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Zhang-Zhang Polynomials of Regular 3- and 4-tier Benzenoid Strips

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Abstract

We present compact, closed-form expressions for Zhang-Zhang (ZZ) polynomials of regular 3- and 4-tier benzenoid strips. It is possible to unify the ZZ polynomials of 11 classes of regular 3- and 4-tier benzenoid strips into a single, universal, three-parameter formula

$$\sum_{k=0}^{Cl}\sum_{l=0}^{2} a_l \binom{n+l}{k}\binom{n-l+Cl-k}{n-l} x^k$$

where $Cl \in \{2,3,4,5,6\}$, $a_0 = 1$, $a_1 \in \{0,1,2,3\}$, and $a_2 \in \{0,1\}$. The parameters a_1 and a_2 partition the 3- and 4-tiers benzenoid strips into four superfamilies; a_1 and a_2 are constant within a given superfamily and Cl enumerates subsequent benzenoid structures. Our finding provides also a compact and universal expression for the number of Kekulé structures for regular 3- and 4-tier benzenoid strips given by

$$K = \sum_{l=0}^{2} a_l \binom{n-l+Cl}{Cl}$$

These expressions are expected to be readily applicable also to wider regular benzenoid strips.

1 Introduction

The process of enumeration of Clar covers for a given benzenoid structure B was greatly simplified when Zhang and Zhang introduced [1-4] a new theoretical concept, a combinatorial polynomial known today as the Clar covering polynomial or as the Zhang-Zhang (ZZ) polynomial. Clar covers can be considered as an extension of the concept of a Kekulè structure (from the chemical point of view) or the concept of a perfect matching (from the graph-theoretical point of view). A Clar cover of a hexagonal graph B with n vertices is such a set of k hexagons and $(n-6k)/2$ edges that each graph vertex is covered once and only once. In chemical terminology, a Clar cover is such an arrangement of aromatic sextets and double bonds that each carbon atom maintains its tetravalent character. Graphically, aromatic sextets are depicted with a circle placed in the center of a selected hexagon and double bonds, with a segment of a double line placed over a selected graph edge. We say that a Clar cover has an order k if exactly k aromatic sextets have been used for its construction. The maximal number of aromatic sextets that can be placed in a hexagonal graph B, i.e., the maximal order of the Clar covers of B, is called the Clar number [5]; it is usually denoted by the symbol Cl. The ZZ polynomial $ZZ(B,x)$ of a benzenoid structure B is given then by

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

where c_k is the number of permissible Clar covers of order k. Clearly, the only function of the dummy variable x is accounting for the number of aromatic sextets *via* its exponent.

ZZ polynomials offer a transparent and convenient way of enumeration of conceivable Clar covers. [6, 7] However, the main strength of ZZ polynomials relies on the inviting recursive properties they possess, permitting their fast and straightforward brute force computation. [7, 8] The most useful of these recursive properties were reviewed elsewhere [1, 4, 6-8] together with an appropriate algorithm that served us as the base of a computer program (ZZCalculator) applicable for evaluation of the ZZ polynomial of small and medium-size benzenoid structures. [7] This code can be routinely applied to dense pericondensed benzenoids containing up to 500 carbon atoms [9] and for catacondensed and quasi-linear pericondensed benzenoid systems containing up to 10000 carbon atoms. For larger structures, alternative approaches must be used. One of such alternatives is determination of general, closed-form ZZ polynomial formulas for particular classes of benzenoid structures (e.g., parallelograms, chevrons, multiple zigzag chains, hexagons, etc.) characterized by a set of general indices $(k, l, m, n, ...)$ defining their size and shape. A beautiful example [10] of such a formula is the ZZ polynomial of the parallelogram $M(m, n)$ given by

$$ZZ(M(m,n), x) = {}_2F_1\left[\begin{matrix}-m, -n\\ 1\end{matrix}; 1 + x\right] \quad (2)$$

where ${}_2F_1$ is the Gauss hypergeometric function, [11] often appearing in combinatorial analysis. (Note that such an analysis reveals also a number of new and interesting facts about the number of Kekulè structures; here, the number of Kekulè structures of $M(m, n)$ is equal to ${}_2F_1\left[\begin{matrix}-m, -n\\ 1\end{matrix}; 1\right]$.) Such closed-form formulas have been already determined—either from heuristic analysis of isostructural benzenoids [7, 12] or from formal decomposition techniques [8, 10, 13-15]—for various families of benzenoid structures. Analogous formulas for other classes of benzenoid structures remain to be discovered. The current manuscript is supposed to summarize, organize, and complete the current state of knowledge about the ZZ polynomials for two important general families of benzenoid structures, regular 3- and 4-tier benzenoid strips. Analogous work for the regular 5-tier benzenoid strips will be presented shortly. [16] These two manuscripts are supposed to generalize the available body of knowledge about the Kekulè structures of the regular 3-, 4-, and 5-tier benzenoid strips to more capacious concept of Clar covers. Note that Kekulè structures are nothing more than the Clar covers of order 0 and their number is simply given by the zeroth-order coefficient c_0 of the ZZ polynomial.

