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Algebraic Structure Count of Cyclobutadieno-Annelated Unbranched Phenylenes

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Summary. The calculation of the algebraic structure count of a cyclobutadieno-annelated unbranched phenylene is reduced to an enumeration of the Kekulé structures of an unbranched catacondensed benzenoid system. For the latter computation, easy and well-known algorithms exist.

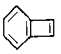
Keywords. Structure Count, Phenylene, Kekulé.

Algebraische Strukturzählung von cyclobutadieno-annelierten unverzweigten Phenylenen

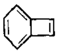
Zusammenfassung. Die Berechnung des algebraischen Strukturzählers eines unverzweigten cyclobutadieno-annelierten Phenylens wird auf die numerische Ermittlung der Kekulé-Strukturen eines unverzweigten cactakondensierten benzenoiden Systems zurückgeführt. Für letztere stehen einfache und bekannte Algorithmen zur Verfügung.

Introduction

Kekulé valence structures have long been important in organic chemistry because, in general, the more such structures that can be drawn for a molecule, the more likely it is that the molecule will be stable. Furthermore, polyhexagonal systems with no Kekulé structures are predicted to be definitely unstable [1]. This intuitive and empirical relationship was given quantitative expression with the publication of estimates of the resonance energy of benzenoid hydrocarbons derived from the number of Kekulé structures (K), either alone [2–4] or with other simple descriptors [5, 6]. However, whilst this rationale is very satisfactory for benzenoid hydrocarbons, it was known from quite early work [7] to be inadequate for a full understanding of conjugated polycyclic non-benzenoid structures. To improve matters the concept of parity was introduced [7], where Kekulé structures are distinguished as K^+ (even) or K^- (odd). The assignment plus or minus is arbitrary, depending upon the initial labelling of the molecule, but two Kekulé structures are said to be of the same parity if one can be obtained from the other by cyclically rearranging an odd number of bonds [8–13]. Conversely, their parities oppose if interconversion requires the cyclic rearrangement of an even number of bonds. This is illustrated by the simple example of benzocyclobutadiene, which has three Kekulé structures (shown below as K_a, K_b and K_c).



K_a



K_b

K_c

K_a and K_b are of the same parity because one can be converted into the other by rotating the conjugated three-double-bond 6-ring by 60°. K_a can only be converted to K_c, however, by rotating two bonds around the 4-ring, while K_b requires movement of four bonds around the perimeter. Needless to say, as structures become larger, it soon becomes much more difficult to count Kekulé structures directly and accurately.

It is the absolute value of the difference between these quantities ($K^+ - K^-$), called the *algebraic structure count* [8,9] or *corrected structure count* [10,11] that is important for understanding and rationalizing the π-electron properties of the wider range of conjugated polycyclic structures in general, and the thermodynamic stability of non-benzenoid aromatic compounds increases with increasing magnitude of this count [2,14]. If the algebraic structure count (ASC) is zero, then the simple Hückel model (see [12,13]) implies that the molecule's π-system has an open-shell electron configuration and is thus likely to be unstable and difficult to synthesise (see reference [15] and citations therein).

A number of methods are available for enumerating Kekulé structures (see for example [13,16–20]), and a relatively easy method [19,20] makes use of the simple recursive relationship

$$K\{G\} = K\{G-(e)\} + K\{G-[e]\} \tag{1}$$

where G is an arbitrary molecular graph, and e can be any edge of it. Deletion of edge e alone gives the subgraph $G-(e)$, while deletion of edge e and its pair of vertices results in subgraph $G-[e]$.

No analogous relationship is known for the algebraic structure count, although it has been demonstrated [21] that the ASC conforms to one of the following three equalities:

$$\mathrm{ASC}\{G\} = \mathrm{ASC}\{G-(e)\} + \mathrm{ASC}\{G-[e]\} \tag{2}$$

$$\mathrm{ASC}\{G\} = \mathrm{ASC}\{G-(e)\} - \mathrm{ASC}\{G-[e]\} \tag{3}$$

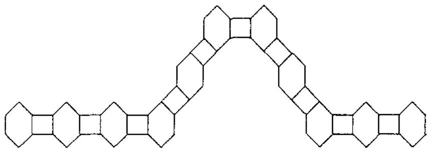
$$\mathrm{ASC}\{G\} = -\mathrm{ASC}\{G-(e)\} + \mathrm{ASC}\{G-[e]\} \tag{4}$$

but whether (2), (3) or (4) is applicable depends on the graph G and its edge e. Thus combinatorial formulae for the ASC have been obtained for only a few classes of non-benzenoid aromatic structures [22–25], in sharp contrast to the great variety of such formulae known for the Kekulé structure count (see within the references given above).

