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A simple mathematical model for the effect of benzo-annelation on cyclic conjugation

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Abstract: In a series of earlier studies, it was established that benzo-annelation in the angular (resp. linear) position relative to a ring *R* of a polycyclic conjugated π-electron system, increases (resp. decreases) the intensity of the cyclic conjugation in the ring R. Herein, it is shown how this regularity can be explained by means of a simple, Kekulé-structure-based argument, itself based on an idea of Randić from the 1970s.

Keywords: cyclic conjugation; Kekulé structure; benzo-annelation; local aromaticity.

INTRODUCTION

The fact that various parts of a polycyclic conjugated molecules have different π-electron properties (often referred to as differences in their local aromaticity or differences in the magnitude of cyclic conjugation in individual rings) was recognized a long time ago;[1–5] see also recent works along these lines.[6–16] In 2004, within a study[17] of the effect of benzo-annelation on cyclic conjugation in perylene, it was found that in the case of its central six-membered ring:

a) benzo-annelation in an angular position increases the intensity of cyclic conjugation in this ring and that

b) benzo-annelation in a linear position decreases the intensity of cyclic conjugation in this ring.

Several years were needed to recognize that the regularities a and b are not restricted to perylene, but are generally valid, both for benzenoid[18–21] and non-benzenoid[22–26] polycyclic conjugated systems. Initially,[17–26] the rules a and b were verified by calculating the energy effects (*ef*) of the respective rings. This quantity is known[5] to provide a reliable measure of the magnitude of cyclic conjugation in individual rings. Details of the theory on which the *ef*-method is based,

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as well as on its numerous applications, are outlined in two reviews.[27,28] Eventually, in order to eliminate the doubt that the results obtained are artifacts of the *ef*-method, the rules a and b were corroborated by means of several other (more advanced) quantum-theoretical approaches.[29–31] In addition, a general mathematical theory of this phenomenon was elaborated,[32,33] and its applicability demonstrated on the case of benzo-annelated perylenes.[34,35]

In the present paper, it is shown that results equivalent to rules a and b can be deduced by means of a simple approach[3] for quantifying the intensity of cyclic conjugation in a particular ring (or, as it was originally stated,[3] of local aromaticity).

Let G be the molecular graph[36] of a polycyclic conjugated π-electron system, R one of the rings of G, and G–R the subgraph obtained from G by deleting the vertices of R; for an illustrative example see Fig. 1.

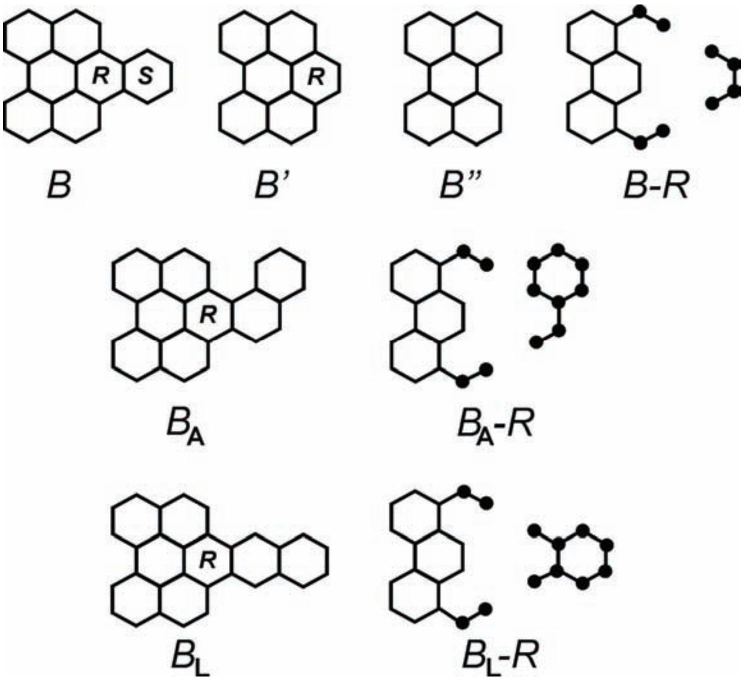

Fig. 1. An example illustrating the notation used in this paper. In naphtho[1,2,3,4-ghi]perylene (B) the ring R has $ef = 0.0261$ and $\Lambda = 0.5263$. In the angularly benzo-annelated derivative (B_A), $ef = 0.0323$, $\Lambda = 0.6897$, and $\Delta = +0.1634$, whereas in the linearly benzo-annelated derivative (B_L), $ef = 0.0223$, $\Lambda = 0.3704$, and $\Delta = -0.1559$.

Let $K(G)$ and $K(G-R)$ be the number of Kekulé structures of G and G–R, respectively. In the following, it is assumed that G is Kekuléan, *i.e.*, that $K(G) > 0$.

