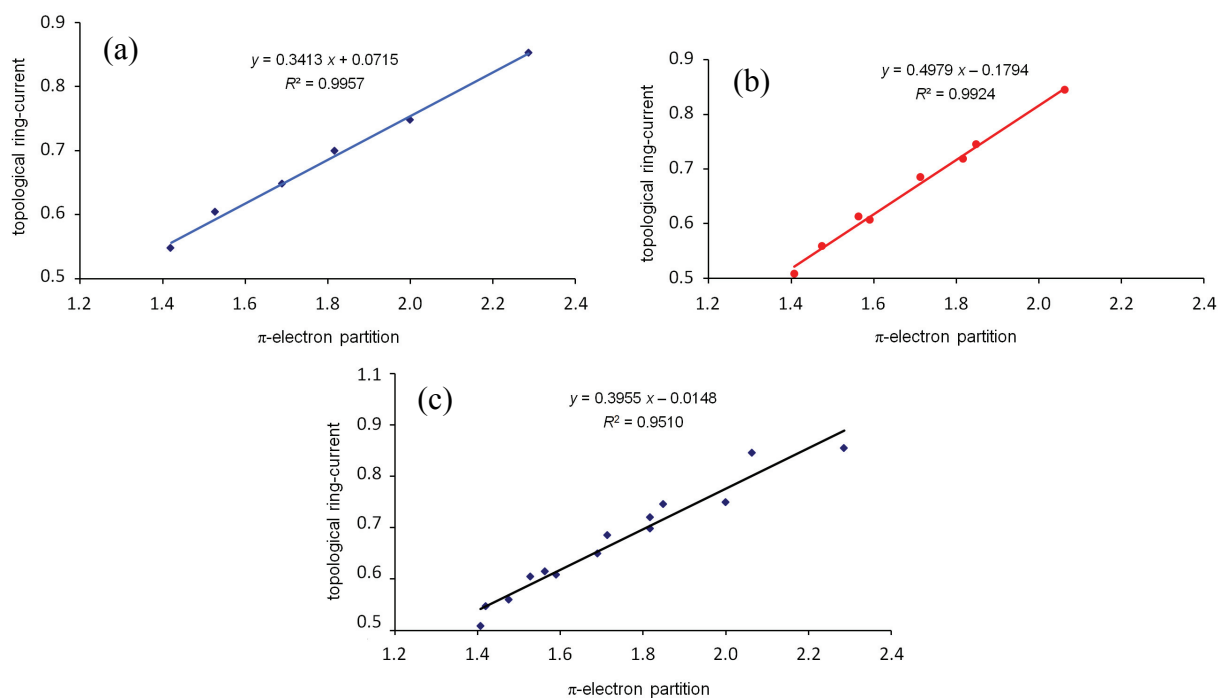
^(a) There are no significant correlations for types *b* and *d''*.

^(b) The correlations have the form: Ring Current = $s \times$ (Ring Partition) + t

^(c) Ring Types are according to the geometrical classifications described in Table 1 and depicted in Figure 2.

^(d) R^2 is the square of the respective correlation-coefficient.

^(e) "Place on Map of Figure 4" refers to the region of Figure 4 in which the plotted points being considered actually occur.

**Figure 5.** Linear correlations between topological π -electron ring-currents and π -electron partitions for ring types *g* (a), *i* and *k* (b), and all three of these ring types combined (c).

rather than an aromatic character. Both for anthracene and phenanthrene, Clar structures^{27,58} also assign a lower "sextet character" to the central rings. This aspect agrees with the fact that the slope of correlations between topological π -electron ring-currents and π -electron partitions for the highest values of the latter parameter become negative.

In order to investigate how ring types affect the local aromaticity we now consider a third criterion of local aromaticity in polycyclic benzenoids – the six-centre delocalisation-indices, denoted as Δ_6 . These may also be regarded as a measure of "local aromaticity" and were recently introduced by Mandado *et al.*^{36,68} Table 5 compares the previous two local-aromaticity parameters

Table 5. Three local-aromaticity indices. The numbers that are here denoted "M#", identifying the compounds under discussion, are replicated directly from Mandado *et al.*³⁶





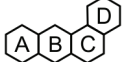
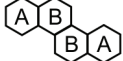