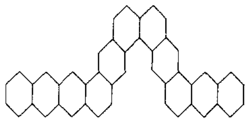
It was recently shown by one of us that the difficult problem of calculating the algebraic structure count for phenylenes can be reduced to the easy (and by now well known) problem of enumerating the Kekulé structures of an appropriate catacondensed benzenoid system [26,27]. In this paper we show how to derive the ASC of cyclobutadieno-annelated phenylenes. Very few of these compounds are known at present, but available details can be found in the recent review by Toda and Garrat [15].

Unbranched Phenylenes and some of their Structural Characteristics

Unbranched phenylenes are polycyclic conjugated systems composed of six-membered rings that are arranged in a chain and coupled to each other via cyclobutadiene units. They are referred to as [*n*]phenylenes. For example, **1** represents an unbranched [*11*]phenylene.



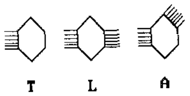
1



2

Every unbranched [*n*]phenylene is associated with an *n*-cyclic unbranched catacondensed benzenoid system to which it can be converted by eliminating the four-membered rings from the phenylene, *i.e.* by collapsing onto each other the hexagons that share a common cyclobutadiene unit. This is called the hexagonal squeeze (*HS*). For instance, the benzenoid system **2** is the hexagonal squeeze of **1**.

The hexagons in both an unbranched phenylene and its hexagonal squeeze are of three types. Two of the hexagons are terminal (*T*), and the remaining $n-2$ hexagons are annelated in either a linear (*L*) or an angular (*A*) mode.



An important part of the topology of these molecules (but not their complete structure!) is described by the so-called *LA*-sequence (first used in reference [28]; with details to be found in reference [26]).

If $\chi_1, \chi_2, \ldots, \chi_n$, are the hexagons of an unbranched phenylene, labelled consecutively from left to right, then the corresponding *LA*-sequence is an ordered *n*-tuple $\mathscr{L} = (S_1, S_2, \ldots, S_n)$, such that for i = 1 and i = n,

$$S_i = L$$

whereas for $i = 2, \ldots, n-1$,

$$S_i = \begin{cases} L & \text{if the hexagon } \chi_i \text{ is annelated in a linear mode} \\ A & \text{if the hexagon } \chi_i \text{ is annelated in an angular mode.} \end{cases}$$

For example, $\mathscr{L}(1) = \mathscr{L}(2) = LLLALAALALL$.

Using the conventions $L \equiv L^1$, $LL \equiv L^2$, $LLL \equiv L^3, \ldots$, as well as $L^0 \equiv 1$ (i.e. no symbol *L*), we can rewrite the right hand side as $L^3AL^1AL^0AL^1AL^2$, and in general write an *LA*-sequence as

$$\text{REM } \mathscr{L} = L^{t_0}AL^{t_1}AL^{t_2}A \ldots L^{t_{p-1}}AL^{t_p} \tag{5}$$

where $t_0 \geqslant 1$, $t_p \geqslant 1$, and $t_i \geqslant 0$ for $i = 1, \ldots, p-1$.

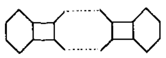
The significance of the LA-sequence is seen from the following results:

Theorem 1. $\mathscr{L}$ determines the Kekulé structure count of an unbranched catacondensed benzenoid system (references [20] and [26] and references thererein).

Theorem 2. $\mathscr{L}$ determines the algebraic structure count of an unbranched phenylene [27]. Furthermore, $\mathrm{ASC}\{\mathscr{L}\} = \mathrm{K}\{\mathscr{L}\}_{HS}$ where $\{\mathscr{L}\}_{HS}$ indicates that the Kekulé structure count is computed for the corresponding hexagonal squeeze.

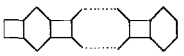
Cyclobutadieno-annelated Unbranched Phenylenes and some of their Structural Characteristics

In what follows an arbitrary unbranched phenylene will be represented by the diagram below and denoted by U. It is understood that U has n hexagons.

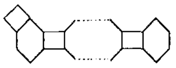


U

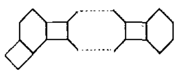
One additional cyclobutadiene unit can be attached to a terminal hexagon in two different ways: linearly (λ) or angularly (α). The respective conjugated systems will be denoted by λU and αU, respectively. From the point of view of the computation of ASC, the actual direction of the angular annelation is immaterial (see below); therefore we will not distinguish between systems αU and $\alpha' U$, although they may correspond to chemically distinct isomers (for the central section need not be linear).



