A FORMULA FOR THE ALGEBRAIC STRUCTURE COUNT OF MULTIPLE PHENYLENES

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Abstract

It is demonstrated that the algebraic structure count (A) of a class of pericondensed nonbenzenoid alternant hydrocarbons $X_{m,n}$, called multiple phenylenes, conforms to the recursion relation: $A\{X_{m,n}\} = (n+1) A\{X_{m-1,n}\} - \lfloor n^2/4 \rfloor A\{X_{m-2,n}\}$ with initial conditions $A\{X_{0,n}\} = 1$ and $A\{X_{1,n}\} = n+1$, $n > 0$.

Introduction

The systematic study of the algebraic structure count (ASC) [1] of nonbenzenoid [2] alternant [3] conjugated hydrocarbons started relatively recently [4-9]. The first results along these lines were obtained for cata-condensed molecules [4,5,7], whereas the finding of the ASC-values of peri-condensed systems turned out to be a much harder problem. (Recall that a polycyclic conjugated molecule is said to be pericondensed if at least one of its atoms is shared by three rings; otherwise the molecule is catacon-densed [10]).

In a recent work [9] we examined a class of pericondensed nonbenzenoid

conjugated systems which we named "multiple phenylenes". Their structure is shown in **Fig. 1**, where also the meaning of the parameters m and n is indicated.
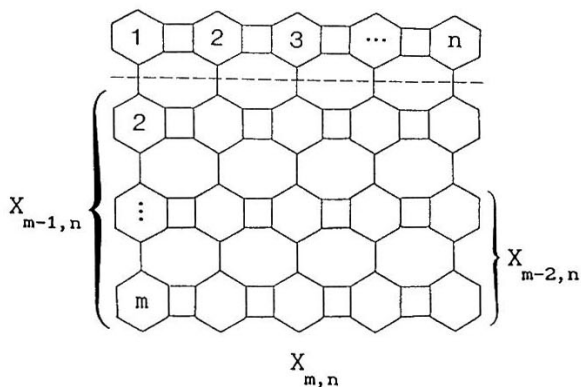

Fig. 1

The graph depicted in Fig. 1 is a standard molecular graph (or more precisely: a skeleton or hydrogen-depleted graph). Its vertices represent carbon atoms, and two vertices are adjacent if the respective carbon atoms are chemically bonded; the type of the chemical bond (single, double or intermediate) is immaterial for the adjacency relation. As usual, hydrogen atoms are not represented by vertices. The vertices of a molecular graph of a fully conjugated hydrocarbon are of degree one, two or three. In the case of the graph $X_{m,n}$ only vertices of degree two and three are encountered. Vertices of degree three represent carbon atoms to which no hydrogen is attached; vertices of degree two represent carbon atoms to which a hydrogen

atom is attached. More details on the construction and properties of mole-
cular graphs can be found elsewhere [10-12].

From **Fig.1** is seen that the multiple phenylene denoted by $X_{m,n}$ consists
of m × n hexagons, arranged in m rows and n columns. If m = 1 , then $X_{m,n}$
is the linear [n]phenylene, namely the linear phenylene with n hexagons. If
m > 1 , then every row of $X_{m,n}$ is just a linear [n]phenylene fragment. In
what follows, instead of "linear [n]phenylene" we will simply say "phenyl-
ene".

In [9] we arrived at a recursion relation and a general expression for
the algebraic structure count of $X_{m,n}$, namely at

$$A\{X_{m,n}\} = (n + 1) \ A\{X_{m-1,n}\} - \lfloor n^2/4 \rfloor \ A\{X_{m-2,n}\} \tag{1}$$

and

$$A\{X_{m,n}\} = (1/R) \left[\left(\frac{n + 1 + R}{2} \right)^{m+1} - \left(\frac{n + 1 - R}{2} \right)^{m+1} \right] \tag{2}$$

where $R = \sqrt{2n+1}$ if n is even and $R = \sqrt{2n+2}$ if n is odd. Recall that $\lfloor n^2/4 \rfloor$
$= n^2/4$ if n is even, and $\lfloor n^2/4 \rfloor = (n^2-1)/4$ if n is odd.

