

Pairwise energy effect of cyclic conjugation in benzo-annelated perylenes

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Received: 25 November 2009 / Accepted: 16 February 2010 / Published online: 27 March 2010
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Abstract Previous analysis of cyclic conjugation in benzo-annelated perylenes has revealed that annelation of a benzene ring in the angular position increases the extent of cyclic conjugation in the central ring whereas annelation of a benzene ring in the linear position reduces it. We now present a general method for assessing the effect of a ring on the energy effect of cyclic conjugation in another ring. The respective quantity, referred to as the pairwise energy effect, is used to rationalize specific modes of cyclic conjugation in benzo-annelated perylenes.

Keywords Cyclic conjugation · Energy effect · Pairwise energy effect · Perylene · Benzo-annelated perylenes

Introduction

Investigations of cyclic conjugation in polycyclic conjugated molecules have a long history [1–3]. Several different approaches are used to quantify cyclic conjugation [1, 3]. Recent studies of cyclic conjugation in acenaphthylene and fluoranthene-type benzenoid hydrocarbons [4–6] provided some new insight into the details of these phenomena [4–7]. In particular, by using the standard methodology in the analysis of cyclic conjugation [1, 3],

one was not able to assess the mutual interaction of cyclic conjugation in different rings present in the molecule.

In this work we are mainly concerned with the regularities observed in Ref. [8], trying to provide a theoretical explanation thereof. In Ref. [8] it was found that annelation of a ring in the angular position increases the energy effect of the central (“empty”) ring of perylene. The increase of the extent of cyclic conjugation in this ring is proportional to the number of such angular annelations. Another regularity was that annelation in the linear position reduces the energy effect of the central ring of perylene. Characteristic examples illustrating these regularities are given in Fig. 1. It should be noted that the (stabilizing) effect of rings in the angular position is significantly greater than the analogous (destabilizing) effect of rings in the linear position. The regularities communicated in Ref. [8] were found at the HMO level of theory, but in our recent work [9] these were corroborated by using more sophisticated ab initio DFT methods.

Comparing the molecules from Fig. 1 it might look “self-evident” and “immediate” that the reason for the changes of cyclic conjugation in the central ring of perylene derivatives is caused by the annelated rings. But, in principle, when we compare cyclic conjugation (or whichever property) of perylene (**1**) with cyclic conjugation (or whichever property) of any of its derivatives (molecules **2**, **3**, **4**, **5**) we should not neglect the fact that these molecules differ significantly: they have different numbers of carbon and hydrogen atoms, different number of π -electrons, different Kekulé structure counts, etc. In order to overcome the problems arising when different molecules are compared, we developed a method which makes it possible to extract the effect of an individual ring on the energy effect of another ring within the same molecule [10]. The quantity that measures that effect is

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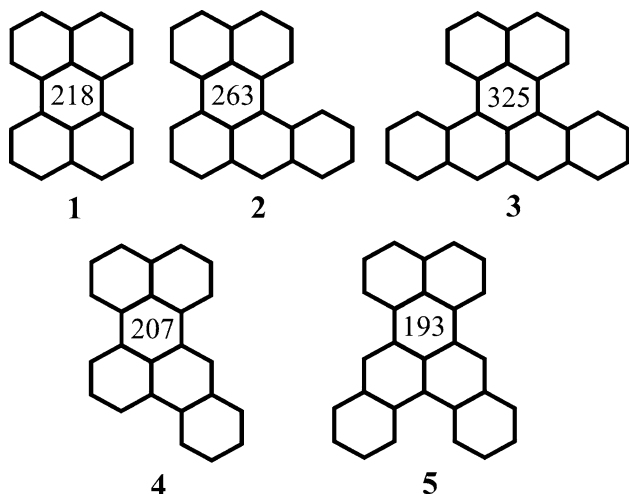


Fig. 1 The energy effect (in β -units $\times 10^4$) of the central ring in perylene (1), and its benzo and dibenzo derivatives (2, 3, 4, 5). From the point of the central ring, the annelated ring(s) can be in the angular position (2 and 3) or in the linear position (4 and 5). For details see Ref. [8]

referred to as the pairwise energy effect (*pef*). In this paper we briefly describe the theory on which *pef* is based, and apply it in the analysis of cyclic conjugation of perylene derivatives.

