MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **86** (2021) 121-140

ISSN 0340 - 6253

Clar Theory for Hexagonal Benzenoids with Corner Defects

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(Received March 6, 2020)

Abstract

We present here a study of Clar covering polynomials (*aka* Zhang-Zhang or ZZ polynomials) for a family of structural derivatives of hexagonal benzenoids $O(n_1, n_2, n_3)$ with some of its corners removed. This family consists of 64 distinct structures. The ZZ polynomials of structures in this family are interrelated by a network of 192 algebraic recurrence relations. Symmetry considerations allow us to reduce the studied network to 96 recurrence relations involving 36 symmetry-distinct structures. Equations defining 25 of these structures are purely algebraic and can be completely solved. The ZZ polynomials of the remaining 11 structures, interrelated by 15 recurrence relations, are characterized in terms of generating function for one of these structures, e.g., $O(n_1, n_2, n_3)$. The presented result is not fully satisfactory: one more recurrence relation is missing to find the explicit form of the generating function for the ZZ polynomials of $O(n_1, n_2, n_3)$. We believe that the presented results constitute an important step toward finding a closed-form ZZ polynomial formulas for hexagonal flakes and their derivatives and completing the theory of Clar covers for hexagonal flakes.

1 Introduction

Characterization of Clar covers [12] of pericondensed polycyclic benzenoids [16] is in general a challenging and tedious task [2, 18, 19, 23, 25, 31, 35, 39]. The typical research questions that are usually asked in this context are: (*i*) Does a benzenoid $\boldsymbol{B}$ permit any Clar covers? (*ii*) If yes, how many Clar covers does it permit? (*iii*) What is the

maximal number of aromatic sextets (Clar number, Cl) that can be accommodated in $\boldsymbol{B}$? (iv) How many Clar structures (Clar covers with Cl aromatic sextets) can be constructed for $\boldsymbol{B}$? (v) How many Clar covers with a prespecified number k of aromatic sextets can be constructed for $\boldsymbol{B}$ for every $0 \leq k < Cl$? (vi) What is the average distribution of aromatic sextets (local aromaticity) in various hexagons of $\boldsymbol{B}$? (vii) What is the distribution of single and double bonds in $\boldsymbol{B}$? ($viii$) Are there any regions with fixed bonds in $\boldsymbol{B}$? (ix) Are the regions with fixed bonds in $\boldsymbol{B}$ located in such a way that $\boldsymbol{B}$ is essentially disconnected? (x) How to establish the aforementioned properties of $\boldsymbol{B}$ in a robust and efficient manner? Answering many of these questions became much simpler after introducing by Zhang and Zhang the Clar covering polynomial $\mathrm{ZZ}(\boldsymbol{B}, x)$ [34, 36–38], which is nowadays customarily referred to as the Zhang-Zhang polynomial or more concisely, as the ZZ polynomial [14]. For example, the maximal degree of x in $\mathrm{ZZ}(\boldsymbol{B}, x)$ is equal to Cl, the coefficient in front of x^{Cl} denotes the number of Clar structures, the coefficient in front of x^0, $c_0 \equiv \mathrm{ZZ}(\boldsymbol{B}, 0)$, denotes the number of Kekulé structures, and the value $\mathrm{ZZ}(\boldsymbol{B}, 1)$ reproduces the total number of Clar covers. The problem of robust determination of $\mathrm{ZZ}(\boldsymbol{B}, x)$ was solved by Gutman, Furtula, and Balaban by proposing an iterative algorithm [17]; this algorithm was further refined and efficiently implemented by Chou and Witek, first in a form of a on-line ZZCalculator [4,5] and later in a form of freely-downloadable ZZDecomposer [7–9, 40, 41]. The latter program, in addition to the tool for determination of the ZZ polynomials for an arbitrary benzenoid that can be conveniently defined using a mouse drawing pad, incorporates also various tools for deriving closed-form formulas for various families of benzenoid structures. In its most typical depth decomposition mode, ZZDecomposer generates a recurrence relation for an analyzed benzenoid structure, which relates its ZZ polynomial to the ZZ polynomials of structurally related benzenoids. In many cases, it is possible to decouple the set of the resulting recurrence relations and find a closed-form recurrence relation that expresses the ZZ polynomial of some structured benzenoid $\boldsymbol{B}_n$ in terms of ZZ polynomials of the isostructural benzenoids $\boldsymbol{B}_m$ with $m < n$. This strategy has been successfully applied by us to various families of pericondensed benzenoids, allowing for finding closed-form formulas for the ZZ polynomials of regular 3-, 4-, and 5-tier benzenoid strips [32, 33], parallelograms $M(m, n)$ [7], chevrons $Ch(k, m, n)$ [9], prolate rectangles $Pr(m, n)$ [11], multiple zigzag chains $Z(m, n)$ [27], and their various generalizations [6, 10, 26–30]. A

successful application of this algorithm to ribbons $Rb(k,m,n)$ will be reported by us soon. However, there exist two classes of structures, oblate rectangles $Or(m,n)$ and hexagonal flakes $O(k,m,n)$, which up-to-date almost completely escape the possibility of their full characterization in terms of closed-form ZZ polynomial formulas. Partial results for constrained subfamilies of these structures (for example: $Or(m,2)$, $O(2,2,n)$, $O(2,3,n)$, $O(3,3,n)$) have been obtained [3,8], but their extension to general structures $Or(m,n)$ and $O(k,m,n)$ constitute a real challenge in the theory of ZZ polynomials.

