

# Effect of benzo-annellation on cyclic conjugation

Alexandru T. Balaban · Ivan Gutman ·  
Svetlana Jeremić · Jelena Đurđević

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**Abstract** Earlier studies revealed that the effect of benzo-annellation on cyclic conjugation in the central ring of a polycyclic conjugated molecule obeys certain general regularities. We now elaborate quantitative models of this effect, showing that the main factors that need to be taken into account are the numbers of angularly, linearly, and geminally annelated rings.

**Keywords** Aromaticity · Electronic structure ·  $\pi$ -Electron partition ·  $\pi$ -Electron energy · Arenes · Polycyclic aromatic hydrocarbons

## Introduction

The effect of benzo-annellation on the intensity of cyclic conjugation of the central (“empty”) ring of perylene was studied several years ago [1]. The fact that the regularities observed that study are generally valid was recognized only recently, initially based on the investigations of benzo-annellated fluoranthene congeners [2–5], and eventually also on other alternant (benzenoid and non-benzenoid) polycyclic aromatic hydrocarbons [6–8]. The main findings of these

studies can be stated as follows, using the notation explained in Fig. 1:

*Rule 1a:* Suppose that the size of the considered ring (X) is not divisible by four. If the annelated benzo-ring (R) is in angular or geminal position with regard to X (as in **2** and **4** in Fig. 1), then the intensity of cyclic conjugation in X is increased relatively to the non-annelated system (**1** in Fig. 1).

*Rule 1b:* Suppose that the size of the considered ring (X) is divisible by four. If the annelated benzo-ring (R) is in angular or geminal position with regard to X (as in **2** and **4** in Fig. 1), then the intensity of cyclic conjugation in X is decreased relatively to the non-annelated system (**1** in Fig. 1).

*Rule 2a:* Suppose that the size of the considered ring (X) is not divisible by four. If the annelated benzo-ring (R) is in linear position with regard to X (as in **3** in Fig. 1), then the intensity of cyclic conjugation in X is decreased relatively to the non-annelated system (**1** in Fig. 1).

*Rule 2b:* Suppose that the size of the considered ring (X) is divisible by four. If the annelated benzo-ring (R) is in linear position with regard to X (as in **3** in Fig. 1), then the intensity of cyclic conjugation in X is increased relatively to the non-annelated system (**1** in Fig. 1).

Rules 1 and 2 were discovered by means of the energy effects ( $ef$ ) of cyclic conjugation (whose details are outlined in a review [9] and elsewhere [10, 11]; recall that the  $ef$  values are expressed in the units of the Hückel molecular orbital (HMO) carbon–carbon resonance integral  $\beta$ , whose value for thermochemical purposes is around  $-137 \text{ kJ mol}^{-1}$  [12]). Eventually, the rules were corroborated by several other theoretical approaches [4, 13–16].

Another recently developed method for quantifying the cyclic conjugation in a ring of a polycyclic conjugated molecule is to assess the partition of the  $\pi$  electrons into

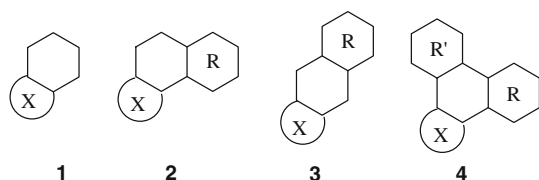
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A. T. Balaban  
Texas A & M University at Galveston,  
Galveston, TX 77551, USA  
e-mail: balabana@tamug.tamu.edu

I. Gutman (✉) · S. Jeremić · J. Đurđević  
Institute of Chemistry, Faculty of Science,  
University of Kragujevac, Kragujevac, Serbia  
e-mail: gutman@kg.ac.rs



**Fig. 1** Two modes of benzo-annulation with regard to the ring X in the non-annelated system (1): If the annelated benzo-ring R is connected to X by a single carbon–carbon bond (as in 2) then R is in an angular position with regard to X. Otherwise (as in 3), R is in a linear position with regard to X. If two benzo rings (R and R') are both angularly annelated (as 4), then these are said to be geminal with regard to ring X

individual rings. Within this approach, one establishes the  $\pi$ -electron content ( $EC$ ) of the respective ring; recall that the  $EC$  values are in fact the number of  $\pi$  electrons in the corresponding ring. The details of the  $EC$  approach can be found in a review [17] and other papers [18–22].

