

Partitioning of π -electrons in rings of polycyclic conjugated hydrocarbons: Part 6. Comparison with other methods for estimating the local aromaticity of rings in polycyclic benzenoids

Alexandru T. Balaban*

Texas A & M University at Galveston, MARS, 5007 Avenue U, Galveston TX 77551, USA
E-mail: balabana@tamug.edu

Milan Randić

3225 Kingman Rd, Ames IA 50014, USA
E-mail: mrandic@msn.com

Received 17 September 2004; revised 20 september 2004

By adopting the convention that shared double bonds in polycyclic conjugated hydrocarbons contribute with one π -electron and unshared ones with two π -electrons, a partition of π -electrons in each ring (π -electron content, EC) can be obtained by averaging over all Kekulé structures, which are assumed to have equal weights. This affords a simple measure of local aromaticity that is comparable with other such local aromaticity indices in polycyclic benzenoids.

KEY WORDS: local aromaticity, Clar structures, Kekulé structures, polycyclic hydrocarbons

1. Introduction, conventions, and definitions

Double bonds in the usual (geometric) Kekulé structures (KSs) of polycyclic benzenoid hydrocarbons (benzenoids, for short) may be either shared by two condensed rings, or unshared. A simple method for partitioning the π -electrons to each ring of a benzenoid consists in assigning one π -electron for each shared double bond and two π -electrons for an unshared double bond. By assuming equal weight for all KSs and by averaging the number of π -electrons for each ring, one obtains the π -electron partitioning (π -electron content, EC, of each ring, or the algebraic KS) [1–3]. Alternatively, the partitioning may be obtained by using Pauling bond orders, as indicated in preceding parts of this series, where we have examined cata-condensed benzenoids (catafusenes) [4], coronoids

* Corresponding author.

[5], peri-condensed benzenoids (perifusenes) [6], and nonalternant conjugated hydrocarbons [7]. Sometimes several different geometric KSs correspond to the same algebraic Kekulé structure [8].

Throughout this article, we adopt the convention to write benzenoid rings so as to have a vertical pair of bonds. The number of KSs is denoted by K , the number of carbon atoms and π -electrons by n , and the number of benzenoid rings by R .

As an example for finding π -electron partitions in rings of benzenoids, let us examine the two isomeric catafusenes anthracene (**1**) and phenanthrene (**6**) whose KSs have seven double bonds, i.e. 14 π -electrons.

Anthracene has four KSs; in two of them, one terminal (outermost) vertical double bond is double, and no double bonds are shared; π -electron counts for the three rings (starting from one terminal ring) are 6, 4, 4 and 4, 4, 6; in the remaining pair of KSs with one shared double bond the π -electron counts are 5, 5, 4 and 4, 5, 5. Therefore the averaged partition for the three benzenoid rings in anthracene is 19/4, 18/4, 19/4.

Phenanthrene is the first catafusene in the class of fibonacenes, i.e. non-branched catafusenes that have no anthracenic subgraph (in other words, their dualist graphs have notations that differ only in interchanging digits 1 and 2, which indicate "left-kink" and "right-kink"). Examples of isomeric fibonacenes are chrysene (**7**) and [4] helicene (**11**); picene (**8**) and [5] helicene (**12**); or the dibenzanthracenes (**16** and **17**). Irrespective of their geometry, fibonacenes with the same number of rings and with dualist graphs differing only by above-mentioned interchange of digits 1 and 2 in their notation, possess the same K values and lead to the same partitions. Phenanthrene has five KSs; the unique Fries structure with two shared double bonds corresponds to a π -electron count 5, 4, 5; the two KSs with one shared double bond have π -electron counts 5, 3, 6 and 6, 3, 5; in the two KSs with no shared double bond the π -electron counts are 4, 6, 4 and 6, 2, 6. Therefore the averaged partition for the three benzenoid rings in phenanthrene is 26/5, 18/5, 26/5.

By comparing the results for these two isomeric catafusenes, one sees that the terminal rings of phenanthrene have a larger share of the 14 π -electrons than the terminal rings of anthracene, having in both its terminal rings a circle symbolizing a sextet of π -electrons. By contrast, anthracene has only one circle in one of its rings in the clar structure.

In the first part of this series [4], which discussed the partition of π -electrons in rings of catafusenes, it was shown that the terminal rings of an acene have a share (part) of π -electrons equal to $(n + 5)/K = (4R + 7)/(R + 1)$. All other rings have a share of $(n + 4)/K$, as can be easily verified for anthracene with $R = 3$, $K = 4$, and $n = 14$. By contrast, in fibonacenes, K is a Fibonacci number (hence the name), and the partition in various rings is much more varied than in acenes.

