

Partial Ordering of Locally Fixed Kekulé Structures in Carbocyclic and Heterocyclic Compounds

Tetsuo MORIKAWA

Chemistry Department, Joetsu University of Education,
Yamayashiki, Joetsu, Niigata Prefecture 943, Japan

Abstract

A partial ordering relation on a set of Kekulé structures in a class of carbocyclic and heterocyclic compounds is defined such that one double bond fixes another. This binary relation gives a partial order to both numbers of Kekulé structures and Pauling bond orders. The partial ordering structure makes it possible for us to estimate upper and/or lower bounds for the Pauling bond order, the Randić index (local aromaticity index in benzenoid hydrocarbons), and the number of Kekulé structures in the compounds.

1 Introduction

Let G be a polygonal skeleton (graph) in a class of carbocyclic and heterocyclic compounds; assume that every vertex x_i of G is connected with two or three vertices [1]. When a double bond connects x_i and x_{i+1} in a Kekulé structure of G , it is denoted by $(x_i = x_{i+1})$, if the context permits, by d_i ; and when a single bond, by $(x_i - x_{i+1})$ or by s_i . Let $K\{G\}$ be the number of Kekulé structures in G , and let $K\{d_i, d_j\}$ be the number of Kekulé structures with d_i and d_j in G . The local (and topological) properties, d_i and s_i , of Kekulé structures often play an important role in the chemistry of carbocyclic and heterocyclic compounds [2, 3]. The Pauling bond order between x_i and x_{i+1} in G , for example, is defined [3, 4] to be $K\{x_i = x_{i+1}\}/K\{G\}$ (if $K\{G\} > 0$); this ratio is written as $p\{d_i\}$, hereafter. A local aromaticity

index for benzenoid hexagons, proposed by Randić [5], is another example; the explicit form of his index I_R for a cycle $[x_1 x_2 x_3 \cdots x_{2j+4}]$ ($j \geq 0$) in G is given in more generalized form by

$$\{K\{[x_1 = x_2 - x_3 = \cdots = x_{2j+4} -]\} + K\{[x_1 - x_2 = x_3 - \cdots - x_{2j+4} =]\}\} / K\{G\},$$

which is indicated by $I_R\{[x_1 x_2 x_3 \cdots x_{2j+4}]\}$, hereafter. The present paper deals with the local properties of Kekulé structures that can be expressed in terms of $K\{d_i\}$, $K\{d_i, d_j, \dots\}$, $p\{d_i\}$, and $I_R\{[x_1 x_2 x_3 \cdots x_{2j+4}]\}$ in G .

The list below should be noticed from the point of view of the enumeration of Kekulé structures in G , as was used in [1, 6]. Here (a) stands for a conjugated vertex that is connected with two vertices; (b) for a conjugated vertex that is connected with three vertices; the prime mark for an unconjugated vertex; also see the **Glossary of Symbols**.

$$K\{x_i a_{i+1} a_{i+2} a_{i+3}\} = K\{x_i a_{i+1}\}, \quad (1)$$

$$K\{x_i a_{i+1} a_{i+2} a_{i+3} a_{i+4}\} = K\{x_i a_{i+1} a_{i+2}\}, \quad (2)$$

$$K\{x_i b_{i+1} a_{i+2} a_{i+3}\} = K\{x_i b_{i+1}\}, \quad (3)$$

$$K\{x_i = x_{i+1}\} = K\{x'_i x'_{i+1}\}, \quad (4)$$

$$K\{[x_1 = x_2 - x_3 = \cdots = x_{2j+4} -]\} = K\{[x_1 - x_2 = x_3 - \cdots - x_{2j+4} =]\}, \quad (5)$$

$$K\{x_i x_{i+1}\} = K\{x_i = x_{i+1}\} + K\{x_i - x_{i+1}\}, \quad (6)$$

$$K\{x_i - x_{i+1}, x_j = x_{j+1}\} \leq K\{x_i - x_{i+1}, x_j x_{j+1}\}, \quad (7)$$

$$K\{x_i - x_{i+1}, x_j - x_{j+1}\} \leq K\{x_i - x_{i+1}, x_j x_{j+1}\}. \quad (8)$$