2 Results

ZZ polynomials can be represented in a number of equivalent ways. The most natural form of a ZZ polynomial is obtained by expressing it as a polynomial in the variable x like in Eq. (1); then, the coefficients c_k directly correspond to the number of Clar covers of order k available for a given benzenoid. A more compact expression for a ZZ polynomial can be obtained by representing it as a polynomial in the variable $1 + x$

$$ZZ(B, x) = \sum_{k=0}^{Cl} d_k (1 + x)^k \quad (3)$$

The coefficients c_k in Eq. (1) and the coefficients d_k in Eq. (3) are obviously closely related

$$c_k = \sum_{l=0}^{Cl} \binom{l}{k} d_l \tag{4a}$$

$$d_k = (-1)^k \sum_{l=0}^{Cl} \binom{l}{k} (-1)^l c_l \tag{4b}$$

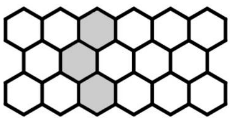
Often, it is possible to evaluate the sums appearing in Eqs. (1) and (3) in closed form, obtaining compact expressions for a given ZZ polynomial in either multiplicative or special function representation. Among all special functions appearing in the ZZ polynomial theory, the Gauss hypergeometric functions seem to occupy particularly exposed place, which should not be too surprising taking into account the role they play in the theory of infinite sums involving binomial coefficients. [17]

The ZZ polynomials of 3- and 4-tier strip benzenoids presented below are given in both polynomial forms defined by Eqs. (1) and (3). In addition to these polynomial forms, additional compact representations are provided whenever available. For each of the 3- and 4-tier strip benzenoids, schematic graphical representation is provided for quick reference with the shaded area symbolizing a horizontal strip of width $n-5$.

3-tier benzenoid strips

Prolate rectangle $Pr(2,n)$

The ZZ polynomials of prolate rectangles $Pr(2,n)$ is a special case of the ZZ polynomials of general prolate rectangles $Pr(m,n)$, which have been first given by Zhang and Zhang [4] and subsequently rederived by Chou and Witek. [18] We have



***Pr*(2,*n*)**

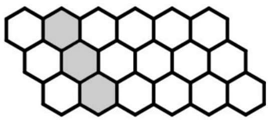
$$\begin{aligned} ZZ(Pr(2,n),x) &= \sum_{k=0}^{2} \binom{2}{k} n^k (1+n)^{2-k} x^k && (5a) \\ &= \sum_{k=0}^{2} \binom{2}{k} n^k (1+x)^k && (5b) \\ &= \big(1+n(1+x)\big)^2 && (5c) \\ &= {}_1F_0\left[{-2 \atop -}; -n(1+x)\right] && (5d) \end{aligned}$$

The multiplicative form in Eq. $(5c)$ highlights the essentially disconnected character of $Pr(2,n)$, which can be seen as two polyacenes $L(n)$ connected by a sequence of fixed single bonds. The hypergeometric expression in Eq. $(5d)$ is readily obtained from Eq. $(5b)$ using basic properties of binomial coefficients $\binom{n}{k}$ and Pochhammer symbols $(a)_k$ (for quick reference see [19] or Appendix I of [11])

$$\sum_{k=0}^{2} \binom{2}{k} n^k (1+x)^k = \sum_{k=0}^{\infty} (-2)_k \frac{\left(-n(1+x)\right)^k}{k!} = {}_1F_0 \left[{-2 \atop -} ; -n(1+x) \right] \qquad (6)$$

Parallelogram $M(3,n)$

The ZZ polynomial of a parallelogram $M(3,n)$ is a special case of the ZZ polynomials of general parallelograms $M(m,n)$, which have been derived originally by Gutman and Borovićanin [20] and put in a compact form by Chou and Witek. [7, 8, 10] We have



***M*(3,*n*)**

$$ZZ(M(3,n),x) = \sum_{k=0}^{3} \binom{3}{k} \binom{n+3-k}{3} x^k \qquad (7a)$$

$$= \sum_{k=0}^{3} \binom{3}{k} \binom{n}{k} (1+x)^k \qquad (7b)$$

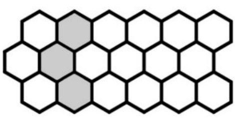
$$= {}_2F_1 \left[{-3, -n \atop 1} ; 1+x \right] \qquad (7c)$$