Rules 1 and 2 are qualitative: they speak of increase or decrease of the intensity of cyclic conjugation, but say nothing on the magnitude of these effects. In order to overcome this shortcoming, in our recent work [7] a quantitative, additive scheme was put forward. Namely, it was shown that the  $\pi$ -electron content and the energy effect of the ring X could be reproduced fairly accurately by means of the additive formulas

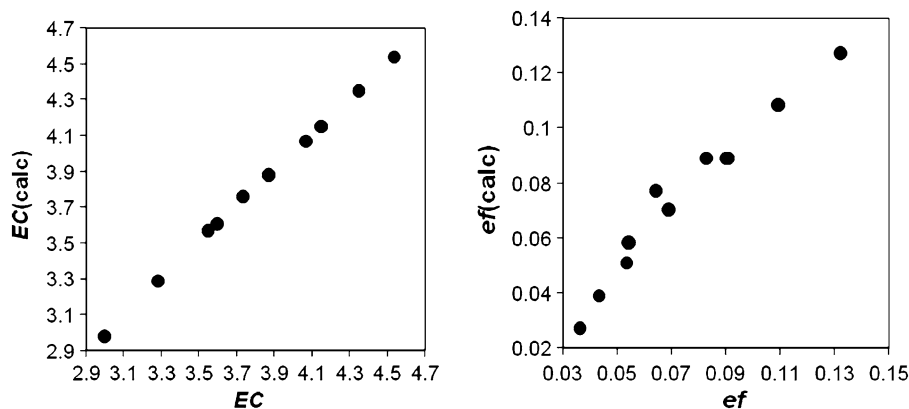
$$EC \approx EC_0 + x_1 A + x_2 L + x_3 G \quad (1)$$

$$ef \approx ef_0 + y_1 A + y_2 L + y_3 G \quad (2)$$

where  $A$ ,  $L$ , and  $G$  are the number of angularly, linearly, and geminally annelated rings, respectively (cf. Fig. 1), whereas  $EC_0$ ,  $x_1$ ,  $x_2$ ,  $x_3$  and  $ef_0$ ,  $y_1$ ,  $y_2$ ,  $y_3$  are empirically determined constants.

As an illustration of the applicability of these proposed models, we consider here phenanthrene and its benzo-annelated congeners. In Fig. 2 the plots of the calculated values of  $EC$  and  $ef$  (according to Eqs. 1, 2) versus their exact values are shown.

**Fig. 2** Application of Eqs. 1 and 2 in the case of benzo-annelated phenanthenes:  $EC(\text{calc})$  are the  $EC$  values calculated according to Eq. 1 with parameters  $EC_0 = 3.60$ ,  $x_1 = 0.27$ ,  $x_2 = -0.31$ ,  $x_3 = 0.23$ ;  $ef(\text{calc})$  are the  $ef$  values calculated according to Eq. 2 with parameters  $ef_0 = 0.051$ ,  $y_1 = 0.019$ ,  $y_2 = -0.012$ ,  $y_3 = 0.019$  (cf. Tables 2, 3)



Analogous plots for several other alternant polycyclic hydrocarbons were communicated in [7] (see also in the “Electronic supplementary material”).

For the considerations that follow, it is important to notice that in the case of benzo-annelated phenanthenes the results of Eq. 1 are visibly better than those of Eq. 2. This happens to be the case with practically all polycyclic alternant hydrocarbons that were examined (both in [7] and the present work, see the “Electronic supplementary material”).

