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Closed-Form Formulas for the Zhang–Zhang Polynomials of Benzenoid Structures: Chevrons and Generalized Chevrons

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Abstract

Closed-form, general formulas for the Zhang-Zhang (ZZ) polynomials for two important classes of benzenoid structures, chevrons $Ch(k,m,n)$ and generalized chevrons $Ch(k,m,n_1,n_2)$, are formally derived. The derivations rely on a new and important theorem, which states that the ZZ polynomial of two fused parallelograms can be represented as the product of the ZZ polynomials of the two separated fragments. This theoretical result seems to play an important role in the theory of pericondensed benzenoids and may prove useful for the process of discovering closed-form formulas of Zhang-Zhang polynomials of for a wide class of benzenoid structures.

1. Introduction

Zhang–Zhang (ZZ) polynomial [1-6] is an important combinatorial tool for enumerating and classifying conceivable Clar covers that can be written for a given benzenoid structure. [7] Clar covers [1-4] can be thought as a generalization of Kekulé structures used by organic chemists to analyze and predict stability and reactivity of various polycyclic compounds. [2, 8-12] In contrast to Kekulé structures, [13] which use single and double bonds to ensure the tetravalent character of each carbon atom, Clar covers employ in addition also the concept of so-called aromatic sextet [14], which can be considered as a linear combination of two Kekulé structures that can be written for a single benzene ring. A single aromatic sextet located in a given benzene ring—usually visualized in the form of a circle—ensures the tetravalent character of all six carbon atoms constituting this ring. A trivial consequence of this fact is that two aromatic sextets cannot occupy two neighboring hexagonal rings; such an arrangement would necessarily invoke pentavalent character of two carbon atoms shared between the two rings. The maximal number of aromatic sextets that can be written inside a given benzenoid system is called the Clar numer Cl. Needless to say, such an arrangement of aromatic sextets can be considered valid, only if the remaining part of the benzenoid structure not covered by the aromatic sextets can be made tetravalent by a feasible arrangement of single and double bonds.

The enumeration of Kekulé structures is in principle not an easy task. A representative account of the enormous amount of work of a few generations of chemists and graph theorists devoted to this problem is probably best reflected in the monumental work of Cyvin and Gutman [7, 13]. The enumeration of Clar covers turns out to be even a more complex task. The introduction of Clar covering polynomials [1] by Zhang and Zhang, which are known better as ZZ polynomials [5] was a great step forward in the enumeration process of Clar covers owing to the inviting recursive properties of the ZZ polynomials. (For details, see the next Section.) The ZZ polynomial structure for a given benzenoid S is very simple and can be given by the following formula

$$ZZ(S,x)=\sum_{k=0}^{Cl} c_k x^k, \tag{1}$$

where c_k is the number of conceivable Clar structures of order k, i.e., containing exactly k aromatic sextets. The variable x is an auxiliary variable used only to distinguish between Clar covers of different order. From the definition of the ZZ polynomial it is immediately clear that the coefficient c_0 is equal to the number of possible Kekulé structures. The ZZ polynomials for the simplest benzenoid structures have been determined by Zhang and Zhang. [1-3] The recursive properties of the ZZ polynomials could be used for finding closed form formulas for various families of catacondensed benzenoids. [1-6, 15-18] The techniques developed for this purpose can be considered general and applicable to any family of catacondensed structures. The situation for the pericondensed benzenoids is much more complex; closed-form formula has been found only for two families of pericondensed structures, parallelograms [17] and prolate rectangles [3, 18]. The situation was slightly improved with the introduction of an efficient computer program, [6] which is applicable for determination of the ZZ polynomials for pericondensed benzenoid structures containing up to 500 carbon atoms using the decomposition properties of the ZZ polynomials in an automatized recursive fashion. The application of this program allowed us to find closed-form formulas for various subfamilies of pericondensed benzenoid structures. Formally, the discovered formulas were conjectures deduced from an analysis of a finite number of members of each subfamily. Analogous, though more theoretically sound, interpolation approaches were used to derive other topological indices. [19, 20] The development of an interactive graphical computer tool (ZZDecomposer), described in the preceding paper, [21] allowed us to prove these conjectures using formal decomposition techniques for many classes of benzenoid hydrocarbons. [22] The ZZDecomposer program was developed mainly as a proof tool for finding and justifying closed forms of the ZZ polynomials for an arbitrary family of benzenoid systems. However, it is flexible enough for other purposes, e.g., computing ZZ polynomial for small and medium-size benzenoids, studying various decomposition paths that can be used for finding optimal decomposition route of a given benzenoid family, [22-24] book-keeping of various fragments appearing in a given decomposition route, and finally fast and convenient definition of polyhex graphs together with a possibility of saving them using graphical format. We believe that the ZZDecomposer program should be in the working arsenal of every chemist and graph theorist interested in the properties and determination of ZZ polynomials of benzenoid structures.

In the current paper, we employ the ZZDecomposer proof environment to find general closed-form formulas for the ZZ polynomials of two important families of benzenoid structures, chevrons $Ch(k,m,n)$ and generalized chevrons $Ch(k,m,n_1,n_2)$. (For definitions, see **Figure 8** and/or [13].) In our previous work [18], we have employed an efficient computer algorithm (and associated ZZ polynomial calculator program) [6] to determine and analyze the ZZ polynomials for two subfamilies of chevron structures, $Ch(2,2,n)$ and $Ch(3,3,n)$. Closed-form formulas of the ZZ polynomials for these two subfamilies were quite complicated, escaping the possibility of generalizing them to other subfamilies of chevron structures and preventing one from discovering general formula for the whole family of the $Ch(k,m,n)$ structures. Fortunately, this difficulty could be circumvented using the ZZDecomposer proof tool. The formulas discovered here have surprisingly simple form and show close connection with the previously developed ZZ polynomials of parallelograms. [17]

The main theoretical result of this paper (**Theorem 7**), used to find the ZZ polynomials of chevrons and generalized chevrons, has different scope and is probably more important from the methodological point of view than the discovered formulas for chevrons. Namely, we are able to show that the ZZ polynomial of two fused parallelograms $P_1||P_2$ can be expressed as a product of the ZZ polynomials of its constituents: $ZZ(P_1||P_2,x) = ZZ(P_1,x)\cdot ZZ(P_2,x)$. (For the definition of "fusing two parallelograms", see **Theorem 7** and **Figure 7**.) Moreover, we are able to show that the fusion is independent of the actual number of bonds defining the fusion. Another way of stating this important result is by saying that a benzenoid structure obtained by fusion of two parallelograms is essentially disconnected, which implies that all the fusing bonds have single character. We expect that this result will be of importance for discovering closed-form formulas also for other families of benzenoid structures.

