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Correlations between Local Aromaticity Indices of Bipartite Conjugated Hydrocarbons

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Local aromaticity in rings of conjugated hydrocarbons can be measured in a variety of ways. In the present paper, we concentrate on two of these, namely, EC, i.e., the π-electron content or π-electron partition, and ef, the energy effect of cycles. For the central ring in five bipartite conjugated hydrocarbons (anthracene, triphenylene, perylene, coronene, and biphenylene), it was found that EC and ef values are modified in a consistent and predictable manner by annelation with benzenoid rings. Equations are presented for computing EC and ef values for the central ring in terms of three integers representing the numbers of annelated benzenoid rings (A, L, and G for *angular, linear,* and *geminal* annelation, respectively). The coefficients of A and G are positive (A > G) and the coefficient of L is negative for benzenoids, but for biphenylene, the situation is reversed for coefficients in the correlation for ef values.

1. Introduction

In conjugated alternant hydrocarbons having n sp^2-hybridized carbon atoms (therefore also n π-electrons) and h rings, it is possible to ascribe local ring-counts of π-electrons either by *atomic* or by *molecular (bond) contributions*. In polyphenyls, where benzenoid rings are isolated, both of these contributions result in six π-electrons per ring.

In the following, we will examine conjugated alternant hydrocarbons possessing at least one Kekulé structure that have condensed rings, so that two adjacent rings share a CC bond. Restricting provisionally the discussion to polycyclic benzenoids,[1] whenever a carbon atom belongs to no more than two rings, we are dealing with cata-condensed benzenoids (catafusenes), but when there are carbon atoms belonging to three rings ("internal carbon atoms"), we are dealing with peri-condensed benzenoids (perifusenes).[1] The same dichotomy is obtained on considering dualists of benzenoids, i.e., a special type of graphs formed by points situated in centers of benzenoid rings, and by edges connecting points corresponding to adjacent rings (unlike usual graphs, in such dualists, the unbounded face is not associated with a vertex, and angles between edges do matter). Catafusenes have acyclic dualists, and perifusenes have dualists containing three-membered rings. In this report, we will ignore coronafusenes whose dualists have larger rings. The general formula of a linear or branched catafusene is $C_{4h+2}H_{2h+4}$ or C_nH_{n+2-2h}, and the general formula of a perifusene with a "internal carbon atoms" is C_nH_{n+2-2h} or $C_{4h+2-a}H_{2h+4-a}$.[1]

2. The π-Electron Sextet

Although it was recognized as the cause of aromatic character and stabilization by Kekulé and Bamberger in Germany during the late 19th century, the π-electron "aromatic sextet" began to be understood in the 1920s and 1930s by Crocker in the USA, by Armit and Robinson in England, by Pauling and Wheland in the USA, and especially by Erich Hückel in Germany, who recognized that this was one particular case of the Hückel rule

involving $4k + 2$ π-electrons in planar ring with continuous conjugation.[2] However, it was Eric Clar in Germany, then Britain, and then Spain who showed the real power of Robinson's circle symbol for the aromatic sextet, as will be shown briefly further below.[3]

3. Atomic Contributions

Considering catafusenes, from atomic contributions, benzene ($h = 1$) has six π-electrons per ring and naphthalene ($h = 2$) has five π-electrons per ring, but for $h \geq 2$, the situation becomes slightly more complicated. From a formal point of view,[4] a ring sharing only one CC bond, i.e., two π-electrons with another ring (such as the rings in naphthalene $C_{10}H_8$, or the marginal rings anthracene or phenanthrene $C_{14}H_{10}$), gets $4 + 2/2 = 5$ π-electrons per ring, whereas the central ring of these two latter benzenoids, sharing two CC bonds with other rings, gets $2 + 4/2 = 4$ electrons. When a ring shares three CC bonds with other rings, for instance, the central ring of triphenylene $C_{18}H_{12}$, it gets $6/2 = 3$ π-electrons from atomic contributions. The central ring of perylene has two carbon atoms common to three rings and four carbon atoms common to two rings; therefore, it gets 2.667 electrons. A ring in an infinite graphene sheet gets $6/3 = 2$ π-electrons. The same number of electrons results for the central ring of coronene having six carbon atoms to three rings, and for the central ring of biphenylene having four carbon atoms to two rings. However, such formal partitions of the n π-electrons from atomic contributions differ from what is found in reality and may be used only for reference and comparison with more refined π-electron partitions.[4] It will be seen in the following discussion that for the central ring of triphenylene, perylene, coronene, and biphenylene the above electron count is higher than EC values that will be discussed in the next section, whereas for anthracene it is lower.

4. π-Electron Partitions (π-Electron Content (EC), Bond Contributions)

Several other ways were devised for "local aromaticity" indices in benzenoid rings. One of these relies on π-electron

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partitions based on how these electrons are assigned from all resonance (Kekulé) structures to each ring's share. Randić formulated three assumptions,[5] namely, (i) a shared C=C bond contributes with one π-electron to each ring; (ii) an unshared C=C bond in a ring contributes with both π-electrons; and (iii) all resonance structures have equal weights, so that the final partition is the arithmetical average of all C=C bond contributions. The resulting local aromaticity index, which represents the partition of all π-electrons to each ring, is called the π-electron content (EC); this acronym also evokes Eric Clar's name. On the basis of the above assumptions, Randić and Balaban applied this approach to benzenoid catafusenes, perifusenes, coronafusenes, and other conjugated alternant or nonalternant hydrocarbons,[6–9] and compared their π-electron partitions with local aromaticity indices devised by other authors.