#### Improving the model (Eq. 2)

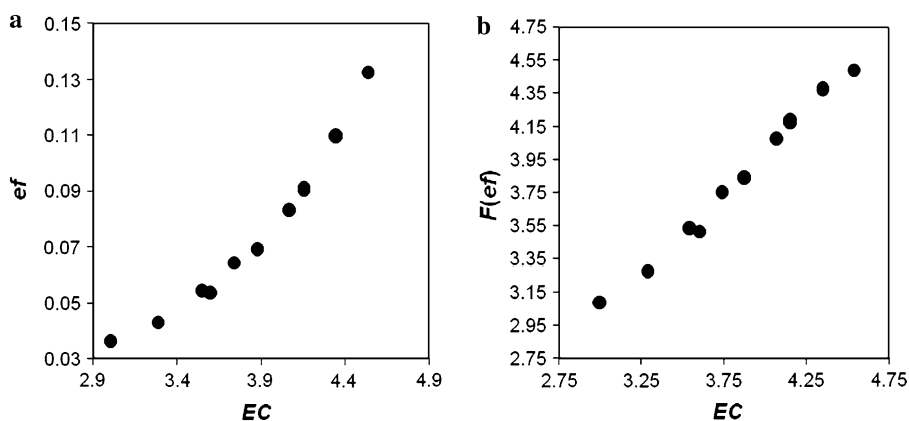
In order to understand why Eq. 2 is less accurate than Eq. 1 it is instructive to view the correlation between  $EC$  and  $ef$ . A characteristic example is provided by the benzo-annelated phenanthenes, see Fig. 3a.

Both in the example shown in Fig. 3a and in the case of other polycyclic aromatic species (see in the “Electronic supplementary material”), the correlation between  $EC$  and  $ef$  is non-linear. Then, since both models (Eqs. 1, 2) are linear, they cannot be both correct at the same time. Since in all studied cases, Eq. 1 yielded better results than Eq. 2, it was a reasonable choice to replace the latter model (Eq. 2) by a non-linear variant:

$$F(ef) \approx ef_0^* + y_1^* A + y_2^* L + y_3^* G \quad (3)$$

where  $F(x)$  is a pertinently chosen function, adjusted so that the correlation between  $EC$  and  $F(ef)$  becomes as close to linear as possible. A trial and error search resulted in a somewhat disappointing finding, namely that the algebraic form of  $F(x)$  depends on the particular class of benzo-annelated conjugated molecules for which it is determined. In order to avoid ambiguities of this kind, we decided to choose the simplest possible non-linear function, i.e., the parabola  $F(x) = \alpha + \beta x + \gamma x^2$ . By this choice the linearization of the  $EC$  versus  $F(ef)$  correlation would not be the best possible, but the model (Eq. 2) would certainly be improved.

**Fig. 3** **a** Correlation between the  $\pi$ -electron contents ( $EC$ ) and energy effect ( $ef$ ) of the central ring of phenanthrene and its benzo-annulated congeners. The correlation is visibly curvilinear. **b** The same data points after linearization; for details see text



That this indeed is the case was confirmed by the detailed numerical testing whose results are outlined in the subsequent section. An example of this kind is shown in Fig. 3b.

#### Numerical work

In order to test Eq. 3, calculations were performed on all benzo-annulated derivatives of five benzenoid (5–9) and four alternant non-benzenoid hydrocarbons (10–13), depicted in Fig. 4. The way in which these benzo-annulated derivatives are labeled is explained by the examples shown in Fig. 5.

Details of the calculations done in the case of phenanthrene (5) are given in Table 1. The analogous results for the remaining eight polycyclic conjugated systems (6–13) can be found in the “Electronic supplementary material”.