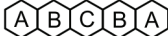
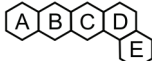
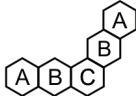
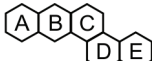
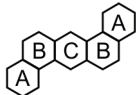
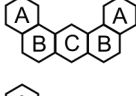
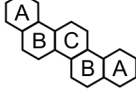
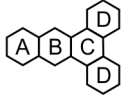
Compound	M#	K	Ring	Partition	$100 \times \Delta_6$	Ring Current	Ring Type	Structure
C1	2	3	AA	5.00	2.63	1.09	<i>a</i>	
C2	3	4	AA	4.75	1.99	1.09	<i>a</i>	
			B	4.50	1.89	1.28	<i>d''</i>	
C3	8	5	AA	5.20	3.14	1.13	<i>a'</i>	
			B	3.60	1.19	0.975	<i>c</i>	
C4	4	5	AA	4.60	1.72	1.07	<i>a</i>	
			BB	4.40	1.59	1.31	<i>d''</i>	
C5	12	7	A	4.86	2.22	1.12	<i>a</i>	
			B	4.57	2.05	1.27	<i>d'</i>	
			C	3.29	0.86	0.891	<i>c</i>	
			D	5.29	3.32	1.12	<i>a'</i>	
C6	10	8	AA	5.13	2.98	1.15	<i>a'</i>	
			BB	3.88	1.49	1.07	<i>c</i>	
C7	11	9	AAA	5.33	3.47	1.11	<i>a'</i>	
			B	2.00	0.51	0.747	<i>g</i>	
C8	5	6	AA	4.50	1.59	1.06	<i>a</i>	
			BB	4.33	1.43	1.30	<i>d''</i>	
			C	4.33	1.41	1.35	<i>d''</i>	
C9	17	9	A	4.67	1.84	1.09	<i>a</i>	
			B	4.44	1.69	1.32	<i>d''</i>	
			C	4.44	1.66	1.35	<i>d''</i>	
			D	3.11	0.73	0.847	<i>c</i>	
			E	5.33	3.38	1.11	<i>a'</i>	
C10	18	10	AA	4.90	2.32	1.11	<i>a</i>	
			BB	4.60	2.07	1.23	<i>d'</i>	
			C	3.00	0.63	0.784	<i>c</i>	
C11	21	11	A	4.82	2.14	1.12	<i>a</i>	
			B	4.55	2.01	1.30	<i>d'</i>	
			C	3.55	1.09	0.993	<i>c</i>	
			D	4.00	1.61	1.08	<i>c</i>	
			E	5.09	2.90	1.15	<i>a'</i>	
C12	14	12	AA	5.25	3.24	1.14	<i>a'</i>	
			BB	3.42	0.97	0.943	<i>c</i>	
			C	4.67	2.33	1.29	<i>d</i>	
C12	15	12	AA	5.25	3.24	1.14	<i>a'</i>	
			BB	3.42	0.97	0.944	<i>c</i>	
			C	4.67	2.30	1.29	<i>d</i>	
C13	20	13	AA	5.15	3.03	1.16	<i>a'</i>	
			BB	3.77	1.39	1.06	<i>c</i>	
			C	4.15	1.86	1.15	<i>c</i>	
C14	19	13	A	4.92	2.30	1.12	<i>a</i>	
			B	4.62	2.19	1.21	<i>d'</i>	
			C	1.69	0.37	0.648	<i>g</i>	
			DD	5.39	3.57	1.08	<i>a'</i>	