5. Energy Effects of Cycles

One of the present authors put forward a method by means of which it was possible to assess the contribution of any individual cycle (present in a polycyclic conjugated molecule) on the total π-electron energy. Details on this "energy effect" (ef) can be found in the reviews[10,11] and elsewhere.[12–16]

The quantity ef is conceived as the difference between the total π-electron energy (tentatively but not necessarily) calculated within the Hückel molecular orbital (HMO) approximation and a quasi-energy, in which the contributions coming from the considered cycle are neglected, whereas contributions coming from any other structural feature are regularly taken into account. Using the mathematical formalism of chemical graph theory,[17] it can be shown that

$$\text{ef} = \text{ef}(G, Z) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z, ix)} \right| dx$$

where G is the molecular graph[17] of the considered polycyclic conjugated molecule, Z is the considered cycle (or ring), and $G - Z$ is the subgraph obtained by deleting the vertices of Z from the molecular graph G. By $\phi(G, x)$ is denoted the characteristic polynomial[17] of the graph G, and $i = (-1)^{1/2}$ is the imaginary unit. The ef values calculated according to the above expression are assumed to be in the (usual) HMO β-units, where β stands for the HMO carbon–carbon resonance integral. Because β is a negative-valued quantity, positive $\text{ef}(G, Z)$ values imply thermodynamic stabilization (caused by the cycle Z). Analogously, if a particular $\text{ef}(G, Z)$ is negative, then the cycle Z destabilizes the underlying conjugated π-electron system. Partisans of "aromaticity" and "local aromaticity" may view rings having positive $\text{ef}(G, Z)$ as aromatic (the greater $\text{ef}(G, Z)$, the greater would be the aromaticity of the ring Z) and rings having negative $\text{ef}(G, Z)$ as antiaromatic (the more negative $\text{ef}(G, Z)$, the greater would be the antiaromaticity of the ring Z).

6. Clarlology

Eric Clar and other chemists formulated several formal requirements for using correctly the circle symbol in benzenoids:[1,3,18,19] (i) circles are never drawn in adjacent hexagons; (ii) the remaining rings must have a Kekulé structure with zero, one, or two double bonds; (iii) as many circles as possible must be drawn subject to the two previous constraints. This last provision ends up in one or several sextet-maximal sextets. When all benzenoid rings are either "empty" or sextet rings, the benzenoid is called "fully benzenoid", "sextet-resonant", or "claromatic" for short.[20] Experimental support for many of

Clar's ideas was obtained from the reactivity or lack of reactivity of polycyclic benzenoids in Diels–Alder reactions,[1,3,21–24] as first demonstrated by Clar and Zander[25] by synthesizing a nonreactive fully benzenoid perifusene with five sextet rings and a reactive isomeric benzenoid with only four such rings. Also, electronic absorption spectra and NMR spectra support many of Clar's ideas.[3]

In polyphenyls, all rings have Clar sextets and this explains the high stability against thermal or radiative degradation of such compounds. The organic moderated and cooled nuclear reactors are using a mixture of *meta-* and *para-*terphenyl. In his lectures, Herman Mark used to show how a transparent sheet of poly(*para-*terphenyl) could be heated with a blow torch until it became red-hot without burning, and was returning to the initial state after cooling.

Clar structures represent the most drastic "winner-takes-all" partition of the n π-electrons in a benzenoid, as exemplified by claromatic benzenoids, e.g., by the assignment of six π-electrons to the two marginal rings of phenanthrene and only two π-electrons to the central ring.

7. A Simple Correlation for π-Electron Partition and Electron Energy

In this communication, we present data revealing the effect of adding a benzenoid ring on the local aromaticity index of a 4- or 6-membered ring once removed from the newly added benzenoid ring. Also, a simple topological correlation will be shown to hold for these effects.

The partition of the 14 π-electrons in phenanthrene according to Randić's convention places 5.2 π-electrons in the marginal rings (whose Clar structure corresponds to sextet rings in a biphenyl-like arrangement) and only 3.6 π-electrons in the central ring. By contrast, in the isomeric anthracene (which, like all acenes, has only one migrating Clar sextet), the marginal rings are assigned 4.75 π-electrons and the central ring 4.50 π-electrons. The 18 π-electrons of triphenylene are partitioned into 2.00 π-electrons in the central ring and 5.33 π-electrons in the marginal rings.

In passing, one should note that most local aromaticity indices indicate higher aromaticity for the marginal rings of anthracene and phenanthrene, in contrast to calculated ring currents or NICS values.[26,27]

It is easy to understand that, on adding to the naphthalene structure a chain of four butadienic CH groups resulting in a new ring in *linear constellation*, the tug-of-war between adjacent rings for the shared π-electrons will take away some of the five π-electrons in the naphthalene ring which becomes the central ring of anthracene. It is also understandable that as a consequence a small part of the π-electron density in the second naphthalene ring will migrate into what is now the middle ring of anthracene. However, it is less easy to provide a rational explanation for what happens when one adds one or two new rings to naphthalene in *angular constellation*, resulting in phenanthrene and triphenylene, respectively. Why is the second naphthalene ring enriched in electrons in these cases? Clar formulas and biphenyl-like conjugation may provide the answer.

In the following paragraphs, we will add in all possible locations a new benzenoid ring at a time to *anthracene, triphenylene, perylene,* and *coronene* for finding what happens to the π-electron partition and energy effects of their central ring. In Figure 1, one can see how the CC outer bonds of these four benzenoids are labeled so that the structure of the expanded system is denoted by the CC bonds that have new benzenoid rings attached to these outer bonds. *Biphenylene* will be a fifth
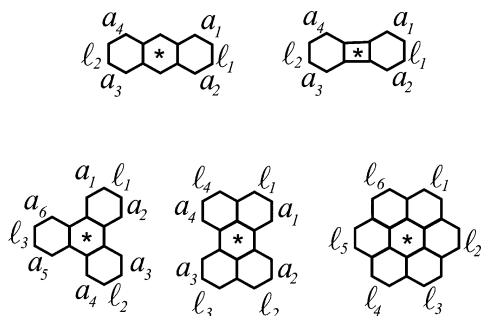
Figure 1. Labeling of outer CC bonds in anthracene, biphenylene, triphenylene, perylene, and coronene.