The current paper reports an important step toward finding a closed-form formulas for the hexagonal flakes $O(k,m,n)$. Namely, we have analyzed the network of recurrence relations obtained for the complete set of structural derivatives of $O(k,m,n)$ obtained by removing its corners. It turns out that the resulting network is closed and comprises of 192 recurrence relations interrelating ZZ polynomials of 64 structural derivatives of $O(k,m,n)$ obtained by removing from it 0, 1, 2, 3, 4, 5, or 6 of its corners. Many of these derivatives are related by symmetry, which allows us to express the network in form of 96 recurrence relations for 36 symmetry-distinct structural derivatives of $O(k,m,n)$. Further, we are able to partially solve the set of recurrence relations for 25 of these symmetry-distinct derivatives, reducing the original set of 96 recurrence relations to 15 recurrence relations interrelating 11 symmetry-distinct structures. Further solution of this problem is given in terms of generating functions, which allow to reduce the problem completely and express ZZ polynomials (or the corresponding generating function) of all of the derivatives of $O(k,m,n)$ in terms of the generating function for the ZZ polynomials of $O(k,m,n)$ or in terms of the generating function for the ZZ polynomials of $G(k,m,n)$, i.e., the derivative of $O(k,m,n)$ obtained by removing its three alternating corners. The obtained result is not fully satisfactory: a single recurrence relation is missing in the whole network in order to provide a mean to its complete solution. However, the partial result obtained here shows that the ZZ polynomials for all of the structural derivatives of $O(k,m,n)$ obtained by introducing corner defects can be readily obtained once the ZZ polynomials of $O(k,m,n)$ or $G(k,m,n)$ are known. We believe that this results constitutes an important step toward developing the complete theory of Clar covers and ZZ polynomials of hexagonal graphene flakes.

2 Preliminaries

A benzenoid is a planar hydrocarbon $\boldsymbol{B}$ consisting entirely of fused benzene rings. Every carbon atom in $\boldsymbol{B}$ forms three σ bonds with its three closest neighbor atoms; the fourth bond, fulfilling the requirement of tetravalent character of each carbon atom, is either a localized π bond formed with one of its neighbor carbon atoms or a delocalized aromatic π sextet involving five other carbon atoms located in the same benzene unit. The arrangement of σ bonds in $\boldsymbol{B}$ is fully and uniquely determined by the topology of $\boldsymbol{B}$, but the arrangement of π bonds can be usually decided in many distinct ways. Each of such arrangements of localized π bonds and delocalized aromatic sextets, resulting in tetravalent character of each carbon atom in $\boldsymbol{B}$, is referred to as a Clar cover [12]. The maximal number, Cl, of aromatic sextets that can be accommodated within the benzenoid $\boldsymbol{B}$ is referred to as the Clar number. The Clar covers with exactly Cl aromatic sextets are called Clar structures. The Clar covers with k aromatic sextets are referred to as the Clar covers of order k. Clar covers involving only localized π bonds (i.e., Clar covers of order 0) are called Kekulé structures. Sometimes, the topology of carbon atom connections in $\boldsymbol{B}$ does not permit for constructing even a single Clar cover; such benzenoids are referred to as non-Kekuléan. In graph-theoretical context, the theory of Clar covers is often expressed as a theory of perfect coverings of graphs of an infinite hexagonal lattice. A Clar cover is a spanning subgraph such that its every component is either K_2 or C_6, where K_2 corresponds to the localized π bonds and C_6 corresponds to the delocalized aromatic sextets.

A convenient way to enumerate Clar covers for a given benzenoid $\boldsymbol{B}$ is given by a combinatorial polynomial in a dummy variable x usually referred to as the ZZ polynomial (*aka* Zhang-Zhang polynomial or Clar covering polynomial), which is given by

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

The ZZ polynomial of $\boldsymbol{B}$ is the most compact source of information about the Clar covers of $\boldsymbol{B}$: the order of the ZZ polynomial is equal to the Clar number Cl of $\boldsymbol{B}$ and the coefficient c_{Cl} is the number of Clar structures, the coefficient c_k denotes the number of Clar covers of order k, and the coefficient c_0 corresponds to the number of Kekulé structures of $\boldsymbol{B}$. It is also easy to see that the total number of Clar covers for $\boldsymbol{B}$ is

simply given as ZZ($\boldsymbol{B}$, 1) and the total number of Kekulé structures for $\boldsymbol{B}$ is simply given as ZZ($\boldsymbol{B}$, 0). The ZZ polynomial of $\boldsymbol{B}$ can be conveniently determined using recursive decomposition algorithms [4, 7, 17] or can be conveniently computed using interface theory of benzenoids [26, 27, 29, 30]. An useful theoretical tool for determination of the ZZ polynomials for an arbitrary benzenoid is ZZDecomposer [7, 8]. With this program, one can conveniently define a benzenoid using a mouse drawing pad and subsequently use the underlying graph representation of the benzenoid to find its ZZ polynomial, manipulate its Clar covers, and determine its structural similarity to other, related benzenoids. In its most typical depth decomposition mode, ZZDecomposer generates a recurrence relation for an analyzed benzenoid structure, which relates its ZZ polynomial to the ZZ polynomials of structurally related benzenoids and often allows for determination of a closed-form formulas for the whole family of structures.

3 Definition of the problem

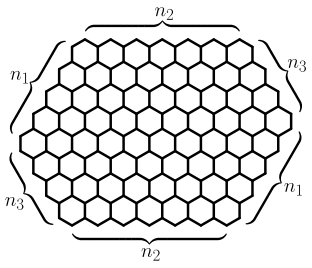

Figure 1. An example of a hexagonal flake $O(n_1, n_2, n_3)$ with $n_1 = 5$, $n_2 = 7$, and $n_3 = 4$.