Chevron $Ch(2,2,n)$

The ZZ polynomial of chevrons $Ch(2,2,n)$ was first deduced empirically by Chou, Li, and Witek (Eq. (40) of [12]) in the following form

$$ZZ(Ch(2,2,n),x) = 1 + 3n(1+x) + \binom{2n}{2}(1+x)^2 + \frac{1}{4}\binom{2n}{3}(1+x)^3 \qquad (8)$$

This formula has been confirmed *via* formal graph decomposition of chevron structures. (For details, see Eqs. (13)–(16) of [10].) It is possible to cast Eq. (8) in a compact form. We have



***Ch*(2,2,*n*)**

$$ZZ(Ch(2,2,n),x) =$$

$$= \sum_{k=0}^{3} \left[\binom{3}{k}\binom{n+3-k}{3} + \binom{n+1}{k}\binom{n+2-k}{3-k} \right] x^k \qquad (9a)$$

$$= \sum_{k=0}^{3} \frac{1}{k+1} \binom{3}{k} \binom{2n}{k} (1+x)^k \qquad (9b)$$

$$= {}_2F_1 \left[{-3, -2n \atop 2} ; 1+x \right] \qquad (9c)$$

The hypergeometric representation is obtained from Eq. $(9b)$ by the following set of transformations

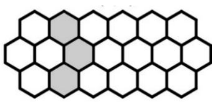
$$\sum_{k=0}^{3} \frac{1}{k+1} \binom{3}{k} \binom{2n}{k} (1+x)^k = \sum_{k=0}^{\infty} \frac{(-3)_k (-2n)_k}{(2)_k} \frac{(1+x)^k}{k!} = {}_2F_1 \left[{-3, -2n \atop 2} ; 1+x \right] \qquad (10)$$

Hexagon $\boldsymbol{O(2,2,n)}$

The ZZ polynomial of hexagons $O(2,2,n)$ was first deduced by Chou, Li, and Witek (Eq. (35) of [12])

$$\begin{aligned} ZZ(O(2,2,n),x) &= 1+4n(1+x)+\frac{1}{2}n(7n-5)(1+x)^2 \\ &+ 2\binom{n}{2}\binom{n-1}{1}(1+x)^3+\frac{1}{3}\binom{n}{2}\binom{n-1}{2}(1+x)^4 \end{aligned} \tag{11}$$

from the analysis of the ZZ polynomials for the first nine members of this family. This formula has been confirmed *via* formal graph decomposition techniques (Eqs. (53)–(57) of [14]). It is possible to cast Eqs. (11) in a compact form. We have



***O*(2,2,*n*)**

$$ZZ(O(2,2,n),x) =$$

$$= \sum_{k=0}^{4}\binom{4}{k}\left[\binom{n-k+4}{4}+\frac{1}{6}\binom{n+1}{2}\binom{n-k+3}{2}\right]\cdot x^k \tag{12a}$$

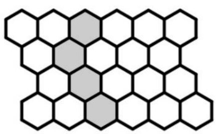
$$= \sum_{k=0}^{4}\left[\binom{4}{k}\binom{n}{k}+\binom{2}{k-2}\binom{n+1}{k}\right]\cdot(1+x)^k \tag{12b}$$

$$\begin{aligned} &= {}_2F_1\left[{-4,-n \atop 1};1+x\right]+ \\ &\quad +(1+x)^2\binom{n+1}{2}\ {}_2F_1\left[{-2,-n+1 \atop 3};1+x\right] \end{aligned} \tag{12c}$$

4-tier benzenoid strips

Goblet $\boldsymbol{X(2,3,n)}$

The ZZ polynomials of goblets $X(2,3,n)$ have been never formally reported before. We have



***X*(2,3,*n*)**

$$ZZ(X(2,3,n),x) = \sum_{k=0}^{2}\binom{2}{k}n^k(1+n)^{2-k}x^k \tag{13a}$$

$$= \sum_{k=0}^{2}\binom{2}{k}n^k(1+x)^k \tag{13b}$$

$$= \big(1+n(1+x)\big)^2 \tag{13c}$$

$$= {}_1F_0\left[{-2 \atop -};-n(1+x)\right] \tag{13d}$$

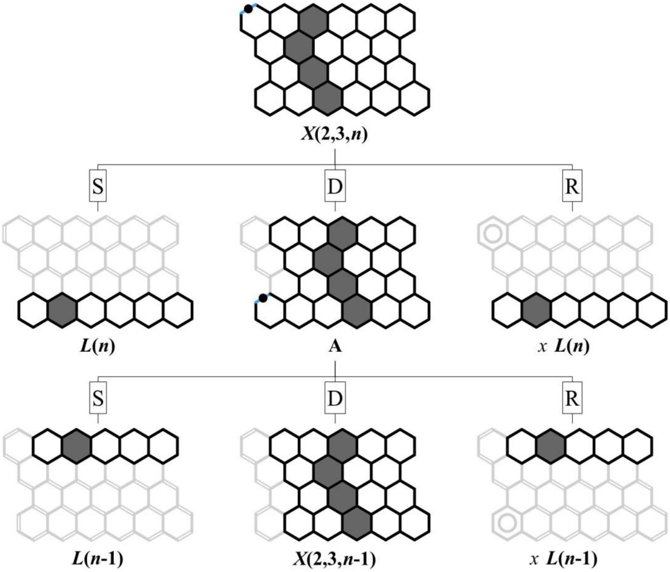


Figure 1. Recursive decomposition of a goblet $X(2,3,n)$, demonstrated here for $n = 6$ and readily generalized to an arbitrary value of n, leads to the recursive relation given by Eq. (15).

