

Algebraic structure count of linear phenylenes and their congeners*

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Abstract: The algebraic structure count of the linear phenylene with h six-membered rings is known to be equal to $h + 1$. We show that the same expression applies if each four-membered ring in the phenylene is replaced by a linear array consisting of k four-membered rings, where $k = 4, 7, 10, \dots$. For any other value of k , the algebraic structure count is either 0 or 1 or 2, and does not increase with increasing h .

Keywords: algebraic structure count, Kekulé structures, phenylenes.

INTRODUCTION

Whereas linear polyacenes (naphthalene, anthracene, tetracene, ...) belong among the best and longest known polycyclic conjugated hydrocarbons,¹ the analogous linear phenylenes were synthesized only in the recent past; for details on the chemistry of phenylenes see the review,² the recent works³⁻⁶ and the references cited therein. The structure of the linear polyacenes (L_h) and the linear phenylenes ($P(1, h)$) is shown in Fig. 1.

The π -electron properties of linear polyacenes are well understood.⁷ In particular, the Kekulé structure count of the linear polyacene with h hexagons is $h + 1$, which, at the same time, is its algebraic structure count.

The π -electron properties of phenylenes are of great interest for theoretical chemistry, because phenylenes are conjugated systems composed of both 6-membered rings (causing bond-length equalization and aromatic stabilization) and 4-membered rings (causing double-bond fixation and antiaromatic destabilization).² In 1993 an unexpected result in this field was obtained,⁸ which eventually stimulated a large amount of additional research.⁹⁻¹⁶ Namely, it was shown⁸ that the algebraic structure count of a phenylene is equal to the number of Kekulé structures of the benzenoid hydrocarbon obtained by formally abandoning the 4-membered rings (so-called "hexagonal squeeze"). In particular, the algebraic structure count of the linear phenylene $P(1, h)$ is equal to the number of Kekulé structures of the linear polyacene L_h , and is thus equal to $h + 1$. (This special case was known¹⁷ before the general regularity⁸ was discovered.)

* Dedicated to Professor Miroslav J. Gašić on the occasion of his 70th birthday.

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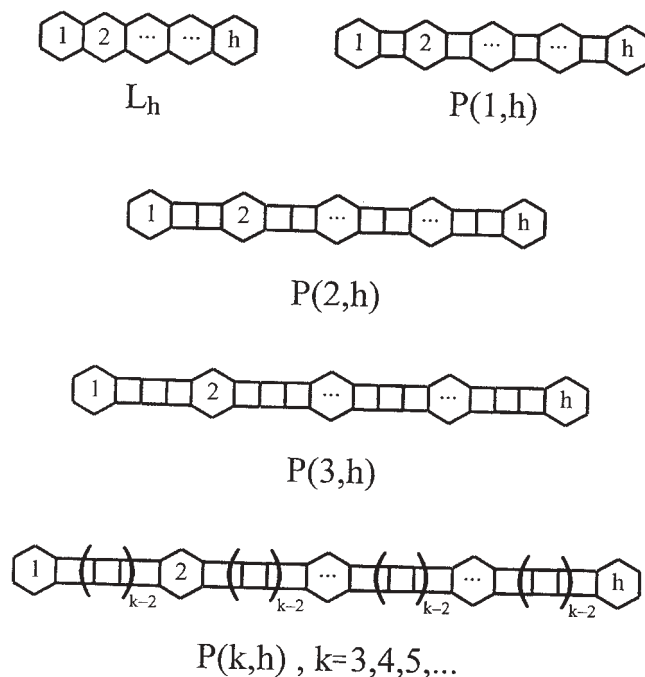


Fig. 1. The polycyclic conjugated π -electron systems, the algebraic structure counts of which are studied in this work.