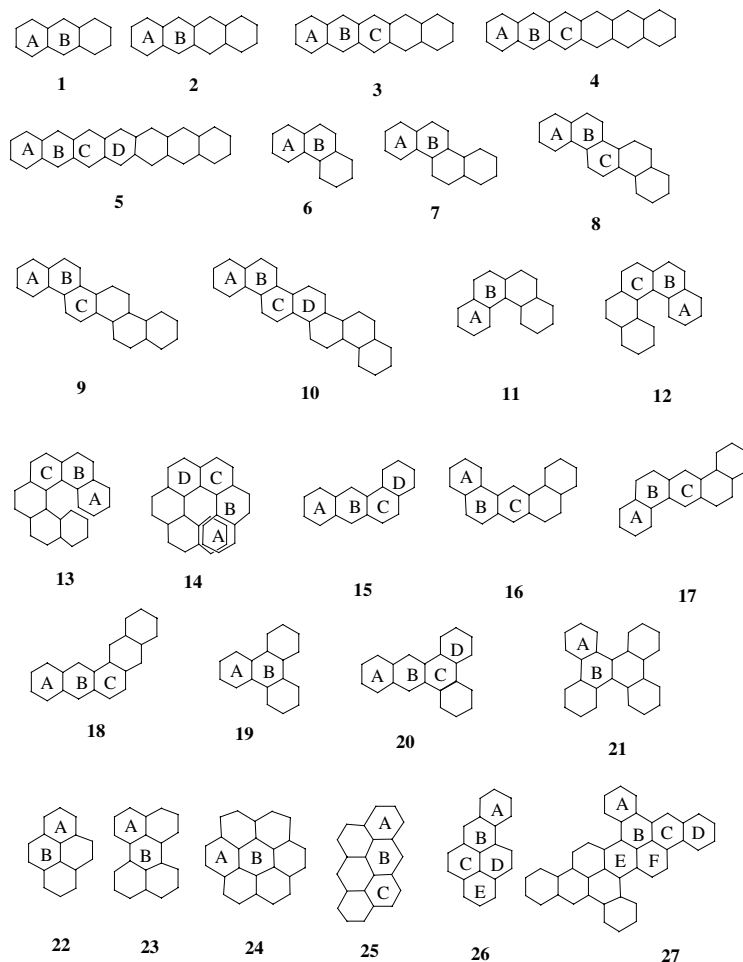


Figure 1. Structures of benzenoids.

2. Local aromaticity in benzenoids

Starting with Polansky and Derflinger's seminal paper [9], theoretical chemists have assigned to rings in benzenoids a more or less pronounced "benzenoid character" or "aromaticity degree" using various criteria such as results of quantum-chemical calculations (VB, HMO, PPP, etc.), or experimentally determined interatomic bond distances. Prominent among the latter local aromaticity criteria are harmonic oscillator model of aromaticity (HOMA) values introduced by Kruszewski and Krygowski [10–18]. More recently, as shown by Schleyer [19], calculations allow the determination of nucleus-independent chemical shifts (NICS) at various distances from the molecular plane (in Ångströms), most often NICS(0) and NICS(1). Some benzenoids, which are non-planar due to

overcrowding, have geometries that disagree with the symmetry of their constitutional formulas; in such cases the literature data have been recalculated taking average values for the symmetrical rings, and the corresponding values are italicized in the tables. Symmetry non-equivalent rings (*r*) are denoted by capital letters A, B, etc. as indicated in figure 1.

In the present paper we shall compare literature data for local aromaticities in rings of polycyclic benzenoids with our simple partitioning of π -electrons (EC) taking into account that the latter data need only quick, simple calculations, and can often be performed without computers.

The comparison will be made with the following quantitative measures of local aromaticity in six-membered rings of benzenoids that in most cases are relative to the aromaticity of benzene (ordered approximately alphabetically; only a selective bibliography is provided, but a more detailed comparison will be published separately, with extensive bibliography):