Results and discussion

The *pef* method

In earlier works [11–14] a method was elaborated for assessing the energy effect (*ef*) of cyclic conjugation in an individual ring of a polycyclic conjugated molecule (for details see Gutman's review [15]). Using the same reasoning as in the original *ef* approach, we introduce the pairwise energy effect, a quantity aimed at measuring the effect of an individual ring on the energy effect of another ring in the same molecule. This consideration is based on the Sachs theorem. Therefore we first recall the basic concepts used for the formulation of the Sachs theorem; details on these matters can be found elsewhere [3, 16–18].

The Sachs theorem establishes the relationship between the structure of a molecular graph and its characteristic polynomial. Bearing in mind that the energy of a conjugated molecule can be obtained from the respective characteristic polynomial, the Sachs theorem provides a relationship between molecular structure and molecular energy.

The Sachs graphs of the given molecular graph are any subgraphs consisting of disjoint rings and/or connected two-vertex graphs K_2 . Also the empty graph (possessing no rings and no K_2 -graphs) is considered a Sachs graph of the

given graph. The set of all Sachs graphs of a molecular graph G will be denoted by $\mathbb{S}(G)$. The Sachs theorem can then be written in the following way:

$$\phi(G, \lambda) = \sum_{S \in \mathbb{S}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} \quad (1)$$

where summation is over all the Sachs graphs contained in G , and where n , $p(S)$, $c(S)$, and $n(S)$ denote the number of vertices of the molecular graph G (i.e. the number of carbon atoms), and the number of components, cyclic components, and vertices of the Sachs graph S , respectively.

We now show how the effect of some rings can be excluded from the characteristic polynomial.

From the definition of Sachs graphs and Eq. 1 we see that $\phi(G, \lambda)$ contains contributions from all the rings present in the molecular graph G . Now, we will be interested in expressions in which the contributions of some particular rings are excluded. Let us consider two disjoint rings Z_a and Z_b contained in the graph G . In the case of the molecular graphs of perylene derivatives, Z_a may be the central ring, and Z_b an annelated ring (Fig. 2). By $\mathbb{S}_a(G)$, $\mathbb{S}_b(G)$, and $\mathbb{S}_{ab}(G)$ we denote, respectively, the set of Sachs graphs of G which contain (as component) Z_a , the set of Sachs graphs of G which contain (as component) Z_b , and the set of Sachs graphs of G which contain (as components) both Z_a and Z_b .

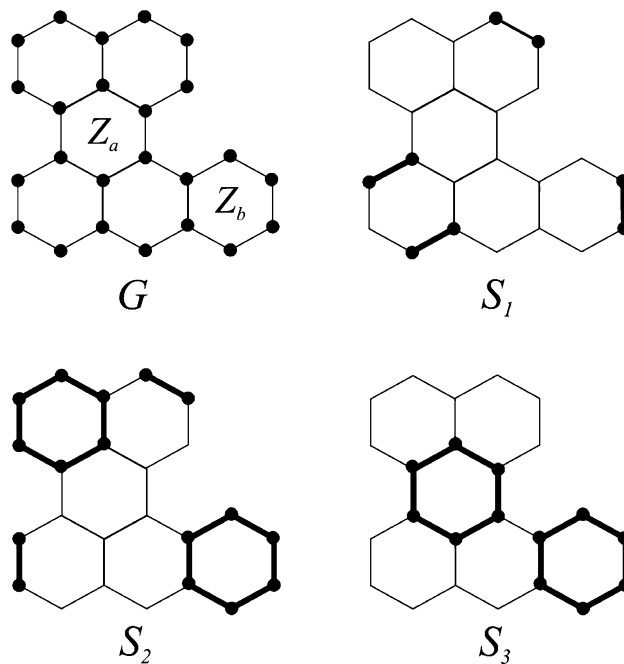


Fig. 2 The molecular graph of benzoperylene (G) and its rings Z_a and Z_b . Heavy lines indicate three Sachs graphs of G . The Sachs graph S_1 has four components, $p(S_1) = 4$, of which none is cyclic, $c(S_1) = 0$, and 10 vertices, $n(S_1) = 10$. Analogously, $p(S_2) = 4$, $c(S_2) = 2$, $n(S_2) = 16$; $p(S_3) = 2$, $c(S_3) = 2$, $n(S_3) = 12$