Table 5. Continued

Compound	M#	K	Ring	Partition	$100 \times \Delta_6$	Ring Current	Ring Type	Structure
C16	6	7	AA	4.43	1.52	1.05	<i>a</i>	
			BB	4.29	1.35	1.29	<i>d''</i>	
			CC	4.29	1.31	1.35	<i>d''</i>	
P1	9	6	AA	4.67	2.43	1.33	<i>b</i>	
			BB	3.33	1.23	0.964	<i>e</i>	
P3	13	9	A	5.00	2.64	1.21	<i>a'</i>	
			B	3.67	1.29	1.29	<i>f</i>	
			C	3.11	0.95	0.848	<i>e</i>	
			D	4.67	2.40	1.30	<i>b</i>	
			E	3.56	1.56	1.08	<i>e</i>	
P4	16	11	A	5.36	3.50	1.10	<i>a''</i>	
			B	1.82	0.54	0.719	<i>i</i>	
			CC	4.73	2.65	1.29	<i>b</i>	
			D	3.36	1.21	0.987	<i>e</i>	
P6	23	10	AA	4.60	2.15	1.34	<i>b</i>	
			BB	3.30	1.31	1.30	<i>h</i>	
			CC	3.10	0.97	0.854	<i>e</i>	
P17	25	17	A	5.06	2.71	1.20	<i>a'</i>	
			B	3.65	1.38	1.23	<i>f</i>	
			C	3.59	1.52	1.09	<i>e</i>	
			D	4.71	2.57	1.26	<i>b</i>	
			E	1.59	0.41	0.606	<i>i</i>	
			F	5.41	3.58	1.06	<i>a''</i>	
P18	24	20	AA	5.35	3.48	1.11	<i>a''</i>	
			BB	1.85	0.53	0.745	<i>i</i>	
			CC	4.80	2.90	1.27	<i>b</i>	

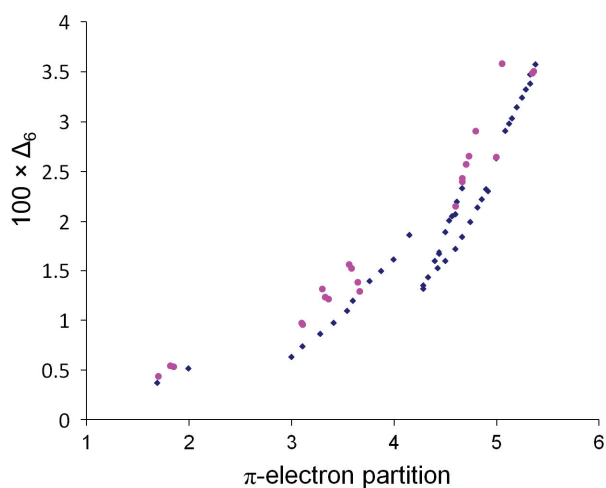


Figure 6. Plot of Δ_6 -values (from Ref. 36) along the vertical axis vs. π -electron partitions,^{33,34} on the horizontal axis. The blue and the purple colours indicate catafusenes and perifusenes, respectively.

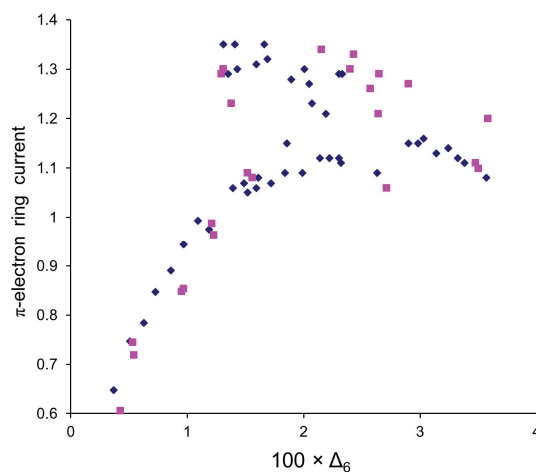


Figure 7. Plot of topological π -electron ring-currents (from Ref. 35) along the vertical axis vs. Δ_6 -values (from Ref. 36), along the horizontal axis. The blue and the purple colours indicate catafusenes and perifusenes, respectively.

(topological π -electron ring-currents and π -electron partitions), with this third one, Δ_6 , by means of the data provided in Ref. 36.

In connexion with Table 5, it should be noted that two isoarithmic catafusenes were listed separately in the paper by Mandado *et al.*,³⁶ as items **14** and **15** – but they both here correspond to the structure that we have labelled³⁴ as **C12**.

As seen in Figure 6, the plot of a convenient multiple (100) of Δ_6 vs. π -electron partitions is as fragmented as the plot of π -electron ring-currents vs. π -electron partitions shown in Figure 4, but it has only *positive* slopes, indicating that these two criteria are congruent, at least to some extent. One might, therefore, construct several distinct local (fragmented) linear-correlations between these parameters according to various ring types, conserving the classification of such ring types from the previous tables.