In this work, we attempt to determine closed-form ZZ polynomials for a family of structurally related benzenoids obtained from hexagonal graphene flakes $O(n_1, n_2, n_3)$ by introducing corner defects. To be more precise, we start with a hexagonal graphene flake $O(n_1, n_2, n_3)$ with the indices $n_1, n_2, n_3 \geq 2$ (see Fig. 1 for a graphical definition) and we construct all possible structural derivatives of $O(n_1, n_2, n_3)$ by removing a certain number (from zero to six) of its corners. The number of the derivative structures of $O(n_1, n_2, n_3)$ that can be obtained in this way is 64. For each of these 64 structures, one can construct decomposition pathways (similar to those shown below in Figs. 2 and 3) by selecting a

bond in one of the remaining corners. The number of decomposition pathways that can be obtained in this way is 192. The ZZ polynomials for the 64 derivative structures of $O(n_1, n_2, n_3)$ are not all different owing to high symmetry possessed by these structures. In fact, the ZZ polynomial of $O(n_1, n_2, n_3)$ is invariant with respect to any permutation of the parameters n_1, n_2, and n_3. Thus it is possible to identify a subset of 36 derivative structures, such that every structural derivative is distinct from all the others from the point of view of symmetry. All these 36 structures together with their labeling scheme are shown in Fig. 4. The original set of 192 decomposition pathways corresponding to the 64 derivative structures reduces now to 96 possible decomposition pathways involving only 36 symmetry-distinct derivatives. These decomposition pathways are symbolically represented below by Eqs. (10)–(15) in form of the resulting recurrence relations for their ZZ polynomials.

The members of the family of symmetry-distinct structural derivatives of $O(n_1, n_2, n_3)$ are closely morphologically and structurally related, so it does not come as a surprise that their ZZ polynomials are also closely related. In fact, for this family of structures, it is possible to construct with the help of the ZZDecomposer program [7] and using the recurrence relation technique described in detail in [4], a set of linear recurrence relations interrelating their ZZ polynomials. To derive this set, let us consider first a few examples. Before doing so, let us introduce a notation convention for the ZZ polynomials that will be used till the end of the current manuscript. Namely, instead of denoting the ZZ polynomial of a benzenoid $\boldsymbol{B}$ as $\mathrm{ZZ}(\boldsymbol{B}, x)$ we will simply write $\boldsymbol{B}$. In this way, the symbol $\boldsymbol{B}$ denotes two distinct quantities: the benzenoid $\boldsymbol{B}$ itself and its ZZ polynomial; we believe that this dichotomy will not cause the reader any practical problems.

Fig. 2 shows that selecting a bond b (denoted in Fig. 2 in blue with a black dot in its center) in one of the corners of the hexagonal flake $O(n_1, n_2, n_3)$ and assigning it with single, double, and aromatic character determines also the character of some other bonds in this structure. In every resulting Clar cover the selected bond b can only assume three different covering types (single = no covering, double = covering with K_2, and aromatic = covering with C_6), so the set of Clar covers of $O(n_1, n_2, n_3)$ is composed of three disjoint sets of Clar covers: those with single bond b, those with double bond b, and those with aromatic bond b. Note now that selecting the bond b to be single fixes the character of all its neighboring bonds, reducing effectively the set of Clar covers of $O(n_1, n_2, n_3)$

with a single bond b to the set of all Clar covers of $O(n_1, n_2, n_3 - 1)$. Similar reductions (to $A_3(n_1, n_2, n_3)$ or $A_3(n_1, n_2, n_3 - 1)$, respectively) happen also for the cases when b is double or aromatic. Consequently, the number of Clar covers for $O(n_1, n_2, n_3)$ is equal to the total number of Clar covers for its three derivative substructures, $O(n_1, n_2, n_3 - 1)$, $A_3(n_1, n_2, n_3)$, and $A_3(n_1, n_2, n_3 - 1)$. Similar relation holds also for the ZZ polynomial of $O(n_1, n_2, n_3)$, which can be obtained by summing the ZZ polynomials of $O(n_1, n_2, n_3 - 1)$, $A_3(n_1, n_2, n_3)$, and $A_3(n_1, n_2, n_3 - 1)$, with the additional condition that the ZZ polynomial of $A_3(n_1, n_2, n_3 - 1)$ should be multiplied by x to account for the additional aromatic ring shown in Fig. 2 in gray. Similar decompositions can be performed for all the three symmetry-distinct corners of $O(n_1, n_2, n_3)$, leading to the following general recurrence relations interrelating the ZZ polynomials of hexagonal graphene flakes O and hexagonal graphene flakes without a corner A_i

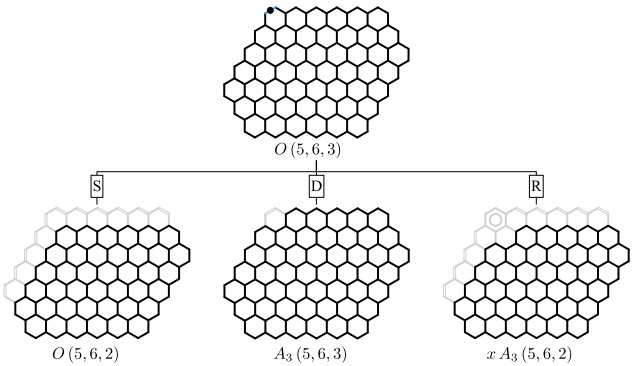

Figure 2. A decomposition of the ZZ polynomial of a hexagonal flake $O(n_1, n_2, n_3)$ (here, $n_1 = 5$, $n_2 = 6$, and $n_3 = 3$) with respect to the bond located in one of the corners (denoted in blue with a black dot in its center) results in a recurrence relation given by Eq. (2), interrelating the ZZ polynomials of these four structures. This recurrence relation constitutes one single entry in the network of 96 recurrence relations considered in the current work (Eqs. (10)–(15)).