The formulas in Eqs. $(13a - d)$ are identical to those for $Pr(2,n)$ in Eqs. $(5a - d)$. This is the consequence of the fact that both structures are essentially disconnected and can be treated as two polyacenes $L(n)$ connected by a network of fixed single bonds. Because for a polyacene $L(n)$, $ZZ(L(n),x) = 1 + n(1 + x)$, [1, 8] we have

$$ZZ(X(2,3,n),x) = ZZ(L(n),x) \cdot ZZ(L(n),x) = ZZ(Pr(2,n),x) \tag{14}$$

confirming the essentially disconnected character of both structures, usually referred to as $L(n) \cdot L(n)$. [21]

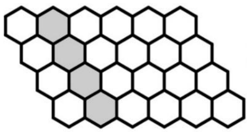
Correctness of the formulas $(13a - d)$ can be readily demonstrated in the following way. The recursive decomposition of a goblet $X(2,3,n)$ shown in **Figure 1** yields the following first-order recursive relation for the ZZ polynomials of goblets $X(2,3,n)$

$$\begin{aligned} ZZ(X(2,3,n),x) &= ZZ(X(2,3,n-1),x) + \\ &+ (x+1) \cdot [ZZ(L(n),x) + ZZ(L(n-1),x)] \end{aligned} \tag{15}$$

which can be immediately solved using standard methods giving Eq. $(13c)$. Other representations follow from the equivalence of Eqs. $(13c)$ and $(5c)$.

Parallelogram $\boldsymbol{M(4,n)}$

The ZZ polynomial of a parallelogram $M(4,n)$ is a special case of the ZZ polynomials of general parallelograms $M(m,n)$, which have been derived originally by Gutman and Borovićanin [20] and put in a compact form by Chou and Witek.[7, 8, 10] We have



$M(4,n)$

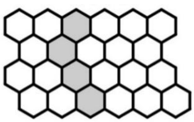
$$ZZ(M(4,n),x) = \sum_{k=0}^{4} \binom{4}{k} \binom{n+4-k}{4} x^k \quad (16a)$$
$$= \sum_{k=0}^{4} \binom{4}{k} \binom{n}{k} (1+x)^k \quad (16b)$$
$$= {}_2F_1 \left[\begin{matrix} -4, -n \\ 1 \end{matrix} ; 1+x \right] \quad (16c)$$

Streamer $\boldsymbol{\Sigma(2,3,n)}$

The ZZ polynomials of streamers $\Sigma(2,3,n)$ have never been reported before. Note that this structure is essentially disconnected and can be written as $M(2,n) \cdot L(n)$. Its ZZ polynomial can be directly computed from **Theorem 7** of [10], which states that the ZZ polynomials of two fused parallelograms is equal to the product of ZZ polynomials of both constituents, $M(2,n)$ and $(1,n) = L(n)$. We have then

$$ZZ(\Sigma(2,3,n),x) = ZZ(M(2,n),x) \cdot ZZ(L(n),x) \quad (17)$$

The right hand side of this expression can be explicitly evaluated giving

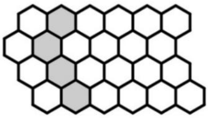


$\Sigma(2,3,n)$

$$ZZ(\Sigma(2,3,n),x) =$$
$$= \sum_{k=0}^{3} \left[n \binom{2}{k-1} \binom{n-k+3}{2} + (n+1) \binom{2}{k} \binom{n-k+2}{2} \right] x^k \quad (18a)$$
$$= \sum_{k=0}^{3} \left[n \binom{2}{k-1} \binom{n}{k-1} + \binom{2}{k} \binom{n}{k} \right] (1+x)^k \quad (18b)$$
$$= {}_2F_1 \left[\begin{matrix} -2, -n \\ 1 \end{matrix} ; 1+x \right] \cdot {}_2F_1 \left[\begin{matrix} -1, -n \\ 1 \end{matrix} ; 1+x \right] \quad (18c)$$
$$= {}_2F_1 \left[\begin{matrix} -3, -n \\ 1 \end{matrix} ; 1+x \right] +$$
$$+ 2(1+x)^2 \binom{n+1}{2} \, {}_2F_1 \left[\begin{matrix} -1, -n+1 \\ 3 \end{matrix} ; 1+x \right] \quad (18d)$$