Formula (2) follows from (1) under the initial conditions $A\{X_{0,n}\} = 1$
and $A\{X_{1,n}\} = n+1$.

Here and later by A{X} is denoted the algebraic structure count of the
conjugated system X. Without loss of generality we may assume that X stands
for the molecular graph.

Whereas (2) is a straightforward consequence of (1), no proof of (1)
was given in [9]. The aim of this paper is to fill this gap and to deduce
the following:

> **Theorem 1.** Formula (1) holds for all m ≥ 2 and n > 0, and its initial
> conditions are $A\{X_{0,n}\} = 1$ and $A\{X_{1,n}\} = n+1$.

In order to prove Theorem 1 we need some preparations.

Some auxiliary considerations

First recall [1] that the ASC-concept is based on the possibility to associate a certain "parity" to every Kekulé structure. Then ASC is equal to the difference between the number of "even" and "odd" Kekulé structures. Two Kekulé structures are of equal (opposite) parity if one is obtained from the other by moving an odd (even) number of double bonds along one cycle. The parity of Kekulé structures has, however, a deeper algebraic foundation; the readers interested in this long-established details should consult the references quoted [1]. Conventionally, the parity of the Kekulé structures is chosen so that the number of even structures is greater than or equal to the number of odd structures. (Then ASC is a positive- or zero-valued quantity.)

Consider now a conjugated system having a four-membered ring. Its Kekulé structures can be divided into five groups (A, B, C, D & E), depending on the arrangement of the double bonds in and around the respective four-membered ring, see **Fig. 2**.
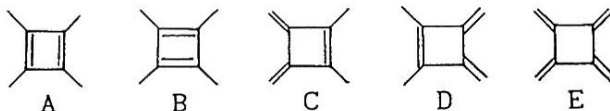

Fig. 2

The Kekulé structures of type A and B differ only in the position of two double bonds within one cycle and are therefore of opposite parity. Hence, they cancel out when ASC is computed. Consequently, in the considerations concerned with ASC, Kekulé structures of the type A and B need not at all be taken into account.

In order that this paper be self-contained we prove again a result from [4]. Besides, parts of the proof of Lemma 1 are used also in the subsequent deliberations.

Lemma 1. For the linear [n]phenylene, $A\{X_{1,n}\} = n + 1$.

Proof. Consider only those Kekulé structures of $X_{1,n}$ in which there are no arrangements of double bonds of the type A or B, see **Fig. 2**. Observe that a Kekulé structure, having the arrangement E in the k-th square is unique, k = 1,...,n-1. We denote this Kekulé structure by L_k (**Fig. 3**). In addition, $X_{1,n}$ has only two more Kekulé structures (L_0 and L_n) in which there are no E-type arrangements of double bonds, see **Fig. 3**.

Now, the structures L_k and L_{k-1} , k = 1,...,n, are of equal parity because one is obtained from the other by moving three (an odd number) double bonds within the k-th hexagon. This implies that ASC is n+1. ■

Proof of Theorem 1

According to what was said in the previous section, we examine only those Kekulé structures of $X_{m,1}$ in which arrangements of the type A and B are absent. Further, let the Kekulé structure which induces the structure L_0 in all phenylene fragments be defined to be even. Then all Kekulé structures of $X_{m,n}$ which induce one of the structures L_k (k = 0,1,...,n) in all phenylene fragments are even; their number is equal to $(n+1)^m$.
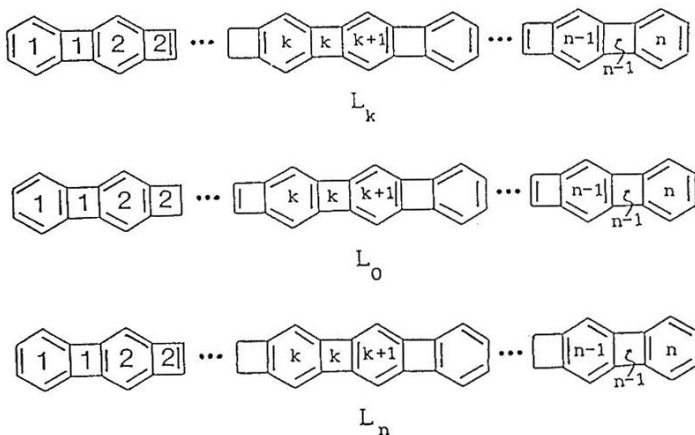
Fig. 3

Assume that n has a fixed value.