In phenylenes each 4-membered ring is adjacent to two 6-membered rings, and no two 6-membered rings are adjacent. In an earlier work¹⁸ we considered the congeners of linear phenylenes, in which there are several mutually adjacent 6-membered rings, and found that then the algebraic structure count increases much faster than $h + 1$. In this work we are concerned with the congeners of linear phenylenes, in which there are several mutually adjacent 4-membered rings, namely the systems $P(k, h)$ whose structure is depicted in Fig. 1. We show that their algebraic structure counts follow a completely different pattern and, irrespective of the value of h , are very small or equal to zero.

INTERLUDE: THE ALGEBRAIC STRUCTURE COUNT

The rule that the stability of polycyclic conjugated systems is proportional to the number K of their Kekulé structures holds for benzenoid hydrocarbons.⁷ Attempts to directly extend this rule to non-benzenoid hydrocarbons failed, because the conclusions thus obtained were in many cases in contradiction to experimental findings. The way out of this difficulty was found by Dewar and Longuet-Higgins¹⁹ and was eventually elaborated in due detail by Wilcox.^{20,21} Each Kekulé structure has a so-called "parity" (even, with sign +1 or odd, with sign -1); instead of counting the Kekulé structures, one has to add their signs. The result is called the "algebraic structure count", ASC . The parities are chosen in such a manner that $ASC \geq 0$.

A non-benzenoid conjugated molecule with algebraic structure count equal to α behaves roughly in the same manner as a benzenoid system with α Kekulé structures. This, in particular, means that systems with $ASC = 0$ are extremely unstable (and usually non-existent) whereas $ASC = 1$ and $ASC = 2$ implies very low stability.

The basic procedure for determining the parity of Kekulé structures is the following: Start with an arbitrary Kekulé structure k_1 and assign to it even parity. The Kekulé structures that are obtained from k_1 by cyclically moving an odd number of double bonds have the same parity, *i.e.*, are also even. The Kekulé structures obtained from k_1 by cyclically moving an even number of double bonds have opposite parity, *i.e.*, are odd. Continuing this procedure we can, step-by-step, determine the parity of all Kekulé structures and then easily compute the ASC . The method is applicable to alternant hydrocarbons (and thus to the conjugated systems considered in this work), whereas in the case of non-alternant species the parity concept is not well defined.²²

We illustrate the calculation of the algebraic structure count for the non-benzenoid conjugated systems BCB, P(2,2) and P(2,3). Their Kekulé structures are depicted in Fig. 2.

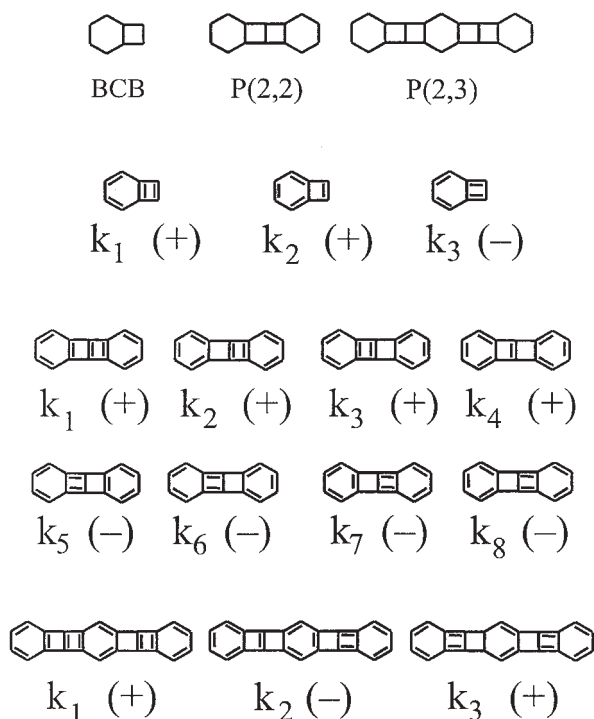


Fig. 2. Three polycyclic conjugated π -electron systems and their Kekulé structures; (+) indicates even and (-) odd parity.