Consider an element S of $\mathbb{S}_a(G)$. By definition, one component of S is the ring Z_a . If this ring is deleted from the Sachs graph S , what remains is a Sachs graph of the subgraph $G - Z_a$. It is easy to see that there is a one-to-one correspondence between the elements of $\mathbb{S}_a(G)$ and $\mathbb{S}(G - Z_a)$ (Fig. 3). If $S' \in \mathbb{S}(G - Z_a)$ corresponds to $S \in \mathbb{S}_a(G)$, then $p(S') = p(S) - 1$, $c(S') = c(S) - 1$ and $n(S') = n(S) - |Z_a|$, where $|Z_a|$ is the number of vertices (= size) of the ring Z_a . Because, in addition, $n(G - Z_a) = n(G) - |Z_a|$ we obtain

$$\sum_{S \in \mathbb{S}_a(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} = (-1)^1 2^1 \\ \times \sum_{S' \in \mathbb{S}(G-Z_a)} (-1)^{p(S')} 2^{c(S')} \lambda^{n-n(S')} = -2\varphi(G - Z_a, \lambda)$$

In a fully analogous manner we have

$$\sum_{S \in \mathbb{S}_b(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} = (-1)^1 2^1 \\ \times \sum_{S' \in \mathbb{S}(G-Z_b)} (-1)^{p(S')} 2^{c(S')} \lambda^{n-n(S')} = -2\varphi(G - Z_b, \lambda)$$

If $S \in \mathbb{S}_{ab}(G)$, then S contains as components both Z_a and Z_b . If these rings are deleted from S , what remains is a Sachs graph of the subgraph $G - Z_a - Z_b$. Again, there is a one-to-one correspondence between the elements of $\mathbb{S}_{ab}(G)$ and $\mathbb{S}(G - Z_a - Z_b)$. If $S' \in \mathbb{S}(G - Z_a - Z_b)$ corresponds to $S \in \mathbb{S}_{ab}(G)$, then $p(S') = p(S) - 2$, $c(S') = c(S) - 2$ and $n(S') = n(S) - |Z_a| - |Z_b|$. In addition, $n(G - Z_a - Z_b) = n(G) - |Z_a| - |Z_b|$, which implies

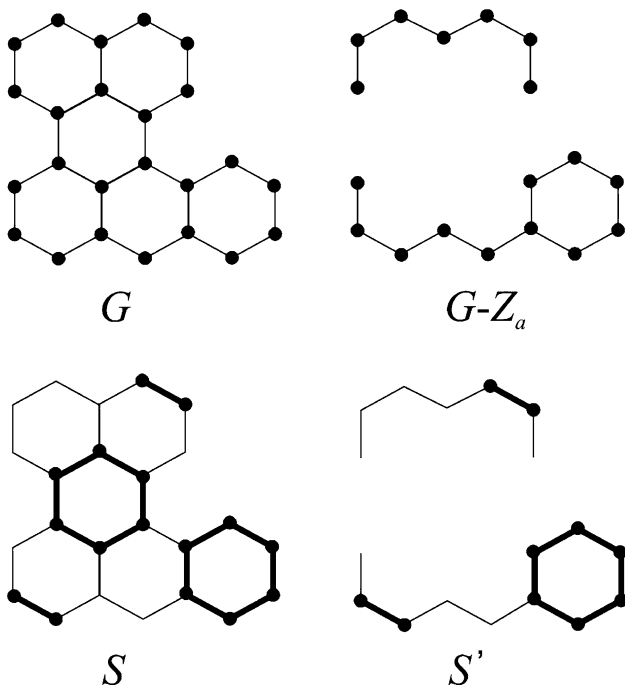


Fig. 3 The molecular graph G and its ring-deleted subgraph $G - Z_a$. The Sachs graphs S of G correspond to the Sachs graph S' of $G - Z_a$; for details see text

$$\sum_{S \in \mathbb{S}_{ab}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} = (-1)^2 2^2 \\ \times \sum_{S' \in \mathbb{S}(G-Z_a-Z_b)} (-1)^{p(S')} 2^{c(S')} \lambda^{n-n(S')} = 4\varphi(G - Z_a - Z_b, \lambda)$$