Chevron $\boldsymbol{Ch(2,3,n)}$

The ZZ polynomials of chevrons $Ch(2,3,n)$ are a special case of the ZZ polynomials for a general chevron $Ch(k,m,n)$ given by Eq. (16) of [10]. The explicit form of $ZZ(Ch(2,3,n),x)$ is given by



Ch(2,3,*n*)

$$ZZ(Ch(2,3,n),x) =$$

$$= \sum_{k=0}^{4} \binom{4}{k} \left[\binom{n-k+4}{4} + \frac{1}{3} \binom{n+1}{2} \binom{n-k+3}{2} \right] \cdot x^k \qquad (19a)$$

$$= \sum_{k=0}^{4} \left[\binom{4}{k} \binom{n}{k} + 2 \binom{2}{k-2} \binom{n+1}{k} \right] \cdot (1+x)^k \qquad (19b)$$

$$= {}_2F_1 \left[\begin{matrix} -4, -n \\ 1 \end{matrix} ; 1+x \right] +$$

$$+ 2(1+x)^2 \binom{n+1}{2} {}_2F_1 \left[\begin{matrix} -2, -n+1 \\ 3 \end{matrix} ; 1+x \right] \qquad (19c)$$

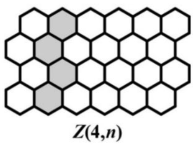
An interesting variation of Eq. $(19a)$ is given by

$$\sum_{k=0}^{4} \left[2 \binom{2}{k} \binom{n-k+3}{4} + B_{4-k}^{(4)} \cdot \binom{n-k+4}{4} + 2 \binom{2}{k-2} \binom{n-k+5}{4} \right] \cdot x^k \qquad (20)$$

where $B_n^{(l)}$ are poly-Bernoulli numbers defined by Kaneko [22] and available in an explicit form as the sequence A099594 in OEIS. [23]

Multiple zigzag chain $Z(4, n)$

The ZZ polynomials of multiple zigzag chains $Z(4, n)$ were deduced empirically by Chou, Li, and Witek (Eq.(44) of [12]) from the analysis of the ZZ polynomials of the first 10 members of this family. The formulas were subsequently re-derived using formal decomposition techniques (Eqs. (33)–(38) of [14]), confirming the heuristic reasoning of [12]. We have



Z(4,*n*)

$$ZZ(Z(4,n),x) =$$

$$= \sum_{k=0}^{4} \left[\binom{3}{k} \binom{n+3-k}{3} + n \binom{4}{k} \binom{n+3-k}{3} + \right.$$

$$\left. + n \binom{3}{k-1} \binom{n+3-k}{2} + \binom{4}{k} \binom{n+2}{4} \right] x^k \qquad (21a)$$

$$= \sum_{k=0}^{4} \left[\binom{4}{k} \binom{n}{k} + 3 \binom{2}{k-2} \binom{n+1}{k} + \right.$$

$$\left. + \binom{0}{k-4} \binom{n+2}{k} \right] (1+x)^k \qquad (21b)$$

$$= \left(1 + n(1+x)\right) \cdot {}_2F_1 \left[\begin{matrix} -3, -n \\ 1 \end{matrix} ; 1+x \right] + \binom{n+2}{4} (1+x)^4 \qquad (21c)$$

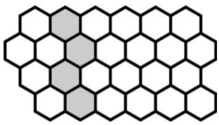
Pentagon $D(2, 3, n)$

The ZZ polynomial of pentagons $D(2,3,n)$ has been implicitly derived by Chou and Witek using formal decomposition techniques. [14] The recurrence relation for pentagons $D(2,3,n)$ is deduced from the lower portion of **Figure 15** of [14]; upon telescopic folding it yields the

ZZ polynomial of pentagons $D(2,3,n)$ expressed in terms of ZZ polynomials of multiple zigzag chains $Z(4,n)$, given by

$$ZZ(D(2,3,n),x) = ZZ(Z(4,n),x) + (1+x)\sum_{k=0}^{n-1} ZZ(Z(4,k),x) \tag{22}$$

Substitution of Eqs. $(21a)$ and $(21b)$ into Eq. (22) gives explicit form of the ZZ polynomials for pentagons $D(2,3,n)$ in the following form