Benzocyclobutadiene (BCB) has three Kekulé structures, k_1, k_2, k_3 . Because k_2 is obtained from k_1 by cyclically rearranging 3 double bonds, k_1 and k_2 are of equal parity. The Kekulé structure k_3 is obtained from k_1 by cyclically rearranging two double bonds, or

from k_2 by cyclically rearranging four double bonds. Hence the parity of k_3 is opposite to that of k_1 and k_2 .

In view of this, the algebraic structure count of benzocyclobutadiene is $ASC(BCB) = +1 + 1 - 1 = 1$.

The conjugated system $P(2,2)$ has a total of 8 Kekulé structures. Of these four are even and four are odd. For instance, the parity of k_2 is even, because k_2 is obtained from k_1 by rearranging three double bonds. The parity of k_4 is also even, because k_4 is obtained from k_2 by rearranging three double bonds. (Note that k_4 cannot be obtained from k_1 by rearranging double bonds within a single cycle.) The parity of k_6 is odd, because k_6 is obtained from k_4 by cyclically rearranging 4 double bonds. *Etc.* As a final result we get $ASC(P(2,2)) = +1 + 1 + 1 + 1 - 1 - 1 - 1 - 1 = 0$.

The conjugated system $P(2,3)$ has 30 Kekulé structures, of which in Fig. 2 are depicted only three. A detailed analysis (same as in the case of BCB and $P(2,2)$) shows that there are 16 even and 14 odd Kekulé structures. Therefore $ASC(P(2,3)) = 16 - 14 = 2$.

In the general case it is not known how to evaluate ASC without actually constructing all the Kekulé structures and determining their parities. In contrast to the counting of Kekulé structures,⁷ no generally applicable recursive method is known for the calculation of the ASC .^{23,24} However, for the systems $P(k, h)$ we were able to find a pertinent method and determine $ASC(P(k, h))$ for all values of the parameters k and h . This is outlined in the subsequent sections.

COMPUTING THE ALGEBRAIC STRUCTURE COUNT OF $P(k, h)$

We first determine $ASC(P(2, h))$. For this consider the carbon-carbon bond indicated in Fig. 3 by an arrow. In some of the Kekulé structures of $P(2, h)$ this bond is double and in some it is single. If this bond is double, then the single/double-character of a few more bonds is fixed, as indicated on diagram **A** in Fig. 3. The non-fixed double bonds belong then to two disjoint fragments, of which one is $P(2, h-2)$ and the other BCB. The contribution of these Kekulé structures to the algebraic structure count of $P(2, h)$ is thus equal to $ASC(P(2, h-2)) \times ASC(BCB)$.

If the bond considered is fixed to be single, then the non-fixed double bonds belong to two disjoint fragments, of which one is $P(2, 2)$ and the other is denoted by **X**, see diagram **B** in Fig. 3. The contribution of these Kekulé structures to the algebraic structure count of $P(2, h)$ is equal to $ASC(X) \times ASC(P(2, 2))$.

Consequently,

$$ASC(P(2, h)) = |ASC(P(2, h-2)) \times ASC(BCB) \pm ASC(X) \times ASC(P(2, 2))|$$

From the previous section we know that $ASC(BCB) = 1$ and $ASC(P(2, 2)) = 0$. Therefore, we arrive at the recursion relation

$$ASC(P(2, h)) = ASC(P(2, h-2))$$

whose initial conditions are $ASC(P(2, 2)) = 0$, $ASC(P(2, 3)) = 2$. This immediately yields