The structure of the current paper is a follows. First we review briefly the recursive properties of ZZ polynomials and summarize the current state of knowledge about the ZZ polynomials for parallelograms $M(m,n)$; proper understanding of these two ingredients is indispensable for further exposition. **Section 4** gives two important general results stated in **Theorems 6** and **7**, which say that: i) ZZ polynomial of a defective parallelogram is necessarily equal to 0 and ii) ZZ polynomial of two fused parallelograms is equal to the product of the ZZ polynomials of the disconnected parallelograms. The remaining **Lemmas** of **Section 4** are very technical and should be skipped in the first reading. **Sections 5** and **6**

give the derivation of the ZZ polynomials for chevrons and generalized chevrons, respectively. The conclusions are given in the **Section 7**.

2. Basic properties of ZZ polynomials

The ZZ polynomials have a number of interesting properties, which can make their evaluation simple and effective. We state them here without proofs, which can be found elsewhere. [1-5] The list of the properties given here is not meant to be complete; we just quote facts important in the context of the work presented here.

Property 1. ZZ polynomial of a structure with no atoms (empty structure) is 1.

Property 2. ZZ polynomial of a structure with an odd number of atoms is 0.

Property 3. ZZ polynomial of a disconnected structure, i.e., a structure with two fragments not connected by a chemical bond is equal to the product of ZZ polynomials of two fragments.

Property 4. Let S be a benzenoid structure containing a terminal carbon atom A, i.e., a carbon atom having only one carbon neighbor B. Then, the ZZ polynomial of the structure S is equal to the ZZ polynomial of the structure S with deleted atoms A and B.

Property 5. Let AB be a bond in a benzenoid structure S not belonging to any hexagonal benzene ring and let the atoms A and B have at least two carbon neighbors each. Then, the ZZ polynomial of the structure S can be expressed as a sum of ZZ polynomials of two simpler structures, $S - AB$ and $S - A - B$, i.e., the structure S with the bond AB deleted and the structure S with the atoms A and B deleted, respectively.

Property 6. Let AB be a bond in a benzenoid structure S belonging to a single hexagonal benzene ring s. Then, the ZZ polynomial of the structure S can be expressed as a sum of $ZZ(S - AB, x)$, $ZZ(S - A - B, x)$, and $x \cdot ZZ(S - s, x)$, where $S - AB$ and $S - A - B$ have the same meaning like in **Property 5** and $S - s$ denotes the structure S with the six carbon atoms belonging to the ring s deleted.

Property 7. Let AB be a bond in a benzenoid structure S shared by two adjacent hexagonal benzene rings s_1 and s_2. Then, the ZZ polynomial of the structure S can be expressed as a sum of $ZZ(S-AB,x)$, $ZZ(S-A-B,x)$, $x\cdot ZZ(S-s_1,x)$, and $x\cdot ZZ(S-s_2,x)$, where $S-AB$ and $S-A-B$ have the same meaning like in **Property 5** and $S-s_i$ denotes the structure S with the six carbon atoms belonging to the ring s_i deleted, $i=1,2$.

3. ZZ polynomial of a parallelogram $M(m,n)$

Consider a hexagon-based parallelogram $M(m,n)$ with edges of length m and n respectively (see **Figure 1**). The ZZ polynomial of this structure was derived by Gutman and Borovićanin [17] as

$$ZZ\left(M\left(m,n\right),x\right)=\sum_{i=0}^{m}\binom{m}{i}\binom{n+m-i}{m}x^i \tag{2}$$

Permutational $m\leftrightarrow n$ symmetry invariance of the $M(m,n)$ ZZ polynomial, clearly visible by a rotation of the structure in **Figure 1** by 60° anticlockwise and by a subsequent mirror reflection—operations obviously not modifying the number of conceivable Clar covers—allows one to write this equation in explicitly symmetric form [6] given by

$$ZZ\left(M\left(m,n\right),x\right)=\sum_{i=0}^{\min(m,n)}\frac{(m+n-i)!}{(n-i)!(m-i)!(i)!}x^i \tag{3}$$

which can be expressed in considerably more compact form in the $(x+1)^i$ basis as

$$ZZ\left(M\left(m,n\right),x\right)=\sum_{i=0}^{\min(m,n)}\binom{m}{i}\binom{n}{i}(x+1)^i \tag{4}$$

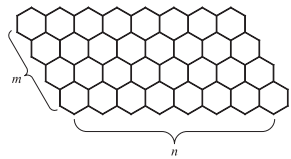


Figure 1. Schematic view of a parallelogram $\boldsymbol{M(m,n)}$. Here, $\boldsymbol{m=4}$ and $\boldsymbol{n=12}$.