By use of Eqs.(1 – 3), it is possible, if needed, to contract and/or enlarge paths and cycles under the requirement of conservation of the number of Kekulé structures in G . Equation (4) points out that $p\{d_i\}$ and the numerator of $I_R\{[x_1 x_2 x_3 \cdots x_{2j+4}]\}$ are equal to $p\{x'_i x'_{i+1}\}$ and $2K\{[x'_1 x'_2 x'_3 \cdots x'_{2j+4}]\}$, respectively; hence the algorithms in [1] are applicable to the calculation of $K\{d_i\}$, $K\{d_i, d_j, \dots\}$, $p\{d_i\}$, and $I_R\{[x_1 x_2 x_3 \cdots x_{2j+4}]\}$ in G . Every bond that meets at the outside vertices in two local conjugated structures, $[x_1 = x_2 - x_3 = \cdots = x_{2j+4} -]$ and $[x_1 - x_2 = x_3 - \cdots - x_{2j+4} =]$, is single; therefore, one obtains Eq.(5). Equation (6), where x_i is adjacent to x_{i+1} , is an identity equation for numbers of Kekulé structures. It is easy to verify Eqs.(7 – 8), because the local conjugated structures in the left-hand side are more restricted than those in the right-hand side. Another inequality below,

Eq.(9), by which the Pauling bond order is joined to the Randić index, can be derived from Eqs.(5, 7), where x_k and x_{k+1} are next to each other in cycle $[x_1 \ x_2 \ x_3 \ \cdots \ x_{2j+4}]$.

$$I_R\{[x_1 \ x_2 \ x_3 \ \cdots \ x_{2j+4}]\} \leq 2p\{x_k = x_{k+1}\}. \quad (9)$$

One often finds that the selection of a double bond in paths and cycles uniquely determines a local conjugated structure containing the double bond; e.g., if the first double bond d_1 in a path $(b_1 \ a_2 \ a_3 \ a_4 \ a_5 \ b_6)$ is selected (and if $K\{b_1 \ a_2 \ a_3 \ a_4 \ a_5 \ b_6\} > 0$), then the remaining double bonds in the path are all fixed by d_1 , that is, d_1 fixes s_2 , s_2 fixes d_3 , d_3 fixes s_4 , and so on. Such a propagation of double bonds from one to another induces a partial ordering on a set of Kekulé structures. The present note shows that a partial ordering relation gives upper and/or lower bounds for $K\{G\}$, $p\{d_i\}$, and $I_R\{[x_1 \ x_2 \ x_3 \ \cdots \ x_{2j+4}]\}$, as well as each equality in Eqs.(7 - 9).

2 Partial Ordering Relation on a Set of Kekulé Structures

(1) Suppose that there is a Kekulé structure of G with a double bond d_i between vertices x_i and x_{i+1} , and suppose that every such Kekulé structure containing this d_i also has a double bond d_j between vertices x_j and x_{j+1} . Then we write

$$d_i \leq d_j,$$

and read " d_i precedes d_j " or " d_j follows d_i ." The binary relation (\leq) is a partial ordering relation [7] because it satisfies three axioms: $d_i \leq d_i$ (reflexivity); if $d_i \leq d_j$, and if $d_j \leq d_k$, then $d_i \leq d_k$ (transitivity); if $d_i \leq d_j$, and if $d_j \leq d_i$, then $d_i = d_j$ (antisymmetry).

Noting Eq.(6), we have the inverse (\geq) of the partial ordering relation (\leq):

$$s_i \geq s_j,$$

which shows a dualism.