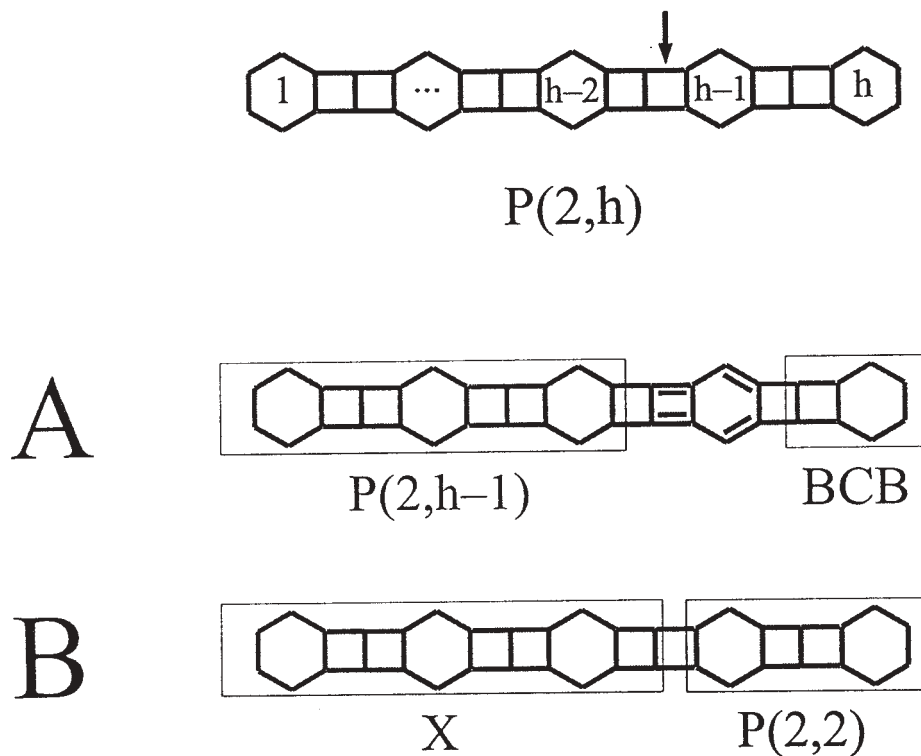


Fig. 3. Diagrams needed for the derivation of the formula for the algebraic structure count of $P(2, h)$.

$$ASC(P(2, h)) = \begin{cases} 0 & \text{if } h = 2, 4, 6, \dots \\ 2 & \text{if } h = 3, 5, 7, \dots \end{cases}$$

In an analogous, yet somewhat more laborious manner, we obtain

$$ASC(P(3, h)) = \begin{cases} 1 & \text{if } h = 2, 4, 6, \dots \\ 2 & \text{if } h = 3, 5, 7, \dots \end{cases}$$

and

$$ASC(P(4, h)) = h + 1.$$

Hence, $ASC(P(4, h)) = ASC(P(1, h))$, which – as will be seen in a while – is a special case of a more general result.

We could continue along these lines and deduce expressions for $ASC(P(5, h))$, $ASC(P(6, h))$, etc. This however is not necessary, in view of Eq. (1) from the subsequent section.

The finding that the ASC -values of the conjugated systems $P(2, h)$ and $P(3, h)$ are zero or near-to-zero, and that these values do not increase with the increasing size of the molecule are in agreement with the fact that the respective compounds have never been synthe-

sized. Another reason for the poor stability of these species would be the enormous steric strain caused by several concatenated 4-membered rings.

A GENERAL RULE FOR THE ALGEBRAIC STRUCTURE COUNT

Denote by F_1 and F_2 two arbitrary alternant conjugated-hydrocarbon fragments. Let H and H^* be conjugated hydrocarbons whose structures are shown in Fig. 4. Then,

$$ASC(H) = ASC(H^*). \quad (1)$$

In order to prove Eq. (1) consider first the Kekulé structures of H . These can be classified into five types, **1**, **2**, **3**, **4**, and **5**, as shown in Fig. 4. The number of even and odd Kekulé structures of each type are denoted by $K_i(\text{even})$ and $K_i(\text{odd})$, $i = 1, 2, 3, 4, 5$. Then the algebraic structure count of H is given by

$$ASC(H) = \sum_{i=1}^5 [K_i(\text{even}) - K_i(\text{odd})] \quad (2)$$

The summands in (2) corresponding to types **4** and **5** cancel out because of

$$K_4(\text{even}) = K_5(\text{odd}) ; K_4(\text{odd}) = K_5(\text{even})$$

The Kekulé structures of H^* can be classified into several types. Of these **11**, **12**, and **13** pertain to Kekulé structures of H of type **1** (see Fig. 4). Now, bearing in mind the way in which the parities of Kekulé structures are determined, we have