An intriguing aspect of Figure 7 – π -electron ring-currents vs. a convenient multiple (100) of the Δ_6 -values – is that it qualitatively mirrors the plot of Figure 4 (of π -electron ring-currents vs. π -electron partitions). The two are not dissimilar in that there is an approximate positive correlation up to ring-current values of about 1.2 – or, rather, two, separate, parallel ones: one for ring currents up to values of about 0.8 and another for ring-current values between about 0.8 and 1.2. Again, however – as in Figure 4 – for the highest Δ_6 -values, the slope of the correlation with topological π -electron ring-currents becomes *negative* for the higher ring-current and Δ_6 -values.

CONCLUSIONS

Comparisons of Figures 4 and 6 on the one hand, and of Figures 4 and 7 on the other, inevitably invite the general conclusion that – despite its superficially intuitive appeal – the "ring-current" index is out of step with the other two indices considered here – π -electron partitions and Δ_6 -values – as an index of what might be regarded as "local aromaticity". This conclusion agrees with the idea that aromaticity is a multi-dimensional and scale-dependent phenomenon^{12–19} – but see Ref. 15 for the opposite viewpoint.

It should, though, be observed that the topological π -electron ring-currents for most (but not all) ring types *are* congruent with other indices that are frequently suggested as encapsulating the extent of such "local aromaticity". In particular, the analysis presented here shows that magnetic criteria disagree with other local aromaticity criteria *only* when discussing fragments of polycyclic condensed aromatic hydrocarbons containing linearly-condensed terminal and next-to-terminal benzenoid rings. Finally, it may be noted in passing that recent studies have also shown a remarkable concord-

ance between topological π -electron ring-currents and energy-effect values^{69,70} in the central ring of perylene-like structures⁷¹ and in the five-membered ring of conjugated systems related to fluoranthene.⁵⁴

Note added in proof. Since the submission of this manuscript, the following papers relevant to it have appeared: (a) a review on π -electron partitions;⁷² (b) two papers pertinent to our discussion of anthracene and phenanthrene;^{73,74} (c) further developments⁷⁵ on the topological aspects of the *aufbau* process, dealt with in Refs. 28–32.

REFERENCES

1. C. W. Haigh and R. B. Mallion, *Ring Current Theories in Nuclear Magnetic Resonance*, in: *Progress in Nuclear Magnetic Resonance Spectroscopy*, J. W. Emsley, J. Feeney, and L. H. Sutcliffe (Eds), Pergamon Press, Oxford, 1979/1980, Vol. 13, pp. 303–344.
2. P. Lazzeretti, *Ring Currents*, in: *Progress in Nuclear Magnetic Resonance Spectroscopy* J. W. Emsley, J. Feeney, and L. H. Sutcliffe (Eds), Elsevier, Amsterdam, 2000, Vol. 36, pp. 1–88.
3. L. Salem, *Molecular Orbital Theory of Conjugated Systems*, W. A. Benjamin, New York, 1966, Chapter 9.
4. J. A. N. F. Gomes and R. B. Mallion, *The Concept of Ring Currents*, in: D. H. Rouvray (Ed), *Concepts in Chemistry: A Contemporary Challenge*, Research Studies Press, Taunton, Somerset (England, United Kingdom), 1997, pp. 205–253.
5. J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.* (1961), pp. 859–866.
6. J. A. Elvidge, *Chem. Commun.* (1965), pp. 160–161.
7. R. J. Abraham and W. A. Thomas, *J. Chem. Soc. B* (1966), pp. 127–131.
8. J. A. N. F. Gomes and R. B. Mallion, *Chem. Rev.* **101** (2001) 1349–1383.
9. J.-F. Labarre and F. Crasnier, *Fort. Chem. Forsch. (Topics Current Chem.)* **24** (1971) 33–54.
10. A. T. Balaban, *Pure Appl. Chem.* **52** (1980) 1409–1429.
11. R. B. Mallion, *Pure Appl. Chem.* **52** (1980) 1541–1548.
12. M. K. Cyrański, T. M. Krygowski, A. R. Katritzky, and P. v. R. Schleyer, *J. Org. Chem.* **2002**, 67 1333–1338.
13. P. Bultinck, S. Fias, and R. Ponec, *Chem. Eur. J.* **12** (2006) 8813–8818.
14. S. Fias, S. Van Damme, and P. Bultinck, *J. Comput. Chem.* **29** (2007) 358–366.
15. S. Fias, P. W. Fowler, J. L. Delgado, U. Hahn, and P. Bultinck, *Chem. Eur. J.* **14** (2008) 3093–3099.
16. A. Ciesielski, T. M. Krygowski, M. K. Cyrański, A. Dobrowolski, A. T. Balaban, and P. Bultinck, *J. Chem. Inf. Model.* **49** (2009) 369–376.
17. R. Ponec, S. Fias, S. van Damme, P. Bultinck, I. Gutman, and S. Stanković, *Coll. Czech. Chem. Commun.* **74** (2009) 147–166.
18. S. Fias, S. Van Damme, and P. Bultinck, *J. Comput. Chem.* **31** (2010) 2286–2293.
19. M. Mandado, *Theoret. Chem. Accounts* **126** (2010) 339–349.
20. A. T. Balaban, D. C. Oniciu, and A. R. Katritzky, *Chem. Rev.* **104** (2004) 2777–2812.
21. A. T. Balaban, *Aromaticity of Six-membered Rings with one Heteroatom*, in: T. M. Krygowski and M. K. Cyrański, (Eds), *Aromaticity in Heterocyclic Compounds*, Springer, New York, 2009, pp 203–246.
22. A. T. Balaban, *Monocyclic Heteroarenes with π -Electron Aromatic Sextet*, in: A. R. Katritzky (Ed.), *Advances in Heterocyclic Chemistry*, Elsevier, Amsterdam, 2010, Vol. 99, pp 69–105.