The most beautiful and compact formula for the ZZ polynomial of this structure is probably given in terms of Gauss hypergeometric function and reads

$$ZZ\left(M\left(m,n\right),x\right)={}_2F_1\left[\begin{matrix}-m,-n\\1\end{matrix};x+1\right] \tag{5}$$

Note that this form, despite of its simplicity, clearly reflects the $m \leftrightarrow n$ symmetry invariance (as ${}_2F_1$ is symmetric under permutation of its upper indices), finite polynomial form (since ${}_2F_1$ reduces to a polynomial for a negative upper index), and the importance of the $x+1$ representation. Note also that the Kekulé number of $M(m,n)$ is readily extracted as ${}_2F_1\left[\begin{matrix}-m,-n\\1\end{matrix};1\right]$ and the total number of Clar covers for $M(m,n)$ is given by ${}_2F_1\left[\begin{matrix}-m,-n\\1\end{matrix};2\right]$. Finally, notice that the hypergeometric representation can be further converted to a Jacobi polynomial representation

$$ZZ\left(M(m,n),x\right)=P_n^{(0,-n-m-1)}\left(-1-2x\right)=P_m^{(0,-n-m-1)}\left(-1-2x\right) \tag{6}$$

4. ZZ polynomials of defective parallelograms *M*(*m*,*n*)

The ZZ polynomial of the parallelogram $M(m,n)$ is clearly non-vanishing for all choices of non-negative indices m and n. In the current Section, we show (**Theorem 6**) that certain types of defects introduced in the parallelogram $M(m,n)$ necessarily invoke vanishing of its ZZ polynomial. This result does not seem to be of particular interest *per se*, but it proves to be of great importance for deriving close forms of ZZ polynomials for two important classes of pericondensed benzenoids, chevrons and generalized chevrons, as demonstrated in **Sections 5** and **6**. The main result of the current **Section** used to prove these facts is **Theorem 7**; its derivation is preceded by a number of definitions and auxiliary lemmas, which make the proof possible. For a reader not interested in technical details of the proof, we suggest to jump directly to the **Theorems 6** and **7** and equipped with them, proceed to **Section 5**.

Before proceeding to the definition of the edge defects considered here, we analyze shortly the edge structure of a parallelogram $M(m,n)$. As shown schematically in **Figure 2**, a periphery of $M(m,n)$ consists of n (or respectively m) hexagonal rings $s_1, s_2, s_3, \ldots, s_n$

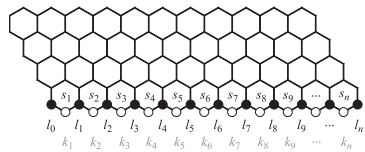


Figure 2. Schematic classification of peripheral vertices in the structure $\boldsymbol{M(m,n)}$.

forming a single polyacene-like zigzag chain of length n. Two types of edge vertices can be distinguished: i) $k_1, k_2, k_3, \dots, k_n$ located in the first layer and depicted using open circles in **Figure 2** and ii) $l_0, l_1, l_2, l_3, \dots, l_n$ located in the second layer and depicted using solid circles in **Figure 2**.

The class of defective parallelograms studied here comprises of all structures $\tilde{M}(m,n)$ obtained from $M(m,n)$ by first deleting $N > 0$ vertices $k_{i_1}, k_{i_2}, k_{i_3}, \dots, k_{i_N}$, where for convenience we assume that $1 \leq i_1 < i_2 < \cdots < i_N \leq n$, and subsequently deleting P vertices $l_{j_1}, l_{j_2}, l_{j_3}, \dots, l_{j_P}$, where $0 < j_1 < j_2 < \cdots < j_P < n$. We further stipulate that the vertex l_j can be deleted only if both the vertices k_j and k_{j+1} have been previously deleted. A careful reader will notice that the class constructed here corresponds precisely to the class of defective structures that can be obtained via recursive decomposition of two fused parallelograms, when the decomposition process is performed along the sequence of fusing edges until the two parallelograms become disconnected. (For more details, see **Figure 7**) Four typical examples of defective structures belonging to the class defined above are shown in **Figure 3**. To demonstrate that the ZZ polynomials of all the structures in the considered class vanish identically, let use consider one of them, $\tilde{M}(m,n)$, in detail. For the convenience of demonstration, let us assume without loss of generality that $n \geq m$ and that the vertices are removed from the longer edge. Note that the most left of the removed vertices is k_{i_1} and that the most right of the removed vertices is k_{i_N}, i.e., that the ordered list of the removed vertices

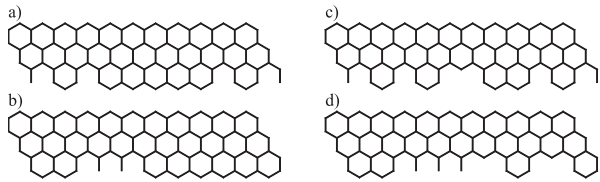


Figure 3. Four examples of defective structures $\tilde{\boldsymbol{M}}$ formed from $\boldsymbol{M(3,11)}$ after removing the vertices: a) $\boldsymbol{k_1, k_3, k_9, k_{11}}$, b) $\boldsymbol{k_3, k_4, k_5}$, c) $\boldsymbol{k_1, k_3, k_5, k_6, k_9, k_{11}, l_5}$, and d) $\boldsymbol{k_3, k_4, k_5, k_6, k_7, k_9, k_{10}, l_6, l_9}$.

always starts with k_{i_1} and finishes with k_{i_N}.

Lemma 1. If only one vertex has been removed from $M(m,n)$, the ZZ polynomial of $\widetilde{M}$ is 0.

Proof: The structure $M(m,n)$ contains an even number of vertices, so $\widetilde{M}$ has an odd number of vertices and its ZZ polynomial is identically equal to 0 by **Property 2**. [5] □

In the following we can consequently assume that at least two vertices k_i have been removed from $M(m,n)$ when forming $\widetilde{M}$. Thus, $k_1 \neq k_{i_N}$. The further reasoning is organized in a sequence of **Lemmas**, which eventually allow us to cover the most general case.

Lemma 2. If the vertex k_1 has been removed, the ZZ polynomial of $\widetilde{M}$ is 0.