Clearly the partial ordering $d_i \leq d_j$ implies that

$$K\{d_i, x_j \ x_{j+1}\} = K\{d_i, d_j\} \leq K\{x_i \ x_{i+1}, d_j\}. \quad (10)$$

Dividing both sides of this inequality by $K\{G\}(> 0)$, one has

$$p\{d_i\} \leq p\{d_j\}, \quad (11)$$

which is also a partial ordering relation. The dual of this partial ordering relation is given by

$$p\{s_i\} \geq p\{s_j\}, \quad (12)$$

because $p\{d_i\} + p\{s_i\} = p\{d_j\} + p\{s_j\} = 1$. Each equality in Eqs.(10 - 12) holds when d_i and d_j precede each other.

(2) A path $(x_1 x_2 \cdots x_{2j+1} x_{2j+2})$ with $j \geq 0$ is given such that every two x_{2k-1} and x_{2k} for $k = 1, 2, \dots, j+1$ is related, namely, such that $d_1 \leq d_3, d_3 \leq d_5$, and so on. Then one uses the notation

$$d_1 \leq d_3 \leq \cdots \leq d_{2j+1},$$

and calls it a chain [7]. Such a chain implies that

$$K\{d_1\} \leq K\{d_3\} \leq \cdots \leq K\{d_{2j+1}\}. \quad (13)$$

(3) A set of d_k with $k = 1, 2, \dots, j+1$ ($j \geq 0$), is called an antichain [7] if no two distinct d_k are related. For $i, k \leq j+1$,

$$K\{d_i, x_k x_{k+1}\} = K\{d_i, d_k\} + K\{d_i, s_k\}, \quad (14)$$

$$K\{s_i, x_k x_{k+1}\} = K\{s_i, d_k\} + K\{s_i, s_k\}. \quad (15)$$

(4) A set of $d_1 \leq d_{2k-1}$ for $k = 1, 2, \dots, j+1$ ($j \geq 0$), is given. Then

$$K\{d_1\} = K\{d_1, d_3, \dots, d_{2j+1}\}. \quad (16)$$

(5) Remember that b_k in a conjugated path has one of three kinds of bond at the outside of the path; namely, double, single, and unfixed; such b_k are denoted by $b_k(=)$, $b_k(-)$, and $b_k(\)$, respectively. An algorithm below tries to construct a sequence, composed of d_k , s_k , $b_k(=)$, $b_k(-)$, and $b_k(\)$, from a path $(x_i x_{i+1} \cdots x_k \cdots x_j x_{j+1})$, and also tries to fix three bonds that meet at b_k .

1. Make d_i .

2. Set k to be $i + 1$.
3. Loop:
 - (a) Either if d_{k-1} , and
 - i. if x_k is a , make s_k ,
 - ii. if x_k is a' , Failure,
 - iii. if x_k is $b_k(=)$, Failure,
 - iv. if x_k is $b_k(-)$, make s_k ,
 - v. if x_k is $b_k()$, make s_k and $b_k(-)$,
 - vi. if x_k is b' , Failure.
 - (b) Or if s_{k-1} , and
 - i. if x_k is a , make d_k ,
 - ii. if x_k is a' , make s_k ,
 - iii. if x_k is $b_k(=)$, make s_k ,
 - iv. if x_k is $b_k(-)$, make d_k ,
 - v. if x_k is $b_k()$, Failure,
 - vi. if x_k is b' , make s_k .
 - (c) Increase k by 1.
4. Repeat the loop until either $k = j$ or Failure.

If no sequence beginning at d_i and ending at d_j for a given path $(x_i x_{i+1} \cdots x_k \cdots x_j x_{j+1})$ is complete, then search for another path. We can conclude that $d_i \leq d_j$, if there is at least one sequence of d_k and s_k from d_i to d_j .