23. R. B. King, *Chem. Rev.* **101** (2001) 1119–1152.
24. Z. Chen and R. B. King, *Chem. Rev.* **105** (2005) 3613–3642.
25. C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19** (1963) 527–544.
26. C. W. Haigh and R. B. Mallion, *Mol. Phys.* **22** (1971) 955–970.
27. E. Clar, *The Aromatic Sextet*, Wiley: London, 1972.
28. R. B. Mallion and D. H. Rouvray, *Mol. Phys.* **36** (1978) 125–128.
29. R. B. Mallion and D. H. Rouvray, *Studia Scientiarum Mathematicarum Hungarica* **13** (1978) 229–243.
30. R. B. Mallion, *Some Chemical Applications of the Eigenvalues and Eigenvectors of Certain Finite, Planar Graphs*, in: *Applications of Combinatorics*, R. J. Wilson (Ed.), Shiva Publishing Ltd., Nantwich, Cheshire (England, United Kingdom), 1982, Chapter 7, pp. 87–117.
31. R. B. Mallion, *Croat. Chem. Acta* **56** (1983) 477–490.
32. R. B. Mallion, *The Topological Nature of the Aufbau Process and of Quantities Calculated via Simple Molecular-Orbital Theory*, in: *Mathematical Methods and Modelling for Students of Chemistry and Biology: Proceedings of the Conference "Mathematical Methods in Chemistry"*, Split, Croatia, September 22–24, 2007, A. Graovac, I. Gutman, and D. Vukičević (Eds.). Hum naklada d.o.o., Zagreb, 2009, pp. 55–86.
33. M. Randić and A. T. Balaban, *Int. J. Quant. Chem.* **108** (2008) 865–897.
34. A. T. Balaban and M. Randić, *Int. J. Quant. Chem.* **108** (2008) 898–926.; Erratum, *ibid.* **III** (2011) 3643–3646.
35. R. B. Mallion, *Croat. Chem. Acta* **81** (2008) 227–246.
36. M. Mandado, P. Bultinck, M. J. González-Moa, and R. A. Mosquera, *Chem. Phys. Lett.* **433** (2006) 5–9.
37. M. Randić, *Chem. Rev.* **103** (2003) 3449–3636.
38. M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 365–372.
39. M. Randić and A. T. Balaban, *Polycyclic Arom. Comp.* **24** (2004) 173–193.
40. A. T. Balaban and M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 50–59.
41. A. T. Balaban and M. Randić, *New J. Chem.* **28** (2004) 800–806.
42. D. Vukičević, M. Randić, and A. T. Balaban, *J. Math. Chem.* **36** (2004) 271–279.
43. A. T. Balaban and M. Randić, *J. Chem. Inf. Comput. Sci.* **44** (2004) 1701–1707.
44. A. T. Balaban and M. Randić, *J. Math. Chem.* **37** (2005) 443–453.
45. M. Randić and A. T. Balaban, *J. Chem. Inf. Comput. Sci.* **46** (2006) 57–64.
46. A. T. Balaban and M. Randić, *New J. Chem.* **32** (2008) 1071–1078.
47. A. T. Balaban, M. Pompe, and M. Randić, *J. Phys. Chem A* **112** (2008) 4148–4157.
48. A. T. Balaban, J. Đurđević, I. Gutman, S. Jeremić, and S. Radenković, *J. Phys. Chem. A* **114** (2010) 5870–5877.
49. C. A. Coulson, B. O'Leary, and R. B. Mallion, *Hückel Theory For Organic Chemists*, Academic Press, London, 1978.