Proof: Removing vertex k_1 results in vertex l_0 having degree one. As shown in **Figure 4**, recursive reduction of the ZZ polynomial of the structure $\widetilde{M}$ starting from vertex l_0 imposes a global double-single bond pattern with an unavoidable defect in the part of the structure $\widetilde{M}$ not involving the vertices $\{l_1, k_2, l_2, k_3, \dots, l_{i_N-1}\}\backslash\{k_{i_2}, k_{i_3}, \dots, k_{i_{N-1}}\}\backslash\{l_{j_1}, l_{j_2}, \dots, l_{j_P}\}$ located inside the rectangular boxes in **Figure 4**. It is always possible to localize the defect in the position l_n. Such a unique defective pattern is explicitly shown in **Figure 4** for two structures $\widetilde{M}$ obtained from $M(4,12)$: a) with $i_N \neq n$ and b) with $i_N = n$. Note that the number of removed vertices and their actual distribution—depicted symbolically using a rectangular frame in **Figure 4**—is irrelevant for the flow of arguments presented here. The

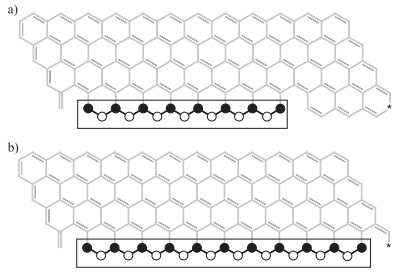


Figure 4. Bond pattern imposed on $\widetilde{\boldsymbol{M}}$ by removing the vertices $\boldsymbol{k_1}$ and $\boldsymbol{k_{i_N}}$ unavoidably results in a disconnected vertex (depicted with $*$) that can be localized at position $\boldsymbol{l_n}$. Note that the pattern of single and double bonds given here is independent of $\boldsymbol{m, n \geq 1}$ and of the unspecified sequence of removed vertices inside the black frame.

specified recursive decomposition of $\tilde{M}$ leads to two disconnected graphs: one involving the sole vertex l_n and one involving the vertices $\{l_1, k_2, l_2, k_3, \ldots, l_{i_N-1}\}\backslash\{k_{i_2}, k_{i_3}, \ldots, k_{i_{N-1}}\}\backslash\{l_{j_1}, l_{j_2}, \ldots, l_{j_P}\}$ located inside the rectangular frame. Consequently, by **Property 3**, the ZZ polynomial of $\tilde{M}$ can be expressed as a product of two ZZ polynomials with one of them—$ZZ(l_n, x)$—identically equal to zero by **Property 2**, which proves our proposition. Short inspection of **Figure 4** clarifies that the arguments used here remain valid for any choice of $m, n \geq 1$ and for any location of k_{i_N}.

Lemma 3. If $m > 1$ and the first removed vertex is k_2, then

$$ZZ\left(\tilde{M}(m,n), x\right) = ZZ\left(\tilde{M}(m-1,n), x\right) \tag{7}$$

where $\tilde{M}(m-1,n)$ is obtained from $M(m-1,n)$ by removing the vertices $k_{i_1}, k_{i_2}, k_{i_3}, \ldots, k_{i_N}$ and $l_{j_1}, l_{j_2}, l_{j_3}, \ldots, l_{j_P}$.

Proof: Recursive decomposition of the ZZ polynomial of $\tilde{M}(m,n)$ with respect to the most left vertical edge of $\tilde{M}(m,n)$ (see the arrow in **Figure 5**) gives [17]

$$ZZ\left(\tilde{M}(m,n), x\right) = ZZ\left(\tilde{M}(m,n-1), x\right) + ZZ\left(\tilde{M}(m-1,n), x\right) + x \cdot ZZ\left(\tilde{M}(m-1,n-1), x\right) \tag{8}$$

as shown schematically for a structure $\tilde{M}(4,10)$ in **Figure 5**. However, the structures $\tilde{M}(m,n-1)$ and $\tilde{M}(m-1,n-1)$ can be treated as defective structures $M(m,n-1)$ and $M(m-1,n-1)$, respectively, with the vertex k_1 removed. Therefore, by **Lemma 2**, their ZZ polynomials vanish, which proves our proposition. □

Lemma 4. If $m > 1$ and the first removed vertex k_{i_1} has an index $i_1 > 2$, then

$$ZZ\left(\tilde{M}(m,n), x\right) = ZZ\left(\tilde{M}(m,n-1), x\right) + ZZ\left(\tilde{M}(m-1,n), x\right) + x \cdot ZZ\left(\tilde{M}(m-1,n-1), x\right) \tag{9}$$

where $\tilde{M}(m-1,n)$ is obtained from $M(m-1,n)$ by removing the vertices $k_{i_1}, k_{i_2}, k_{i_3}, \ldots, k_{i_N}$ and $l_{j_1}, l_{j_2}, l_{j_3}, \ldots, l_{j_P}$, and $\tilde{M}(m,n-1)$ and $\tilde{M}(m-1,n-1)$ are obtained from $M(m,n-1)$ and $M(m-1,n-1)$, respectively, by removing the vertices $k_{i_1-1}, k_{i_2-1}, k_{i_3-1}, \ldots, k_{i_N-1}$ and and $l_{j_1-1}, l_{j_2-1}, l_{j_3-1}, \ldots, l_{j_P-1}$. In other words, it is possible to

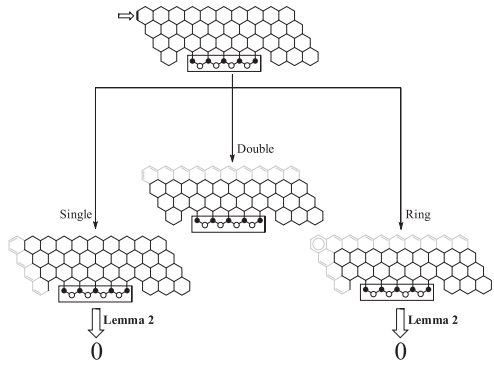


Figure 5. Recursive decomposition of a defective parallelogram $\widetilde{M}(m,n)$ with $m > 1$ and $i_1 = 2$ effectively results in reducing the number of rows by one.

reduce the problem of finding the ZZ polynomial of a defective structure $\widetilde{M}(m,n)$ to the problem of finding the ZZ polynomials of three analogous structures with smaller dimensions m and/or n.

