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On Algebraic and Geometric Kekulé Structures in Benzenoid Rotagraphs

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• Kekulé structures
• Kekulé structure count
• geometric and algebraic Kekulé structures
• benzenoids
• rotagraph

Recently introduced algebraic Kekulé structures (AKS) describe the π-electron distribution within rings of a conjugated network. The ratio of the AKS count to the classical Kekulé structures count was studied in benzenoid rotagraphs. By considering three representative classes of such rotagraphs, it was shown that this ratio tends towards either 1 or 0, or its value lies between 0 and 1.

INTRODUCTION

The notion of Kekulé structures is of use in organic chemistry as a means for quick estimation of molecular thermodynamic stability, and is especially useful when benzenoid molecules are considered.[1] Recently, Randić introduced another concept of algebraic Kekulé structures (AKS).[2–10] These structures are obtained from the classical Kekulé structures by inscribing into each hexagon the number of π-electrons that belong to this hexagon. Let us call this the Randić number (or ring partition value) and denote it by ρ. Double bonds shared by two hexagons are assumed to contribute one π-electron to each hexagon while other double bonds are viewed as contributing both of their π-electrons to the hexagon in which they lie. The Randić numbers can take values from 0 up to 6. Of course, the sum of all Randić numbers over all cycles gives the number of π-electrons in a benzenoid.

The traditional Kekulé structures are called here geometric Kekulé structures (GKS). Each GKS uniquely determines its AKS, but the opposite is not true.[5–7] Namely, there are different Kekulé structures that have the same AKS.

We denote the number of AKS by α and the number of GKS by γ. α is smaller than or equal to γ, and herein we study the ratio $\frac{\alpha}{\gamma}$ of these two numbers on a few selected examples of benzenoids. They belong to benzenoid strips closed on themselves and, using graph-theoretical terminology, they are called benzenoid rotagraphs.

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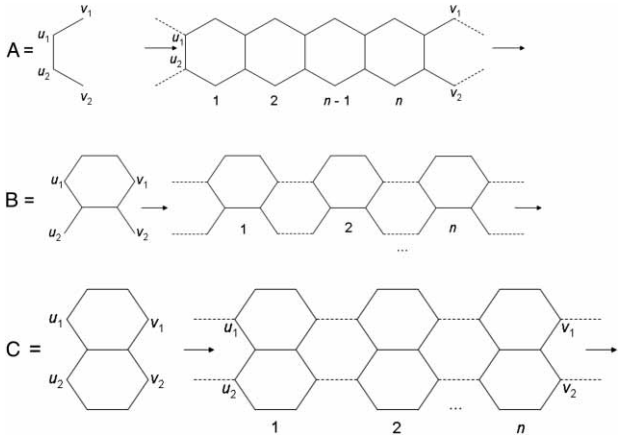

Figure 1. Monographs and their rotagraphs.

Fasciagraphs were introduced as mathematical models: in the same way as a polymer is built from monomers, a fasciagraph is obtained from monographs.[11] In this paper, we assume that all monographs are the same and that linking between them remains the same throughout the fasciagraph. When a fasciagraph is closed on itself, we call it a rotagraph.

A few examples of benzenoid rotagraphs are shown in Figure 1.

The monographs (A, B, C) serve as building blocks to form rotagraphs R_N (A), R_N (B), R_N (C). The number of linking edges in all examples shown in Figure 1 equals 2. The left linking vertices of monographs are denoted by u_1 and u_2, and the right ones by v_1 and v_2. The total number of monographs is denoted by N. The closure of a rotagraph on itself is indicated by arrows; namely, they show that the last monograph is linked with the first one.

RATIO OF ALGEBRAIC TO GEOMETRIC KEKULÉ STRUCTURE COUNTS FOR THREE REPRESENTATIVE CLASSES OF GRAPHS

Acene Rotagraphs

It is easy to see that polyacene closed on itself, R_N(A), has only four GKS, which are shown in Figure 2.