λU

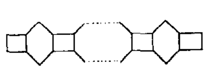


αU

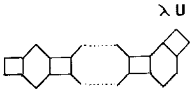


$\alpha' U$

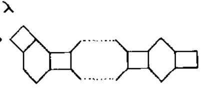
If to both terminal hexagons of an unbranched phenylene, U, a cyclobutadiene unit is annelated, then four cases have to be distinguished: $\lambda U \lambda$, $\lambda U \alpha$, $\alpha U \lambda$ and $\alpha U \alpha$:



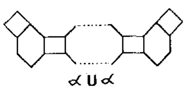
$\lambda U \lambda$



$\lambda U \alpha$



$\alpha U \lambda$



$\alpha U \alpha$

Results and Discussion

Denote the LA-sequence on the unbranched phenylene by $\mathscr{L}$ and assume that it has the form given by Eq. (5). Then the algebraic structure counts of the cyclobutadieno-annelated derivatives of U are equal to the Kekulé structure counts of certain benzenoid systems. The respective results are summarised in Theorems 3–6.

Theorem 3. If $t_1 > 0$, then $\mathrm{ASC}\{\lambda U\} = K\{L^{t_1}AL^{t_2}A \dots L^{t_{p-1}}AL^{t_p}\}_{HS}$. If $t_1 = 0$ then $\mathrm{ASC}\{\lambda U\} = K\{L^{t_2+1}A \dots L^{t_{p-1}}AL^{t_p}\}_{HS}$.

Theorem 4. If $t_0 > 1$, then $\mathrm{ASC}\{\alpha U\} = K\{L^{t_0-1}AL^{t_1}A \dots L^{t_{p-1}}AL^{t_p}\}_{HS}$. If $t_0 = 1$ then $\mathrm{ASC}\{\alpha U\} = K\{L^{t_1+1}AL^{t_2}A \dots L^{t_{p-1}}AL^{t_p}\}_{HS}$.

Theorem 5. If $\mathrm{ASC}\{\lambda U\lambda\} = \mathrm{ASC}\{\lambda U'\}$ and $\mathrm{ASC}\{\alpha U\lambda\} = \mathrm{ASC}\{\alpha U'\}$ where U' is a phenylene system whose LA-sequence is $L^{t_0}AL^{t_1}A \dots L^{t_{p-1}}$ if $t_{p-1} > 0$, and $L^{t_0}AL^{t_1}AL^{t_2}A \dots L^{t_{p-2}+1}$ if $t_{p-1} = 0$. The ASC-values of $\lambda U'$ and $\alpha U'$ are obtained from Theorems 3 and 4.

Theorem 6. $\mathrm{ASC}\{\lambda U\alpha\} = \mathrm{ASC}\{\lambda U''\}$ and $\mathrm{ASC}\{\alpha U\alpha\} = \mathrm{ASC}\{\alpha U''\}$ where U'' is a phenylene system whose LA sequence is $L^{t_0}AL^{t_1}A \dots L^{t_{p-1}}AL^{t_p-1}$ if $t_p > 1$ and $L^{t_0}AL^{t_1}AL^{t_2}A \dots L^{t_{p-1}+1}$ if $t_p = 1$. The ASC values of $\lambda U''$ and $\alpha U''$ are obtained from Theorems 3 and 4.

In order to illustrate these theorems, we compute the algebraic structure counts of λU, αU, $\lambda U\lambda$, $\lambda U\alpha$, $\alpha U\lambda$ and $\alpha U\alpha$ for U being the [*11*]phenylene **1**. In this case (see above), $p = 4$, $t_0 = 3$, $t_1 = 1$, $t_2 = 0$, $t_3 = 1$, $t_4 = 2$.

1. Because $t_1 > 0$, we have from Theorem 3:

   $$\mathrm{ASC}\{\lambda \mathbf{1}\} = K\{\mathbf{3}\}$$

   when the benzenoid system **3** is depicted below and where $\mathscr{L}(\mathbf{3}) = LAALAL^2$. Consequently $K\{\mathbf{3}\} = 27$, and therefore $\mathrm{ASC}\{\lambda \mathbf{1}\} = 27$.
2. Because $t_0 > 1$, we have from Theorem 4:

   $$\mathrm{ASC}\{\alpha \mathbf{1}\} = K\{\mathbf{4}\}$$

   where $\mathscr{L}(\mathbf{4}) = L^2ALAALAL^2$, $K\{\mathbf{4}\} = 91$. Therefore $\mathrm{ASC}\{\alpha \mathbf{1}\} = 91$.
3. The relevant condition is $t_{p-1} > 0$ and Theorem 5 yields:

   $$\mathrm{ASC}\{\lambda \mathbf{1}\lambda\} = \mathrm{ASC}\{\lambda \mathbf{1}'\} \text{ and } \mathrm{ASC}\{\alpha \mathbf{1}\lambda\} = \mathrm{ASC}\{\alpha \mathbf{1}'\}$$

   where the auxiliary system **1′** is depicted below. By means of Theorems 3 and 4 we now readily obtain:

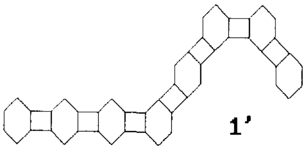
   $$\mathrm{ASC}\{\lambda \mathbf{1}'\} = \mathrm{K}\{\mathbf{5}\} = 8 \text{ and therefore } \mathrm{ASC}\{\lambda \mathbf{1}\lambda\} = 8$$
   $$\mathrm{ASC}\{\alpha \mathbf{1}'\} = \mathrm{K}\{\mathbf{6}\} = 27 \text{ and therefore } \mathrm{ASC}\{\alpha \mathbf{1}\lambda\} = 27$$

   Notice that **6** is isomorphic to **3**.
4. The relevant condition is $t_p > 1$ and Theorem 6 thus yields:

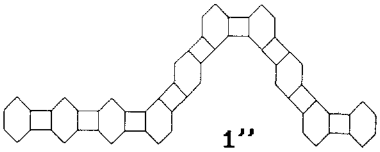
   $$\mathrm{ASC}\{\lambda \mathbf{1}\alpha\} = \mathrm{ASC}\{\lambda \mathbf{1}''\} \text{ and } \mathrm{ASC}\{\alpha \mathbf{1}\alpha\} = \mathrm{ASC}\{\alpha \mathbf{1}''\}.$$

   By means of Theorems 3 and 4 we further get that:

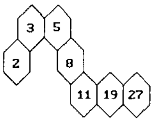
   $$\mathrm{ASC}\{\lambda \mathbf{1}''\} = K\{\mathbf{7}\} = 19 \text{ and therefore } \mathrm{ASC}\{\lambda \mathbf{1}\alpha\} = 19$$
   $$\mathrm{ASC}\{\alpha \mathbf{1}''\} = K\{8\} = 64 \text{ and therefore } \mathrm{ASC}\{\alpha \mathbf{1}\alpha\} = 64.$$



1'



1''



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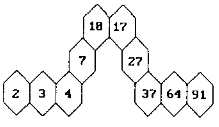

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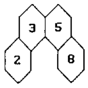

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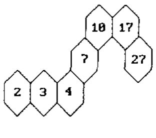

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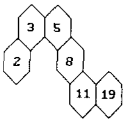
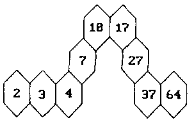


7



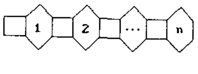
8

Note: In **3**–**8**, the figures for calculating K by the well-known Gordon–Davidson "numeral in hexagon" method [29] are shown. For this, start at one end and insert "2" and "3", respectively, in the first two hexagons. The "addition constant" is now one. For each subsequent hexagon; form its numeral by adding this addition constant to the value of the preceding ring, but immediately after each kink, change the value of the addition constant to that of the last ring before the kink. The last figure obtained is then the number of Kekulé structures.

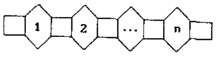
The application of these rules seems complicated when the details are elaborated in this way. For practical paper and pencil enumeration, however, it is worth pointing out that once it is determined which equations are applicable, then the actual operations required are very simple, and remain consistent for the various combinations. Thus, for the example shown above, the algebraic structure count of U is equal to $K\{\mathbf{2}\}$; if a cyclobutadiene is annelated λ then, from the appropriate end of **2**, hexagons are deleted up to and including the first angular hexagon; if it is annelated α, then one hexagon is deleted from the appropriate end, to provide a graph **G** where $K\{\mathbf{G}\} = \mathrm{ASC}\{\mathbf{1}\}$.

The only cases where the above theorems are (formally) inapplicable are the linear systems **9** and **10**. If these are encountered, then their algebraic structure counts can be calculated by means of the simple formulae [22]:

$$\mathrm{ASC}\{\mathbf{9}\} = 1; \quad \mathrm{ASC}\{\mathbf{10}\} = 0 \text{ for all } n \geqslant 1.$$



9



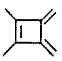
10

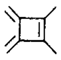
The fact that the algebraic structure count is equal to the Kekulé structure count of its hexagonal squeeze was proved earlier [27].