TABLE 1: π-Electron Partitions and Energy Effects for the Central Ring of (Poly)benzanthracenes

compound	A	L	G	partition (EC)	energy effect (ef)	partition (EC) calc	energy effect (ef) calc
anthracene	**0**	**0**	**0**	**4.500**	**0.0653**	**4.4930**	**0.0632**
l_1	0	1	0	4.400	0.0535	4.3922	0.0505
a_1	1	0	0	4.571	0.0796	4.5768	0.0811
l_1l_2	0	2	0	4.333	0.0453	4.2914	0.0378
a_1l_2	1	1	0	4.444	0.0633	4.4760	0.0684
a_1a_3	2	0	0	4.667	0.1001	4.6606	0.0990
a_1a_4	2	0	0	4.667	0.1002	4.6606	0.0990
a_1a_2	0	0	2	4.615	0.0908	4.6308	0.0966
$a_1a_2l_2$	0	1	2	4.471	0.0710	4.5300	0.0839
$a_1a_2a_3$	1	0	2	4.727	0.1166	4.7146	0.1145
$a_1a_2a_3a_4$	0	0	4	4.800	0.1380	4.7686	0.1300

TABLE 2: π-Electron Partitions and Energy Effects for the Central Ring of (Poly)benzotriphenylenes

compound	A	L	G	partition (EC)	energy effect (ef)	partition (EC) calc	energy effect (ef) calc
triphenylene	**0**	**0**	**0**	**2.0000**	**0.0242**	**1.9918**	**0.0213**
a_1	1	0	0	2.2857	0.0304	2.2898	0.0304
l_1	0	1	0	1.6923	0.0204	1.676	0.0160
a_1a_2	0	0	2	2.5000	0.0360	2.5152	0.0401
a_1a_3	2	0	0	2.5909	0.0390	2.5878	0.0395
a_1a_4	2	0	0	2.5909	0.0390	2.5878	0.0395
a_2a_3	2	0	0	2.5909	0.0389	2.5878	0.0395
l_1a_3	1	1	0	1.9500	0.0249	1.974	0.0251
l_1a_4	1	1	0	1.9500	0.0249	1.974	0.0251
l_1l_2	0	2	0	1.4211	0.0179	1.3602	0.0107
$a_1a_2a_3$	1	0	2	2.8158	0.0466	2.8132	0.0492
$a_1a_2a_4$	1	0	2	2.8158	0.0467	2.8132	0.0492
$a_1a_3a_5$	3	0	0	2.9143	0.0511	2.8858	0.0486
$a_1a_3a_6$	3	0	0	2.9143	0.0510	2.8858	0.0486
$a_1a_2l_2$	0	1	2	2.1471	0.0289	2.1994	0.0348
$a_1a_3l_3$	2	1	0	2.2258	0.0310	2.2720	0.0342
$a_1a_4l_3$	2	1	0	2.2258	0.0310	2.2720	0.0342
$a_2a_3l_3$	2	1	0	2.2258	0.0309	2.2720	0.0342
$a_1l_2l_3$	1	2	0	1.6552	0.0212	1.6582	0.0198
$l_1l_2l_3$	0	3	0	1.1786	0.0161	1.0444	0.0054
$a_1a_2a_3a_4$	0	0	4	3.0455	0.0562	3.0386	0.0589
$a_1a_2a_3a_5$	2	0	2	3.1475	0.0616	3.1112	0.0583
$a_1a_2a_3a_6$	2	0	2	3.1475	0.0615	3.1112	0.0583
$a_1a_2a_4a_5$	2	0	2	3.1475	0.0617	3.1112	0.0583
$a_1a_2a_3l_3$	1	1	2	2.4340	0.0364	2.4974	0.0439
$a_1a_2l_2a_5$	1	1	2	2.4340	0.0365	2.4974	0.0439
$a_1a_2l_2l_3$	0	2	2	1.8367	0.0242	1.8836	0.0295
$a_1a_2a_3a_4a_5$	1	0	4	3.3832	0.0748	3.3366	0.0680
$a_1a_2a_3a_4l_3$	0	1	4	2.6484	0.0432	2.7228	0.0536
$a_1a_2a_3a_4a_5a_6$	0	0	6	3.6190	0.0910	3.5620	0.0777

Figure 2. For the central ring of (poly)benzanthracenes, plots of EC(calc) (=EC calculated according to eq 1) versus the exact EC values (a), ef(calc) (=ef calculated according to eq 2) versus the exact ef values (b), and ef versus EC (c).

bipartite conjugated hydrocarbon to become expanded by addition of benzenoid rings, and the outer CC bonds will be labeled exactly as for anthracene.