Denote the set of all Kekulé structures of $X_{m,n}$ without arrangements of the type A and/or B by $\mathscr{S}_m$. The even and odd structures from $\mathscr{S}_m$ form the subsets $\mathscr{E}_m$ and $\mathcal{O}_m$, respectively. Of course, $\mathscr{E}_m \cup \mathcal{O}_m = \mathscr{S}_m$; $\mathscr{E}_m \cap \mathcal{O}_m = \varnothing$.

The edges of $X_{m,n}$ which connect the first and second phenylene fragment will be referred to as cut-edges, because by their removal $X_{m,n}$ decomposes into $X_{m-1,n}$ and an [n]phenylene (= $X_{1,n}$). In **Fig. 1** the cut edges are those which intersect the horizontal dashed line; $X_{m,n}$ has n cut-edges.

Denote by $\mathscr{S}_m^1$ the set of all structures (from $\mathscr{S}_m$) which induce one of the structures L_k (k = 0, 1, ..., n) in the first phenylene fragment. In these Kekulé structures all the cut-edges correspond to single bonds. Let further $\mathscr{E}_m^1$ and $\mathcal{O}_m^2$ be the subsets of $\mathscr{S}_m^1$, formed by the even and odd structures,

respectively. Let $\mathscr{S}_m^2 = \mathscr{S}_m \setminus \mathscr{S}_m^1$, $\mathcal{E}_m^2 = \mathcal{E}_m \setminus \mathcal{E}_m^1$ and $\mathcal{O}_m^2 = \mathcal{O}_m \setminus \mathcal{O}_m^1$. Evidently, $\mathscr{S}_m^1 = \mathcal{E}_m^1 \cup \mathcal{O}_m^1$, $\mathcal{E}_m^1 \cap \mathcal{O}_m^1 = \varnothing$ and $\mathscr{S}_m^2 = \mathcal{E}_m^2 \cup \mathcal{O}_m^2$, $\mathcal{E}_m^2 \cap \mathcal{O}_m^2 = \varnothing$.

Note that by removing from $X_{m,n}$ the first phenylene fragment we obtain $X_{m-1,n}$ whereas by removing both the first and the second phenylene fragments, we obtain $X_{m-2,n}$ (see **Fig. 1**).

We are now ready to prove Theorem 1 by means of mathematical induction on the parameter m.

Lemma 1 validates the statement of Theorem 1 for the case m = 1.

Assume now m > 1 and consider the set $\mathscr{S}_m^1 \subseteq \mathscr{S}_m$ of Kekulé structures whose cut-edges do not pertain to double bonds. Exactly one (induced) structure of $X_{m-1,n}$ (i.e. an element from $\mathscr{S}_{m-1}$) is assigned to each structure from $\mathscr{S}_m^1$. Bearing in mind the criteria for determining the mutual parity of Kekulé structures (stated at the beginning of the preceding section, it is not difficult to show that all these structures are of equal parity.

Conversely, exactly (n+1) elements from $\mathscr{S}_m^1$ are assigned to each element from $\mathscr{S}_{m-1}$. This is because (according to Lemma 1) the number of structures of the (first) phenylene fragment is n+1. They too all are of equal parity.

Now, we immediately obtain

$$|\mathcal{E}_m^1| = (n + 1)|\mathcal{E}_{m-1}^1| \quad \text{and} \quad |\mathcal{O}_m^1| = (n + 1)|\mathcal{O}_{m-1}^1| \tag{3}$$

where $|\mathfrak{X}|$ stands for the cardinality (= number of elements) of the set $\mathfrak{X}$.

Consider now $\mathscr{S}_m^2$ - the set of all Kekulé structures from $\mathscr{S}_m$ for which at least one cut-edge corresponds to a double bond. Since the number of vertices in the (first) phenylene fragment is even, the number of such cut-edges is even.

Choose an arbitrary Kekulé structure $K_m(k,p)$ from $\mathscr{S}_m^2$. Let the ordinal numbers of the first two cut-edges corresponding to double bonds of this

Kekulé structure be k and p (k < p). Note that k and p must have opposite parities, i.e., p-k must be odd.