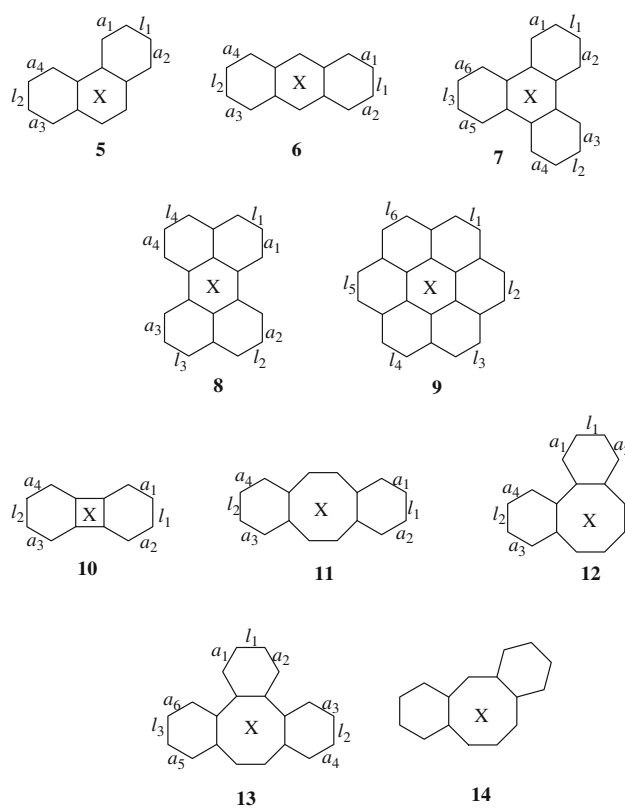
The parameters (obtained by least-squares fitting) needed for the application of Eqs. 1, 2, and 3 are given in Tables 2, 3 and 4, respectively. The parameters  $\alpha$ ,  $\beta$ , and  $\gamma$ , needed for the linearization of the  $EC/F(ef)$  correlation are given in Table 5.

In the case of phenanthrene (5), the quality of the achieved linearization of the correlation between  $\pi$ -electron content ( $EC$ ) and  $\pi$ -electron energy effect ( $ef$ ) is seen in Fig. 3b. The analogous diagrams for the systems 6–13 can be found in the “Electronic supplementary material”.

In all studied cases the model based on Eq. 3 gave better (often, significantly better) results than the one based on Eq. 2. This can be seen from the correlation coefficients given in Table 6.

## Results and discussion

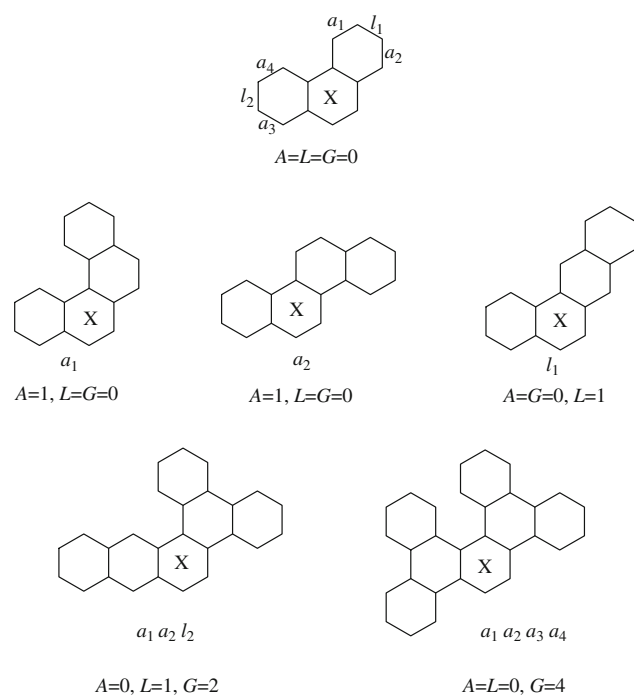
For reasons explained below, we will discuss separately the results obtained for benzenoid molecules (5–9) and for those in which the central ring X is four-membered (10) or eight-membered (11–13).



**Fig. 4** The polycyclic conjugated compounds whose benzo-annulated derivatives are studied in this work, their ring X to which our studies pertain, and the labeling of the sites of annellation, cf. Fig. 5. The conjugated system 14 (structurally similar to 11 and 12) was not analyzed, because it and several of its benzo-annulated derivatives possess non-bonding MOs and therefore their  $ef$  values are not reliable

#### Benzenoid molecules

What first needs to be noticed is that in Table 2 all  $x_1$  and  $x_3$  values are positive, whereas all  $x_2$  values are negative. From Tables 3 and 4 it is seen that the same holds also for the respective  $y$  and  $y^*$  values. These results are in perfect



**Fig. 5** Examples illustrating the labeling of benzo-annulated derivatives of phenanthrene (**5**) in Table 1, and the corresponding values of the parameters  $A$ ,  $L$ , and  $G$  (occurring in Eqs. 1, 2, 3). The labeling of the benzo-annulated derivatives of the compounds **6–13** is analogous, see the “Electronic supplementary material”