According to Randić,[3] the local aromaticity (Λ) pertaining to the ring R in a conjugated system G can be measured by means of the expression:

$$\Lambda = \Lambda(G,R) = \frac{2K(G-R)}{K(G)} \tag{1}$$

A ring is fully aromatic if $\Lambda = 1$, and devoid of any cyclic conjugation if $\Lambda = 0$. The difference between the local aromaticity (of the ring R) after and before benzo-annelation is denoted by $\Delta = \Delta(R)$.

APPLICATION OF EQUATION (1)

The notation used in this section is explained in Fig. 2 (and illustrated by a particular example in Fig. 1).

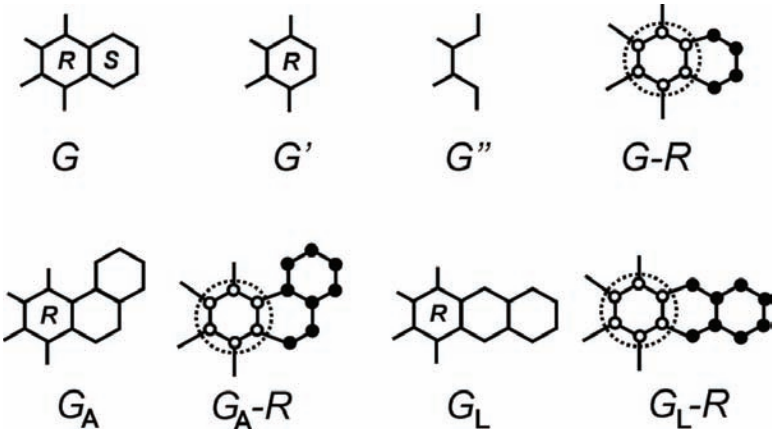

Fig. 2. The notation used. The encircled vertices are those that have been deleted.

Thus, let G be the molecular graph of a polycyclic conjugated system, R the ring whose cyclic conjugation is to be examined, and S the ring adjacent to R. It should be noted that the ring S must be six-membered, but the ring R need not be. In G' the ring S is missing, whereas in G'' both rings R and S are missing. The subgraph $G–R$ is obtained by deleting from G all vertices belonging to the ring R. The angularly and linearly benzo-annelated derivatives of G are denoted by G_A and G_L, respectively, and their subgraphs $G_A–R$ and $G_A–R$ are constructed in full analogy with $G–R$.

In order to apply Eq. (1), the Kekulé structure counts of G, G_A, and G_L must be computed. This can be realized using standard recursive methods,[37,38] namely:

$$K(G) = K(G-e) + K(G-u-v) \tag{2}$$

where e is an edge of G, connecting the vertices u and v, and

$$K(G) = K(G-u-v) \tag{3}$$

if either the vertex *u* or the vertex *v* are pendent (have a single neighbor). The manner in which the formula:

$$K(G) = K(G') + K(G'') \tag{4}$$

is obtained by using Eqs. (2) and (3) is shown in Fig. 3.

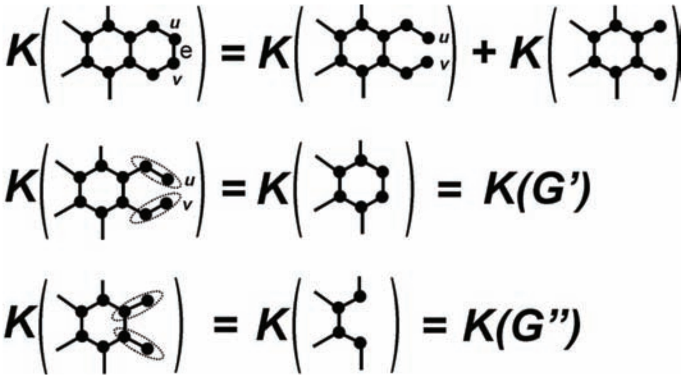

Fig. 3. Deducing Eq. (4).

In an analogous manner, one obtains:

$$K(G_\mathrm{A}) = K(G) + K(G') \text{ and } K(G_\mathrm{L}) = K(G) + K(G'')$$

which combined with Eq. (4) yield:

$$K(G_\mathrm{A}) = 2K(G') + K(G'') \text{ and } K(G_\mathrm{L}) = K(G') + 2K(G'')$$

It should be noted that since $K(G) > 0$, then $K(G')$ and $K(G'')$ must also be > 0.