3 Partial Ordering in Cyclic Subskeletons

(1) For a cycle $[x_1 x_2 \cdots x_{2j+4}]$ in G with $j \geq 0$, suppose that $d_1 \leq d_{2k+1}$ for $k = 1, 2, \dots, j + 1$. One can then make sure that:

$$\begin{aligned}
 & K\{[x_1 = x_2 x_3 \cdots x_{2j+4}]\} \\
 &= K\{[x_1 = x_2 x_3 = x_4 \cdots x_{2j+3} = x_{2j+4}]\} \\
 &= K\{[x_1 = x_2 - x_3 = x_4 - \cdots - x_{2j+3} = x_{2j+4} -]\} \\
 &= K\{[x_1 - x_2 = x_3 - x_4 = \cdots = x_{2j+3} - x_{2j+4} =]\} \\
 &\leq K\{[x_1 - x_2 x_3 \cdots x_{2j+4}]\}.
 \end{aligned}$$

The first equality implies that $(x_1 = x_2)$ precedes all other double bonds in $[x_1 = x_2 \ x_3 = x_4 \cdots x_{2j+3} = x_{2j+4}]$; the second equality is derived from the assumption that each vertex of G is connected with at most three vertices; in other words, if the double bond $(x_1 = x_2)$ in $[x_1 \ x_2 \cdots x_{2j+4}]$ is fixed, then the single and double bonds arrange by turn in the cycle, and then the local conjugated structure of the cycle is uniquely determined. Equation (5) gives the third equality, and Eqs.(7 - 8) lead to the inequality in the last line. That is,

$$K\{[x_1 = x_2 \ x_3 \cdots x_{2j+4}]\} \leq K\{[x_1 - x_2 \ x_3 \cdots x_{2j+4}]\}. \quad (17)$$

Using Eq.(17) and noting Eq. (6), we have that:

$$2K\{[x_1 = x_2 \ x_3 \cdots x_{2j+4}]\} \leq K\{G\} \leq 2K\{[x_1 - x_2 \ x_3 \cdots x_{2j+4}]\}, \quad (18)$$

$$p\{x_1 = x_2\} \leq \frac{1}{2} \leq p\{x_1 - x_2\} \text{ (if } K\{G\} > 0), \quad (19)$$

$$I_R\{[x_1 \ x_2 \cdots x_{2j+4}]\} = 2p\{x_1 = x_2\} \leq 1 \text{ (if } K\{G\} > 0). \quad (20)$$

Each equality in Eqs.(17-19) holds when $K\{[x_1 = x_2 \ x_3 \cdots x_{2j+4}]\} = K\{[x_1 - x_2 \ x_3 \cdots x_{2j+4}]\}$. $p\{d_1\}$ is the smallest value in the set of $p\{d_{2k-1}\}$ for $k = 1, 2, \dots, j+2$.

(2) For a cycle $[x_1 \ x_2 \cdots x_{2j+4}]$ in G with $j \geq 0$, suppose that $d_1 \geq d_{2k+1}$ for $k = 1, 2, \dots, j+1$. The dualism of partial ordering suggests that $s_1 \leq s_{2k+1}$ for $k = 1, 2, \dots, j+1$ in $[x_1 - x_2 \ x_3 - x_4 \cdots x_{2j+3} - x_{2j+4}]$. Hence,

$$\begin{aligned} & K\{[x_1 - x_2 \ x_3 \cdots x_{2j+4}]\} \\ &= K\{[x_1 - x_2 \ x_3 - x_4 \cdots x_{2j+3} - x_{2j+4}]\} \\ &\geq K\{[x_1 - x_2 = x_3 - x_4 = \cdots = x_{2j+3} - x_{2j+4} =]\} \\ &= K\{[x_1 = x_2 - x_3 = x_4 - \cdots - x_{2j+3} = x_{2j+4} -]\}. \end{aligned} \quad (21)$$

Notice that the inequality in the third line is different from the equality discussed in the derivation of Eq.(17). Then one gets:

$$2p\{x_1 - x_2\} \geq I_R\{[x_1 \ x_2 \cdots x_{2j+4}]\} \text{ (if } K\{G\} > 0). \quad (22)$$

The equality holds when $K\{[x_1 - x_2 \ x_3 - x_4 \cdots x_{2j+3} - x_{2j+4}]\} = K\{[x_1 - x_2 = x_3 - x_4 = \cdots = x_{2j+3} - x_{2j+4} =]\}$. $p\{s_1\}$ is the smallest value in the set of $p\{s_{2k-1}\}$ for $k = 1, 2, \dots, j+2$.