However, all of them have the same AKS and all ρ are the same and equal to 4. The ratio $\frac{\alpha}{\gamma}$ is then equal to $\frac{1}{4}$ for R_N(A) regardless of how large N is.

Zig-zag Rotagraphs

Benzenoids and benzenoid rotagraphs have a number of striking properties. One of them, discovered by Klein *et al.*,[12] is that the number of double bonds δ sitting on linking edges is conserved throughout the rotagraph. Therefore, as shown in Figure 3, all Kekulé structures of

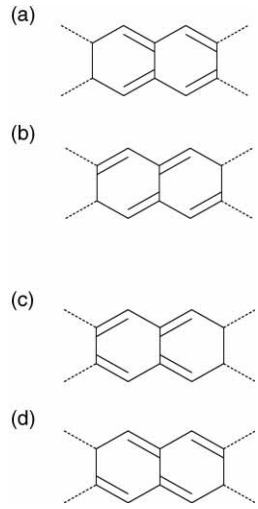

Figure 2. Four Kekulé structures of R_N(A) have the same AKS with all χ equal to 4.

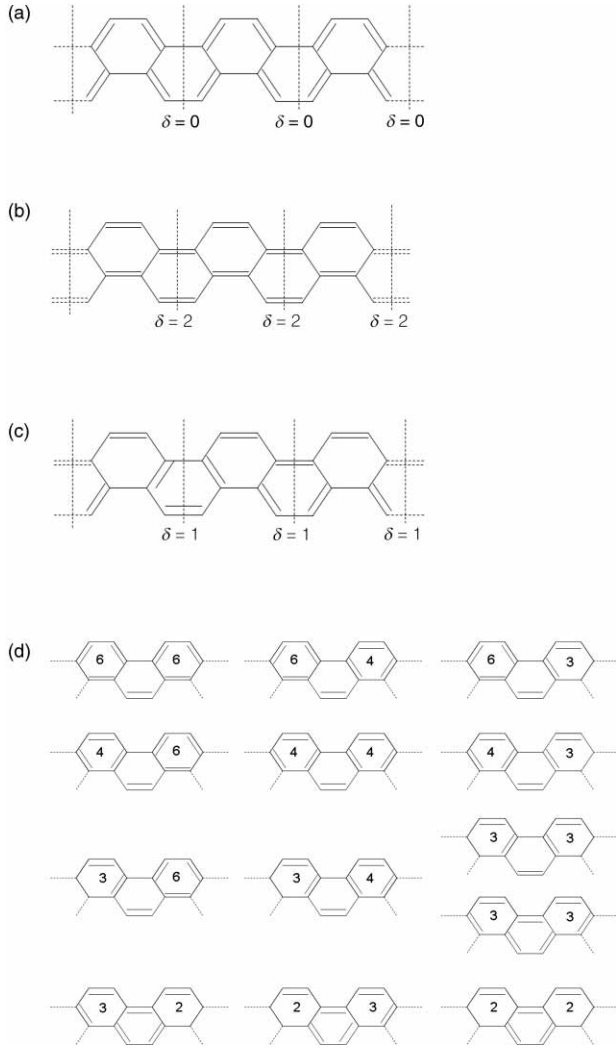

Figure 3. Breaking of Kekulé structures of rotagraph R_N(B) according to their value of δ into three classes (a) – (c). For $\delta = 1$, there are 12 possible combinations (d) of consecutive Randić numbers. Note that one of them (3,3) breaks into two further cases.

R_N(B) break into three classes. The class with $\delta = 0$ has only one member, shown in Figure 3a, where all ρ are the same and equal to 4. The second class, with $\delta = 2$, also contains only one member, shown in Figure 3b, where all ρ are the same and equal to 4.

The third class, with $\delta = 1$, has an exponentially (in N) growing number of members with one example shown in Figure 3c. Note that the double bond on a given pair of linking edges could be located either on the lower linking edge (which we will denote by l) or on upper linking edge (which we will denoted by u). We write information on the position of double bonds on the left and right sides of monographs, for pairs which written lexicographically read *ll*, *lu*, *ul*, *uu*. Note that doublet *ll* splits into two different cases and therefore the five situations shown in Figure 4 exist.