$$O\left(n_1,n_2,n_3\right)=O\left(n_1,n_2,n_3-1\right)+A_3\left(n_1,n_2,n_3\right)+x\,A_3\left(n_1,n_2,n_3-1\right) \tag{2}$$

$$O\left(n_1,n_2,n_3\right)=O\left(n_1,n_2-1,n_3\right)+A_2\left(n_1,n_2,n_3\right)+x\,A_2\left(n_1,n_2-1,n_3\right) \tag{3}$$

$$O\left(n_1,n_2,n_3\right)=O\left(n_1-1,n_2,n_3\right)+A_1\left(n_1,n_2,n_3\right)+x\,A_1\left(n_1-1,n_2,n_3\right) \tag{4}$$

The next example concerns the structure $A_3\left(n_1,n_2,n_3\right)$. Since this structure has five symmetry-distinct corners, it is possible to construct five symmetry-distinct decomposition pathways. These possible recursive decompositions of $A_3\left(n_1,n_2,n_3\right)$ are shown in Fig. 3. All these decomposition pathways allow to express the ZZ polynomial of $A_3\left(n_1,n_2,n_3\right)$ as a sum of ZZ polynomials of its derivative structures, producing five distinct recurrence relations given by

$$A_3\left(n_1,n_2,n_3\right)=\ O\ \left(n_1-1,n_2,n_3\right)+B^2\left(n_1,n_2,n_3\right)+x\,A_1\left(n_1-1,n_2,n_3\right) \tag{5}$$

$$A_3\left(n_1,n_2,n_3\right)=\ O\ \left(n_1,n_2-1,n_3\right)+B^1\left(n_1,n_2,n_3\right)+x\,A_2\left(n_1,n_2-1,n_3\right) \tag{6}$$

$$A_3\left(n_1,n_2,n_3\right)=A_3\left(n_1,n_2,n_3-1\right)+D_3\left(n_1,n_2,n_3\right)+x\,D_3\left(n_1,n_2,n_3-1\right) \tag{7}$$

$$A_3\left(n_1,n_2,n_3\right)=A_3\left(n_1,n_2-1,n_3\right)+C^1\left(n_1,n_2,n_3\right)+x\,C^1\left(n_1,n_2-1,n_3\right) \tag{8}$$

$$A_3\left(n_1,n_2,n_3\right)=A_3\left(n_1-1,n_2,n_3\right)+C^2\left(n_1,n_2,n_3\right)+x\,C^2\left(n_1-1,n_2,n_3\right) \tag{9}$$

Similar decomposition process applied to the remaining 33 structures (note that no decomposition pathway can be derived for $L\left(n_1,n_2,n_3\right)$ as this structure has no corners) produces the remaining 88 recurrence relations. Since the derivations are rather obvious and can be performed easily by an attentive reader using ZZDecomposer, we do not give them here. Moreover, since listing the remaining 88 recurrence relations would occupy a considerable part of this manuscript, we have decided to skip a few steps in the derivation process and list only an equivalent family of relations that have been obtained by simple algebraic transformations of the set of the original recurrence relations derived in the same fashion like Eqs. (2)–(9). This family of 96 equations can be symbolically represented as

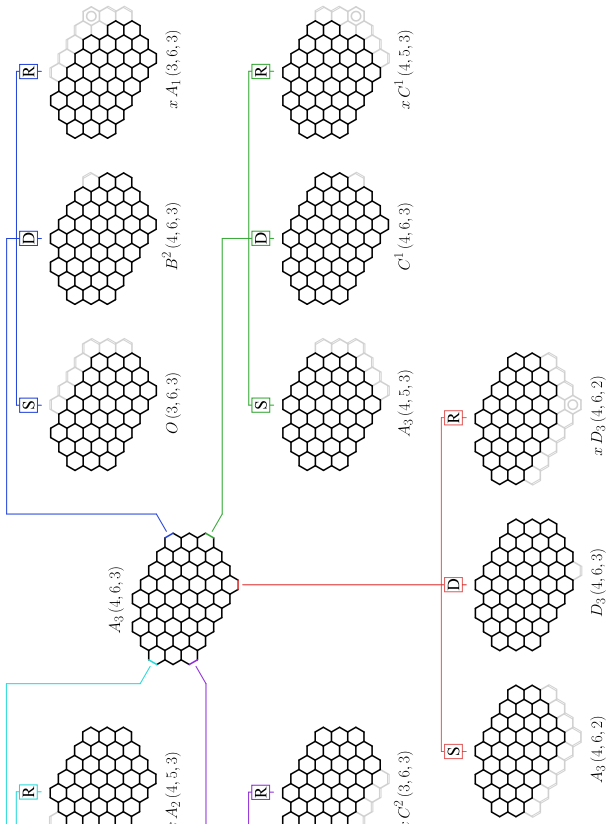

Figure 3. Five distinct corner decomposition pathways available for the structure $A_3\,(n_1, n_2, n_3)$ lead to the recurrence relations given in Eqs. (5)–(9). Here, $n_1 = 4$, $n_2 = 6$, and $n_3 = 3$. Note that the S, D, and R indicate the pathways where the bond is assigned as a single bond (S), a double bond (D), and a part of the aromatic ring (R), respectively.

