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

IVAN GUTMAN[1]*# and ALEXANDRU T. BALABAN[2]

[1]Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia and [2]Texas A & M University at Galveston, 200 Seawolf Parkway, Galveston, TX 77553, USA

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,

---

* Corresponding author. E-mail: gutman@kg.ac.rs
# Serbian Chemical Society member.

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.
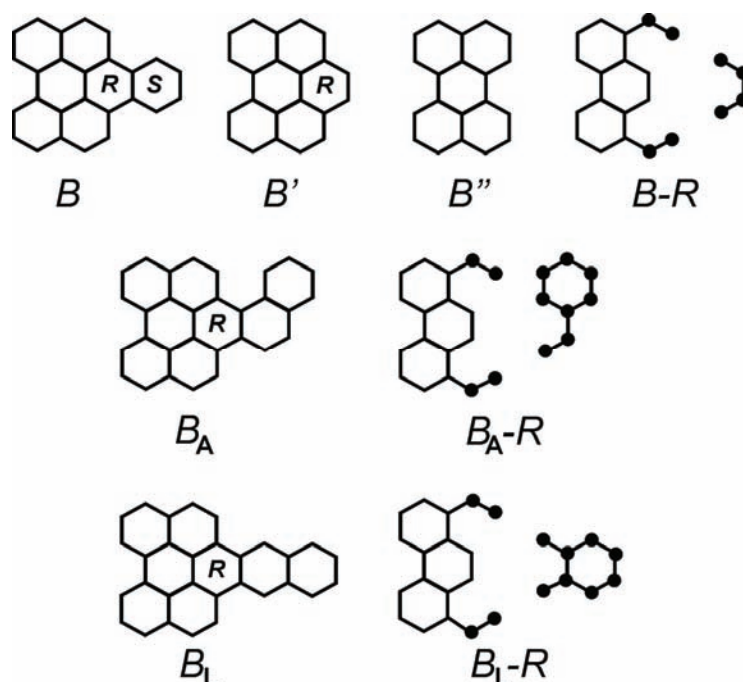

Fig. 1. An example illustrating the notation used in this paper. In naphtho[1,2,3,4-ghi]perylene (B) the ring R has $ef = 0.0261$ and $\Lambda = 0.5263$. In the angularly benzo-annelated derivative (B$_A$), $ef = 0.0323$, $\Lambda = 0.6897$, and $\Delta = +0.1634$, whereas in the linearly benzo-annelated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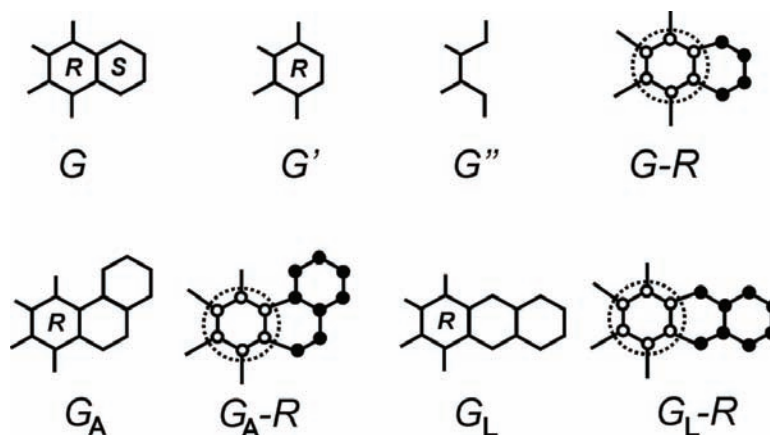

Fig. 2. The notation used. The encircled vertices are those that have been deleted.

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:

$$K(G) = K(G') + K(G'') \qquad (4)$$

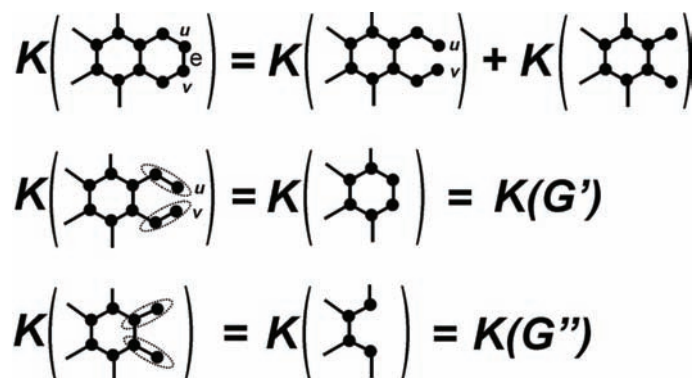is obtained by using Eqs. (2) and (3) is shown in Fig. 3.

Fig. 3. Deducing Eq. (4).

In an analogous manner, one obtains:

$$K(G_A) = K(G) + K(G') \text{ and } K(G_L) = K(G) + K(G'')$$

which combined with Eq. (4) yield:

$$K(G_A) = 2K(G') + K(G'') \text{ and } K(G_L) = K(G') + 2K(G'')$$

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 $K(G_A$–$R) = 2K(G$–$R)$. On the other hand, the subgraph G_L–R possesses an o-xylylene fragment, the Kekulé structure count of which is unity. Therefore, $K(G_L - R) = K(G - R)$. Bearing these relations in mind one readily arrives at:

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

$$\Lambda(G_A, R) = \frac{2K(G_A - R)}{K(G)} = \frac{4K(G - R)}{2K(G') + K(G'')} \qquad (6)$$

and

$$\Lambda(G_L, R) = \frac{2K(G_L - R)}{K(G)} = \frac{K(G - R)}{2K(G') + K(G'')} \qquad (7)$$

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.,

$$\Delta_L^*(R) = \Lambda^*(G_L, R) - \Lambda^*(G, R) < 0 \ \text{ and } \ \Delta_A^*(R) = \Lambda^*(G_A, R) - \Lambda^*(G, R) > 0,$$

that is in harmony with the rules a and b.