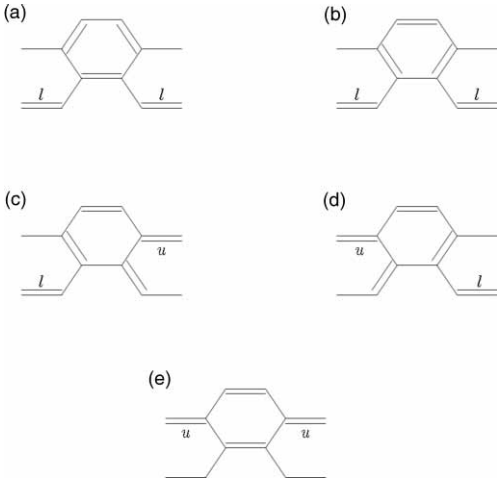

Figure 4. Five possible geometric and algebraic Kekulé structures for the monograph of R_N(B) with $\delta = 1$.

Each of the remaining cases (c)–(e), with doublets *lu*, *ul* and *uu*, leads to a unique ρ of the monograph.

Let us now consider two consecutive monographs for $\delta = 1$. Among all possible combinations of their ρs, it is easy to check that only the following twelve are allowed: (6,6), (6,4), (6,3), (4,6), (4,4), (4,3), (3,6), (3,4), (3,3), (3,2), (2,3), (2,2) and they are presented in Figure 3d.

For example, combination (6,2) is not allowed, because it forces the upper linking edge to be covered and at the same time not to be covered by a double bond.

Let us consider (6,6) as one of the combinations. It is allowed because both 6s force the upper linking edge not to be covered. Note that there is only one way to complete the Kekulé structure by covering a lower edge by a double bond. This unique Kekulé structure uniquely determines the Randić structure 6_26 (Figure 3d, 1st drawing) where the subscript denotes ρ in the linking ring.

All other combinations are treated along the same line, with the exception of (3,3). Namely, this combination gives two possible Kekulé structures corresponding to two different Randić structures: 3_43 and 3_63, as seen in Figure 3d.

Summarizing the case $\delta = 1$, we conclude that there is a 1 : 1 correspondence between Kekulé and Randić structures. Note that when all ρ in R_N(B) are equal to 4, the Randić structure is $...4_44_44_4...$. The same structure was found for $\delta = 0$ and $\delta = 2$, but with different Kekulé structures than for $\delta = 1$. Hence, $\alpha = \gamma - 2$; γ is determined by *e.g.* the application of the transfer matrix[13–17] method as:

$$\gamma = \mathrm{tr}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}^N =$$

$$\mathrm{tr}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -\sqrt{5}/2+3/2 & 0 & 0 \\ 0 & 0 & \sqrt{5}/2+3/2 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}^N =$$

$$2 + (-\sqrt{5}/2 + 3/2)^N + (\sqrt{5}/2 + 3/2)^N$$

and therefore the ratio $\frac{\alpha}{\gamma}$ we have looked at tends towards 1 for large N.

*Benzo[*e*]pyrenic Rotagraphs*

The ratio $\frac{\alpha}{\gamma}$ can tend towards 0 for large N, as well. An example is given in Figure 5.

Computation of γ as well as the estimation of α are possible by noting that there are 6 Kekulé structures (1) – (6) possible for hexagons shaded in Figure 5a. These Kekulé structures are shown in Figure 5b. The first »transfer« from some Kekulé structure (1) to the next Kekulé structure (1) gives rise to the four situations depicted in Figure 5c. Note that there are only three Randić structures *versus* 4 Kekulé structures.

Before further discussion, we denote the three Randić structures of Figure 5d by 5305, 5215, 5135, where the ρs of the central horizontal row obviously suffice to determine all ρs. Note that 5215 corresponds to two Kekulé structures.

Similarly, one could treat in an analogous way the remaining »transfers« among all 36 possibilities.