In **Fig. 4** we present an example of such a Kekulé structure, namely $K_m(k,p)$ for k = 3 and p = 8; heavy lines indicate the positions of double bonds.
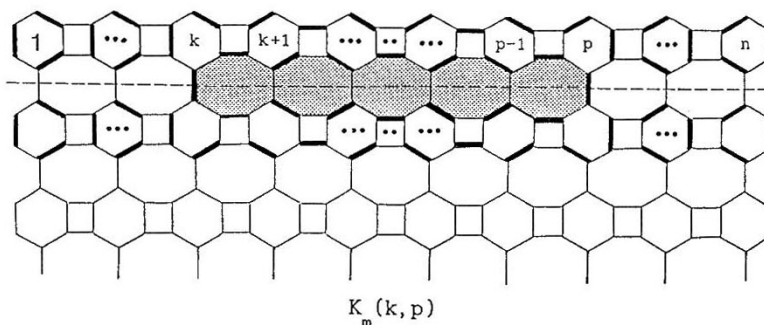

$$K_m(k,p)$$

Fig. 4

It is not difficult to see that in the Kekulé structure $K_m(k,p)$ depicted in **Fig. 4**, all edges indicated by heavy lines have to be present, i.e., their position is fully determined by k and p. (To verify this one may try to construct a Kekulé structure in which one of the indicated edges is not contained. After some trial it becomes evident that such attempts necessarily end in failure. If we want to be completely rigorous, then the examination has to be separately repeated for every edge which in **Fig. 4** is indicated by a heavy line. This is elementary, but lengthy.)

The above observation implies that no more than two cut-edges can correspond to double bonds, and that all edges connecting the second and the third phenylene fragment must correspond to single bonds. Consequently, the remaining double bonds of the Kekulé structure of $X_{m,n}$ (i.e., the double

bonds lying below the first two phenylene fragments of $X_{m,n}$) induce a unique Kekulé structure $K_{m-2} \in \mathscr{S}_{m-2}$.

$K_m(k,p)$ and K_{m-2} have opposite parities. To see this, rearrange cyclically the double bonds embracing the hatched region in **Fig. 4** and observe that the number of these double bonds is even. The Kekulé structure thus obtained is denoted by $K'_m(k,p)$ and is depicted in **Fig.5**. Since $K'_m(k,p)$ does not belong to $\mathscr{S}_m$, we rearrange cyclically the double bonds embracing its hatched regions (see **Fig. 5**). By this the Kekulé structure $K''_m(k,p)$ is obtained. The number of hatched regions in $K'_m(k,p)$ is even, and therefore the parities of $K'_m(k,p)$ and $K''_m(k,p)$ are opposite.

Now, $K''_m(k,p) \in \mathscr{S}^1_m$ induces the structure L_{p-1} in the first and second phenylene fragments. Consequently, $K''_m(k,p)$ has the same parity as K_{m-2} .
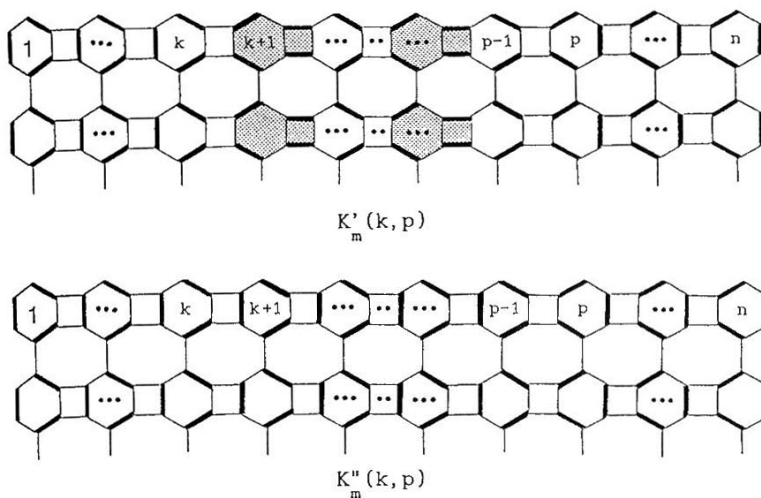

$K'_m(k,p)$

$K''_m(k,p)$

Fig. 5

We thus conclude that exactly one (induced) Kekulé structure from $\mathcal{G}_{m-2}$ is assigned to each Kekulé structure from $\mathcal{G}_m^2$, and that these Kekulé structures have opposite parities.

