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*Short communication*

SHORT COMMUNICATION

# Stability order of isomeric benzenoid hydrocarbons and Kekulé structure count

SLAVKO RADENKOVIĆ[#] and IVAN GUTMAN*[#]

*Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia*

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*Abstract*: The commonly accepted opinion that the thermodynamic stability of isomeric benzenoid hydrocarbons (assessed by their total π-electron energy and various resonance energies) increases with increasing number of Kekulé structures is shown to be violated in numerous cases. The smallest examples of such anomalous behavior are two hexacyclic pericondensed benzenoids of formula $C_{24}H_{14}$ and several pairs of heptacyclic catacondensed benzenoids of formula $C_{30}H_{18}$.

*Keywords*: total π-electron energy; Kekulé structures; benzenoid hydrocarbons.

## INTRODUCTION

One of the basic postulates of resonance theory[1] is that the thermodynamic stability of isomeric conjugated molecules increases with the number $K$ of Kekulé structural formulas. In the early days of quantum chemistry,[2–4] it was discovered that concepts from resonance theory occur also within the molecular orbital theory of benzenoid hydrocarbons. Knowing this, it was then natural to anticipate that the (molecular orbital) total π-electron energy ($E$) and the various (molecular-orbital-based) resonance energies of benzenoid hydrocarbons are all somehow proportional to $K$. The first approximation in which $E$ was related with $K$ was put forward[5] already in the 1940s, and was eventually followed by a large number of other researches in the same direction. Of these are especially relevant those of Hall (claiming that the relation between $E$ and $K$ is linear),[6,7] of Cioslowski (claiming that the parameter influencing $E$ is $K^{2/n}$, where $n$ is the number of carbon atoms)[8–12] and of some other authors[13–15] (according to whom $E$ depends on $K$ in a logarithmic manner). After painstaking studies,[16–21] the linear Hall rule has prevailed, although later work[22–26] required its significant modification. Details of the examination of the ($E$/$K$) dependence in benzenoid sys-

* Corresponding author. E-mail: gutman@kg.ac.yu
[#] Serbian Chemical Society member.
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tems are found in the reviews[27,28] and references quoted therein. For some recent related investigations along these lines see the papers.[29–34]

All the earlier numerical studies on the ($E$/$K$) dependence[18,20,22–26,29–31,33] were performed on large sets of benzenoid isomers, and the conclusions drawn were based on statistical inferences. It is remarkable that until now nobody checked if the simple relation:

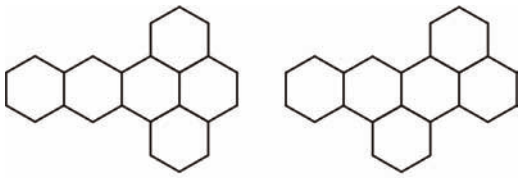
$$K(\mathrm{A}) > K(\mathrm{B}) \Rightarrow E(\mathrm{A}) > E(\mathrm{B}) \tag{1}$$

holds for all pairs A,B of benzenoid isomers. In this study, this checking was performed and it was found that Condition (1) is violated in a large number of cases.

It should be noted that the Requirement (1) is weaker than any of the assumed and previously considered approximate analytical relations between $E$ and $K$. Thus, if (1) is violated, then each of these relations between $E$ and $K$ is violated. A violation of (1) was reported[35] already in the 1970s, but for acyclic systems (for which the Kekulé structure count is either 1 or 0).

## VIOLATIONS FROM CONDITION (1)

The present systematic numerical testing revealed that Condition (1) is, indeed, satisfied by all catacondensed benzenoid hydrocarbons with six and fewer hexagons and by all pericondensed benzenoids with five and fewer hexagons. This fact, combined with the *a priori* expectations originating from the resonance theory, was probably the reason for overlooking the violations from (1) until now. Anyway, the two smallest benzenoid hydrocarbons violating Condition (1) are benzo[*b*]perylene and dibenzo[*de*,*qr*]naphthacene, depicted in Fig. 1. This is the only such pair with six hexagons that was found.