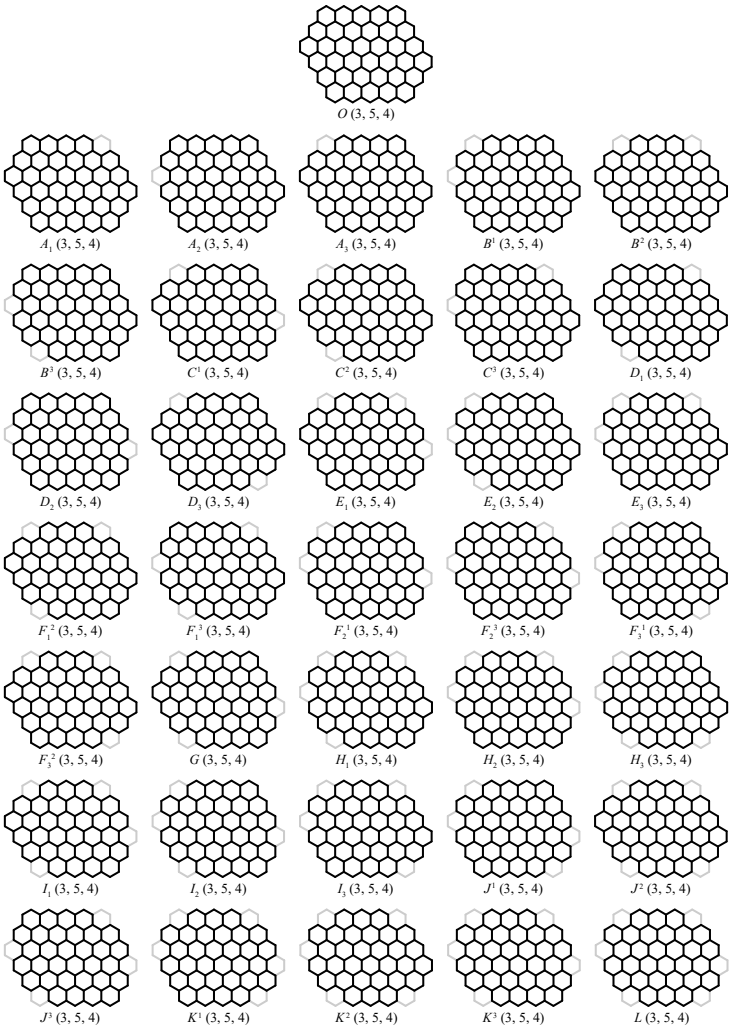

Figure 4. All possible derivative structures that can be obtained from a hexagonal graphene flake $O\,(n_1, n_2, n_3)$ by removing a certain number (from zero to six) of its corners. Here, $n_1 = 3$, $n_2 = 5$, and $n_3 = 4$. It might be helpful to mention that the naming convention is based on subscript indices i corresponding to a missing corner in the direction of n_i and superscript indices j corresponding to an existing corner in the direction of n_j.

follows

$$O - A_i = A_j - B^k = A_k - B^j = C^i - E_i = O\,(i) + x\,A_i\,(i) \tag{10}$$

$$A_i - C^j = B^k - E_j = D_i - F_i^j = F_i^k - H_i = A_i\,(k) + x\,C^j\,(k) \tag{11}$$

$$A_i - D_i = G - I_i = C^j - F_i^j = C^k - F_i^k = A_i\,(i) + x\,D_i\,(i) \tag{12}$$

$$B^i - F_j^i = E_k - H_j = F_k^i - J^i = I_k - K^i = B^i\,(j) + x\,F_j^i\,(j) \tag{13}$$

$$C^i - G = F_j^i - I_j = F_k^i - I_k = J^i - K^i = C^i\,(i) + x\,G\,(i) \tag{14}$$

$$E_i - I_i = H_j - K^k = H_k - K^j = K^i - L = E_i\,(i) + x\,I_i\,(i) \tag{15}$$

where the symbol X without any arguments simply denotes the ZZ polynomial of the structure $X\,(n_1, n_2, n_3)$ and the symbol $X\,(l)$ denotes the ZZ polynomial of the structure $X\,(n_1, n_2, n_3)$ with the index n_l diminished by 1. The indices i, j, and k in Eqs. (10)–(15) are always distinct and correspond to all the permutations of the numbers 1, 2, and 3. For example, the equality between the first and last members of Eq. (10) with the choice of $i = 3$ reproduces Eq. (2), and the equality between the first and last members of Eq. (11) with the choice of $i = 3$, $k = 2$, and $j = 1$ reproduces Eq. (8). Note that the first three equal signs in Eqs. (10)–(15) correspond to 72 algebraic relations involving structures with the same set of indices (n_1, n_2, n_3) and only the first and last columns in Eqs. (10)–(15) correspond to 24 recurrence relations involving structures with different set of indices.

The set of 72 algebraic equations with the same set of indices (n_1, n_2, n_3) in Eqs. (10)–(15) involves 36 symmetry-distinct structures. This set is linearly dependent; its rank is 25, which allows us to solve it for 25 symmetry-distinct structures. The choice of these structures is not unique. Here, we decide to give the solution for the ZZ polynomials of the 25 structures B^i, E_i, F_i^j, H_i, I_i, J^i, K^i and L in terms of the ZZ polynomials of the

11 structures O, A_i, C^i, D_i, and G. The solution is given by

$$B^i = -O + A_j + A_k \tag{16}$$

$$E_i = -O + A_i + C^i \tag{17}$$

$$F_i^j = -A_i + C^j + D_i \tag{18}$$

$$H_i = -2\,A_i + C^j + C^k + D_i \tag{19}$$

$$I_i = -A_i + D_i + G \tag{20}$$

$$J^i = O - 2\,A_j - 2\,A_k + 2\,C^i + D_j + D_k \tag{21}$$

$$K^i = O - 2\,A_j - 2\,A_k + C^i + D_j + D_k + G \tag{22}$$

$$L = 2\,O - 2\,A_i - 2\,A_j - 2\,A_k + D_i + D_j + D_k + 2\,G \tag{23}$$

The indices i, j, and k in Eqs. (16)–(23) are again distinct and correspond to any permutation of the numbers 1, 2, and 3.