From Figs. 1 and 2, it can be seen that the subgraph G_A–R differs from G–R by having a styrene fragment instead of a butadiene fragment. Since styrene has two Kekulé structures, whereas butadiene only one, one has $K(G_\mathrm{A}–R) = 2K(G–R)$. On the other hand, the subgraph G_L–R possesses an *o*-xylylene fragment, the Kekulé structure count of which is unity. Therefore, $K(G_\mathrm{L} - R) = K(G - R)$. Bearing these relations in mind one readily arrives at:

$$\Lambda(G,R) = \frac{2K(G-R)}{K(G)} = \frac{2K(G-R)}{K(G')+K(G'')} \tag{5}$$

$$\Lambda(G_\mathrm{A},R) = \frac{2K(G_\mathrm{A}-R)}{K(G)} = \frac{4K(G-R)}{2K(G')+K(G'')} \tag{6}$$

and

$$\Lambda(G_\mathrm{L},R) = \frac{2K(G_\mathrm{L}-R)}{K(G)} = \frac{K(G-R)}{2K(G')+K(G'')} \tag{7}$$

It is now a matter of elementary calculation to verify that if $K(G–R)$ is non-zero, then Eqs. (5)–(7) imply:

$$\Lambda(G_{\mathrm{L}},R) < \Lambda(G,R) < \Lambda(G_{\mathrm{A}},R)$$

i.e., $\Delta_{\mathrm{L}}(R) = \Lambda(G_{\mathrm{L}},R) - \Lambda(G,R) < 0$ and $\Delta_{\mathrm{A}}(R) = \Lambda(G_{\mathrm{A}},R) - \Lambda(G,R) > 0$, which is in full agreement with rules a and b. In other words, our finding with regard to the effect of benzo-annelation on cyclic conjugation can be rationalized by means of the simple Kekulé-structure-based formula, Eq. (1). However, this is the case only if the subgraph $G–R$ is also Kekuléan, *i.e.*, if $K(G–R) > 0$.

THE CASE $K(G–R) = 0$

The case $K(G–R) = 0$ needs to be analyzed separately. This case is important, because it is encountered if the ring R is odd-membered, as in the much studied acenaphthylene and fluoranthene congeners.[22–26] Also, perylene belongs to this case.[17]

If the subgraph $G–R$ is non-Kekuléan, then from Eqs. (5)–(7), it follows:

$$\Lambda(G,R) = \Lambda(G_{\mathrm{A}},R) = \Lambda(G_{\mathrm{L}},R) = 0$$

i.e.,

$$\Delta_{\mathrm{L}}(R) = \Delta_{\mathrm{A}}(R) = 0$$

a result that would be expected from a model based solely on Kekulé structures.

The way to circumvent this difficulty is evident: Eq. (1) has to be modified to:

$$\Lambda^{*} = \Lambda^{*}(G,R) = \frac{2K^{*}(G-R)}{K(G)}$$

where K^* is the count of some pertinently chosen resonance structures (with one or more unpaired π-electrons).[39,40] For the present analysis, the actual choice of K^* is immaterial, it is only necessary that $K^*(G–R) > 0$. If so, then from the modifications of Eqs. (5)–(7), namely:

$$\Lambda^{*}(G,R) = \frac{2K^{*}(G-R)}{K(G)} = \frac{2K^{*}(G-R)}{K(G')+K(G'')}$$

$$\Lambda^{*}(G_{\mathrm{A}},R) = \frac{2K^{*}(G_{\mathrm{A}}-R)}{K(G)} = \frac{4K^{*}(G-R)}{2K(G')+K(G'')}$$

$$\Lambda^{*}(G_{\mathrm{L}},R) = \frac{2K^{*}(G_{\mathrm{L}}-R)}{K(G)} = \frac{K^{*}(G-R)}{2K(G')+K(G'')}$$

one immediately obtains:

$$\Lambda^{*}(G_{\mathrm{L}},R) < \Lambda^{*}(G,R) < \Lambda^{*}(G_{\mathrm{A}},R)$$

i.e.,

$$\Delta_{\mathrm{L}}^{*}(R)=\Lambda^{*}(G_{\mathrm{L}},R)-\Lambda^{*}(G,R)<0 \text{ and } \Delta_{\mathrm{A}}^{*}(R)=\Lambda^{*}(G_{\mathrm{A}},R)-\Lambda^{*}(G,R)>0,$$

that is in harmony with the rules a and b.

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ИЗВОД

JEDNOSTAVNI

МАТЕМАТИЧКИ МОДЕЛ ЗА УТИЦАЈ БЕНЗО-АНЕЛАЦИЈЕ НА ЦИКЛИЧНУ КОНЈУГАЦИЈУ

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У низу ранијих истраживања установљено је да бензо-анелација у линеарном (одн. ангуларном) положају у односу на прстен *P* у полицикличном конјугованом π-електронском систему, смањује (одн. увећава) интензитет цикличне конјугације у прстену R. У раду показујемо да се ова правилност може објаснити помоћу једног једноставног, на Кекулеовим структурама заснованог, модела.

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