(3) For a cycle $[x_1 \ x_2 \cdots x_{2j+4}]$ in G with $j \geq 0$, suppose that $d_1 \leq d_{2k+1}$, and $d_1 \geq d_{2k+1}$ for $k = 1, 2, \dots, j+1$. Then, if the equality of Eq.(21) is true, then so is the equality of Eq.(17), and vice versa; if the equality is concluded, then

$$\frac{1}{2}K\{G\} = K\{[x_1 = x_2 \ x_3 \cdots x_{2j+4}]\} = K\{[x_1 - x_2 \ x_3 \cdots x_{2j+4}]\}, \quad (23)$$

$$p\{x_i = x_{i+1}\} = p\{x_i - x_{i+1}\} = \frac{1}{2} \text{ for adjacent vertices,} \quad (24)$$

$$I_R\{[x_1 \ x_2 \cdots x_{2j+4}]\} = 1. \quad (25)$$

4 Applications and Discussion

(1) In order to estimate $K\{d_i\}$, $p\{d_i\}$, and $I_R\{[x_1 \ x_2 \cdots x_{2j+4}]\}$ by means of Eqs.(10 - 25), we have to find a preceding and/or following relation among double bonds in a Kekulé structure of G . The application needs several comments:

The partial ordering relation remains unchanged even in the contraction and/or enlargement of paths and cycles by use of Eqs.(1 - 3); for example, $(b = b)$ precedes all the other double bonds in hexagon $[b = b - a = b - a = b -]$, and also in $[b = b - a = b - a = b - (a = a)_{j+1} -]$ ($j \geq 0$).

Fixing a double bond in a cycle does not necessarily mean that single and double bonds alternate in the cycle. For example, a double bond $(b = a)$ in the perimeter $[b \ a \ a \ b \ a \ a \ b \ a \ a]$ of acepentylene decides the local conjugated structure, but there is no alternation of single and double bonds in the perimeter; however, this $(b = a)$ precedes the rest in a cycle $[b = a - a = b - a = a - b = b -]$ of acepentylene. Not all locations between vertices in a cycle uniquely determine the arrangement of double bonds. In a path between d_i and d_j , intermediate vertices might be double bonded to vertices external to the path, so that the bonds along the path are not necessarily alternating single and double.

In Eqs.(10 - 12), the set of $K\{d_i\}$ need no to be a chain, even if d_i precedes the rest.

A bond d_i (or s_i) is called "essential [8]" if it is in every Kekulé structure of G . If d_i is essential, then $K\{d_i\} = K\{G\}$, and then $p\{d_i\} = 1$. Hence, if an essential double bond d_i precedes d_j , then $0 = p\{s_i\} \geq p\{s_j\}$, that is, $p\{d_j\} = 1$ (refer to Eq.(12)). Since $p\{x_1 = x_2\}$ in Eq.(19) do not exceed $1/2$, none of essential double bonds is compatible with the preceding double bond ($x_1 = x_2$).

(2) A preceding double bond d_i occurs in many polygonal skeletons. An edge between x_i and x_{i+1} in polyhexes is called "forcing [9]" if it determines a Kekulé substructure. A list of cycles (4- to 8-membered), called "inclusive" with respect to $(b = b)$, is presented in [6]. In such an inclusive cycle, the double bond $(b = b)$ precedes all other double bonds in the cycle; therefore, Eqs.(17 - 20) are applicable to inclusive cycles.