$$\begin{aligned} K_{11}(\text{even}) &= K_1(\text{even}) ; K_{11}(\text{odd}) = K_1(\text{odd}) \\ K_{12}(\text{even}) &= K_1(\text{odd}) ; K_{12}(\text{odd}) = K_1(\text{even}) \\ K_{13}(\text{even}) &= K_1(\text{odd}) ; K_{13}(\text{odd}) = K_1(\text{even}) \end{aligned}$$

implying

$$\sum_{i=1}^3 [K_{1i}(\text{even}) - K_{1i}(\text{odd})] = -[K_1(\text{even}) - K_1(\text{odd})] \quad (3)$$

The text types of Kekulé structures of H^* are those marked in Fig. 4 by **21**, **22**, **23**, **24**, and **25**. these all pertain to type **2** Kekulé structures of H . By direct inspection we verify that

$$\begin{aligned} K_{21}(\text{even}) &= K_2(\text{even}) ; K_{21}(\text{odd}) = K_2(\text{odd}) \\ K_{22}(\text{even}) &= K_2(\text{odd}) ; K_{22}(\text{odd}) = K_2(\text{even}) \\ K_{23}(\text{even}) &= K_2(\text{odd}) ; K_{23}(\text{odd}) = K_2(\text{even}) \\ K_{24}(\text{even}) &= K_2(\text{odd}) ; K_{24}(\text{odd}) = K_2(\text{even}) \\ K_{25}(\text{even}) &= K_2(\text{even}) ; K_{25}(\text{odd}) = K_2(\text{odd}) \end{aligned}$$

implying

$$\sum_{i=1}^5 [K_{2i}(\text{even}) - K_{2i}(\text{odd})] = -[K_2(\text{even}) - K_2(\text{odd})] \quad (4)$$

Because of symmetry the analysis of Kekulé structures of H^* of the type **31–35** (not shown in Fig. 4), that correspond to the Kekulé structures of H of the type **3** lead to

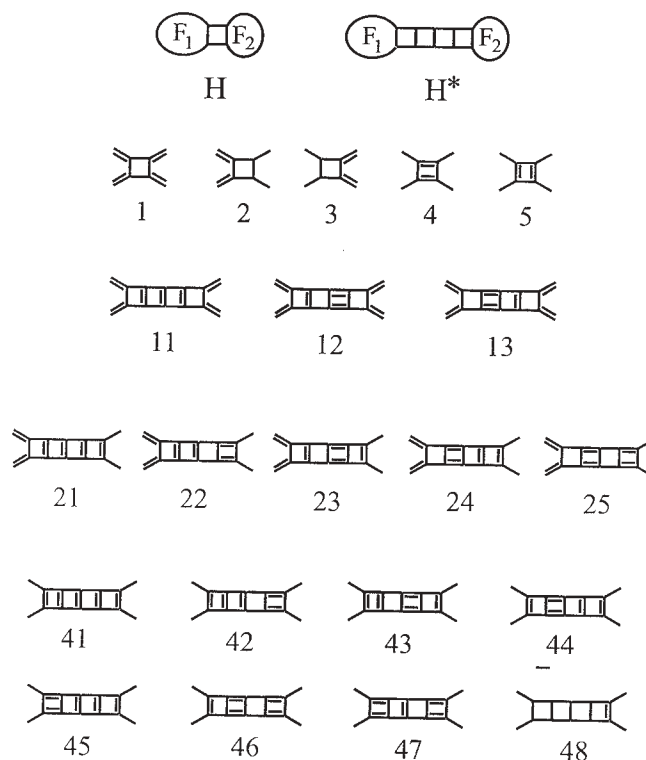


Fig. 4. The general form of the conjugated π -electron systems to which Eq. (1) applies and various types of their Kekulé structures.

$$\sum_{i=1}^5 [K_{3i}(\text{even}) - K_{3i}(\text{odd})] = -[K_3(\text{even}) - K_3(\text{odd})] \quad (5)$$

Finally, we have to examine the Kekulé structures of H^* of the types **41–48**, which are related to the Kekulé structures of H of the types **4** and **5**. Their total contribution is also zero, because four of them (**41, 46, 47, 48**) are of one parity and the other four (**42, 43, 44, 45**) of opposite parity.