Now the reference polynomial, resembling the characteristic polynomial, from which the effect of the ring Z_a is excluded, is obtained as the difference between $\phi(G, \lambda)$ and $-2\phi(G - Z_a, \lambda)$, which (i.e. the difference) thus represents the part of $\phi(G, \lambda)$ in which all structural details contribute, except those associated with the ring Z_a :

$$\phi(G \setminus Z_a) = \phi(G, \lambda) + 2\phi(G - Z_a, \lambda) \quad (2)$$

Analogously, the polynomial from which the contribution of ring Z_b has been excluded is:

$$\phi(G \setminus Z_b) = \phi(G, \lambda) + 2\phi(G - Z_b, \lambda). \quad (3)$$

If we want to exclude from the characteristic polynomial the contributions of both rings Z_a and Z_b , then we have:

$$\phi(G \setminus Z_a, Z_b) = \phi(G, \lambda) + 2\phi(G - Z_a, \lambda) + 2\phi(G - Z_b, \lambda) \\ + 4\phi(G - Z_a - Z_b, \lambda) \quad (4)$$

Note that the last term on the right-hand side of Eq. 4 had to be added because any Sachs graph $S \in \mathbb{S}_{ab}(G)$ is contained in both $\mathbb{S}_a(G)$ and $\mathbb{S}_b(G)$. A more detailed derivation of Eqs. 2–4 is given in Ref. [10].

Within the HMO approximation, the total π -electron energy E_π of a conjugated molecule can be calculated from the characteristic polynomial of the underlying molecular graph. If we restrict our considerations to benzenoid hydrocarbons, then using the Coulson [19] integral formula, E_π can be directly related with the characteristic polynomial. For this, the following form of the Coulson integral formula is suitable:

$$E_\pi(G_1) - E_\pi(G_2) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\phi(G_1, ix)}{\phi(G_2, ix)} dx, \quad (5)$$

where $\phi(G_1, \lambda)$ and $\phi(G_2, \lambda)$ are the characteristic polynomials of the equal-sized molecular graphs G_1 and G_2 , respectively, and $i = \sqrt{-1}$.

The difference between the true molecule energy, calculated from its characteristic polynomial, and the energy-like quantity calculated from the reference polynomial that has no contributions from a particular ring, is interpreted as the energy effect of that ring, ef [11–15]. The quantity ef can be calculated from the following expression, which is obtained by combining Eq. 5 with Eq. 2:

$$ef(G; Z_a) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z_a, ix)} dx$$

Both ef and the below described pef are expressed in units of the HMO carbon–carbon resonance integral β . It is important to note that because the value of β is negative, positive values of ef and pef indicate a stabilizing effect caused by cyclic conjugation in the given ring(s).

The measure of effect of the ring Z_b on the ef value of the ring Z_a can be calculated as the difference between $ef(G; Z_a)$ and the reference energy effect $ef(G \setminus Z_b; Z_a)$ which corresponds to ef of the ring Z_a without contributions from the ring Z_b . Combining Eq. 5 with Eqs. 2, 3, and 4 we obtain:

$$pef(G; Z_a, Z_b) = \frac{1}{\pi} \int_{-\infty}^{\infty} \ln \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z_a, ix)} dx - \frac{1}{\pi} \int_{-\infty}^{\infty} \ln \frac{\phi(G, ix) + 2\phi(G - Z_b, ix)}{\phi(G, ix) + 2\phi(G - Z_a, ix) + 2\phi(G - Z_b, ix) + 4\phi(G - Z_a - Z_b, ix)} dx$$

i.e.,

$$pef(G; Z_a, Z_b) = \frac{1}{\pi} \int_{-\infty}^{\infty} \ln \frac{\phi(G, ix)[\phi(G, ix) + 2\phi(G - Z_a, ix) + 2\phi(G - Z_b, ix) + 4\phi(G - Z_a - Z_b, ix)]}{[\phi(G, ix) + 2\phi(G - Z_a, ix)][\phi(G, ix) + 2\phi(G - Z_b, ix)]} dx \quad (6)$$

It is easy to see that

$$pef(Z_a, Z_b) = pef(Z_b, Z_a) \quad (7)$$

Bearing in mind Eq. 7, $pef(Z_a, Z_b)$ can be viewed as the energy effect caused by the interaction of cyclic conjugation in the pair of rings Z_a and Z_b —a pairwise ring energy effect.