**1** **2**

$E = 34.0059$ $E = 34.0070$

$K = 16$ $K = 15$

Fig. 1. Dibenzo[*de*,*qr*]naphthacene (**1**) and benzo[*b*]perylene (**2**), both with the formula $C_{24}H_{14}$, are the smallest pair of benzenoid isomers for which Condition (1) is violated; $E$ = HMO total $\pi$-electron energy;[27,28] $K$ = Kekulé structure count. The energy difference of **1** and **2** of *ca*. 0.001 $\beta$-units implies that their heats of formation should differ by 0.15 kJ/mol; for details see in the book.[36]

Among the heptacyclic benzenoids, violations from Condition (1) are quite numerous. In the set of heptacyclic catacondensed benzenoids, $C_{30}H_{18}$, already 69 pairs that violate (1) were found. There are a total of 118 such benzenoid hyd-

rocarbons, forming 6903 pairs. Thus, roughly 1 % of these violate Condition (1). A characteristic example is shown in Fig. 2.

Among the 62 heptacyclic Kekuléan pericondensed benzenoids of formula $C_{28}H_{16}$, 30 pairs were found that violate Condition (1), which is around 1.5 % of the total number of pairs (= 1891). Among the 9 heptacyclic Kekuléan pericondensed benzenoids of formula $C_{26}H_{14}$, there is not a single violation from Condition (1). Details can be obtained from the authors, upon request.

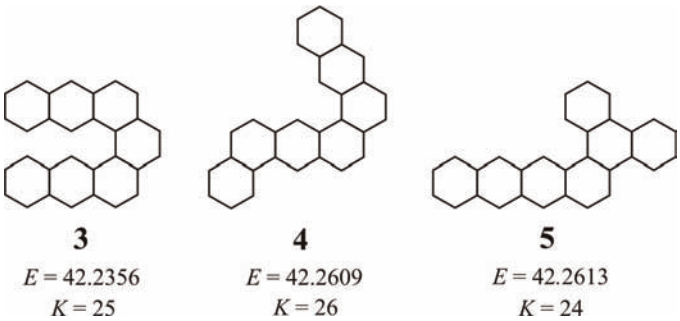



Fig. 2. Three catacondensed benzenoid systems that violate Condition (1): benzo[2,1-*a*:3,4-*a*']-dianthracene (**3**), anthra[1,2-*a*]benz[*h*]anthracene (**4**), and phenanthro[9,10-*a*]naphthacene (**5**), all with the formula $C_{30}H_{18}$; *E* and *K* are the same as in Fig. 1. Note that the difference between the heats of formation of **3** and **5** was estimated[36] to be 3.5 kJ/mol. In fact, because of the non-planarity of **3** and steric strain, the stability difference between **3** and **5** should be even greater (in favor of **5**).

## CONCLUDING REMARKS

The often repeated claim that "the greater is the Kekulé structure count, the greater is the (thermodynamic) stability of a benzenoid hydrocarbon" is simply not true. What is true is that within sets of isomeric benzenoid hydrocarbons there is a (statistically significant) trend that the thermodynamic stability increases with the number of Kekulé structures, but this does not mean that each member of the set with a greater Kekulé structure count is more stable than each member with a smaller Kekulé structure count.

Most remarkable in the above stated "discovery" is that is was not stated in the 1960s or 1970s, but only at the beginning of the 21st century.

ИЗВОД

СТАБИЛНОСТ ИЗОМЕРНИХ БЕНЗЕНОИДНИХ УГЉОВОДОНИКА И БРОЈ KEKULÉ-ОВИХ СТРУКТУРА

СЛАВКО РАДЕНКОВИЋ и ИВАН ГУТМАН

*Природно–математички факултет Универзитета у Крагујевцу, п.пр. 60, 34000 Крагујевац*

Показано је да од опште усвојеног схватања да је термодинамичка стабилност изомерних бензеноидних угљоводоника (која се процењује на основу укупне π-електронске енергије и разних енергија резонанције) тим већа што је већи број Kekulé-ових структура, постоје

бројна одступања. Најмањи примери оваквог аномалног понашања су два хексациклична перикондензована бензеноидна система формуле $C_{24}H_{14}$ и већи број парова хептацикличних катакондензованих бензеноидних система формуле $C_{30}H_{18}$.

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