

LINEARLY ANNELATED CORONENES WITH GREATEST KEKULÉ STRUCTURE COUNTS

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ABSTRACT. In the class of isomeric linearly annelated derivatives of coronene, the species with greatest number of Kekulé structures is determined.

INTRODUCTION

In the theory of benzenoid hydrocarbons [1–3] the Kekulé structures, and especially their number K , play an outstanding role [4,5]. Namely, within classes of benzenoid isomers the following regularities are known to hold:

- The thermodynamic stability (enthalpy of formation and similar) of benzenoid hydrocarbons is a monotonically decreasing function of K [6,7]. In particular, there is a slightly curvilinear dependence of total π -electron energy on K (the Hall rule) [8–12].
- Aromaticity, as measured by various resonance energies, increases with K . In particular, the topological resonance energy and the Dewar resonance energy were, respectively, found to be linearly proportional to K and proportional to the logarithm of K [13,14].
- The first ionization potential increases with K [15].
- Chemical reactivity decreases with increasing K [16–18].

Bearing the above in mind, the identification of the member of a class of benzenoid isomers with greatest K -value is a problem of evident chemical significance. This benzenoid system would be exceptionally stable, both thermodynamically and kinetically. Problems of this kind were studied in several earlier works [19–22]. Here we offer the solution of one more maximum- K problem, namely for isomeric linearly annelated derivatives of coronene.

THE BENZENOID SYSTEM $B(h_1, h_2, h_3, h_4, h_5, h_6)$ AND ITS KEKULÉ STRUCTURE COUNT

The general member of the class of benzenoid systems studied here is denoted by $B(h_1, h_2, h_3, h_4, h_5, h_6)$, where h_1, h_2, \dots, h_6 indicate the length (= number of hexagons) of the linear hexagonal chains annelated to the respective sites of coronene. Thus, in particular, coronene itself would be $B(0, 0, 0, 0, 0, 0)$. For more details see Fig. 1 and observe that $B(h_1, h_2, h_3, h_4, h_5, h_6)$ possesses a total of

$$h = 7 + h_1 + h_2 + \dots + h_6 \quad (1)$$

hexagons.

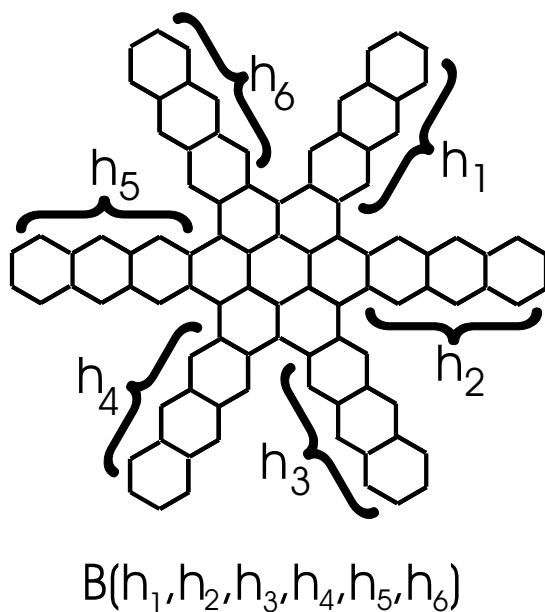


Figure 1. The general formula of the linearly annelated coronene, and the labelling of its six linear hexagonal chains.

It is known for some time [4,23] that when a linear hexagonal chain of length h^* is attached to a molecular graph G , then the number of Kekulé structures of G increases as a linear function of the parameter h^* . Because $B(h_1, h_2, h_3, h_4, h_5, h_6)$ possesses six such linear hexagonal chains, its Kekulé structure count must be a linear function of each of the six parameters h_1, h_2, \dots, h_6 . A lengthy but elementary calculation, based on standard methods [3–5] for the enumeration of Kekulé structures, leads to