Proof: Standard recursive decomposition of the ZZ polynomial of $\widetilde{M}(m,n)$ with respect to the most left vertical edge of $\widetilde{M}(m,n)$ (see the arrow in **Figure 6**) gives [17]

$$ZZ\left(\tilde{M}(m,n),x\right) = ZZ\left(\tilde{M}(m,n-1),x\right) + ZZ\left(\tilde{M}(m-1,n),x\right) + x\cdot ZZ\left(\tilde{M}(m-1,n-1),x\right) \quad (10)$$

as shown schematically for a structure $\widetilde{M}(4,11)$ in **Figure 6**. Again, as far as $m > 1$, the decomposition is independent of the unspecified sequence of removed vertices inside the black frame. Note that for the new structures $\widetilde{M}(m,n-1)$ and $\widetilde{M}(m-1,n-1)$ with $n-1$ columns, the indices of the removed vertices are shifted left by one, which proves our proposition. □

Lemmas 3 and **4** show how to express the ZZ polynomial of a structure $\widetilde{M}(m,n)$ with $m > 1$ in terms of ZZ polynomials of defective parallelograms with a smaller number of rows and/or columns. These **Lemmas** can be used repeatedly to express the ZZ polynomial of any defective parallelogram $\widetilde{M}(m,n)$ as a sum of ZZ polynomials (possibly multiplied by certain polynomials in the variable x) of defective parallelograms $\widetilde{M}(1,s)$ with $s \leq n$ or defective parallelograms $\widetilde{M}(t,s)$ with $s \leq n$, $t \leq m$ and with the vertex k_1 removed. The second class of defective parallelograms vanish by **Lemma 2**. Next **Lemma** shows that defective

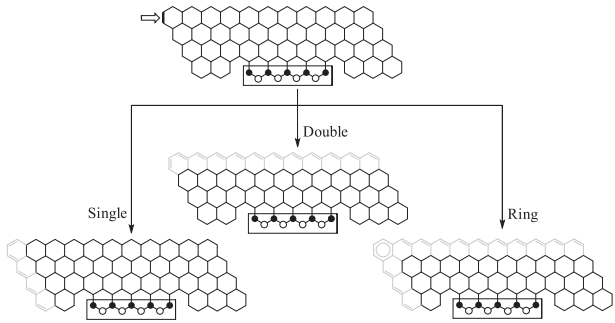
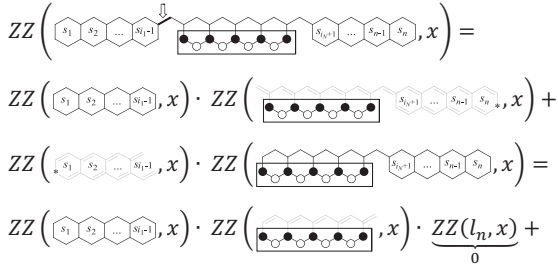


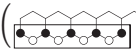
Figure 6. Recursive decomposition of a defective parallelogram $\widetilde{M}(m,n)$ with $m > 1$ and $i_1 > 2$ results in reducing the number of rows by one.

parallelogram of height one (i.e., with $m = 1$), have their ZZ polynomials necessarily equal to 0.

Lemma 5. The ZZ polynomial of a defective structure $\widetilde{M}(1,n)$ is equal to 0.

Proof: If $N = 1$, then the proposition is true by **Lemma 1**. If $N > 1$, any defective structure $\widetilde{M}(1,n)$ can be represented schematically by three segments. The two terminal segments have a well-defined polyacene structure of length $i_1 - 1$ and $n - i_N$, respectively. (Note that a polyacene of length 0 can be interpreted as an ethylene molecule.) The central segment consists of a defected polyacene of length $i_N - i_1 - 1$; the number of removed vertices creating the defects and their distribution is irrelevant to the flow of the current proof and is represented in a form of a rectangular frame in the equations below. Recursive decomposition of the ZZ polynomial of $\widetilde{M}(1,n)$ with respect to the bond marked with an arrow gives by **Property 5**



$$\underbrace{ZZ(l_0,x)}_{0}\cdot ZZ\left(\text{  },x\right)=0 \qquad (11)$$

which proves our proposition. Note that the decompositions discussed here are independent of the unspecified sequence of removed vertices inside the black frame. □

We are sufficiently equipped now to prove the two main results of the current Section.

Theorem 6. The ZZ polynomial of a defective structure $\widetilde{M}(m,n)$ is equal to 0.

Proof: If $N=1$, then the proposition is true by **Lemma 1**. If $k_1=1$, then the proposition is true by **Lemma 2**. If $m=1$, then the proposition is true by **Lemma 5**. If $N>1$, $m>1$, and $k_1>1$, then the ZZ polynomial of any defective structure $\widetilde{M}(m,n)$ can be reduced by repeated application of **Lemmas 3** and **4** to a sum of ZZ polynomials (possibly multiplied by certain polynomials in the variable x) of defective parallelograms $\widetilde{M}(1,p)$ with $p\le n$ and/or defective parallelograms $\widetilde{M}(t,s)$ with $s\le n$, $1<t\le m$ and with the vertex k_1 removed, which vanish by **Lemma 5**, and **Lemma 2**, respectively. Consequently the sum of such vanishing contributions equals to zero, giving $ZZ\left(\widetilde{M}(m,n)\right)=0$. □

Theorem 7. Let the structure $M(m,n)||M(m',n')$ be obtained from two aligned parallelograms $M(m,n)$ and $M(m',n')$ by drawing a certain number p of new edges connecting pairs of vertically aligned vertices (k_i,k_i'). (Two possible ways of fusing the structures $M(3,10)$ and $M(4,6)$ are illustrated in **Figure 7**.) Then, the ZZ polynomial of the fused structure $M(m,n)||M(m',n')$ is equal to the product of the ZZ polynomials of its original components

$$ZZ\left(M(m,n)\,||\,M(m',n'),x\right)=ZZ\left(M(m,n),x\right)\cdot ZZ\left(M(m',n'),x\right) \qquad (12)$$

Proof: Recursive decomposition of the structure $M(m,n)||M(m',n')$ using the **Properties 5** and **6** with respect to the edges fusing both parallelograms results after at most p steps in expressing $ZZ(M(m,n)||M(m',n'),x)$ as a sum of terms in the form $ZZ(M(m,n),x)\cdot ZZ(M(m',n'),x)$ or $ZZ\left(\widetilde{M}(m,n),x\right)\cdot ZZ\left(\widetilde{M}(m',n'),x\right)$, possibly multiplied by certain powers of the variable x. This is easily seen by the following argument.