***D*(2,3,*n*)**

$$\begin{aligned} ZZ(D(2,3,n),x) &= \\ &= \sum_{k=0}^{5}\left[(n+1)\binom{n}{k}\binom{n+4-k}{n} + n\binom{n}{k-1}\binom{n+5-k}{n} - \right. \\ &\qquad \left. - \binom{n+1}{k}\binom{n+4-k}{n-1} + \binom{n+2}{k}\binom{n+3-k}{n-2}\right] x^k && (23a) \\ &= \sum_{k=0}^{5}\left[\binom{5}{k}\binom{n}{k} + 3\binom{3}{k-2}\binom{n+1}{k} + \right. \\ &\qquad \left. + \binom{1}{k-4}\binom{n+2}{k}\right](1+x)^k && (23b) \\ &= {}_2F_1\left[\begin{matrix}-5,-n\\1\end{matrix};1+x\right] + \\ &\qquad + 3(1+x)^2\binom{n+1}{2}\, {}_2F_1\left[\begin{matrix}-3,-n+1\\3\end{matrix};1+x\right] + \\ &\qquad + (1+x)^4\binom{n+2}{4}\, {}_2F_1\left[\begin{matrix}-1,-n+2\\5\end{matrix};1+x\right] && (23c) \end{aligned}$$

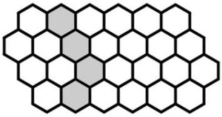
***Hexagon* $\boldsymbol{O(2,3,n)}$**

The ZZ polynomial of hexagons $O(2,3,n)$ has been derived initially by Chou and Witek using formal decomposition techniques (Eq. 65 of [14]). To cast this formula into a closed sum, we use the recurrence relation for hexagons $O(2,3,n)$ deduced from the upper portion of **Figure 12** of [14]; upon telescopic folding (Eq. 53 of [14]) it yields the ZZ polynomial of hexagons $O(2,3,n)$ expressed in terms of ZZ polynomials of pentagons $D(2,3,n)$, given by

$$ZZ(O(2,3,n),x) = ZZ(D(2,3,n),x) + (1+x)\sum_{k=0}^{n-1} ZZ(D(2,3,k),x) \tag{24}$$

Substitution of Eqs. $(23a)$ and $(23b)$ into Eq. (24) gives explicit form of the ZZ polynomials for hexagons $O(2,3,n)$ in the following form

$$ZZ(O(2,3,n),x) =$$
$$= \sum_{k=0}^{6} \left[(n+1)\binom{n}{k}\binom{n+5-k}{n} + n\binom{n}{k-1}\binom{n+6-k}{n} - \right.$$
$$\left. -2\binom{n+1}{k}\binom{n+5-k}{n-1} + \binom{n+2}{k}\binom{n+4-k}{n-2} \right] x^k \quad (25a)$$



$O(2,3,n)$

$$= \sum_{k=0}^{6} \left[\binom{6}{k}\binom{n}{k} + 3\binom{4}{k-2}\binom{n+1}{k} + \right.$$
$$\left. + \binom{2}{k-4}\binom{n+2}{k} \right] (1+x)^k \quad (25b)$$
$$= {}_2F_1\left[{-6,-n \atop 1}; 1+x \right] +$$
$$+3(1+x)^2\binom{n+1}{2}\ {}_2F_1\left[{-4,-n+1 \atop 3}; 1+x \right] +$$
$$+(1+x)^4\binom{n+2}{4}\ {}_2F_1\left[{-2,-n+2 \atop 5}; 1+x \right] \quad (25c)$$

3 Discussion

The ZZ polynomials of 3- and 4-tier benzenoids show surprisingly large degree of similarity. It is possible to express the ZZ polynomials for all 11 types of considered here benzenoids using a single compact formula

$$ZZ(B,x) = \sum_{k=0}^{Cl} \left[\binom{Cl}{k}\binom{n}{k} + a_1\binom{Cl-2}{k-2}\binom{n+1}{k} + a_2\binom{Cl-4}{k-4}\binom{n+2}{k} \right] (1+x)^k \quad (26)$$

where the constants Cl, a_1, and a_2 are summarized in Table 1. The constants Cl, a_1, and a_2 play a role of “quantum numbers” (or topological invariants, for sake of preference) for benzenoids structures. It is reasonable to think that they should serve as a natural basis for a new classification of families of benzenoid structures with possibly more scientific rigor and depth than the current classification based on the shape of each family. The “quantum number” Cl (i.e., Clar number) denotes the maximal number of aromatic sextets in each family and does not require further comment. The transcendental meaning of “quantum numbers” a_1 and a_2, classifying each structure in one of the superfamilies (for details, see below), remains to be understood. The representation of ZZ polynomials in the basis of powers of $1+x$, given by Eq. (26) can be easily transformed into other forms. We have

$$ZZ(B,x) = \sum_{k=0}^{Cl} \left[\binom{n}{k}\binom{n+Cl-k}{n} + a_1\binom{n+1}{k}\binom{n-1+Cl-k}{n-1} + \right.$$
$$\left. +a_2\binom{n+2}{k}\binom{n-2+Cl-k}{n-2} \right] x^k \quad (27)$$

in the basis of monomials x^k and

Table 1. Constants Cl, a_1, and a_2 allowing one to express the ZZ polynomials of 11 families of regular 3- and 4-tier strips benzenoids using a single expression. For various representations of this expression, see Eqs. (26)–(28) and (26*a*)–(28*a*). For analogous expression giving the number of Kekulé structures, see Eqs. (29) and (29*a*). For the discussion of superfamilies, see text below.