$$\begin{aligned}
& K\{B(h_1, h_2, h_3, h_4, h_5, h_6)\} \\
&= (h_1 + 1)(h_2 + 1)(h_3 + 1)(h_4 + 1)(h_5 + 1)(h_6 + 1) \\
&+ [(h_1 + 1)(h_2 + 1)(h_3 + 1)(h_4 + 1)(h_5 + 1) \\
&+ (h_1 + 1)(h_2 + 1)(h_3 + 1)(h_4 + 1)(h_6 + 1) \\
&+ (h_1 + 1)(h_2 + 1)(h_3 + 1)(h_5 + 1)(h_6 + 1) \\
&+ (h_1 + 1)(h_2 + 1)(h_4 + 1)(h_5 + 1)(h_6 + 1) \\
&+ (h_1 + 1)(h_3 + 1)(h_4 + 1)(h_5 + 1)(h_6 + 1) \\
&+ (h_2 + 1)(h_3 + 1)(h_4 + 1)(h_5 + 1)(h_6 + 1)] \\
&+ [(h_1 + 1)(h_2 + 1)(h_3 + 1)(h_5 + 1) + (h_1 + 1)(h_2 + 1)(h_4 + 1)(h_5 + 1) \\
&+ (h_1 + 1)(h_2 + 1)(h_4 + 1)(h_6 + 1) + (h_1 + 1)(h_3 + 1)(h_4 + 1)(h_5 + 1) \\
&+ (h_1 + 1)(h_3 + 1)(h_4 + 1)(h_6 + 1) + (h_1 + 1)(h_3 + 1)(h_5 + 1)(h_6 + 1) \\
&+ (h_2 + 1)(h_3 + 1)(h_4 + 1)(h_6 + 1) + (h_2 + 1)(h_3 + 1)(h_5 + 1)(h_6 + 1) \\
&+ (h_2 + 1)(h_4 + 1)(h_5 + 1)(h_6 + 1)] + 2[(h_1 + 1)(h_3 + 1)(h_5 + 1) \\
&+ (h_2 + 1)(h_4 + 1)(h_6 + 1)] . \tag{2}
\end{aligned}$$

If the sum on the right-hand side of Eq. (1) has a fixed value, then the members of the class $B(h_1, h_2, h_3, h_4, h_5, h_6)$ are isomers with the formula $C_{4(h-1)}H_{2(h-1)}$. Therefore, in what follows we assume that h is a constant. We are thus interested in the maximum value of K within the class of benzenoid molecules $B(h_1, h_2, h_3, h_4, h_5, h_6)$ with h hexagons.

We mention in passing that the minimal value of such benzenoid isomers is attained for $h_1 = h - 7$ and $h_2 = h_3 = \dots = h_6 = 0$, when

$$K_{min}\{B(h_1, h_2, h_3, h_4, h_5, h_6)\} = 14h - 78 .$$

THE MAXIMUM OF $K\{B(h_1, h_2, h_3, h_4, h_5, h_6)\}$

Finding the conditions under which the right-hand side of Eq. (2) becomes maximal (for a fixed value of h , Eq. (1)) appears to be a rather perplexed and difficult mathematical task. This task is left to mathematicians to solve. Instead, we performed an appropriate computer search, by means of which the following results could be established.

Rule 1. For any given value of h , $h \geq 7$, the right-hand side of Eq. (2) becomes maximal if the parameters h_i , $i = 1, 2, \dots, 6$ are almost equal, i. e., if $|h_i - h_j| \leq 1$ for all $1 \leq i, j \leq 6$.

Rule 2. If ℓ is a positive integer, then $K\{B(h_1, h_2, h_3, h_4, h_5, h_6)\}$ becomes maximal if the parameters h_i , $i = 1, 2, \dots, 6$, assume values as given in the following table.

	h_1	h_2	h_3	h_4	h_5	h_6
$h = 6\ell + 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$
$h = 6\ell + 2$	ℓ	$\ell - 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$	$\ell - 1$
$h = 6\ell + 3$	ℓ	$\ell - 1$	ℓ	$\ell - 1$	$\ell - 1$	$\ell - 1$
$h = 6\ell + 4$	ℓ	$\ell - 1$	ℓ	$\ell - 1$	ℓ	$\ell - 1$
$h = 6\ell + 5$	ℓ	ℓ	ℓ	$\ell - 1$	ℓ	$\ell - 1$
$h = 6\ell + 6$	ℓ	ℓ	ℓ	ℓ	ℓ	$\ell - 1$

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