It will be observed that the topology of these hydrocarbons allows three types of annelations for anthracene, triphenylene, and biphenylene, namely, linear annelation (denoted by *l*), a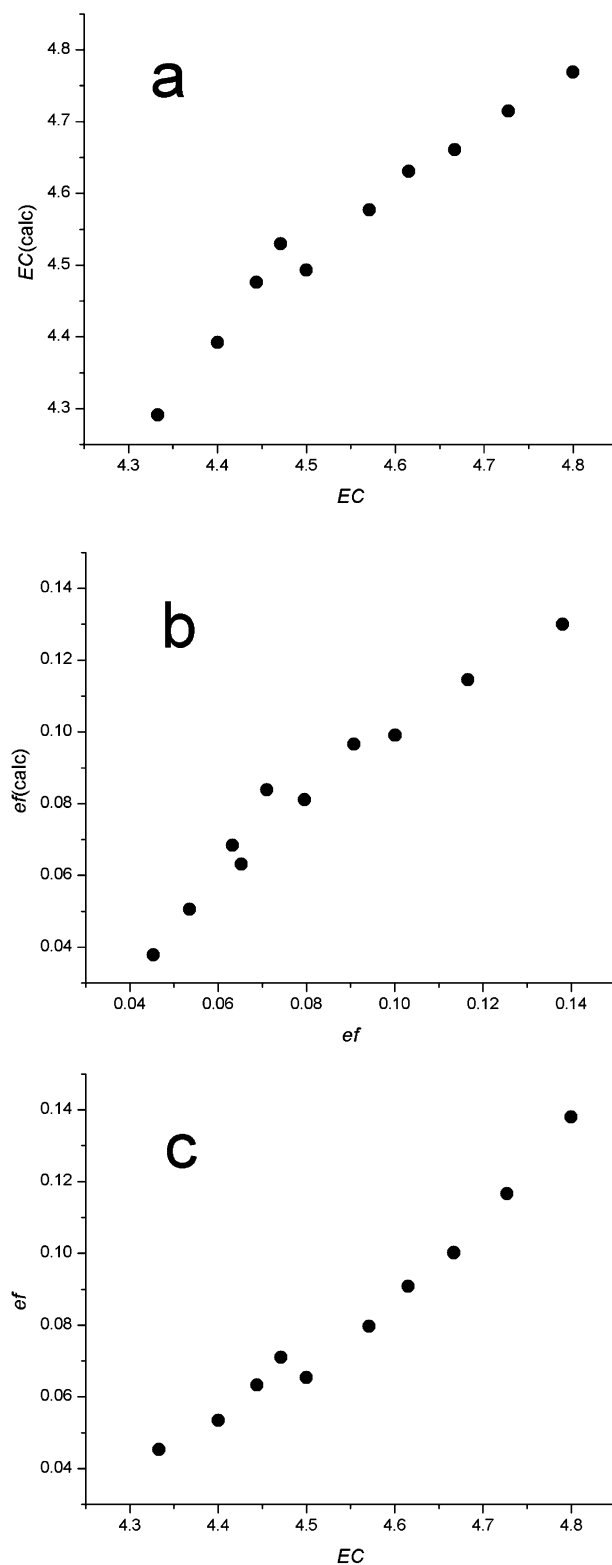ngular annelation (denoted by *a*)—in both of these cases, one new benzenoid ring is attached to a peripheral ring—and geminal annelation (denoted by *g*), when two new rings are attached to a peripheral ring. For perylene, only *l*-type and *a*-type annelations are possible, whereas, for coronene, only *l*-type annelation is possible.

Local Aromaticity of Bipartite Conjugated Hydrocarbons

J. Phys. Chem. A, Vol. 114, No. 18, 2010 **5873**

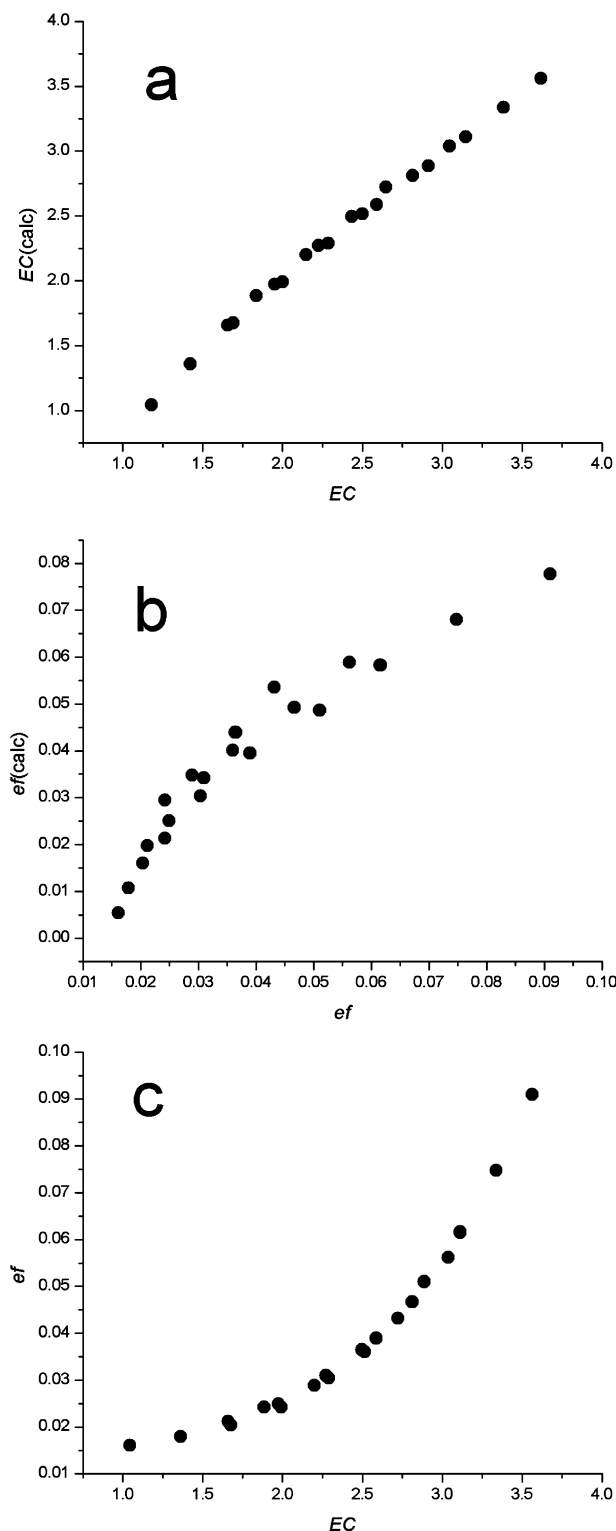**Figure 3.** For the central ring of (poly)benzotriphenylenes, plots of EC(calc) (=EC calculated according to eq 3) versus the exact EC values (a), ef(calc) (=ef calculated according to eq 4) versus the exact ef values (b), and ef versus EC (c).