The number of ways to choose the numbers k and p ($1 \le k < p \le n$), such that p-k is odd, is equal to $\lfloor n^2/4 \rfloor$. Indeed, for even n this number is $1 + 3 + \cdots + (n-1) = n^2/4$ whereas for odd values of n it is equal to $2 + 4 + \cdots + (n-1) = (n^2-1)/4$.

This yields

$$|\mathcal{E}_m^2| = \lfloor n^2/4 \rfloor \ |O_{m-2}| \quad \text{and} \quad |O_m^2| = \lfloor n^2/4 \rfloor \ |\mathcal{E}_{m-2}| \ . \tag{4}$$

Combining Eqs. (3) with (4) we obtain

$$|\mathcal{E}_m| = (n + 1)|\mathcal{E}_{m-1}| + \lfloor n^2/4 \rfloor \ |O_{m-2}|$$

and

$$|O_m| = (n + 1)|O_{m-1}| + \lfloor n^2/4 \rfloor \ |\mathcal{E}_{m-2}|$$

which finally results in

$$|\mathcal{E}_m| - |O_m| = (n + 1)\left(|\mathcal{E}_{m-1}| - |O_{m-1}|\right) - \lfloor n^2/4 \rfloor\left(|\mathcal{E}_{m-2}| - |O_{m-2}|\right) \ . \tag{5}$$

In accordance with the definition of the algebraic structure count [1],

$$|\mathcal{E}_h| - |O_h| = A\{X_{h,n}\} \quad \text{for h = m, m-1 \& m-2}$$

and we see that Eq. (5) is tantamount to Eq. (1).

Knowing that $A\{X_{1,n}\} = n + 1$ (see Lemma 1) as well as that [9] $A\{X_{2,n}\} = \lfloor \frac{1}{4}(3n^2 + 8n + 5) \rfloor$, we easily verify that the initial conditions in (1) are precisely those stated in Theorem 1.

By this the proof of Theorem 1 is completed. ■

References

[1] The algebraic structure count is a concept introduced by Wilcox and, independently, Herndon [C.F.Wilcox, *Tetrahedron Letters*, 795 (1968); W.C.Herndon, *Tetrahedron* **29**, 3 (1973)], based on an earlier conceived notion of the parity of Kekulé structures [M.J.S.Dewar and H.C.Longuet-Higgins, *Proc.Roy.Soc.London* **A214**, 482 (1952)]. The fact that in the case of alternant hydrocarbons the parity of the Kekulé structures is a well-defined concept and that there is a unique partition of the Kekulé structures into even and odd was proven in the 1970s [A.Graovac, I.Gutman, N.Trinajstić and T.Živković, *Theor.Chim.Acta* **26**, 67 (1972); I.Gutman and N.Trinajstić, *Croat.Chem.Acta* **45**, 539 (1973); D.Cvetković I.Gutman and N.Trinajstić, *J.Chem.Phys.* **61**, 2700 (1974)]. In these works the relation between the parity of Kekulé structures and the parity of a certain permutations of vertices of the molecular graph is established and thus the parity concept in the theory of Kekulé structures given a sound foundation. Detailed accounts of the theory of algebraic structure count as well as illustrative examples can be found also in the recently published papers [4] and [5].

[2] In the case of benzenoid hydrocarbons the algebraic structure count coincides with the simple count of Kekulé structures. Therefore, the study of algebraic structure count is purposeful only in the case of nonbenzenoid systems.

[3] Parity of Kekulé structures and, consequently, algebraic structure count are well-defined only in the case of alternant conjugated molecules and, in the general case, are not applicable for non-alternant systems [I.Gutman and N.Trinajstić, *Croat.Chem.Acta* **47**, 35 (1975); I. Gutman, M.Randić and N.Trinajstić, *Rev.Roum.Chim.* **23**, 383 (1978)].

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