At every step of the recursive decomposition, one of the following operations is performed on $M(m,n)||M(m',n')$: ***i***) the edge between the vertices k_i and k_i' is deleted, leaving both vertices intact, *or* ***ii***) the vertices k_i and k_i' are deleted, *or* ***iii***) the vertices k_i, l_i, k_{i+1} and k_i', l_i', k_{i+1}' are deleted; the last operation is permissible only when both edges, (k_i, k_i') and (k_{i+1}, k_{i+1}'), are present in $M(m,n)||M(m',n')$. After $p-s$ steps of recursive decomposition, where s denotes the number of times of choosing the operation ***iii***, the structure $M(m,n)||M(m',n')$ becomes disconnected and consists of two fragments, $\widetilde{M}(m,n)$ and $\widetilde{M}(m',n')$ (or $M(m,n)$ and $M(m',n')$, if the operation ***i*** has been selected all the times). From the general properties of the ZZ polynomials, [1, 5, 6, 21] we know that the contribution from this particular decomposition path to the ZZ polynomial of $M(m,n)||M(m',n')$ can be expressed as $x^s \cdot ZZ\left(\widetilde{M}(m,n)\right) \cdot ZZ\left(\widetilde{M}(m',n')\right)$; the total ZZ polynomial of $M(m,n)||M(m',n')$ can be computed as a sum of such terms over all possible decomposition paths. Now, it is clear that choosing operation ***ii*** or ***iii*** in a given decomposition path results in introducing a defect in $M(m,n)$ and in $M(m',n')$ of exactly the same type as discussed earlier in this **Section**. Therefore, every time when the operations ***ii*** or ***iii*** have been chosen during the decomposition of $M(m,n)||M(m',n')$, the resulting parallelogram structures $\widetilde{M}(m,n)$ and $\widetilde{M}(m',n')$ are defective. Consequently, by **Theorem 6** their ZZ polynomials vanish, giving no contribution to $ZZ\big(M(m,n)||M(m',n')\big)$. The only non-vanishing contribution to the ZZ polynomial of $M(m,n)||M(m',n')$ is given by a path always following the operation ***i*** in each step of the decomposition process. Since the operation ***i*** does not introduce any defects and the operation ***iii*** is never selected, the contribution from this path is equal to $x^0 \cdot ZZ\big(M(m,n)\big) \cdot ZZ\big(M(m',n')\big)$, proving the proposition.

5. ZZ polynomial of a chevron $Ch(k,m,n)$

In the next two **Sections**, we show that the general result given in **Theorem 7** can be used for very convenient and concise evaluation of the ZZ polynomials for two important classes of benzenoid structures: chevrons and generalized chevrons. Graphical definition of this type of structures is given in **Figure 8**.

The determination of the ZZ polynomial for a chevron structure $Ch(k,m,n)$ can be conveniently performed in the way shown in **Figure 9**. The first step of the recursive

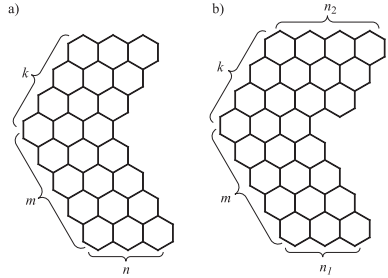


Figure 8. Two important classes of benzenoid structures: a) chevrons $\boldsymbol{Ch(k,m,n)}$ and b) generalized chevrons $\boldsymbol{Ch(k,m,n_1,n_2)}$

decomposition of the $Ch(k,m,n)$ structure using **Property 6** with respect to the edge marked with a dot in **Figure 9** yields the ZZ polynomial of $Ch(k,m,n)$ as a sum of ZZ polynomials of three simpler structures. One of them is immediately identified as the chevron $Ch(k,m,n-1)$ and the remaining two structures are clearly equal to fused parallelogram structures $M(m-1,n)||M(k-1,n)$ and $M(m-1,n-1)||M(k-1,n-1)$. Application of **Theorem 7** yields a recursive formula for computing the ZZ polynomial of the chevron structure $Ch(k,m,n)$

$$\begin{aligned}\mathrm{ZZ}\left(Ch(k,m,n),x\right)=\mathrm{ZZ}\left(Ch(k,m,n-1),x\right)+\mathrm{ZZ}\left(M(k-1,n),x\right)\cdot\mathrm{ZZ}\left(M(m-1,n),x\right)\\+x\cdot\mathrm{ZZ}\left(M(k-1,n-1),x\right)\cdot\mathrm{ZZ}\left(M(m-1,n-1),x\right)\end{aligned}\tag{13}$$

This equation can be treated as a first-order non-homogeneous recurrence relation in variable n with the initial condition $n=1$ given by

$$\mathrm{ZZ}\left(Ch(k,m,1),x\right)=1+x+\mathrm{ZZ}\left(M(k-1,1),x\right)\cdot\mathrm{ZZ}\left(M(m-1,1),x\right)\tag{14}$$

Solution to this recurrence relation is immediate and yields the following closed-form expression for the ZZ polynomial of $Ch(k,m,n)$

$$\begin{aligned}\mathrm{ZZ}\left(Ch(k,m,n),x\right)=\sum_{i=0}^{n-1}(1+x)\cdot\mathrm{ZZ}\left(M(k-1,i),x\right)\cdot\mathrm{ZZ}\left(M(m-1,i),x\right)\\+\mathrm{ZZ}\left(M(k-1,n),x\right)\cdot\mathrm{ZZ}\left(M(m-1,n),x\right)\end{aligned}\tag{15}$$

