Papers

Benzenoid isomers with extremal values of the Kekulé structure count

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In families of benzenoid isomers, the molecules with maximum (minimum) Kekulé structure counts should possess maximum (minimum) stability and other distinguished properties. Identifying these extremal isomers turns out to be a difficult task. In this paper we solve such a problem for the class of isomers $B(m,n)$, obtained from a benzenoid molecule B by attaching to its two fixed sites linear polyacene fragments of length m and n; $m + n =$ constant.

The number of Kekulé structures (K) is a quantity related to, or even determining, a variety of chemical and physical properties of polycyclic conjugated molecules, especially of benzenoid hydrocarbons[1-3]. The stabilities (both thermodynamic[4,5] and kinetic[6,7]) of benzenoid molecules are proportional to their K-values; this fact is reflected in the K-dependence of various resonance energies[8,9], total π-electron energy[10-12], HOMO-LUMO separation[10,13,14] and similar theoretical stability-measures. In particular, within a family of isomers, the most and least stable compounds are those corresponding to the greatest and smallest Kekulé structure counts, respectively. Hence, the identification of these extremal members of benzenoid-isomer families is a problem with clear chemical significance. It may sound somewhat surprising that, in spite of the plethora of results achieved for Kekulé structures of benzenoid systems[1,2] and in spite of almost half a century of research in this area, the problem of benzenoid isomers with extremal values of the Kekulé structure count was so far hardly addressed with a few exceptions. (This problem was examined and fully resolved for unbranched catacondensed benzenoids[15,16]. Also, among benzenoids with a given number of hexagons, the systems possessing maximum K were determined[17]; these happen to be branched catacondensed molecules). In this paper we report the solution of the problem of extremal Kekulé structure counts for a general class of benzenoid systems, whose members are represented by molecular graphs[18] of the type $B(m,n)$.

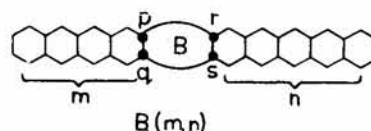The structure of $B(m,n)$ is depicted in Fig. 1.

Fig. 1—The structure of the benzenoid system $B(m,n)$, examined in this work; for details see text[M]

$B(m,n)$ is constructed as follows. Let B be an arbitrary benzenoid system (either peri- or catacondensed) and let (p,q) and (r,s) be its two non-incident edges. We assume that the four vertices p, q, r, s are of degree two, since, otherwise, $B(m,n)$ would not correspond to a benzenoid molecule. Then $B(m,n)$ is obtained by attaching to the edge (p,q) a linear polyacene fragment consisting of m hexagons, and by attaching to the edge (r,s) a linear polyacene fragment consisting of n hexagons. If $m = 0$ or $n = 0$, then nothing is attached to (p,q) or (r,s), respectively. In particular, $B(0,0)$ coincides with B.

In what follows we will examine families of benzenoid systems $B(m,n)$ in which $n + m$ is fixed. Evidently, these systems are isomers.

Statement of the Problem

Let $n + m = h$. Throughout this paper it will be assumed that h has some fixed value. The variable parameters m and n assume then the values 0, 1, 2, ..., $h-1$, h and h, $h-1$, ..., 2, 1, 0, respectively.

For brevity, the number of Kekulé structures of $B(m,n)$, $m+n=h$, will be denoted by $K(h,m)$. Then $K(0,0)$ is equal to the K-value of the parent hydrocarbon B. Further, X, Y and Z will denote

the Kekulé structure counts of the subgraphs $B-p-q$, $B-r-s$ and $B-p-q-r-s$, respectively. (As usual[1,2,18], $B-p-q$ is obtained by deleting the vertices p and q from B; the meaning of the symbols $B-r-s$ and $B-p-q-r-s$ is analogous).

Using previously elaborated methods[1,2,19,20], the Kekulé structures of $B(m,n)$ are easily enumerated:

$$K(h,m) = K(0,0) + mX + nY + mnZ$$

i.e.

$$K(h,m) = K(0,0) + hY + (X-Y)m + m(h-m)Z \quad \dots (1)$$

In order to arrive at Eq. (1), recall[19] that the K value of the polyhex in which a single linear polyacene fragment (with m hexagons) is attached to B is given by $K\{B\} + mK\{B-p-q\}$.