- Aida and Hosoya's "benzene characteristics" [20];
- Aihara's ring currents (in units relative to benzene) [21];
- Gutman and Bosanac's ring energies (in β units) [22];
- Herndon and Ellzey's "ring aromaticity indices" [23];
- Jiang's (with coworkers) six-electron spin-alternation probability, PSESA [24, 25];
- Kruszewski–Krygowski–Cyranski's harmonic oscillator model of aromaticity (HOMA) values, HOMA = 1 – EN – GEO (EN values also listed) [10–18];
- Li and Jiang's relative (to benzene) local hexagon aromaticity, RLHE [26];
- Monev–Fratesc–Polansky–Mehlhorn's ground-state benzene character [27];
- Moyano and Paniagua's ring resonance energies, RRE (in β units) [28];
- Poater et al.'s mean Bader's electron delocalization index DI of *para*-related carbon atoms [29];
- Polansky and Derflinger's "characterograms" [9];
- Randić's graph-theoretical local aromaticity index [30,31];
- Sakurai's "benzene character" [32];
- Schleyer's nucleus-independent chemical shift computed at a distance $d = 0$ or 1 \AA from the center of the corresponding benzenoid ring, NICS(d) [19];

- Suresh–Gadre’s molecular electrostatic potential (MESP) topography at critical points for each ring [33];
- Tarko–Filip’s topographical paths aromaticity, TPA [34].

We start with local aromaticities of rings in acenes, then we continue with other catafusenes (non-branched and branched), and we finish with data for perifusenes.

3. Acenes

In table 1 we present values for local aromaticities of acenes with 3–7 benzenoid rings. Numbers in the heading indicate references. Our EC partitioning is more discriminating than simple VB local aromaticities (which have one and the same value for all rings of a given acene, e.g. 0.333 for the five rings of pentacene). However, most other literature data discriminate better local aromaticities than our EC partitioning, e.g., again for pentacene the values for rings *A*, *B*, and *C* are 0.657, 0.462, and 0.434 (HMO), and 0.581, 0.508, and 0.686 (PPP calculations) [20]. For rings *A* and *B* in anthracene, local aromaticities were reported to be 0.893 and 0.840 in ref. 9, 0.643 and 0.537, [34] or 0.0952 and 0.0652 [22].

Among the literature data from table 1, our EC partitioning leads to correlation factors $r^2 = 0.86$ with EN data [10–18], and 0.76 with data from ref. 33. Other local aromaticities correlate even less satisfactorily with our EC partitioning data.

4. Other non-branched and branched catafusenes

Table 2 contains local aromaticities for three other classes of catafusenes, different from acenes: fibonacenes, other non-branched catafusenes, and branched catafusenes. These classes are separated by dividing lines in table 3. For all such catafusenes, our EC partitioning discriminates well the symmetry-non-equivalent rings, and higher correlation coefficients are obtained in comparing them with other measures of local aromaticity. Among the best correlations with our EC partitions one may mention those with NICS(0) ($r^2 = 0.97$), NICS(1) ($r^2 = 0.95$), HOMA ($r^2 = 0.91$), and EN ($r^2 = 0.84$). Other data are too few for correlations; thus, ring energies for rings *A* and *B* in phenanthrene are 0.159β and 0.053β , and in triphenylene 0.191β and 0.024β , respectively, according to ref. 22; ring currents for rings *A* and *B* in chrysene have relative values of 1.152 and 1.068, and in triphenylene 1.109 and 0.748, respectively, according to ref. 21.

Table 2
Catafusenes excluding acenes.

Catafusene	r	EC	HOMA	EN	NICS(0)	NICS(1)	28	27	33	25	26	32	9	23	30	31
Phenanthrene, 6	A	5.2	0.87	0.005	-10.7	-12.6	0.308	0.18	0.898	0.415	0.956	0.937	0.893	0.88	0.3678	0.744
	B	3.6	0.458	0.181	-6.7	-9.6	0.242	0.409	0.772	0.31	0.885	0.853	0.84	0.56	0.36	0.466
Chrysenes, 7	A	5.125	0.85	0.009	-10.5	-12.5		0.204	0.862	0.408	0.952	0.933	0.923	0.85	0.3675	0.713
	B	3.875	0.568	0.119	-7.9	-10.6		0.353	0.8	0.34	0.896	0.864	0.832	0.55	0.3613	0.539
Picene, 8	A	5.154	0.845	0.012	-10.4	-12.4		0.162		0.41					0.3676	
	B	3.769	0.544	0.119	-7.3	-10.1		0.145		0.33					0.3574	
Fulminene, 9	C	4.154	0.669	0.14	-8.9	-11.4		0.254		0.363					0.3609	
	A	5.143	0.856	0.055	-10.4	-12.4										
B	3.81	0.559	0.237	-7.4	-10.2											
	C	4.048	0.643	0.192	-8.4	-11										
[7] Fibonacene, 10	A	5.147	0.856	0.055	-10.4	-12.4										
	B	3.794	0.553	0.24	-7.3	-10.1										
C	4.088	0.659	0.185	-8.5	-11											
	D	3.941	0.618	0.207	-7.9	-10.4										
Tetrahelicene, 11	A	5.125	0.838	0.009			0.304		0.902	0.407	0.952				0.3674	0.713
	B	3.875	0.503	0.173			0.246		0.8	0.34	0.897				0.3613	0.539
Pentahelicene, 12	A	5.154	0.848	0.007												
	B	3.769	0.469	0.153												
C	4.154	0.573	0.129													
	A	4.857	0.834	0.01												
B	3.81	0.466	0.133													
	C	4.048	0.487	0.081												
Heptahelicene, 14	A	5.147	0.824	0.003												
	B	3.794	0.624	0.159												
C	4.088	0.67	0.129													
	D	3.941	0.737	0.13												
Benz[<i>a</i>]-anthracene, 15	A	4.857					0.292		0.831	0.376	0.937	0.938	0.899	0.686	0.3659	0.581
	B	4.571					0.368		0.815	0.375	0.908	0.838	0.85	0.743	0.3621	0.602
C	3.286						0.045		0.726	0.28	0.872	0.862	0.793	0.4	0.3587	0.353
	D	5.286					0.3		0.886	0.421	0.957	0.915	0.93	0.914	0.368	0.78