Further solution to this problem comes from the analysis of the 15 recurrence relations

$$O - O\,(i) = A_i + x\,A_i\,(i) \tag{24}$$

$$A_k - A_k\,(i) = C^j + x\,C^j\,(i) \tag{25}$$

$$A_i - A_i\,(i) = D_i + x\,D_i\,(i) \tag{26}$$

$$C^i - C^i\,(i) = G + x\,G\,(i) \tag{27}$$

interrelating the ZZ polynomials of the 11 structures O, A_i, C^i, D_i, and G. The solution to these equations is sought in form of generating functions GO, GA_i, GC^i, GD_i, and GG for the 11 structures $X = O, A_i, C^i, D_i,$ and G. The generating function $GX \equiv GX\,(t_1, t_2, t_3)$ for the family of structures $X\,(n_1, n_2, n_3)$ is defined as follows

$$GX \equiv GX\,(t_1, t_2, t_3) = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} X\,(n_1, n_2, n_3)\; t_1^{n_1}\, t_2^{n_2}\, t_3^{n_3} \tag{28}$$

The generating function here is defined in an extended way that we included the ZZ polynomials of the structures $O, A_i, C^i, D_i,$ and G with one or more indices equal to 1. Thus we have to also extend the definition of the structures. We again start with the hexagonal flakes $O\,(n_1, n_2, n_3)$. When one, two, or all of the index equal to 1, $O\,(n_1, n_2, n_3)$ reduces to a parallelogram $M\,(n, m)$, a polyacene, or a single benzene ring, respectively. We can construct structures $A_i, C^i, D_i,$ and G by "removing corners" from a parallelogram,

a polyacene, or a benzene. We then can analyze ZZ polynomials for these structures by ZZDecomposer and the relations below are obtained.

$$O\left(1,n_j,n_k\right)=M\left(n_j,n_k\right)={}_2F_1\left[\begin{array}{c}-n_j,-n_k\\1\end{array};1+x\right] \tag{29}$$

$$A_i\left(1,n_j,n_k\right)=M\left(n_j,n_k\right)-(1+x) \tag{30}$$

$$A_k\left(1,n_j,n_k\right)=M\left(n_j-1,n_k\right) \tag{31}$$

$$C^i\left(1,n_j,n_k\right)=M\left(n_j-1,n_k-1\right) \tag{32}$$

$$C^j\left(1,n_j,n_k\right)=M\left(n_j-1,n_k\right) \tag{33}$$

$$D_i\left(1,n_j,n_k\right)=\left\{\begin{array}{ll}0 & n_j=n_k=1\\ M\left(n_j,n_k\right) & \text{otherwise}\end{array}\right. \tag{34}$$

$$G\left(1,n_j,n_k\right)=M\left(n_j-1,n_k-1\right) \tag{35}$$

Now, multiplication of both sides of Eqs. (24)–(27) by $t_i^{n_i}\,t_j^{n_j}\,t_k^{n_k}$ and summation over all values of $n_j,n_k\geq 1$ and $n_i\geq 2$, transforms Eqs. (24)–(27) into the following set of non-homogeneous linear equations for the functions GO, GA_i, GC^i, GD_i, and GG

$$\frac{1-t_i}{t_i}\,GO=\frac{1+x\,t_i}{t_i}\,GA_i+\sum_{n_j=1}^{\infty}\sum_{n_k=1}^{\infty}\left[O\left(1,n_j,n_k\right)-A_i\left(1,n_j,n_k\right)\right]\,t_j^{n_j}\,t_k^{n_k} \tag{36}$$

$$\frac{1-t_i}{t_i}\,GA_k=\frac{1+x\,t_i}{t_i}\,GC^j+\sum_{n_j=1}^{\infty}\sum_{n_k=1}^{\infty}\left[A_k\left(1,n_j,n_k\right)-C^j\left(1,n_j,n_k\right)\right]\,t_j^{n_j}\,t_k^{n_k} \tag{37}$$

$$\frac{1-t_i}{t_i}\,GA_i=\frac{1+x\,t_i}{t_i}\,GD_i+\sum_{n_j=1}^{\infty}\sum_{n_k=1}^{\infty}\left[A_i\left(1,n_j,n_k\right)-D_i\left(1,n_j,n_k\right)\right]\,t_j^{n_j}\,t_k^{n_k} \tag{38}$$

$$\frac{1-t_i}{t_i}\,GC^i=\frac{1+x\,t_i}{t_i}\,GG+\sum_{n_j=1}^{\infty}\sum_{n_k=1}^{\infty}\left[C^i\left(1,n_j,n_k\right)-G\left(1,n_j,n_k\right)\right]\,t_j^{n_j}\,t_k^{n_k} \tag{39}$$

From Eqs. (29)–(35), we can obtain the following relations which can be used to evaluate the double summations in Eqs. (36)–(39)

$$O\left(1,n_j,n_k\right)-A_i\left(1,n_j,n_k\right)=1+x \tag{40}$$

$$A_k\left(1,n_j,n_k\right)-C^j\left(1,n_j,n_k\right)=0 \tag{41}$$

$$A_i\left(1,n_j,n_k\right)-D_i\left(1,n_j,n_k\right)=\left\{\begin{array}{ll}1 & n_j=n_k=1\\ 1+x & \text{otherwise}\end{array}\right. \tag{42}$$

$$C^i\left(1,n_j,n_k\right)-G\left(1,n_j,n_k\right)=0 \tag{43}$$

After substituting these relations into Eqs. (36)–(39) and eliminating redundant terms, we obtain the following family of non-homogeneous, linear equations interrelating the functions GO, GA_i, GC^i, GD_i, and GG

$$(1-t_i)\;GO-(1+x\,t_i)\;GA_i=\frac{t_i\,t_j\,t_k\;(1+x)}{(1-t_j)\,(1-t_k)} \tag{44}$$

$$(1-t_i)\;GA_k-(1+x\,t_i)\;GC^j=0 \tag{45}$$

$$(1-t_i)\;GA_i-(1+x\,t_i)\;GD_i=\frac{t_i\,t_j\,t_k\;(1+x)}{(1-t_j)\,(1-t_k)}-x\,t_i\,t_j\,t_k \tag{46}$$

$$(1-t_i)\;GC^i-(1+x\,t_i)\;GG=0 \tag{47}$$

The rank of this system of 11 equations is 10. The solution can be written as follows by expressing all the other generating functions in terms of the function GO