This formula becomes slightly more transparent in hypergeometric representation

$$ZZ\left(Ch(k,m,n),x\right)=\sum_{i=0}^{n-1}(1+x)\cdot {}_2F_1\left[\begin{matrix}1-k,-i\\1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,-i\\1\end{matrix};x+1\right]$$
$$+{}_2F_1\left[\begin{matrix}1-k,-n\\1\end{matrix};x+1\right]\cdot {}_2F_1\left[\begin{matrix}1-m,-n\\1\end{matrix};x+1\right] \quad (16)$$

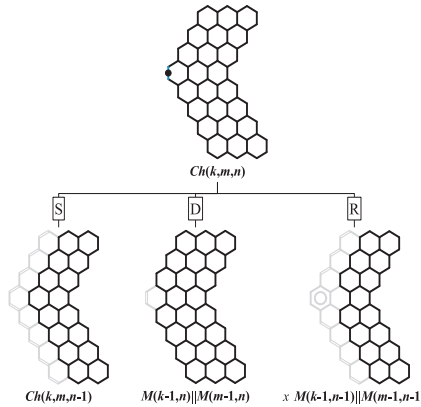


Figure 9. The following graph decomposition of $\boldsymbol{Ch(k,m,n)}$ produces a recurrence relation, which can be readily solved to yield a closed-form formula for $\boldsymbol{ZZ(Ch(k,m,n),x)}$. For details, see text.

Numerical experiments show that the last two formulas are correct.

It is tempting to look for further simplification of this expression. However, such a simplification could be difficult to obtain in practice, because closed-form expressions for the product of two hypergeometric functions and sums of such products are in general unknown. [25] Alternative possible representation in form of Jacobi polynomials seems also of a little use for this purpose.

6. ZZ polynomial of a generalized chevron $Ch(k,m,n_1,n_2)$

Similar approach can be used for finding the ZZ polynomial of a generalized chevron structure $Ch(k,m,n_1,n_2)$. We can assume without loss of generality that $n_2 > n_1$. (Indeed, the ZZ polynomials of $Ch(k,m,n_1,n_2)$and its rotated mirror-reflection are identical.) The first step of recursive decomposition process of the $Ch(k,m,n_1,n_2)$ structure using **Property 6** with respect to the edge marked with a dot in **Figure 10** gives the following recursive relation for the ZZ polynomial of $Ch(k,m,n_1,n_2)$

$$\begin{aligned}\mathrm{ZZ}\left(Ch\left(k,m,n_1,n_2\right),x\right)&=\mathrm{ZZ}\left(Ch\left(k,m,n_1-1,n_2-1\right),x\right)\\&+\mathrm{ZZ}\left(M\left(k-1,n_2\right),x\right)\cdot\mathrm{ZZ}\left(M\left(m-1,n_1\right),x\right)\\&+x\cdot\mathrm{ZZ}\left(M\left(k-1,n_2-1\right),x\right)\cdot\mathrm{ZZ}\left(M\left(m-1,n_1-1\right),x\right)\end{aligned}\tag{17}$$

with the following initialization formula for the base case $n_1 = 1$

$$\begin{aligned}\mathrm{ZZ}\left(Ch\left(k,m,1,n_2-n_1+1\right),x\right)&=\left(x+1\right)\cdot\mathrm{ZZ}\left(M\left(k-1,n_2-n_1\right),x\right)\\&+\mathrm{ZZ}\left(M\left(k-1,n_2-n_1+1\right),x\right)\cdot\mathrm{ZZ}\left(M\left(m-1,1\right),x\right)\end{aligned}\tag{18}$$

Solution of this first-order recursion quite readily yields a closed-form formula for the ZZ polynomial of the $Ch(k,m,n_1,n_2)$ structure given by

$$\begin{aligned}\mathrm{ZZ}\left(Ch\left(k,m,n_1,n_2\right),x\right)&=\sum_{i=1}^{n_1}\left(1+x\right)\cdot\mathrm{ZZ}\left(M\left(k-1,n_2-i\right),x\right)\cdot\mathrm{ZZ}\left(M\left(m-1,n_1-i\right),x\right)\\&+\mathrm{ZZ}\left(M\left(k-1,n_2\right),x\right)\cdot\mathrm{ZZ}\left(M\left(m-1,n_1\right),x\right)\end{aligned}\tag{19}$$

Again, the following representation of this formula in terms of hypergeometric functions can be more suitable for computational purposes and for attempts of its further simplification

$$\begin{aligned}\mathrm{ZZ}\left(Ch\left(k,m,n_1,n_2\right),x\right)&=\sum_{i=1}^{n_1}\left(1+x\right)\cdot{}_2F_1\left[\begin{matrix}1-k,i-n_2\\1\end{matrix};x+1\right]\cdot{}_2F_1\left[\begin{matrix}1-m,i-n_1\\1\end{matrix};x+1\right]\\&+{}_2F_1\left[\begin{matrix}1-k,-n_2\\1\end{matrix};x+1\right]\cdot{}_2F_1\left[\begin{matrix}1-m,-n_1\\1\end{matrix};x+1\right]\end{aligned}\tag{20}$$

Finally, it is useful to lift the assumption $n_2 > n_1$ performed during the derivation of this formula and to arrive at the most general formula for the ZZ polynomial of a generalized chevron $Ch(k,m,n_1,n_2)$ given by

$$\begin{aligned}\mathrm{ZZ}\left(Ch\left(k,m,n_1,n_2\right),x\right)&=\sum_{i=1}^{\min\left(n_1,n_2\right)}\left(1+x\right)\cdot{}_2F_1\left[\begin{matrix}1-k,i-n_2\\1\end{matrix};x+1\right]\cdot{}_2F_1\left[\begin{matrix}1-m,i-n_1\\1\end{matrix};x+1\right]\\&+{}_2F_1\left[\begin{matrix}1-k,-n_2\\1\end{matrix};x+1\right]\cdot{}_2F_1\left[\begin{matrix}1-m,-n_1\\1\end{matrix};x+1\right]\end{aligned}\tag{21}$$

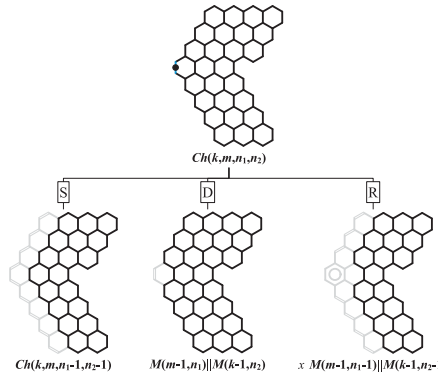


Figure 10. The following graph decomposition of $\boldsymbol{Ch(k,m,n_1,n_2)}$ produces a recurrence relation, which can be readily solved to yield a closed-form formula for $\boldsymbol{ZZ(Ch(k,m,n_1,n_2),x)}$. For details, see text.