A path $(b (a)_{2j+1} b (a)_{2k+1} b \cdots b (a)_{2\ell+1} b)$ ($j, k, \cdots, \ell \geq 0$) is referred to as "alternate" in [6]. In a cycle, composed of two alternate paths, a double bond $(b = b)$ precedes all other double bonds in the cycle; the perimeter

$$[b a a a b a a a b a b b a a a b a a a b a b]$$

of zethrene is an example for such a cycle. A cycle,

$$[b (a)_{2j+1} b (a)_{2k+1} b \cdots b (a)_{2\ell+1}] (j, k, \cdots, \ell \geq 0),$$

is said to be "alternate" in [6]; the perimeter of azulene is a cycle of this kind. In a local conjugated structure of alternate cycles, each of $(b = a)$, $(a = b)$, and $(a = a)$, precedes and follows the rest, and the equality in Eq.(23) is concluded; therefore, $p\{b = a\} = p\{a = b\} = p\{a = a\} = 1/2$, and $I_R = 1$ for alternate cycles.

(3) Table 1 lists all 11 hexagonal cycles, each of which has at least one double bond that precedes and/or follows all other double bonds in the cycle. Mirror images about the horizontal line and/or the vertical line are omitted. In each local conjugated hexagon, a double bond is indicated by either \underline{p} if it precedes or \underline{f} if it follows or \underline{pf} if it precedes and follows all other double bonds in the hexagonal cycle. Neither $[b b b b b a]$ nor $[b b b b b b]$ is included in Table 1. If there is \underline{pf} in a hexagonal cycle, then Eq.(24) implies that one Pauling bond order is equal to another in the hexagon; for

Table 1: All 11 hexagonal subgraphs with double bonds, each of which precedes and/or follows all other double bonds.

$$\begin{aligned}
 [b \stackrel{p}{=} b - a \stackrel{f}{=} a - a \stackrel{f}{=} a -], & \quad [b - b \stackrel{pf}{=} a - a \stackrel{pf}{=} a - a \stackrel{pf}{=} a -], \\
 [b \stackrel{pf}{=} a - b \stackrel{pf}{=} a - a \stackrel{pf}{=} a -], & \quad [b \stackrel{p}{=} a - a \stackrel{p}{=} b - a \stackrel{f}{=} a -], \\
 [b \stackrel{p}{=} b - b \stackrel{f}{=} a - a \stackrel{f}{=} a -], & \quad [b \stackrel{p}{=} b - a = b - a \stackrel{f}{=} a -], \\
 [b - b \stackrel{f}{=} a - b \stackrel{p}{=} a - a \stackrel{p}{=} a -], & \quad [b \stackrel{pf}{=} a - b \stackrel{pf}{=} a - b \stackrel{pf}{=} a -], \\
 [b = b - b = b - a \stackrel{f}{=} a -], & \quad [b \stackrel{p}{=} b - b \stackrel{f}{=} a - b = a -], \\
 [b \stackrel{p}{=} b - a = b - b = a -].
 \end{aligned}$$

example, $p\{[b = a a a b]\} = p\{[b a a = a a b]\} = p\{[b a a a a = b]\}$ (Table 1, top, right). Table 1 presents three hexagonal cycles, $[b b a a a a]$, $[b a b a a a]$ and $[b a b a b a]$, each of which has $\stackrel{pf}{=}$; the latter two alternate, and hence, for example, $p\{[b = a b a b a]\} = p\{[b a = b a b a]\} = 1/2$, and $I_R\{[b a b a b a]\} = 1$ (refer to Eqs.(23 - 25).

(4) Equation (18) is applicable to the estimation of upper and lower bounds for $K\{G\}$. The first step is to find a conjugated cycle in G such that $(x_i = x_{i+1})$ precedes all other double bonds in the cycle. The second step is to make up two skeletons; the one is G with $(x_i - x_{i+1})$, and the other is G with $(x_i = x_{i+1})$. The last step for the first skeleton is to remove the single bond from $(x_i - x_{i+1})$, and for the second skeleton is to remove the double bond from $(x_i = x_{i+1})$; thus, the conjugated cycle in G can be eliminated.