The problem considered in this work is the finding of the greatest and smallest among the numbers $K(h,m)$, $m = 0, 1, 2, \dots, h$, where $K(h,m)$ is given by Eq. (1) and where h has a given, fixed, value. These extremal values will be denoted by K_{max} and K_{min}, respectively. The values of m for which these extrema are achieved are denoted by m_{max} and m_{min}, respectively.

At the first glance the above specified problem may look easy, but as the analysis outlined in the subsequent section shows, its solution happens to be quite perplexing.

At this point we wish to explain the meaning of the symbols $\lfloor x \rfloor$ and $\lceil x \rceil$ (sometimes referred to[21] as "floor" and "ceiling", respectively). These are frequently encountered in the later parts of this paper. By $\lfloor x \rfloor$ is denoted the greatest integer which is not greater than x; for instance, $\lfloor 1.9 \rfloor = 1$, $\lfloor 2.0 \rfloor = 2$, $\lfloor 2.1 \rfloor = 2$. By $\lceil x \rceil$ is denoted the smallest integer which is not smaller than x; for instance $\lceil 1.9 \rceil = 2$, $\lceil 2.0 \rceil = 2$, $\lceil 2.1 \rceil = 3$.

Identifying the $B(m,n)$-isomers with maximum and minimum K-values

In order to find the m-values for which $K(h,m)$ is maximal and minimal, we have to distinguish between four cases:

(i) $X = Y$ and $Z = 0$

(ii) $X = Y$ and $Z > 0$

(iii) $X \neq Y$ and $Z = 0$, and

(iv) $X \neq Y$ and $Z > 0$.

Without loss of generality, we will assume that $X \geq Y$. By this assumption, the considerations that follow are somewhat simplified.

The analysis of the first three of the above cases is elementary.

(i): In this case $K(h,m) = K(0,0) + hY$ and the Kekulé structure count is independent of m. Therefore, $m_{min} = m_{max} = 0, 1, \dots, h$. An example of a B-graph for which (i) applies is **1** depicted in Fig. 2.

(ii): In this case $K(h,m) = K(0,0) + hY + m(h-m)Z$. The minimum K-values are achieved for $m = 0$ and $m = h$: $K_{min} = K(h,0) = K(h,h)$. If h is even, then m_{max} is unique and K_{max} is equal to $K(h,h/2)$. If h is odd, then there are two maximum K-values, for $m_{max} = \lfloor h/2 \rfloor$ and $m_{max} = \lceil h/2 \rceil$. System **2** in Fig. 2 is an example for the case (ii). Notice that this case is usually encountered when in the parent molecular graph B the edges (p,q) and (r,s) are symmetry-equivalent.

(iii): In this case K is an increasing linear function of m, i.e., $K(h,m) = K(0,0) + hY + (X-Y)m$. Consequently, both m_{min} and m_{mix} are unique and $K_{min} = K(h,0)$, $K_{max} K(h,h)$. One should recall that, conventionally, the edges (p,q) and (r,s) of B are selected so that $X > Y$. For an example see **3** in Fig. 2.

The examination of case (iv) is somewhat more complicated. We first transform Eq. (1) into the form

$$K(h,m) = [K(0,0) + hY] + [X-Y+hZ]m - Zm^2 \quad \dots (2)$$

noting that both $[K(0,0) + hY]$ and $[X-Y+hZ]$ depend on h and that $[X-Y+hZ]$ is necesarily positive. If $K(h,m)$ in eq. (2) is considered as a function of a continuous variable m, then we immediately see that $K(h,m)$ has the form of a concave parabola. The maximum of this parabola is at $m = M$, where

$$M = \frac{1}{2}[(X-Y)/Z + h] \quad \dots (3)$$

Evidently, $M > h/2$.

Two subcases of the case (iv) have to be distinguished:

(iv-a) $M \geq h$

(iv-b) $h/2 < M < h$

(iv-a): In this case, for $0 \leq m \leq h$, $K(h,m)$ is a monotonously increasing function of m. Consequently, $m_{min} = 0$, $K_{min} = K(h,0)$; $m_{max} = h$, $K_{max} = K(h,h)$. In view of Eq. (3), the condition $M \geq h$ is tantamount to $(X-Y)/Z \geq h$. Because X, Y, and Z are constants, subcase (iv-a) can occur only for some limited values of h. For instance, if the parent hydrocarbon B is of the form **4** (see
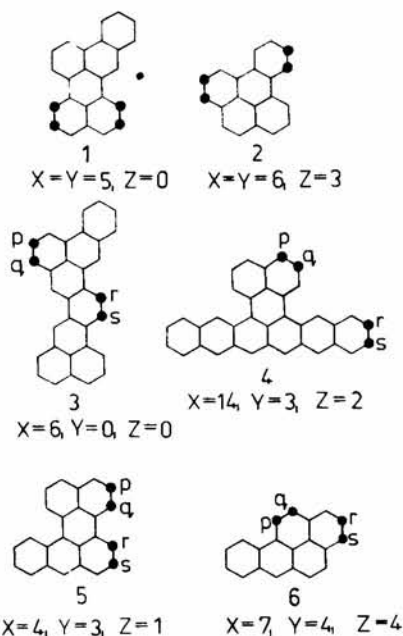
Fig. 2—Examples of various types of parent benzenoid systems $B \equiv B(0,0)$ from which the isomers $B(m,n)$ are constructed by attaching linear polyacene fragments to the sites indicated by heavy dots; for details see text[M]

Fig. 2), then $(X - Y)/Z = 5.5$ and condition (iv-a) is obeyed only for $h \leq 5$.

(iv-b): The determination of the minimum K-value is simple: $m_{min} = 0$, $K_{min} = K(h,0)$. The finding of maximum K is somewhat more complicated:

(1) If M is an integer, then $m_{max} = M$, $K_{max} = K(h,M)$. Example 5, $h = 3, 5, 7, \ldots$ (see Fig. 2).

(2) If M is not an integer and $M - \lfloor M \rfloor < \lceil M \rceil - M$ then the maximum is unique and $m_{max} = \lfloor M \rfloor$. Examples: 4, $h = 7, 9, 11, \ldots$ and 6, $h = 2, 4, 6, \ldots$ (see Fig. 2).

(3) If M is not an integer and $M - \lfloor M \rfloor > \lceil M \rceil - M$ then the maximum is unique and $m_{max} = \lceil M \rceil$. Examples: 4, $h = 6, 8, 10, \ldots$ and 6, $h = 3, 5, 7, \ldots$ (see Fig. 2).

(4) If M is not integer and $M - \lfloor M \rfloor = \lceil M \rceil - M$ then there are two maximal K-values, for $m_{max} = \lfloor M \rfloor$ and $m_{max} = \lceil M \rceil$. Example: 5, $h + 2, 4, 6, \ldots$ (see Fig. 2).

For h being sufficiently large, all examples of type (iv) belong to the subcase (iv-b). For instance, this happens with the system 4 if $h \geq 6$. Numerous benzenoid systems B obey the condition (iv-b) for all values of h, for example 5 and 6 (see Fig. 2).

Concluding Remarks

In the preceding section we determined, case-by-case, the extremal values of the Kekulé structure count of $B(m,n)$. The examination of each in-

dividual case was quite simple and required only elementary mathematical reasoning. What makes the problem relatively difficult is the unusually large number of cases which must be treated separately. Yet, systems of the type $B(m,n)$ seem to pertain to one of the simplest minimax problems as far as Kekulé structures of isomeric benzenoid hydrocarbons are concerned.

The analogous problem for other types of benzenoid isomers turns out to be significantly more perplexing. For instance, if instead of linear polyacene fragments we attach to B zig-zag benzenoid chains (with m and n hexagons), then the corresponding Kekulé structure count is given by

$$F_{m-1}F_{n-1}K(0,0) + F_m F_{n-1}X + F_{m-1}F_n Y + F_m F_n Z$$
$$\ldots (4)$$

where F_k is the k-th Fibonacci number ($F_0 = F_1 = 1$, $F_2 = 2$, $F_3 = 3$, $F_4 = 5$, $F_5 = 8$, ..., $F_k = F_{k-1} + F_{k-2}$). Formula (4) should be compared with Eq. (1). The finding of the minima and maxima of the expression (4) is a hard task.

Further generalizations of the above problem are straightforward: One may consider a given "core" benzenoid B, to which one, two (or more) benzenoids, S, T, ..., are attached. The fragments S, T, ... may be chosen to be cata- and/or peri-condensed benzenoids, subject to some constraints (e.g. that the total number of hexagons is fixed). Chemical sense should be an additional criterion for deciding which of these numerous options to pursue.

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