superfamily	B	Cl	a_1	a_2
1	$M(3,n)$	3	0	0
	$M(4,n)$	4	0	0
$M(1,n)\cdot M(1,n)$	$Pr(2,n)$ $X(2,3,n)$	2	1	0
	$Ch(2,2,n)$	3	1	0
	$O(2,2,n)$	4	1	0
$M(1,n)\cdot M(2,n)$	$\Sigma(2,3,n)$	3	2	0
	$Ch(2,3,n)$	4	2	0
$Z(4,n)$	$Z(4,n)$	4	3	1
	$D(2,3,n)$	5	3	1
	$O(2,3,n)$	6	3	1

$$ZZ(B,x) = {}_2F_1\left[{-Cl,-n \atop 1};1+x\right] + a_1(1+x)^2\binom{n+1}{2}\,{}_2F_1\left[{2-Cl,1-n \atop 3};1+x\right] + \\ + a_2(1+x)^4\binom{n+2}{4}\,{}_2F_1\left[{4-Cl,2-n \atop 5};1+x\right] \tag{28}$$

in the hyperspherical representation. Note that Eq. (27) gives implicitly the number of Kekulé structures $K = c_0$ for each of the 3- and 4-tier benzenoid family; it can be expressed explicitly as

$$K = \binom{n+Cl}{Cl} + a_1\binom{n-1+Cl}{Cl} + a_2\binom{n-2+Cl}{Cl} \tag{29}$$

with the constants Cl, a_1, and a_2 defined in Table 1. This single formula replaces 11 distinct formulas for the number of Kekulé structures K that can be found on pp. 165–166 of [21]. Note finally, that with setting $a_0 = 1$, Eqs. (26)–(29) can be expressed in the most compact form given by

$$ZZ(B,x) = \sum_{k=0}^{Cl}\sum_{l=0}^{2} a_l \binom{n+l}{k}\binom{n-l+Cl-k}{n-l} x^k \tag{27a}$$

$$= \sum_{k=0}^{Cl}\sum_{l=0}^{2} a_l \binom{Cl-2l}{k-2l}\binom{n+l}{k} (1+x)^k \tag{26a}$$

$$= \sum_{l=0}^{2} a_l (1+x)^{2l} \binom{n+l}{2l} \, {}_2F_1\left[\begin{matrix} 2l-Cl, l-n \\ 2l+1 \end{matrix}; 1+x\right] \tag{28a}$$

and

$$K = \sum_{l=0}^{2} a_l \binom{n-l+Cl}{Cl} \tag{29a}$$

A very insightful and possibly useful upon appropriate formalization way of looking at the ZZ polynomials of regular 3- and 4-tier benzenoids uses an umbral [24] operator $\hat{\Sigma}$ defined in action on some function $f(n,x)$ in the following manner

$$\hat{\Sigma}\,[f(n,x)] = \begin{cases} 1 + (1+x)\sum_{j=0}^{n-1} 1 = 1 + (1+x)n & \text{if } f(n,x) = 1 \\ f(n,x) + (1+x)\sum_{j=0}^{n-1} f(j,x) & \text{if } f(n,x) \neq 1 \end{cases} \tag{30}$$

It is possible to express the ZZ polynomials of all considered here structures via the action of the operator $\hat{\Sigma}$ on some simpler objects. We have

$$ZZ(M(m,n),x) = \underbrace{\hat{\Sigma}\big[\hat{\Sigma}[\cdots\hat{\Sigma}}_{m \text{ times}}[1]\cdots]\big] = \hat{\Sigma}^m[1] \tag{31}$$

The parallelograms $M(3,n)$ and $M(4,n)$ belong thus to the same superfamily of benzenoids characterized by $a_1 = 0$ and $a_2 = 0$ and called by us the 1 superfamily. The benzenoids $Pr(2,n)$, $X(2,3,n)$, $Ch(2,2,n)$, and $O(2,2,n)$ belong to the $M(1,n)\cdot M(1,n)$ superfamily characterized by $a_1 = 1$ and $a_2 = 0$ (see Table 1); we have

$$\left.\begin{matrix} ZZ(Pr(2,n),x) \\ ZZ(X(2,3,n),x) \end{matrix}\right\} = \hat{\Sigma}^0[ZZ(M(1,n),x)\cdot ZZ(M(1,n),x)] = \hat{\Sigma}[1]\cdot\hat{\Sigma}[1] \tag{32a}$$

$$ZZ(Ch(2,2,n),x) = \hat{\Sigma}^1[ZZ(M(1,n),x)\cdot ZZ(M(1,n),x)] = \hat{\Sigma}\left[\hat{\Sigma}[1]\cdot\hat{\Sigma}[1]\right] \tag{32b}$$

$$ZZ(O(2,2,n),x) = \hat{\Sigma}^2[ZZ(M(1,n),x)\cdot ZZ(M(1,n),x)] = \hat{\Sigma}^2\left[\hat{\Sigma}[1]\cdot\hat{\Sigma}[1]\right] \tag{32c}$$