ИЗВОД

JEDNOSTAVNI

МАТЕМАТИЧКИ МОДЕЛ ЗА УТИЦАЈ БЕНЗО-АНЕЛАЦИЈЕ
НА ЦИКЛИЧНУ КОНЈУГАЦИЈУ

ИВАН ГУТМАН[1] и ALEXANDRU T. BALABAN[2]

[1]Природно–математички факултет Универзитета у Крагујевцу и [2]Texas A & M University at Galveston, Galveston, USA

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.

REFERENCES

1. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969
2. E. Clar, *The Aromatic Sextet*, Wiley, London, 1972
3. M. Randić, *Tetrahedron* **30** (1974) 2067
4. M. Randić, *Tetrahedron* **31** (1975) 1477
5. I. Gutman, S. Bosanac, *Tetrahedron* **33** (1977) 1809
6. M. Randić, *Chem. Rev.* **103** (2003) 3449
7. A. T. Balaban, *Polyc. Arom. Comp.* **24** (2004) 83
8. A. T. Balaban, M. Randić, *J. Math. Chem.* **37** (2005) 443
9. G. Portella, J. Poater, M. Sola, *J. Phys. Org. Chem.* **18** (2005) 785
10. P. Bultinck, S. Fias, R. Ponec, *Chem. Eur. J.* **12** (2006) 8813
11. J. Aihara, T. Ishida, H. Kanno, *Bull. Chem. Soc. Jpn.* **80** (2007) 1518
12. J. Ou, *MATCH Commun. Math. Comput. Chem.* **64** (2010) 157
13. M. Randić, *MATCH Commun. Math. Comput. Chem.* **64** (2010) 303
14. M. V. Putz, *MATCH Commun. Math. Comput. Chem.* **64** (2010) 391
15. A. Ciesielski, T. M. Krygowski, M. K. Cyranski, A. T. Balaban, *Phys. Chem. Chem. Phys.* **13** (2011) 3737
16. A. T. Balaban, M. Randić, in: *Advances in Physics and Chemistry of Carbon Bonding and Structures*, M. V. Putz, Ed., Springer-Verlag, Berlin, 2011, in press
17. I. Gutman, N. Turković, J. Jovičić, *Monatsh. Chem.* **135** (2004) 1389

18. S. Jeremić, S. Radenković, I. Gutman, *Maced. J. Chem. Chem. Eng.* **29** (2010) 63
19. A. T. Balaban, J. Đurđević, I. Gutman, S. Jeremić, S. Radenković, *J. Phys. Chem., A* **114** (2010) 587
20. S. Jeremić, S. Radenković, I. Gutman, *J. Serb. Chem. Soc.* **75** (2010) 943
21. A. T. Balaban, I. Gutman, S. Jeremić, J. Đurđević, *Monatsh. Chem.* **142** (2011) 53
22. I. Gutman, J. Đurđević, A. T. Balaban, *Polyc. Arom. Comp.* **29** (2009) 3
23. J. Đurđević, I. Gutman, J. Terzić, A. T. Balaban, *Polyc. Arom. Comp.* **29** (2009) 90
24. I. Gutman, J. Đurđević, *J. Serb. Chem. Soc.* **74** (2009) 765
25. I. Gutman, S. Jeremić, V. Petrović, *Indian J. Chem., A* **48** (2009) 658
26. B. Furtula, I. Gutman, S. Jeremić, S. Radenković, *J. Serb. Chem. Soc.* **75** (2010) 83
27. I. Gutman, *Monatsh. Chem.* **136** (2005) 1055
28. I. Gutman, in: *Mathematical Methods and Modelling for Students of Chemistry and Biology*, A. Graovac, I. Gutman, D. Vukičević, Eds., Hum, Zagreb, 2009, pp. 13–27
29. J. Đurđević, S. Radenković, I. Gutman, S. Marković, *Monatsh. Chem.* **140** (2009) 1305
30. J. Đurđević, I. Gutman, R. Ponec, *J. Serb. Chem. Soc.* **74** (2009) 549
31. A. T. Balaban, T. K. Dickens, I. Gutman, R. B. Mallion, *Croat. Chem. Acta* **83** (2010) 209
32. S. Radenković, J. Đurđević, I. Gutman, *Chem. Phys. Lett.* **475** (2009) 289
33. I. Gutman, *J. Math. Chem.* **47** (2010) 1309
34. S. Radenković, W. Linert, I. Gutman, S. Jeremić, *Indian J. Chem., A* **48** (2009) 1657
35. I. Gutman, S. Radenković, W. Linert, *Monatsh. Chem.* **141** (2010) 401
36. I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin, 1986
37. W. C. Herndon, *J. Chem. Educ.* **51** (1974) 10
38. S. J Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1988
39. J. R. Dias, *J. Chem. Inf. Comput. Sci.* **41** (2001) 129
40. J. R. Dias, *J. Chem. Inf. Comput. Sci.* **41** (2001) 686.