**Table 1** Application of Eqs. 1, 2, and 3 to the benzo-annulated derivatives of phenanthrene (**5**)

Compound	$A$	$L$	$G$	$EC$	$ef$	$EC(\text{calc})$	$ef(\text{calc})$	$F(\text{ef})$	$F(\text{ef})(\text{calc})$
<b>5</b>	0	0	0	3.6000	0.0534	3.6010	0.0510	3.5169	3.5829
$a_1$	1	0	0	3.8750	0.0693	3.8760	0.0700	3.8441	3.8483
$a_2$	1	0	0	3.8750	0.0689	3.8760	0.0700	3.8366	3.8483
$l_1$	0	1	0	3.2857	0.0431	3.2880	0.0390	3.2697	3.2732
$a_1a_2$	0	0	2	4.0714	0.0829	4.0690	0.0890	4.0714	4.0283
$a_1a_3$	2	0	0	4.1538	0.0907	4.1510	0.0890	4.1799	4.1677
$a_1a_4$	2	0	0	4.1538	0.0909	4.1510	0.0890	4.1825	4.1677
$a_2a_3$	2	0	0	4.1538	0.0903	4.1510	0.0890	4.1747	4.1677
$a_1l_2$	1	1	0	3.5455	0.0545	3.5630	0.0580	3.5417	3.5927
$l_1a_3$	1	1	0	3.5455	0.0542	3.5630	0.0580	3.5350	3.5927
$l_1l_2$	0	2	0	3.0000	0.0361	2.9750	0.0270	3.0859	3.0177
$a_1a_2a_3$	1	0	2	4.3478	0.1093	4.3440	0.1080	4.3745	4.3477
$a_1a_2l_2$	0	1	2	3.7368	0.0643	3.7560	0.0770	3.7483	3.7727
$a_1a_2a_4$	1	0	2	4.3478	0.1096	4.3440	0.1080	4.3769	4.3477
$a_1a_2a_3a_4$	0	0	4	4.5366	0.1324	4.5370	0.1270	4.4903	4.5277

Compound labels are explained in Figs. 4 and 5.  $F(\text{ef})$  is the transformed value of the  $\pi$ -electron energy effect, calculated by means of  $\alpha + \beta ef + \gamma ef^2$ , cf. Table 5, whereas  $F(\text{ef})(\text{calc})$  is the value calculated by means of Eq. 3, cf. Table 4; for units in which the  $ef$  and  $EC$  values are expressed and for other details see text

agreement with the above stated (qualitative) rules 1a and 2a. In addition, the coefficients given in Tables 2, 3, and 4 make it possible to quantitatively assess the effect of

**Table 2** The fitting parameters occurring in Eq. 1 for the benzo-annulated derivatives of the conjugated compounds shown in Fig. 4

Compound	$EC_0$	$x_1$	$x_2$	$x_3$
<b>5</b>	3.6007	0.2747	-0.3134	0.2336
<b>6</b>	4.4930	0.0838	-0.1008	0.0689
<b>7</b>	1.9918	0.2980	-0.3158	0.2617
<b>8</b>	1.3364	0.0804	-0.0696	
<b>9</b>	1.8203		-0.0777	
<b>10</b>	1.6002	0.2752	-0.3107	0.2332
<b>11</b>	5.6003	0.2751	-0.3107	0.2331
<b>12</b>	5.6007	0.2747	-0.3134	0.2336
<b>13</b>	3.9937	0.2990	-0.3279	0.2608

**Table 3** The fitting parameters occurring in Eq. 2 for the benzo-annulated derivatives of the conjugated compounds shown in Fig. 4

Compound	$ef_0$	$y_1$	$y_2$	$y_3$
<b>5</b>	0.0512	0.0191	-0.0118	0.0186
<b>6</b>	0.0632	0.0179	-0.0127	0.0167
<b>7</b>	0.0213	0.0091	-0.0053	0.0094
<b>8</b>	0.0212	0.0060	-0.0160	
<b>9</b>	0.0298		-0.0013	
<b>10</b>	-0.1496	-0.0695	0.0383	-0.0715
<b>11</b>	-0.0456	-0.0420	0.0245	-0.0432
<b>12</b>	-0.0436	-0.0424	0.0257	-0.0441
<b>13</b>	-0.0080	-0.0153	0.0100	-0.0162