Numerical work

The pef values were calculated for all pairs of the central ring and the annelated benzo rings, for all benzo-annelated perylenes. There are two mono, nine di, eight tri, and seven tetrabenzoperylene, a total of 26 distinct benzo-annelated derivatives (Fig. 4 and Table 1). The results obtained are given in Table 1. The calculated pef values are in complete agreement with previously found regularities [8]: In the case of angular arrangement of the central ring and the annelated rings, the value of pef positive, whereas the value of pef is negative for linear constellations. In addition, the absolute values of pef for the rings in the angular arrangement are an order of magnitude greater than those for linear arrangements. In the next section we present a

mathematical analysis and explanation of the pef results obtained.

Mathematical analysis of the $pefs$ of perylene derivatives

Consider now the special case of Eq. 6 when G is the molecular graph of a benzo-annelated perylene, Z_a is its central “empty” ring, and Z_b is one of the annelated six-membered rings. We assume that the molecule is Kekuléan, which implies that the number n of vertices of G is even.

Then the polynomials occurring in Eq. (6) can be written as:

$$\begin{aligned} \phi(G, ix) &= i^n P(x) \\ \phi(G - Z_a, ix) &= i^{n-6} P_a(x) \\ \phi(G - Z_b, ix) &= i^{n-6} P_b(x) \\ \phi(G - Z_a - Z_b, ix) &= i^{n-12} P_{ab}(x) \end{aligned} \quad (8)$$

Combining Eqs. 6 and 8 we obtain:

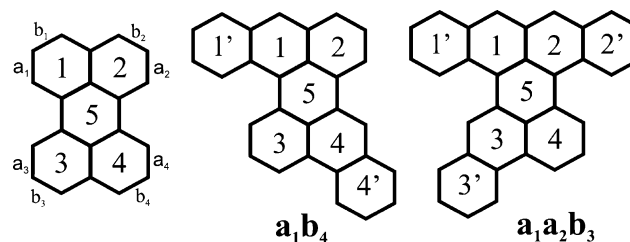


Fig. 4 Labelling of the rings of perylene and its benzo-annelated derivatives; from the point of view of the central ring 5, annelation may be either angular (in positions a_1 , a_2 , a_3 , and a_4) or linear (in positions b_1 , b_2 , b_3 , and b_4). For example, the molecules **2**, **3**, **4**, and **5** from Fig. 1 would be denoted by \mathbf{a}_1 , $\mathbf{a}_1\mathbf{a}_2$, \mathbf{b}_1 , and $\mathbf{b}_1\mathbf{b}_2$. The benzene rings annelated to perylene rings 1, 2, 3, or 4 are labeled $1'$, $2'$, $3'$, or $4'$

Table 1 Pairwise energy effects (in β -units) of the central and annelated rings in benzo-annelated perylenes; for notation see Fig. 4

Compound	Rings	<i>pef</i>
a₁	(5, 1')	0.00185
b₁	(5, 1')	-0.00051
a₁a₂	(5, 1')=(5, 2')	0.00265
a₁a₃	(5, 1')=(5, 3')	0.00254
a₁a₄	(5, 1')=(5, 4')	0.00263
a₁b₂	(5, 1')	0.00180
	(5, 2')	-0.00080
a₁b₃	(5, 1')	0.00165
	(5, 3')	-0.00071
a₁b₄	(5, 1')	0.00166
	(5, 4')	-0.00071
b₁b₂	(5, 1')=(5, 2')	-0.00050
b₁b₃	(5, 1')=(5, 3')	-0.00046
b₁b₄	(5, 4')=(5, 2')	-0.00046
a₁a₂a₃	(5, 1')	0.00366
	(5, 2')	0.00376
	(5, 3')	0.00368
a₁a₂b₃	(5, 1')	0.00234
	(5, 2')	0.00235
	(5, 3')	-0.00100
a₁a₃b₂	(5, 1')	0.00249
	(5, 2')	-0.00011
	(5, 3')	0.00225
a₁a₄b₂	(5, 1')	0.00258
	(5, 2')	-0.00113
	(5, 4')	0.00233
a₁b₂b₃	(5, 1')	0.00160
	(5, 2')	-0.00072
	(5, 3')	-0.00063
a₁b₂b₄	(5, 1')	0.00161
	(5, 2')	-0.00072
	(5, 4')	-0.00064
a₁b₃b₄	(5, 1')	0.00136
	(5, 3')	-0.00069
	(5, 4')	-0.00069
b₁b₂b₃	(5, 1')	-0.00045
	(5, 2')	-0.00045
	(5, 3')	-0.00039
a₁a₂a₃a₄	(5, 1')=(5, 2')=(5, 3')=(5, 4')	0.00526
a₁a₂a₃b₄	(5, 1')	0.00323
	(5, 2')	0.00331
	(5, 3')	0.00366
	(5, 4')	-0.00016
a₁a₂b₃b₄	(5, 1')=(5, 2')	0.00189
	(5, 3')=(5, 4')	-0.00097
a₁a₃b₂b₄	(5, 1')=(5, 3')	0.00220
	(5, 2')=(5, 4')	-0.00100