Again, numerical experiments show that the formulas in this **Section** are correct.

7. Conclusion

We present a formal derivation of the ZZ polynomials for two important classes of pericondensed benzenoids structures, chevrons and generalized chevrons. The final formulas (Eqs. (16) and (21)) are surprisingly simple, especially taking into account the complexity of previously presented formulas of the ZZ polynomials for some subfamilies of the chevron structures with prespecified values of some of the indices. [18], [new paper 2] The simplicity of the final formulas presented here is obtained owing to the important result for defective parallelogram structures, for which we give a proof that a certain class of defects introduced in the perimeter necessarily invokes vanishing of the ZZ polynomials of such defective structures. We expect that this important result can be used for finding closed form formulas of the ZZ polynomial for other important classes of benzenoids structures. [23, 24]

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References

[1] H. P. Zhang, F. J. Zhang, The Clar covering polynomial of hexagonal systems. 1, *Discr. Appl. Math.* **69** (1996) 147–167.

[2] F. J. Zhang, H. P. Zhang, Y. T. Liu, The Clar covering polynomial of hexagonal systems. 2. An application to resonance energy of condensed aromatic hydrocarbons, *Chin. J. Chem.* **14** (1996) 321–325.

[3] H. P. Zhang, F. J. Zhang, The Clar covering polynomial of hexagonal systems III, *Discr. Math.* **212** (2000) 261–269.

[4] H. P. Zhang, The Clar covering polynomial of hexagonal systems with an application to chromatic polynomials, *Discr. Math.* **172** (1997) 163–173.

[5] I. Gutman, B. Furtula, A. Balaban, Algorithm for simultaneous calculation of Kekulé and Clar structure counts, and Clar number of benzenoid molecules, *Polycyc. Arom. Comp.* **26** (2006) 17–35.

[6] C. P. Chou, H. A. Witek, An algorithm and fortran program for automatic computation of the Zhang–Zhang polynomial of benzenoids, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 3–30.

[7] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer, Berlin, 1989.

[8] H. Hosoya, How can we explain the stability of conjugated hydrocarbon- and heterosubstituted networks by topological descriptors? *Curr. Comput. Aided Drug Des.* **6** (2010) 225–234.

[9] S. Gojak, I. Gutman, S. Radenković, A. Vodopivec, Relating resonance energy with the Zhang–Zhang polynomial, *J. Serb. Chem. Soc.* **72** (2007) 673–679.

[10] I. Gutman, S. Gojak, B. Furtula, S. Radenković, A. Vodopivec, Relating total π-electron energy and resonance energy of benzenoid molecules with Kekulé- and Clar-structure-based parameters, *Monatsh. Chem.* **137** (2006) 1127–1138.

[11] I. Gutman, S. Gojak, B. Furtula, Clar theory and resonance energy, *Chem. Phys. Lett.* **413** (2005) 396–399.

[12] A. J. Page, C. P. Chou, B. Q. Pham, H. A. Witek, S. Irle, K. Morokuma, Quantum chemical investigation of epoxide and ether groups in graphene oxide and their vibrational spectra, *Phys. Chem. Chem. Phys.* **15** (2013) 3725–3735.

[13] S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer, Berlin, 1988.

[14] E. Clar, *The Aromatic Sextet*, Wiley, London, 1972.

[15] C. P. Chou, H. A. Witek, Comment on "Zhang–Zhang polynomials of cyclo–polyphenacenes" by Q. Guo, H. Deng, and D. Chen, *J. Math. Chem.* **50** (2012) 1031–1033.

[16] Q. Z. Guo, H. Y. Deng, D. Chen, Zhang–Zhang polynomials of cyclo–polyphenacenes, *J. Math. Chem.* **46** (2009) 347–362.

[17] I. Gutman, B. Borovićanin, Zhang–Zhang polynomial of multiple linear hexagonal chains, *Z. Naturforsch.* **61a** (2006) 73–77.

[18] C. P. Chou, Y. Li, H. A. Witek, Zhang–Zhang polynomials of various classes of benzenoid systems, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 31–64.

[19] Z. Alizadeh, S. Klavžar, Interpolation method and topological indices: 2-parametric families of graphs, *MATCH Commun. Math. Comput. Chem.* **69** (2013) 523–534.

[20] Z. Alizadeh, A. Iranmanesh, S. Klavžar, Interpolation method and topological indices: The case of fullerenes C_{12k+4}, *MATCH Commun. Math. Comput. Chem.* **68** (2012) 303–310.

[21] C. P. Chou, H. A. Witek, ZZdecomposer: A graphical toolkit for analyzing the Zhang–Zhang polynomials of benenoids, *MATCH Commun. Math. Comput. Chem.* **71** (2014) 741–764.

[22] C. P. Chou, H. A. Witek, Determination of ZZ polynomials for various classes of benzenoid systems: Non-heuristic approach, *MATCH Commun. Math. Comput. Chem.* **72** (2014) 75–104.

[23] C. P. Chou, H. A. Witek, Closed-form formulas for the Zhang–Zhang polynomials of benzenoid structures: Prolate rectangles and their generalizations, *submitted*.

[24] C. P. Chou, H. Witek, Closed-form formulas for the Zhang–Zhang polynomials of benzenoid structures: Ribbons and their generalized ribbons, *in preparation*.

[25] A. Erdélyi (Ed.), *Higher Transcendental Functions*, McGraw–Hill, New York, 1953.