The benzenoids $\Sigma(2,3,n)$ and $Ch(2,3,n)$ belong to the $M(1,n)\cdot M(2,n)$ superfamily characterized by $a_1 = 2$ and $a_2 = 0$; we have

$$ZZ(\Sigma(2,3,n),x) = \hat{\Sigma}^0[ZZ(M(1,n),x)\cdot ZZ(M(2,n),x)] = \hat{\Sigma}[1]\cdot\hat{\Sigma}^2[1] \tag{33a}$$

$$ZZ(Ch(2,3,n),x) = \hat{\Sigma}^1[ZZ(M(1,n),x)\cdot ZZ(M(2,n),x)] = \hat{\Sigma}\left[\hat{\Sigma}[1]\cdot\hat{\Sigma}^2[1]\right] \tag{33b}$$

Finally, the benzenoids $\mathrm{Z}(4,n)$, $D(2,3,n)$, and $O(2,3,n)$ belong to the $\mathrm{Z}(4,n)$ superfamily characterized by $a_1 = 3$ and $a_2 = 1$; we have

$$ZZ(\mathrm{Z}(4,n),x) = \hat{\Sigma}^0[ZZ(\mathrm{Z}(4,n),x)] \tag{34a}$$

$$ZZ(D(2,3,n),x) = \hat{\Sigma}^1[ZZ(\mathrm{Z}(4,n),x)] \tag{34b}$$

$$ZZ(O(2,3,n),x) = \hat{\Sigma}^2[ZZ(\mathrm{Z}(4,n),x)] \tag{34b}$$

No compact expression for $ZZ(\mathrm{Z}(4,n),x)$ in terms of the operator $\hat{\Sigma}$ has been discovered. It is instructive to evaluate explicitly an exemplary expression involving the operator $\hat{\Sigma}$. For $O(2,2,n)$, we have

$$\begin{aligned} ZZ(O(2,2,n),x) &= \hat{\Sigma}^2\left[\hat{\Sigma}[1]\cdot\hat{\Sigma}[1]\right] \\ &= \hat{\Sigma}^2\left[\left(1+(1+x)\sum_{j=0}^{n-1}1\right)^2\right] \\ &= \left(1+(1+x)\sum_{j=0}^{n-1}1\right)^2 + 2(1+x)\sum_{k=0}^{n-1}\left(1+(1+x)\sum_{j=0}^{k-1}1\right)^2 \\ &\quad + (1+x)^2\sum_{k=0}^{n-1}\sum_{l=0}^{k-1}\left(1+(1+x)\sum_{j=0}^{l-1}1\right)^2 \end{aligned} \tag{35}$$

These results suggest that the operator $\hat{\Sigma}$ together with parallelograms $M(m,n)$ and multiple zigzag chains $Z(m,n)$ constitute the basic building blocks useful for efforts of developing a general theory of ZZ polynomials. [25, 26] These results also show that regular 1-, 2-, 3-, and 4-tier strips benzenoids can be conveniently classified into 4 superfamilies: 1, $M(1,n)\cdot M(1,n)$, $M(1,n)\cdot M(2,n)$, and $\mathrm{Z}(4,n)$. Similar regularities are expected for wider regular benzenoid strips.[16]

4 Conclusions

Compact, closed form expressions for the ZZ polynomials of regular 3- and 4-tiers benzenoid strips have been presented in various representations. It has been possible to unify the ZZ polynomials of 11 classes of apparently different benzenoid structures into a single, universal formula, depending only on three parameters: Cl, a_1, and a_2. The parameters a_1 and a_2 partition the 3- and 4-tiers benzenoid strips into four superfamilies that can be conveniently referred to as the 1, $M(1,n) \cdot M(1,n)$, $M(1,n) \cdot M(2,n)$, and $\mathrm{Z}(4,n)$ superfamilies. The parameters a_1 and a_2 are constant within a given superfamily and the parameter Cl enumerates subsequent families of benzenoid structures. The partition of the regular 3- and 4-tiers benzenoid strips into superfamilies is further rationalized using an umbral operator $\hat{\Sigma}$, which together with parallelograms $M(m,n)$ and multiple zigzag chains $Z(m,n)$ seem to constitute the basic building blocks for the general theory of ZZ polynomials of benzenoid structures.

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