$$GA_i=\frac{1-t_i}{1+x\,t_i}\,GO-\frac{t_i\,t_j\,t_k\,(1+x)}{(1+x\,t_i)\,(1-t_j)\,(1-t_k)} \tag{48}$$

$$GC^i=\frac{(1-t_j)\,(1-t_k)}{(1+x\,t_j)\,(1+x\,t_k)}\,GO-\frac{t_i\,t_j\,t_k\,(1+x)}{(1-t_i)\,(1+x\,t_j)\,(1+x\,t_k)} \tag{49}$$

$$GD_i=\frac{(1-t_i)^2}{(1+x\,t_i)^2}\,GO-\frac{t_i\,t_j\,t_k\,(1+x)\,[t_i\;(x-1)+2]}{(1+x\,t_i)^2\,(1-t_j)\,(1-t_k)}+\frac{t_i\,t_j\,t_k\,x}{1+x\,t_i} \tag{50}$$

$$GG=\frac{(1-t_i)\,(1-t_j)\,(1-t_k)}{(1+x\,t_i)\,(1+x\,t_j)\,(1+x\,t_k)}\,GO-\frac{t_i\,t_j\,t_k\;(1+x)}{(1+x\,t_i)\,(1+x\,t_j)\,(1+x\,t_k)} \tag{51}$$

or alternatively, by expressing all the other generating functions in terms of the function GG

$$GO=\frac{t_i\,t_j\,t_k\;(1+x)}{(1-t_i)\,(1-t_j)\,(1-t_k)}+\frac{(1+x\,t_i)\,(1+x\,t_j)\,(1+x\,t_k)}{(1-t_i)\,(1-t_j)\,(1-t_k)}\,GG \tag{52}$$

$$GA_i=\frac{(1+x\,t_j)\,(1+x\,t_k)}{(1-t_j)\,(1-t_k)}\,GG \tag{53}$$

$$GC^i=\frac{1+x\,t_i}{1-t_i}\,GG \tag{54}$$

$$GD_i=\frac{t_i\,t_j\,t_k\,x}{1+x\,t_i}-\frac{t_i\,t_j\,t_k\;(1+x)}{(1+x\,t_i)\,(1-t_j)\,(1-t_k)}+\frac{(1-t_i)\,(1+x\,t_j)\,(1+x\,t_k)}{(1+x\,t_i)\,(1-t_j)\,(1-t_k)}\,GG \tag{55}$$

It is possible by using Eq. (28) together with the following identities

$$\frac{t}{1-t}=\sum_{n=1}^{\infty}t^n \qquad \frac{1+x\,t}{1-t}=1+(1+x)\sum_{n=1}^{\infty}t^n$$
$$\frac{t}{1+x\,t}=-\frac{1}{x}\sum_{n=1}^{\infty}(-x)^n\;t^n \qquad \frac{1-t}{1+x\,t}=1+\frac{(1+x)}{x}\sum_{n=1}^{\infty}(-x)^n\;t^n$$

to expand all the generating functions in Eqs. (48)–(55) into power series and by appropriate sum rearrangements and equating coefficients at both sides of each equation for identical powers of $t_1^{n_1}\,t_2^{n_2}\,t_3^{n_3}$ find explicit formulas for $X\,(n_1,n_2,n_3)$ as a function of $O\,(m_1,m_2,m_3)$ (for Eqs. (48)–(51)) and as a function of $G\,(m_1,m_2,m_3)$ (for Eqs. (52)–(55)). These formulas, unfortunately, are often exceedingly complicated and involve multiple finite summations of $O\,(m_1,m_2,m_3)$ or $G\,(m_1,m_2,m_3)$ over various indices m_i. The simplest of these relations obtained by expanding Eq. (54) and given explicitly by

$$C^1\,(n_1,n_2,n_3)=G\,(n_1,n_2,n_3)+(1+x)\sum_{k=1}^{n_1-1}G\,(k,n_2,n_3) \tag{56}$$

$$C^2\,(n_1,n_2,n_3)=G\,(n_1,n_2,n_3)+(1+x)\sum_{k=1}^{n_2-1}G\,(n_1,k,n_3) \tag{57}$$

$$C^3\,(n_1,n_2,n_3)=G\,(n_1,n_2,n_3)+(1+x)\sum_{k=1}^{n_3-1}G\,(n_1,n_2,k) \tag{58}$$

might be useful, but for example the formula relating $O\,(n_1,n_2,n_3)$ and $G\,(m_1,m_2,m_3)$ obtained by expanding Eq. (52) and given explicitly by

$$\begin{aligned}O\,(n_1,n_2,n_3)&=G\,(n_1,n_2,n_3)+(1+x)^3\sum_{k_1=1}^{n_1-1}\sum_{k_2=1}^{n_2-1}\sum_{k_3=1}^{n_3-1}G\,(k_1,k_2,k_3)\\&+(1+x)\left[1+\sum_{k_1=1}^{n_1-1}G\,(k_1,n_2,n_3)+\sum_{k_2=1}^{n_2-1}G\,(n_1,k_2,n_3)+\sum_{k_3=1}^{n_3-1}G\,(n_1,n_2,k_3)\right]\\&+(1+x)^2\left[\sum_{k_1=1}^{n_1-1}\sum_{k_2=1}^{n_2-1}G\,(k_1,k_2,n_3)+\sum_{k_1=1}^{n_1-1}\sum_{k_3=1}^{n_3-1}G\,(k_1,n_2,k_3)+\sum_{k_2=1}^{n_2-1}\sum_{k_3=1}^{n_3-1}G\,(n_1,k_2,k_3)\right]\end{aligned} \tag{59}$$

might be of little practical importance due to its complexity. We believe that the explicit expressions for the ZZ polynomials of the 25 structures B^i, E_i, F_i^j, H_i, I_i, J^i, K^i and L given by Eqs. (16)–(23) and the implicit expressions for the ZZ polynomials of the 10 structures A_i, C^i, D_i, and G given by Eqs. (48)–(51) as a function of the generating function $GO\equiv GO\,(t_1,t_2,t_3)$ can be made fully useful and robust only by discovering an

explicit expression for the last missing tile of the studied here puzzles, the ZZ polynomial of the hexagonal flakes $O(n_1, n_2, n_3)$ and its associated generating function GO, or alternatively, the ZZ polynomial of the hexagonal flakes without three alternating corners $G(n_1, n_2, n_3)$ and its associated generating function GG.