Table 2 (Continued)

Catafusene	r	EC	HOMA	EN	NICS(0)	NICS(1)	28	27	33	25	26	32	9	23	30	31
Dibenz[<i>a,f</i>]-anthracene, 16	A	5.25														0.3679
	B	3.42														0.3591
	C	4.67														0.3627
Dibenz[<i>a,h</i>]-anthracene, 17	A	5.25					0.304	0.129					0.929	0.9	0.3679	
	B	3.42					0.144	0.438					0.8	0.467	0.3591	
	C	4.67					0.384	0.208					0.863	0.8	0.3622	
Pentaphene, 18	A	4.9					0.294						0.901		0.366	
	B	4.6					0.303						0.851		0.3623	
	C	3					-0.032						0.772		0.3573	
Triphenylene, 19	A	5.333					0.205	0.245		0.43	0.963	0.948	0.94	0.933	0.3686	0.8
	B	2					0.311	0.47		0.294	0.821	0.777	0.714	0.356	0.353	0.318
Dibenz[<i>a,c</i>]-anthracene, 20	A	4.923						0.277					0.903	0.738	0.3661	
	B	4.615						0.251					0.859	0.769	0.3629	
	C	1.692						0.53					0.694	0.246	0.3516	
	D	5.385						0.11					0.942	0.954	0.3688	
Dibenzo[<i>e,n</i>]-chrysene, 21	A	5.25											0.013			
	B	2.5											0.473			

5. Perifusenes

Data for local aromaticity in rings of peri-condensed benzenoids are displayed in table 3. Because HOMA and EN indices are determined from molecular geometries determined experimentally either by X-ray or by neutron diffraction, data for pyrene are given for both techniques. A special mention should be made for the last benzenoid (**27**) in table 3: it has a center-symmetric structure, but because of steric repulsions the molecule is not perfectly planar [35]. Local aromaticities for its rings were estimated by Randić's graph-theoretical procedure (GT) [30], and by the relative ring energy content [14]. Again, our EC partitioning correlates fairly well with other, more complicated, measures of local aromaticity such as HOMA ($r^2 = 0.94$) and EN ($r^2 = 0.90$).

Other data are two few correlations; thus for rings *A* and *B* in pyrene have ring resonance values of 0.362 and 0.118, respectively, according to ref. 28; rings *A* and *B* in perylene have local hexagon aromaticity (RLHE) of 0.929 and 0.814 according to ref. 26; rings *A*, *B*, and *C* in anthanthrene (dibenzo[*def,mno*]chry-sene) have aromaticity indices according to Aida and Hosoya of 0.414, 0.404, and 0.609 (HMO) and 0.284, 0.454, and 0.686, respectively (PPP calculations) [20].

On attempting correlations between partitions and other local aromaticity indices for *all* benzenoids **1–27**, despite the similar trends that are evident from the tables, lower correlation coefficients are obtained, e.g., with HOMA values one finds $r^2 = 0.59$.

6. Conclusions

By comparing our recently proposed EC partitions of π -electrons in rings of polycyclic benzenoids with various other local aromaticity indices proposed earlier in the literature it was found that there exists a pronounced parallelism with the HOMA and EN indices, and with NICS values. The highest correlations were found for non-linear catafusenes, and the lowest ones with linear catafusenes (acenes); perifusenes fall in-between.

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