TABLE 3: π-Electron Partitions and Energy Effects for the Central Ring of (Poly)benzoperylenes

compound	A	L	EC	energy effect (ef)	EC calc	energy effect (ef) calc
perylene	**0**	**0**	**1.3333**	**0.0218**	**1.3364**	**0.0212**
a_1	1	0	1.4167	0.0263	1.4169	0.0272
l_1	0	1	1.2667	0.0207	1.2669	0.0196
a_1a_2	2	0	1.5000	0.0322	1.4973	0.0332
a_1a_3	2	0	1.5000	0.0324	1.4973	0.0332
a_1a_4	2	0	*1.4667*	*0.0325*	1.4973	0.0332
a_1l_2	1	1	1.3500	0.0248	1.3473	0.0256
a_1l_3	1	1	1.3500	0.0248	1.3473	0.0256
a_1l_4	1	1	*1.3810*	*0.0247*	1.3473	0.0256
l_1l_2	0	2	1.2000	0.0197	1.1973	0.0180
l_1l_3	0	2	1.2000	0.0197	1.1973	0.0180
l_1l_4	0	2	*1.1667*	*0.0193*	1.1973	0.0180
$a_1a_2a_3$	3	0	1.5500	0.0407	1.5777	0.0392
$a_1a_2l_4$	2	1	1.4643	0.0300	1.4277	0.0316
$a_1a_3l_4$	2	1	1.4643	0.0302	1.4277	0.0316
$a_1a_4l_2$	2	1	*1.4000*	*0.0303*	1.4277	0.0316
$a_1l_2l_4$	1	2	1.3143	0.0234	1.2777	0.0240
$a_1l_3l_4$	1	2	1.3143	0.0234	1.2777	0.0240
$a_1l_2l_3$	1	2	*1.2500*	*0.0227*	1.2777	0.0240
$l_1l_2l_4$	0	3	1.1000	0.0184	1.1277	0.0164
$a_1a_2a_3a_4$	4	0	1.6000	0.0522	1.6581	0.0452
$a_1a_2a_3l_4$	3	1	1.5143	0.0376	1.5081	0.0376
$a_1a_2l_3l_4$	2	2	1.4286	0.0281	1.3581	0.0300
$a_1a_3l_2l_4$	2	2	1.4286	0.0283	1.3581	0.0300
$a_1a_4l_2l_3$	2	2	*1.3000*	*0.0274*	1.3581	0.0300
$a_1l_2l_3l_4$	1	3	1.2143	0.0216	1.2081	0.0224
$l_1l_2l_3l_4$	0	4	1.0000	0.0173	1.0581	0.0148

agreement with those of Aihara's paper.[15] The numbers of benzenoid rings attached by *a*-, *l*-, and *g*-type annelation are indicated in columns designated by *A*, *L*, and *G*.

On comparing the EC and ef values for the central ring of anthracene before and after annelation, it can be observed that *a*-type and *g*-type annelations always increase, and *l*-type annelation decreases the value for the central ring. This difference for EC is not influenced at all by the annelation according to a_1a_3 or a_1a_4 topologies, and for the ef effect, the values for these two isomers of dibenzanthracene are practically identical.

What is even more interesting is that the EC and ef values depend practically linearly on three integers (*A*, *L*, and *G*) representing the numbers of *a*-type, *l*-type, and *g*-type annelations, as shown by eq 1 and by the plot of Figure 2a, in which the EC value calculated according to this equation is represented as a function of the original EC value. For the ef values, a similar equation (eq 2) holds. The plot of Figure 2b is analogous to Figure 2a. As shown in Figure 2c, EC and ef values are well correlated with other.

$$EC \approx EC_0 + x_1A + x_2L + x_3G \qquad (1)$$

$EC_0 = 4.4930$; $x_1 = 0.0838$; $x_2 = -0.1008$; $x_3 = 0.0689$; correlation coefficient $= 0.9814$.

$$ef \approx ef_0 + y_1A + y_2L + y_3G \qquad (2)$$

$ef_0 = 0.0632$; $y_1 = 0.0179$; $y_2 = -0.0127$; $y_3 = 0.0167$; correlation coefficient $= 0.9765$.

Table 2 presents the analogous data for all possible (=30) (poly)benzotriphenylenes; the first entry (boldface) is for triph-
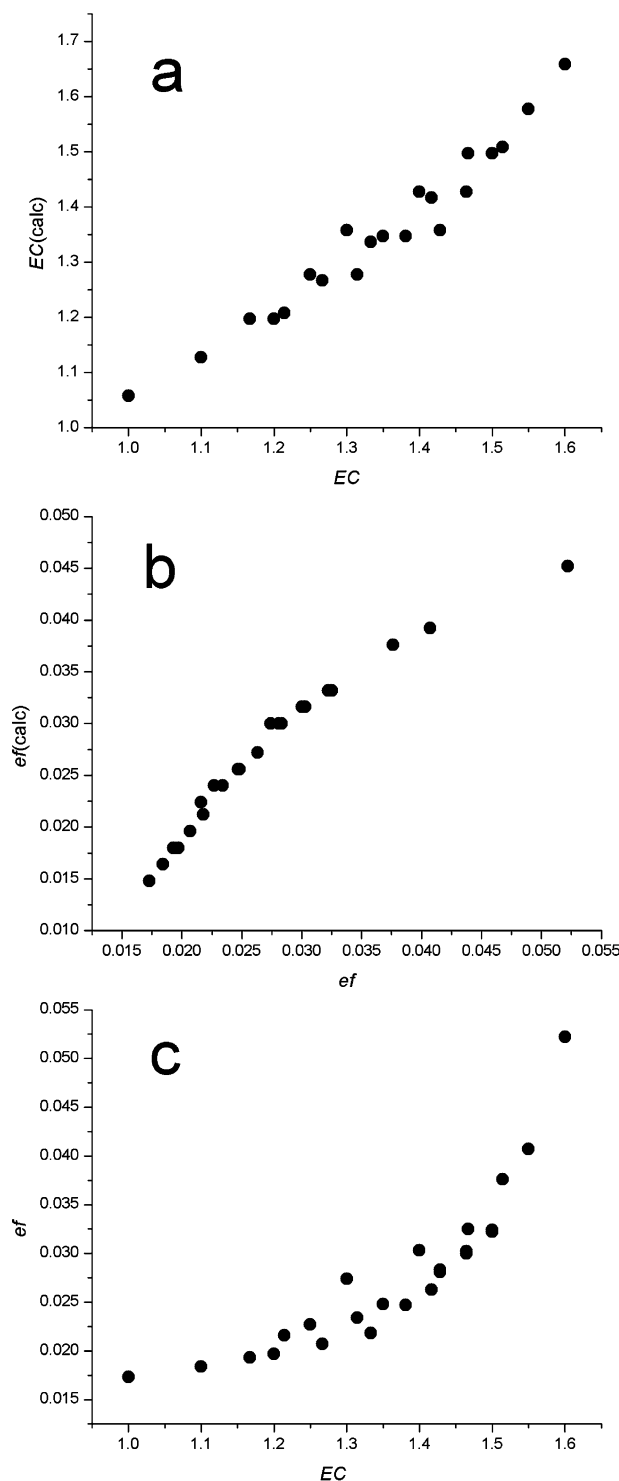
8. Results and Discussion