4 Conclusion

We have presented a detailed analysis of the recurrence relations involving the ZZ polynomials of a family of structural derivatives of $O(n_1, n_2, n_3)$. The analyzed network of equations comprises of 192 recurrence relations interrelating the ZZ polynomials of 64 structural derivatives of $O(n_1, n_2, n_3)$ obtained by removing from 0 to 6 of its corners. Symmetry considerations allow to reduce this family to 96 recurrence relations for 36 symmetry-distinct structural derivatives of $O(n_1, n_2, n_3)$. The solution to this set of equations is obtained in two steps. First, the explicit expressions for the ZZ polynomials of the 25 structures B^i, E_i, F_i^j, H_i, I_i, J^i, K^i and L are given by Eqs. (16)–(23) as a function of the ZZ polynomials of the remaining 11 structures: O, A_i, C^i, D_i, and G. Further solution is given in terms of generating functions. This approach allows to reduce the problem completely and express the ZZ polynomial generating functions of the remaining structures (O, A_i, C^i, D_i, and G) by a single generating function; the explicit expressions are given by Eqs. (48)–(51) as a function of the generating function $GO \equiv GO(t_1, t_2, t_3)$ for the hexagonal flakes $O(n_1, n_2, n_3)$, or by Eqs. (52)–(55) as a function of the generating function $GG \equiv GG(t_1, t_2, t_3)$ for the derivatives $G(n_1, n_2, n_3)$ obtained by removing the three alternating corners of $O(n_1, n_2, n_3)$.

The presented here result is not fully satisfactory: a single recurrence relation is missing in the studied network of recurrence relations in order to provide a mean to its complete solution. However, the partial result obtained here shows that the ZZ polynomials for all of the structural derivatives of $O(n_1, n_2, n_3)$ obtained by introducing corner defects can be readily obtained once the ZZ polynomials of $O(n_1, n_2, n_3)$ or $G(n_1, n_2, n_3)$ are known. We believe that the presented results constitute an important step toward finding a closed-form formulas for the hexagonal graphene flakes $O(n_1, n_2, n_3)$ and completing the theory of Clar covers and ZZ polynomials for hexagonal graphene flakes. The reader should be also aware that the presented results can be cast in fully functional from only by discovering an explicit expression for the last missing tile of the studied here puzzles, the ZZ polynomial

of the hexagonal graphene flakes $O(n_1, n_2, n_3)$ and its associated generating function GO, or alternatively, the ZZ polynomial of the hexagonal graphene flakes without three alternating corners $G(n_1, n_2, n_3)$ and its associated generating function GG. Note that the lowest order coefficient, $c_0 \equiv K\{O(n_1, n_2, n_3)\}$, in the ZZ polynomial of $O(n_1, n_2, n_3)$, denoting the number of Kekulé structures of this bezenoid, is given as

$$K\{O(n_1, n_2, n_3)\} = \prod_{k=0}^{n_1-1} \frac{\binom{n_2+n_3+k}{n_3}}{\binom{n_3+k}{n_3}} = \frac{\prod_{j=0}^{n_1+n_2+n_3-1} j!}{\prod_{j_1=n_1}^{n_2+n_3-1} j_1! \prod_{j_2=n_2}^{n_3+n_1-1} j_2! \prod_{j_3=n_3}^{n_1+n_2-1} j_3!} \tag{60}$$

This formula was first found by Cyvin [13] as a generalization of earlier results of Woodger and Everett reported originally by Gordon and Davison [15]. The first formal demonstration and derivation of this formula was given by Bodroža and collaborators [1] using extensively a novel method of computing the number of Kekulé structures as a determinant of the path matrix developed by John and Sachs [20–22, 24]. Unfortunately, higher order generalizations of this formula are not known up to date.

The substitution of Eq. (60) into Eq. (28) with $X(n_1, n_2, n_3) = O(n_1, n_2, n_3)$ evaluated at $x = 0$ can be used to find the generating function for the number of Kekulé structures of O. This development can lead to a closed form of generating functions for the number of Kekulé structures for A_i, C^i, D_i, and G by using Eqs. (48)–(51). The coefficients of $t_1^{n_1} t_2^{n_2} t_3^{n_3}$ in these generating functions indicate the numbers of Kekulé structures of $O(n_1, n_2, n_3)$, $A_i(n_1, n_2, n_3)$, $C^i(n_1, n_2, n_3)$, $D_i(n_1, n_2, n_3)$, and $G(n_1, n_2, n_3)$. By substituting these numbers into Eqs. (16)–(23) evaluated at $x = 0$, one can calculate the numbers of Kekulé structures of the rest of structurally related benzenoids, namely, $B^i(n_1, n_2, n_3)$, $E_i(n_1, n_2, n_3)$, $F_i^j(n_1, n_2, n_3)$, $H_i(n_1, n_2, n_3)$, $I_i(n_1, n_2, n_3)$, $J^i(n_1, n_2, n_3)$, $K^i(n_1, n_2, n_3)$ and $L(n_1, n_2, n_3)$. The task of explicit derivation of this formulas is not pursued further in the current paper. We hope that this work will stimulate the community to efforts leading to achieve this goal.

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