50. K. H. Yates, *Hückel Molecular Orbital Theory*, Academic Press, New York, 1978.
51. F. London, *J. Phys. Radium (7^e série)* **8** (1937) 397–409.
52. J. A. Pople, *Mol. Phys.* **1** (1958) 175–180.
53. R. McWeeny, *Mol. Phys.* **1** (1958) 311–321.
54. A. T. Balaban, T. K. Dickens, I. Gutman, and R. B. Mallion, *Croat. Chem. Acta* **83** (2010) 209–215.
55. D. Janežič, A. Miličević, S. Nikolić, and N. Trinajstić, *Graph Theoretical Matrices in Chemistry*. Mathematical Chemistry Monographs, Faculty of Science, University of Kragujevac (Serbia), 2007.
56. R. B. Mallion, *Mol. Phys.* **25** (1973) 1415–1432.
57. R. B. Mallion, *Proc. Royal Soc. (London) Ser. A* **341** (1974/1975) 429–449.
58. I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag: Berlin (West), 1989.
59. A. T. Balaban and F. Harary, *Tetrahedron* **24** (1968) 2505–2516.
60. I. Gutman, R. B. Mallion, and J. W. Essam, *Mol. Phys.* **50** (1983) 859–877.
61. A. T. Balaban and I. Tomescu, *MATCH Commun. Math. Comput. Chem.* **14** (1983) 155–182.
62. A. T. Balaban, *MATCH Commun. Math. Comput. Chem.* **24** (1989) 29–38.
63. T. M. Krygowski and M. K. Cyrański, *Chem. Rev.* **101** (2001) 1385–1419.
64. C. W. Haigh and R. B. Mallion, *J. Chem. Phys.* **76** (1982) 4063–4066.
65. P. v. R. Schleyer and H. Jiao, *Pure Appl. Chem.* **68** (1996) 209–218.
66. P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **118** (1996) 6317–6318.
67. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. v. R. Schleyer, *Chem. Rev.* **105** (2005) 3842–3888.
68. M. Mandado, M. J. González Moa, and R. A. Mosquera, *Aromaticity: Exploring Basic Chemical Concepts with the Quantum Theory of Atoms in Molecules*, Nova Science Publishers, Hauppauge, New York, 2008.
69. I. Gutman, *Monatsh. Chem.* **136** (2005) 1055–1069.
70. I. Gutman, *Mathematical Modeling of Chemical Phenomena*, in: *Mathematical Methods and Modelling for Students of Chemistry and Biology: Proceedings of the Conference "Mathematical Methods in Chemistry"*, Split, Croatia, September 22–24, 2007, A. Graovac, I. Gutman, and D. Vukičević (Eds.). Hum naklada d.o.o., Zagreb, 2009, pp. 13–27.
71. T. K. Dickens and R. B. Mallion, *J. Phys. Chem. A* **115** (2011) 331–356.
72. A. T. Balaban and M. Randić, *Structural Approach to Aromaticity and Local Aromaticity in Conjugated Polycyclic Systems*, in: *Carbon Bonding and Structures: Advances in Physics and Chemistry. Carbon Materials: Chemistry and Physics 5*, M. V. Putz (Ed.), Springer Science+Business Media B. V., 2011, pp. 159–204.
73. P. v. R. Schleyer, M. Manoharan, H. Jiao, and F. Stahl, *Org. Lett.* **3** (2001) 3643–3646.
74. S. Sakai and Y. Kita, *J. Phys. Org. Chem.* (2012).
75. A. Ceulemans, E. Lijnen, P. W. Fowler, R. B. Mallion, and T. Pisanski, *Proc. R. Soc. A* (2011).