In Table 1, we present for all possible (=10) (poly)benzanthracenes the π-electron partitions and energy effects of the central ring (indicated by an asterisk in Figure 1). Here, benzenoid rings are attached by *a*-type, *l*-type, and *g*-type annelation to anthracene (whose EC and ef values are indicated in boldface in the first row). The ef values are in complete

Balaban et al.

$$EC \approx EC_0 + x_1A + x_2L + x_3G \qquad (3)$$

$EC_0 = 1.9918$; $x_1 = 0.2980$; $x_2 = -0.3158$; $x_3 = 0.2617$; correlation coefficient = 0.9971.

$$ef \approx ef_0 + y_1A + y_2L + y_3G \qquad (4)$$

$ef_0 = 0.0213$; $y_1 = 0.0091$; $y_2 = -0.0053$; $y_3 = 0.0094$; correlation coefficient = 0.9540.

In Table 3, we present data for all possible (=26) (poly)benzoperylenes and for perylene itself (first row with boldface values). As it is well-known, unlike the benzenoids disussed so far, perylene is the smallest essentially disconnected benzenoid because in all of its resonance structures the central ring has two fixed single bonds, separating the two naphthalene subgraphs. We can speak of a North/South barrier between these naphthalene subgraphs. In this case, even for isomeric systems having the same pairs of A and L values, there is a difference, marked by the fact that one isomer (indicated by italicized numbers with smaller values) with annelations involving no crossing of this barrier has slightly different EC values than those for other isomers that do involve such crossings. For the ef values, a similar situation occurs but the differences are smaller. Equation 5 for EC values and eq 6 for ef values give rise to the plots presented in Figure 4 by analogy with previous cases. Here again, EC and ef values are not correlated linearly.

$$EC \approx EC_0 + x_1A + x_2L \qquad (5)$$

$EC_0 = 1.3364$; $x_1 = 0.0804$; $x_2 = -0.0696$; correlation coefficient = 0.9702.

$$ef \approx ef_0 + y_1A + y_2L \qquad (6)$$

$ef_0 = 0.0212$; $y_1 = 0.0060$; $y_2 = -0.016$; correlation coefficient = 0.9678.

For (poly)benzocoronenes, EC and ef values are displayed in Table 4. It will be observed that isomeric systems with the same L values present differences according to whether they involve annelated rings that are or are not in biphenyl-type conjugation. Equation 7 for EC values and eq 8 for ef values lead to plots a, b, and c in Figure 5 showing fair linearity.

Figure 4. For the central ring of (poly)benzoperylenes, plots of EC(calc) (=EC calculated according to eq 5) versus the exact EC values (a), ef(calc) (=ef calculated according to eq 6) versus the exact ef values (b), and ef versus EC (c).

enylene itself. It can be observed that, whenever the triplet values for A, L, and G are the same, the partitions EC are identical and the ef values have almost identical values. Again, eq 3 holds for EC values and eq 4 for ef values. The plot of Figure 3a indicates that calculated and original EC values present an excellent correlation, but the plot of Figure 3b shows that ef values provide only a satisfactory correlation with values calculated according to eq 4. The plot of Figure 3c indicates that EC and ef values are far from being linearly correlated.

TABLE 4: π-Electron Partitions and Energy Effects for the Central Ring of (Poly)benzocoronenes

compound	L	partition (EC)	energy effect (ef)	partition (EC) calc	energy effect (ef) calc
coronene	**0**	**1.800**	**0.0298**	**1.8203**	**0.0298**
l_1	1	1.735	0.0284	1.7426	0.0284
l_1l_2	2	1.643	0.0266	1.6649	0.0271
l_1l_3	2	1.695	0.0276	1.6649	0.0271
l_1l_4	2	1.649	0.0269	1.6649	0.0271
$l_1l_2l_3$	3	1.575	0.0254	1.5872	0.0258
$l_1l_2l_4$	3	1.583	0.0257	1.5872	0.0258
$l_1l_3l_5$	3	1.673	0.0271	1.5872	0.0258
$l_1l_2l_3l_4$	4	1.487	0.0241	1.5095	0.0245
$l_1l_2l_4l_5$	4	1.500	0.0245	1.5095	0.0245
$l_1l_2l_3l_5$	4	1.537	0.0248	1.5095	0.0245
$l_1l_2l_3l_4l_5$	5	1.424	0.0232	1.4318	0.0232
$l_1l_2l_3l_4l_5l_6$	6	1.333	0.0219	1.3542	0.0219