Table 1 continued

Compound	Rings	<i>pef</i>
a₁a₄b₂b₃	(5, 1')=(5, 4')	0.00227
	(5, 2')=(5, 3')	-0.00100
a₁b₂b₃b₄	(5, 1')	0.00133
	(5, 2')	-0.00059
	(5, 3')	-0.00061
	(5, 4')	-0.00062
b₁b₂b₃b₄	(5, 1')=(5, 2')=(5, 3')=(5, 4')	-0.00038

$$pef(G; Z_a, Z_b) = \frac{2}{\pi} \int_0^\infty \ln \frac{P(x)[P(x) - 2P_a(x) - 2P_b(x) + 4P_a(x)P_b(x)]}{[P(x) - 2P_a(x)][P(x) - 2P_b(x)]} dx \tag{9}$$

A convenient way to write Eq. 9 is:

$$pef(G; Z_a, Z_b) = \frac{2}{\pi} \int_0^\infty \ln[1 + \Gamma(G; Z_a, Z_b, x)] dx \tag{10}$$

where, for the sake of brevity, we introduce the auxiliary function

$$\Gamma(x) = \Gamma(G; Z_a, Z_b, x) = 4 \frac{P(x)P_{ab}(x) - P_a(x)P_b(x)}{[P(x) - 2P_a(x)][P(x) - 2P_b(x)]} \tag{11}$$

It can be shown that the expression

$$\frac{P(x)[P(x) - 2P_a(x) - 2P_b(x) + 4P_a(x)P_b(x)]}{[P(x) - 2P_a(x)][P(x) - 2P_b(x)]}$$

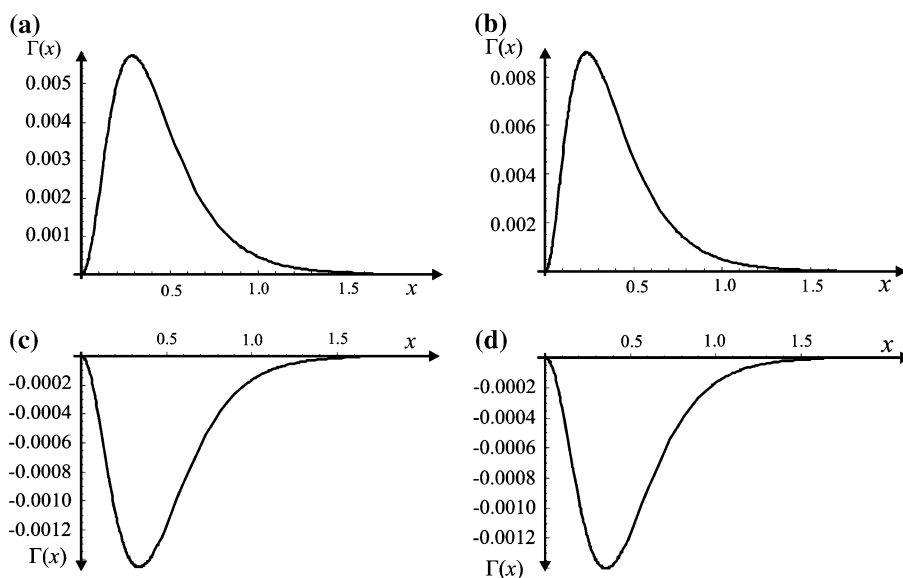
occurring in Eq. 9, is greater than zero for all values of the variable x , $0 \leq x < \infty$. Therefore, $\Gamma(x) > -1$. In fact, our numerical studies indicate that for all values of x , $0 \leq x < \infty$, the value of $|\Gamma(x)|$ is orders of magnitude smaller than unity. A few characteristic examples illustrating these findings are shown in Fig. 5.