In summary, the algebraic structure count of H^* depends on the number of even and odd Kekulé structures of the types **1i, 2i, and 3i** and in view of Eqs. (3)–(5),

$$\begin{aligned} ASC(H^*) &= \left| \sum_{i=1}^3 [K_{1i}(\text{even}) - K_{1i}(\text{odd})] + \sum_{i=1}^5 [K_{2i}(\text{even}) - K_{2i}(\text{odd})] + \right. \\ &+ \left. \sum_{i=1}^5 [K_{3i}(\text{even}) - K_{3i}(\text{odd})] \right| = \left| - \sum_{i=1}^3 [K_i(\text{even}) - K_i(\text{odd})] \right| = \\ &= \left| -ASC(H) \right| = ASC(H) \end{aligned}$$

which is just the result stated as Eq. (1).

BACK TO THE CONGENERS OF LINEAR PHENYLENES

Bearing in mind Eq. (1), we see that the identity

$$ASC(P(k+3, h)) = ASC(P(k, h)) \quad (6)$$

must hold for any $k \geq 1$ and $h \geq 2$. This means that it is sufficient to determine the expressions for the algebraic structure counts of $P(1, h)$, $P(2, h)$, and $P(3, h)$ (what we already did), whereas for all higher values of k the formulas are readily obtained by means of Eq. (6).

Thus the general expression for the algebraic structure count of the congeners of linear phenylenes studied in this work (*cf.* Fig. 1) reads:

$$ASC(P(k, h)) = \begin{cases} h+1 & \text{for } h=2, 3, 4, 5, \dots \text{ and } k=1, 4, 7, 10, \dots \\ 0 & \text{for } h=2, 4, 6, 8, \dots \text{ and } k=2, 5, 8, 11, \dots \\ 1 & \text{for } h=2, 4, 6, 8, \dots \text{ and } k=3, 6, 9, 12, \dots \\ 2 & \text{for } h=3, 5, 7, 9, \dots \text{ and } k \neq 1, 4, 7, 10, \dots \end{cases}$$

The main chemical consequence of the above formulas is the following. Linear phenylenes $P(1, h)$ (possessing one four-membered ring between the six-membered rings) are slightly less stable than the corresponding linear polyacenes L_h . Introduction of additional four-membered rings drastically reduces the stability of the thus obtained π -electron systems. This is implied both by the extremely low ASC -values (a feature studied in this work) and by the extremely increased steric strain (a feature not considered in this work).

In order to help understanding how small are the ASC -values of the phenylenes and their congeners, we mention that in the case $h=5$ (*cf.* Fig. 1), the systems $P(1, h)$, $P(2, h)$, and $P(3, h)$ possess 79, 418, and 3038 Kekulé structures, respectively. Yet their behavior is such as if they had 6, 2, and 2 Kekulé structures, respectively. There is no (stabilizing) effect originating from the numerous Kekulé structures, because nearly half of them are of one and half of the opposite parity.

ИЗВОД

АЛГЕБАРСКИ БРОЈ СТРУКТУРА ЛИНЕАРНИХ ФЕНИЛЕНА И СРОДНИХ
ЈЕДИЊЕЊА

ИВАН ГУТМАН

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Познато је да је алгебарски број структура линеарног фенилена са h шесточланих прстенова једнак $h+1$. У раду показујемо да исти израз важи и ако се сваки четворочлани прстен у фенилену замени са k линеарно поређаних четворочланих прстенова, за $k=4, 7, 10, \dots$. За све остале вредности k , алгебарски број структура је или 0 или 1 или 2, и не расте са порастом h .

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