**Table 4** The fitting parameters occurring in Eq. 3 for the benzo-annulated derivatives of the conjugated compounds shown in Fig. 4

Compound	$ef_0^*$	$y_1^*$	$y_2^*$	$y_3^*$
<b>5</b>	3.5288	0.3194	-0.2556	0.2497
<b>6</b>	4.4677	0.0951	-0.0806	0.0788
<b>7</b>	1.8649	0.3421	-0.2368	0.2841
<b>8</b>	1.2680	0.1014	-0.0393	
<b>9</b>	1.8208		-0.0779	
<b>10</b>	1.5239	0.3279	-0.2413	0.2456
<b>11</b>	5.5425	0.3202	-0.2527	0.2361
<b>12</b>	5.5461	0.3115	-0.2555	0.2361
<b>13</b>	3.9351	0.3135	-0.2592	0.2605

benzo-annulation on the intensity of cyclic conjugation measured by either  $EC$  or  $ef$ .

The correlation between  $EC$  and  $ef$ , although not linear, is monotonically increasing. This implies that, in the case of benzenoid hydrocarbons, the (stabilizing) effect of cyclic conjugation is proportional (yet not linear) to the amount of  $\pi$  electrons in the underlying ring. This, in turn, causes the signs of  $x$  and  $y$  parameters to be identical.

**Table 5** The parameters used for calculating the transformed value of the  $\pi$ -electron energy effect,  $F(ef) = \alpha + \beta ef + \gamma ef^2$ , for the benzo-annulated derivatives of the conjugated compounds shown in Fig. 4

Compound	$\alpha$	$\beta$	$\gamma$
5	1.93	36.62	-130.79
6	3.95	9.66	-25.29
7	0.38	70.93	-403.43
8	0.31	56.54	-621.39
9	-1.22	158.04	-1,906.10
10	0.15	-10.29	-11.31
11	4.88	-14.06	-30.58
12	4.92	-13.56	-29.70
13	3.43	-35.24	-151.50

**Table 6** Correlation coefficients for the correlation between  $\pi$ -electron content ( $EC$ ) and  $\pi$ -electron energy ( $ef$ ) before and after transformation of  $ef$  by means of Eq. 3

Compound	NBAD	$EC$ versus $ef$	$EC$ versus $F(ef)$
5	11	0.984	0.994
6	30	0.952	0.991
7	27	0.871	0.954
8	13	0.996	0.999
9	11	0.938	0.988
10	15	0.967	0.996
11	11	0.933	0.984
12	15	0.938	0.984
13	70	0.910	0.972

NBAD number of benzo-annulated derivatives of the conjugated compounds shown in Fig. 4

#### Nonbenzenoid molecules (containing 4- and 8-membered rings)

By comparing the data for molecules **10–13** in Tables 2 and 3, we notice that their signs differ in all cases. This is a consequence of the fact that for such molecules the considered ring X is antiaromatic. Thus, the increase of the  $\pi$ -electron content in the ring X (as measured by  $EC$ ) increases its antiaromaticity, i.e., causes an additional energetic destabilization (as measured by  $ef$ , which for antiaromatic rings has negative values [9, 10]). The signs

of the coefficients  $\gamma$  are in direct agreement with rules 1b and 2b, and make it possible to quantitatively assess the effect of benzo-annulation on the cyclic conjugation in rings whose size is divisible by 4. On the other hand, inferences on cyclic conjugation in such rings, based on the  $\pi$ -electron content ( $EC$ , Table 2) should be done cum grano salis.

When  $ef$  is properly transformed into  $F(ef)$ , cf. Eq. 3, then this disagreement between the two approaches to cyclic conjugation is eliminated: the signs of the coefficients  $\gamma^*$  (in Table 4) agree with those of  $x$  (in Table 2).

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