In view of this, and recalling that for near-zero t the approximation $\ln(1 + t) \approx t$ can be used, we arrive at:

$$pef(G; Z_a, Z_b) \approx \frac{2}{\pi} \int_0^\infty \Gamma(G; Z_a, Z_b, x) dx \tag{12}$$

From both Eqs. 10 and 12 it is seen that the sign of *pef* depends on the sign of the function $\Gamma(x)$. In particular, if $\Gamma(x) \geq 0$ for all x , $0 \leq x < \infty$, then *pef* will necessarily be positive. Similarly, if $\Gamma(x) \leq 0$ for all x , $0 \leq x < \infty$, then *pef* < 0. In the general case, however, $\Gamma(x)$ may change sign, and then it is less straightforward to predict the sign

Fig. 5 The functions $\Gamma(x) = \Gamma(G; Z_a, Z_b, x)$, defined via Eq. 11, where G is the molecular graph. In diagrams **a**, **b**, **c**, and **d** the graph G pertains to the molecules **2**, **3**, **4**, and **5** from Fig. 1. Z_a is the central “empty” ring, and Z_b the annelated ring of the respective molecule. Note that $\Gamma(x) > 0$ in cases **a** and **b** (angular annelation), whereas $\Gamma(x) < 0$ in cases **c** and **d** (linear annelation)



of pef . Our numerical studies showed that in the case of all perylene derivatives, the sign of the function $\Gamma(x)$ is the same in the entire interval $0 < x < \infty$. Using this (fortunate) fact, the sign of pef can be predicted as follows.

The sign of the function $\Gamma(x)$ (i.e., the sign of pef) is determined by the sign of the polynomial $P(x)P_{ab}(x) - P_a(x)P_b(x)$, occurring in Eq. 11, because $[P(x) - 2P_a(x)][P(x) - 2P_b(x)] > 0$ for all values of the variable x , $0 < x < \infty$. Thus, analysis of the sign of $\Gamma(x)$ is based on examination of the expression $P(x)P_{ab}(x) - P_a(x)P_b(x)$.

The constant term of the characteristic polynomials of benzenoid molecules is equal to the square of the Kekulé structure count. Therefore, because Z_a is the “empty” ring, $P_a(0) = 0$ and $P_{ab}(0) = 0$, implying that $P(x)P_{ab}(x) - P_a(x)P_b(x) = 0$ for $x = 0$, and thus $\Gamma(0) = 0$.

In the case of benzenoid molecules, the polynomials $P(x)$, $P_a(x)$, $P_b(x)$ and $P_{ab}(x)$, defined above by Eq. 8, have the form:

$$c_0x^h + c_1x^{h-2} + c_2x^{h-4} + c_3x^{h-6} + \dots$$

where $c_0, c_1, c_2, c_3, \dots$ are non negative numbers. From the Sachs theorem we know (see, e.g. Ref. [16]) that $c_1 =$ number of edges and $c_2 =$ number of pairs of disjoint edges in the underlying graph. In addition, $c_0 = 1$. Bearing this in mind, consider the edge-set $E(G)$ of the molecular graph G and partition it into subsets $E_a(G)$, $E_b(G)$, and $E_x(G)$, so that:

$E_a(G)$ contains the edges belonging to or incident to Z_a ,
 $E_b(G)$ contains the edges belonging to or incident to Z_b ,
 $E_x(G)$ contains the edges that neither belong to nor are incident to Z_a or Z_b .

In Fig. 6 the edges belonging to $E_a(G)$ are indicated by heavy lines, and the edges belonging to $E_b(G)$ by dashed

lines. One should note that for angular annelation a single edge (marked by an arrow) belongs both to $E_a(G)$ and $E_b(G)$.