Local Aromaticity of Bipartite Conjugated Hydrocarbons

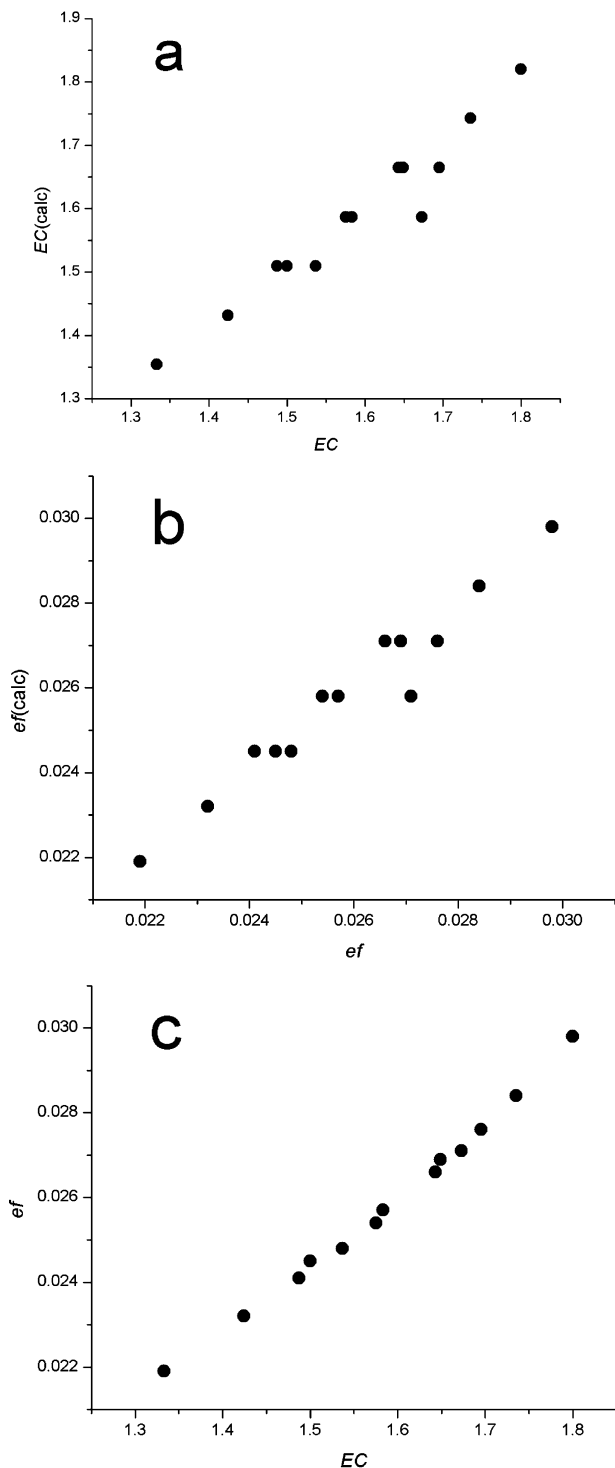*J. Phys. Chem. A, Vol. 114, No. 18, 2010* **5875**

Figure 5. For the central ring of (poly)benzocoronenes, plots of EC(calc) (=EC calculated according to eq 7) versus the exact EC values (a), ef(calc) (=ef calculated according to eq 8) versus the exact ef values (b), and ef versus EC (c).

$$EC \approx EC_0 + x_2 L \qquad (7)$$

$EC_0 = 1.8203$; $x_2 = -0.0777$; correlation coefficient $= 0.9715$.

$$ef \approx ef_0 + y_2 L \qquad (8)$$

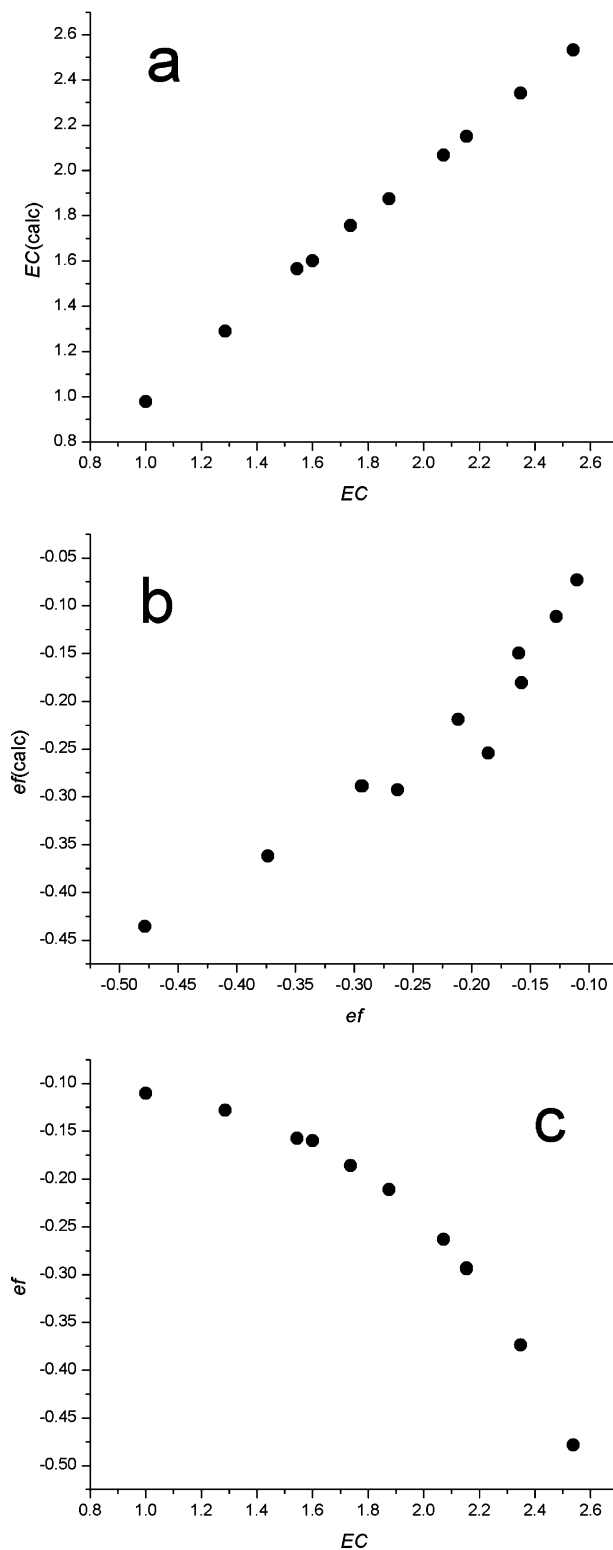$ef_0 = 0.0298$; $y_2 = -0.0013$; correlation coefficient $= 0.9767$.