For example, the »transfer« from (1) to (6) gives rise to only one Kekulé structure and therefore only one Randić structure, and transfer from (1) to (4) is not consistent, because for such a transfer there is no Kekulé structure for the unshaded fragment.

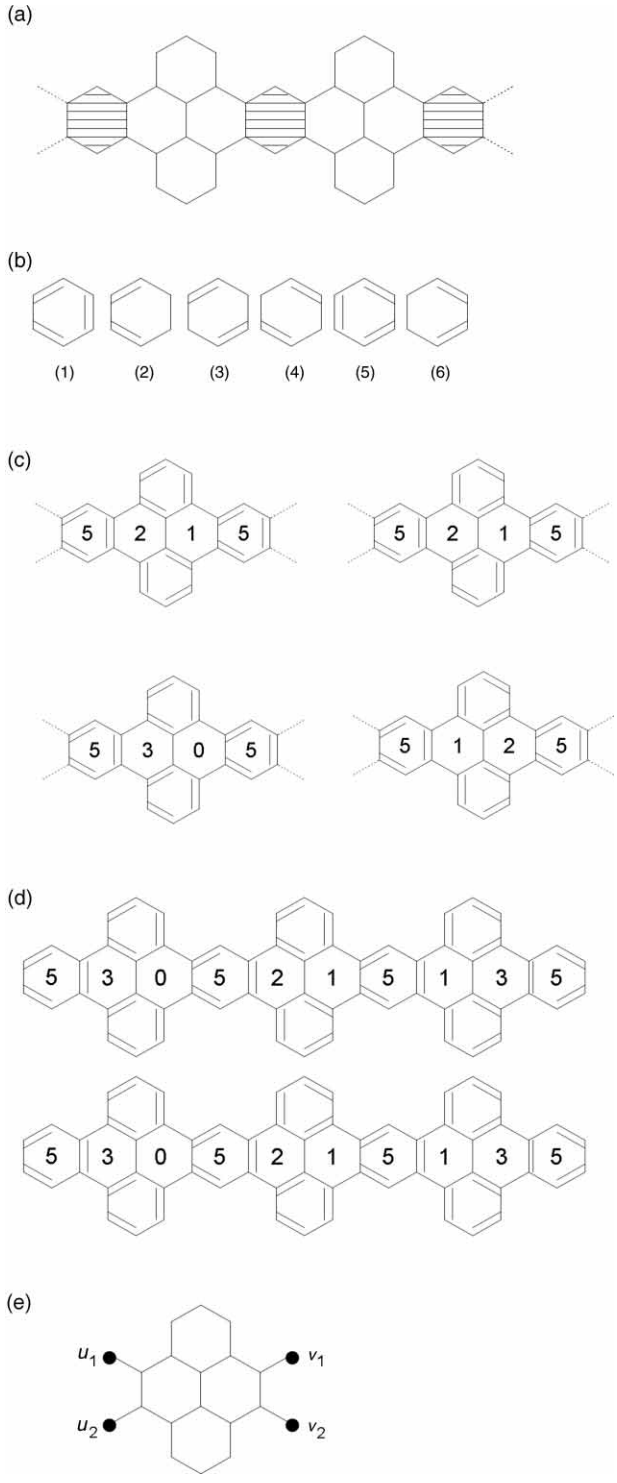

Figure 5. Benzenoid rotagraph whose linking hexagons are shaded in (a). Six Kekulé structures of the linking hexagon are shown in (b). All four possible »transfers« from (1) to (1) are depicted in (c). Two fragments with the same AKS and different GKS are shown in (d). Linking vertices used in the computation of GKS are shown in (e).