Preparatory to treating the case of cyclobutadieno-annelated phenylenes, consider first a phenylene molecule and examine the arrangements of double bonds in one of its 4-membered cycles. Five distinct arrangements are possible: **A**, **B**, **C**, **D** and **E**:


A


B


C


D


E

In view of the definition of ASC, Kekulé structures having arrangements **A** and **B** have opposite parities and they mutually cancel (for details see [27] and the references quoted therein). Therefore, the Kekulé structures possessing 4-membered cycles with double-bond-arrangements **A** or **B**, do not contribute to the ASC. In the case of phenylenes, ASC is equal to the number of remaining Kekulé structures, namely those in which in all 4-membered cycles the double bonds have arrangements **C**, **D** or **E**. In other words, in order to determine the ASC-value of a phenylene, we have to count its Kekulé structures in which the arrangements **A** and **B** are absent.

This conclusion applies also to cyclobutadieno-annelated phenylenes. Here we have additional requirement that of the three possible arrangements of double bonds in the terminal 4-membered rings (**A**′, **B**′, **C**′), the arrangement **A**′ and **B**′ are absent:

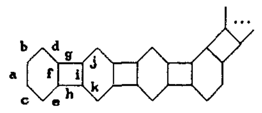

A'

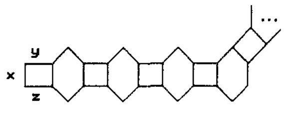

B'


C'

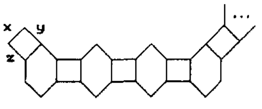
Without loss of generality we may consider the effect of the annelation of a cyclobutadiene unit to the left hand side of the phenylene chain, Further, for the sake of simplicity we choose a concrete value for t_0 (in our case: $t_0 = 3$), but the reasoning is applicable in an obvious manner to any other value of t_0.

Consider thus an unbranched phenylene and its two cyclobutadieneo-annelated derivatives, whose structures are shown in the diagram below:





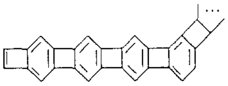
λ



α

Case 1: linear annelation of cyclobutadiene unit (λ)

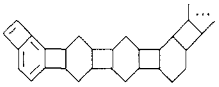
As already explained, we have to count the Kekulé structures in which the double bonds occupy neither the positions y and z, nor the positions x and a. Hence, the double bonds must be in positions x, b and c. Then the bonds d and e must be single. If the bond f were single too, then the bonds g and h would have to be double, implying a configuration of type **A**. Since such a configuration is not permitted, f must be double and g and h single. If bond i were double, then we would have a configuration of type **B**. Since this is not permitted, i must be single. Consequently, j and k must be double, etc. Continuing this argument, we conclude that until the first angularly annelated hexagon (inclusive), the double bonds must have a fixed arrangement, as indicated below.



The above conclusion, combined with Theorem 2, results in Theorem 3. A fully equivalent reasoning leads to Theorem 5.

Case 2: angular annelation of cyclobutadiene unit (α)

In this case the only permissible arrangement of double bonds in the terminal cyclobutadiene fragment is x, a and d. Then the bond e also must be double. Consequently, the bonds g and h must be single. Now the bond i can be either single (resulting in a configuration of type **E**) or double (resulting in a configuration of the type **D**). Since both **D**- and **E**-type arrangements are permitted, we see that an angular annelation of the cyclobutadiene fragment influences the arrangements of the double bonds only in the (adjacent) terminal hexagon:



This conclusion, together with Theorem 2, results in Theorem 4. A fully analogous reasoning yields Theorem 6.

Conclusions

The algebraic structure count is an important quantity for understanding the generality of conjugated systems, but with polycyclic structures of more than a very few rings it is quite impracticable to evaluate it directly. In this and the preceding paper we have shown that for at least some classes of structure the problem can be reduced to that of counting Kekulé structures, for which many published methods are available. Here, specifically, the remarkably simple method for dealing with phenylenes has been extended to cover cyclobutadieno-annelated phenylenes, with only slightly greater complication.

Because all catacondensed benzenoids possess two or more Kekulé structures, our results imply that ASC $\geqslant 2$ for both phenylenes (as noted earlier [27]) and, in general, cyclobutadieno-annelated phenylenes as shown here. The only exceptions are the systems **9**, where ASC = 1, and **10**, for which ASC = 0. These are known to be very unstable.

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