Let us consider a cycle $[b_1 a_2 a_3 b_4 a_5 a_6 a_7 a_8 b_9 b_{10}]$ (10-membered) of G ; two cycles, $[b_1 a_2 a_3 b_4 b_{10}]$ (pentagon) and $[b_4 a_5 a_6 a_7 a_8 b_9 b_{10}]$ (heptagon), are connected by sharing only the path $(b_4 b_{10})$. The cycle is first contracted by use of Eqs.(1 - 3):

$$K\{[b_1 a_2 a_3 b_4 a_5 a_6 a_7 a_8 b_9 b_{10}]\} = K\{[b_1 b_4 b_9 b_{10}]\}.$$

The double bond $(b_1 = a_2)$ precedes all other double bonds in the cycle $[b_1 = a_2 - a_3 = b_4 - a_5 = a_6 - a_7 = a_8 - b_9 = b_{10} -]$. Then Eq.(18) gives the following:

$$2K\{[b_1 = b_4 b_9 b_{10}]\} \leq K\{G\} \leq 2K\{[b_1 - b_4 b_9 b_{10}]\},$$

$$2K\{[[b'_1 = b'_4 b_9 b_{10}]]\} \leq K\{G\} \leq 2K\{[b_1 - b_4 b_9 b_{10}]\},$$

$$2K\{a'_1 \ b_{10} \ a'_4 \ b_9\} \leq K\{G\} \leq 2K\{a_1 \ b_{10} \ a_4 \ b_9\},$$

$$2K\{a'_1 \ a_{10} \ a_9\} \leq K\{G\} \leq 2K\{a_1 \ a'_{10} \ a_9\} + 2K\{a_1 \ a_{10} \ a'_9\}.$$

Glossary of Symbols

a_i	conjugated vertex, connecting with two vertices, in G
a'_i	unconjugated vertex, connecting with two vertices, in G
b_i	conjugated vertex, connecting with three vertices, in G
b'_i	unconjugated vertex, connecting with three vertices, in G
d_i	double bond ($x_i = x_{i+1}$)
G	skeleton (graph)
$I_R\{[\cdots]\}$	Randić index of cycle $[\cdots]$ in G
$K\{G\}$	number of Kekulé structures in G
$K\{[\cdots]\}$	number of Kekulé structures with cycle $[\cdots]$ in G
$K\{d_i, d_j, \dots\}$	number of Kekulé structures with d_i, d_j, \dots
$p\{x_i = x_{i+1}\}$	Pauling bond order between x_i and x_{i+1} in G
$p\{x_i - x_{i+1}\}$	$= 1 - p\{x_i = x_{i+1}\}$
s_i	single bond ($x_i - x_{i+1}$)
x_i	a_i, b_i
x'_i	a'_i, b'_i
$(x_i = x_{i+1})$	x_i and x_{i+1} are connected by a double bond
$(x_i - x_{i+1})$	x_i and x_{i+1} are connected by a single bond

References

- [1] T. Morikawa, *Z. Naturforsch.*, **49a**, 511 (1994).
- [2] N. Trinajstić, *Chemical Graph Theory II*, CRC Press, Boca Raton, 1983.
- [3] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960, Chap. 7.
- [4] W. C. Herndon and C. Párkányi, *J. Chem. Educ.*, **53**, 689 (1976).
- [5] M. Randić, *Tetrahedron* **31**, 1477 (1975).
- [6] T. Morikawa, *Z. Naturforsch.*, **49a**, 973 (1994).

- [7] C. L. Liu, *Elements of Discrete Mathematics*, second ed., McGraw-Hill, New York, 1985, Chap. 4.
- [8] M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum, New York, 1975, p. 99.
- [9] F. Harary, D. J. Klein and T. P. Živković, *J. Math. Chem.*, **6**, 295 (1991).
- [10] M. Randić and D. J. Klein, *Kekulé Valence Structures Revisited. Innate Degrees of Freedom of Pi-Electron Couplings in Mathematical and Computational Concepts in Chemistry*, ed. by N. Trinajstić, Ellis Horwood, New York, 1986, Chap. 23.