Figure 6. For the central ring of (poly)benzobiphenylenes, plots of EC(calc) (=EC calculated according to eq 9) versus the exact EC values (a), ef(calc) (=ef calculated according to eq 10) versus the exact ef values (b), and ef versus EC (c).

Finally, Table 5 presents data for all possible (=10) *(poly)-benzobiphenylenes,* in addition to biphenylene, which appears in boldface characters on the first row. For the central four-membered ring, the ef values are negative so that the coefficients of all equations have now changed signs. In this case, eq 9 leads to an excellent correlation for EC values, and eq 10 to a satisfactory correlation for ef values, as further

5876 *J. Phys. Chem. A, Vol. 114, No. 18, 2010*

Balaban et al.

TABLE 5: π-Electron Partitions and Energy Effects for the Central Ring of (Poly)benzobiphenylenes

compound	A	L	G	partition	energy effect	partition calc	energy effect calc
biphenylene	**0**	**0**	**0**	**1.600**	**−0.1598**	**1.6002**	**−0.1496**
l_1	0	1	0	1.286	−0.1280	1.2895	−0.1113
a_1	1	0	0	1.875	−0.2113	1.8754	−0.2191
l_1l_2	0	2	0	1.000	−0.1104	0.9788	−0.0730
a_1l_2	1	1	0	1.545	−0.1573	1.5647	−0.1808
a_1a_3	2	0	0	2.154	−0.2939	2.1506	−0.2886
a_1a_4	2	0	0	*2.154*	*−0.2930*	2.1506	−0.2886
a_1a_2	0	0	2	2.071	−0.2630	2.0666	−0.2926
$a_1a_2l_2$	0	1	2	1.737	−0.1859	1.7559	−0.2543
$a_1a_2a_3$	1	0	2	2.348	−0.3737	2.3418	−0.3621
$a_1a_2a_3a_4$	0	0	4	2.537	−0.4784	2.5330	−0.4356

revealed by the plots shown in Figure 6a and b. Interestingly, unlike all other nonlinear c-type plots between EC and ef values, the concavity of the plot in Figure 6c is oriented in the opposite direction from all previous cases because of the changed sign for ef. Also, whereas the signs of coefficients in eq 9 are the same as those for the other topological correlations for EC values, the signs of coefficients in eq 10 are exactly opposite to those of the other correlations for ef values. The explanation for this observation is that the Hückel $4n + 2$ π-electron rule is inherent in ef values (positive for aromatic rings and negative for antiaromatic rings), whereas this rule is ignored when calculating EC values.

$$EC \approx EC_0 + x_1A + x_2L + x_3G \qquad (9)$$

$EC_0 = 1.6002$; $x_1 = 0.2752$; $x_2 = −0.3107$; $x_3 = 0.2332$; correlation coefficient = 0.9997.

$$ef \approx ef_0 + y_1A + y_2L + y_3G \qquad (10)$$

$ef_0 = −0.1496$; $y_1 = −0.0695$; $y_2 = 0.0383$; $y_3 = −0.0715$; correlation coefficient = 0.9601.

It comes as no surprise to see that, in all equations analyzed here, the coefficient of G is slightly lower than the coefficient of A; this means that two angular annelations on the same ring cannot increase the EC value as much as two angular annelations on different rings. This fact had been noted earlier in Clar's book.[3]

According to eqs 1−10, the isomers with the same set of triplet values for A, L, and G have the same *calculated EC* and ef values, as seen in Tables 1−5. However, as one may see in these tables, the EC and ef values may differ slightly according to the topology of annelation, and one isomer in each group has italicized values in Table 3, which could (with additional topological parameters) improve the correlations.

Finally, we would like to mention that in the present paper we did not propose to make a detailed statistical analysis of the correlations shown in Figures 2−6, and thus we included only the linear correlation coefficients in terms of A, L, and G, without elaborating on curvilinear correlations. Readers interested in such statistical fine details may easily arrive at them from data provided in Tables 1−5.

9. Conclusion

In perfect analogy with the ef effect discussed for nonbenzenoid systems having a five-membered central ring (acenaphthylene, fluoranthene, and corannulene), the EC and ef values of the 4- or 6-membered central ring in polycyclic bipartite conjugated molecules are decreased when annelation with a benzenoid ring occurs in linear constellation and increased for angular constellation. However, in such cases, a simple topological regularity was observed in terms of at most three integers indicating the number of annelated benzenoid rings (A, L, and G for the *a*-type, *l*-type, and *g*-type annelation, respectively). Satisfactory or excellent correlations involving these integers are found for annelation effects of the central ring of anthracene, triphenylene, perylene, coronene, and biphenylene. The EC and ef values are correlated with each other in an analogous, but not linear, fashion. No such simple correlations have been found earlier for acenaphthylene, fluoranthene, and corannulene.

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J. Phys. Chem. A, Vol. 114, No. 18, 2010 **5877**

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