It is convenient to write all possible »transfers« in the matrix form. The transfer matrix for Kekulé structure count is given by (with the entries in matrix taken from Figure 5e):

$$\boldsymbol{A} = \begin{array}{c} \\ \varnothing \\ u_1 \\ u_2 \\ u_1 u_2 \end{array} \begin{array}{c} \begin{array}{cccc} \varnothing & v_1 & v_2 & v_1 v_2 \end{array} \\ \begin{bmatrix} 5 & 0 & 0 & 4 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 5 & 0 & 0 & 5 \end{bmatrix} \end{array} \tag{1}$$

The information on the upper bound of the Randić structure count can be obtained by the following matrix:

$$\boldsymbol{R} = \begin{array}{c} \\ \varnothing \\ u_1 \\ u_2 \\ u_1 u_2 \end{array} \begin{array}{c} \begin{array}{cccc} \varnothing & v_1 & v_2 & v_1 v_2 \end{array} \\ \begin{bmatrix} 4 & 0 & 0 & 3 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 4 & 0 & 0 & 4 \end{bmatrix} \end{array} \tag{2}$$

Note that matrix $\boldsymbol{R}$ is not a transfer matrix for enumeration of Randić structures, because some Randić structures are counted in more than one matrix entry, *e.g.*, 4334 is counted in both entries $(R)_{5,5}$ and $(R)_{6,6}$.

Recall that the trace $\mathrm{tr}(A^N)$ of the Nth power A^N of the transfer matrix $\boldsymbol{A}$ is equal to the Kekulé structure count of the rotagraph.[14,15] For the example shown in Figure 5, one obtains:

$$\mathrm{tr}(A^N) = \mathrm{tr}\begin{bmatrix} 5 & 0 & 0 & 4 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 5 & 0 & 0 & 5 \end{bmatrix}^N =$$

$$\mathrm{tr}\begin{bmatrix} -2\sqrt{5}+5 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 2\sqrt{5}+5 \end{bmatrix}^N =$$

$$(-2\sqrt{5}+5)^N + (2\sqrt{5}+5)^N + 2 \tag{3}$$

and

$$\mathrm{tr}(R^N) = \mathrm{tr}\begin{bmatrix} 4 & 0 & 0 & 3 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 4 & 0 & 0 & 4 \end{bmatrix}^N =$$

$$\mathrm{tr}\begin{bmatrix} -2\sqrt{3}+4 & 0 & 0 & 0 \\ 0 & 2\sqrt{3}+4 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}^N =$$

$$(-2\sqrt{3}+4)^N + (2\sqrt{3}+4)^N + 2 \tag{4}$$

However, $\mathrm{tr}(R^N)$ is only an upper bound for the Randić structure count and therefore:

$$\frac{\alpha}{\gamma} < \frac{\mathrm{tr}(R^N)}{\mathrm{tr}(A^N)} \qquad (5)$$

which implies that the ratio $\frac{\alpha}{\gamma}$ tends towards zero as $N \to \infty$. It can be shown that the number of Randić structures α is given by:

$$\alpha = \mathrm{tr}(R^N) - (1+2^N) = (-2\sqrt{3}+4)^N + (2\sqrt{3}+4)^N - 2^N + 1.$$

CONCLUSIONS

Kekulé structures describe pairings of π-electrons along bonds in molecular networks while the novel Randić structures describe π-electron counts within structural details of networks, herein within hexagons of benzenoid rotagraphs, *i.e.,* rotagraphs built up from hexagons. These structures have generally different counts, denoted here by α and γ. The ratio $\frac{\alpha}{\gamma}$ is studied in the present paper in three representative classes. The first class is an example for $0 < \frac{\alpha}{\gamma} < 1$, the second for $\frac{\alpha}{\gamma} = 1$ and the third for $\frac{\alpha}{\gamma}$, which tends towards zero when the number of monographs in a rotagraph extends to infinity.

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SAŽETAK

O algebarskim i geometrijskim Kekuléovim strukturama u benzenoidnim rotagrafovima

Ante Graovac, Damir Vukičević i Janez Žerovnik

Nedavno uvedene algebarske Kekuléove strukture opisuju raspodjelu π-elektrona unutar prstenova konjugirane mreže. Omjer njihovog broja i broja klasičnih Kekuléovih struktura za benzenoidne rotagrafove proučavan je u ovom radu. Razmatranjem triju reprezentativnih klasa ovih rotagrafova pokazano je da promatrani omjer teži prema 1 ili 0, ili pak da njegova vrijednost leži između 0 i 1.