For what follows we need to consider pairs of disjoint edges e, f in the graph G and its subgraphs. Denote the number of such pairs by:

$$\begin{aligned} b_{aa} & \text{ if } e \in E_a(G), f \in E_a(G) \\ b_{bb} & \text{ if } e \in E_b(G), f \in E_b(G) \\ b_{xx} & \text{ if } e \in E_x(G), f \in E_x(G) \\ b_{ab} & \text{ if } e \in E_a(G), f \in E_b(G) \text{ or } e \in E_b(G), f \in E_a(G) \\ b_{ax} & \text{ if } e \in E_a(G), f \in E_x(G) \text{ or } e \in E_x(G), f \in E_a(G) \\ b_{bx} & \text{ if } e \in E_b(G), f \in E_x(G) \text{ or } e \in E_x(G), f \in E_b(G) \end{aligned}$$

Then, in view of the fact that the polynomial $P(x)$ pertains to the molecular graph G , whereas $P_a(x)$, $P_b(x)$, and

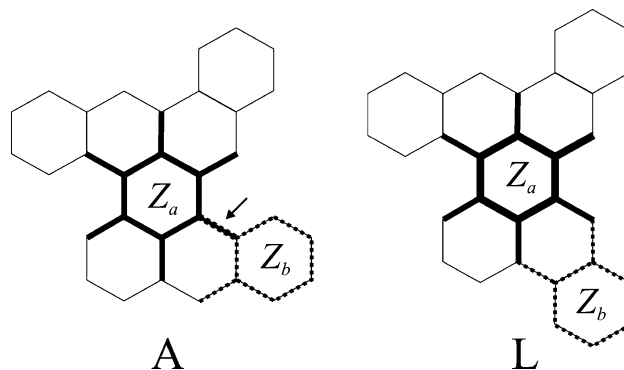


Fig. 6 Angularly and linearly annelated benzoperylenes, **A** and **L**. The edges belonging to or incident to the ring Z_a are marked by heavy lines and form the set $E_a(G)$; the edges belonging to or incident to the ring Z_b are marked by dashed lines and form the set $E_b(G)$. The edge indicated by an arrow (which occurs only in the case of angular annelation) belongs to both $E_a(G)$ and $E_b(G)$

$P_{ab}(x)$ pertain to the subgraphs $G - Z_a$, $G - Z_b$, and $G - Z_a - Z_b$, we have:

$$P(x) = x^h + mx^{h-2} + (b_{aa} + b_{bb} + b_{xx} + b_{ax} + b_{bx} + b_{ab})x^{h-4} + \dots,$$

$$P_a(x) = x^{h-6} + (m-12)x^{h-8} + (b_{bb} + b_{xx} + b_{bx})x^{h-10} + \dots,$$

$$P_b(x) = x^{h-6} + (m-8)x^{h-8} + (b_{aa} + b_{xx} + b_{ax})x^{h-10} + \dots,$$

and

$$P_{ab}(x) = x^{h-12} + (m-19)x^{h-14} + (b_{xx})x^{h-16} + \dots$$

if Z_b is in the angular position, and

$$P_{ab}(x) = x^{h-12} + (m-20)x^{h-14} + (b_{xx})x^{h-16} + \dots$$

if Z_b is in the linear position.

By direct calculation this yields:

$$P(x)P_{ab}(x) - P_a(x)P_b(x) = 1 \cdot x^{2n-14} + (b_{ab} + m - 96)x^{2n-16} + \dots$$

if Z_b is in the angular position, and

$$P(x)P_{ab}(x) - P_a(x)P_b(x) = (b_{ab} - 12 \cdot 8)x^{2n-16} + \dots = -2 \cdot x^{2n-16} + \dots$$

if Z_b is in the linear position, because then $b_{ab} = |E_a(G)| \cdot |E_b(G)| - 2 = 12 \cdot 8 - 2$.

Thus, for large values of x , $P(x)P_{ab}(x) - P_a(x)P_b(x)$ is positive for angular annelation and negative for linear annelation. Because $P(x)P_{ab}(x) - P_a(x)P_b(x) = 0$ for $x = 0$, and assuming that $P(x)P_{ab}(x) - P_a(x)P_b(x)$ does not change sign, we arrive at our final conclusions.

Angularly annelated benzenoid rings increase the intensity of cyclic conjugation in the central “empty” ring

of perylene, i.e., the pairwise energy effect pef is positive. Linearly annelated benzenoid rings reduce the intensity of cyclic conjugation in the central “empty” ring of perylene, i.e., the pairwise energy effect pef is negative.

Acknowledgments S.R. and I.G. were supported by the Serbian Ministry of Science, through Grant no. 144015G. W.L. was supported by the Austrian Science Fund (FWF) (Project 19335-N17).

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