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Automatic Computation of Generalized Zhang-Zhang Polynomials of Benzenoids

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Abstract

We present an algorithm for automatic computation of generalized Zhang-Zhang (GZZ) polynomials of benzenoids. The Fortran 95 implementation of the presented algorithm has been used for the determination of GZZ polynomials for several basic classes of benzenoids. Correctness of the derived formulas has been demonstrated using standard decomposition recurrence relations.

1 Introduction

Determination of physical and chemical properties of benzenoids is nowadays usually performed with the help of quantum chemical calculations [16, 18, 24, 26, 29, 30, 36, 44]. However, for larger benzenoid systems, for which quantum calculations are not permissible or require prohibitive computer resources, traditional qualitative concepts—such as Kekulé structures [15] and Clar aromatic sextets [2, 14, 20]—can be used to understand the stability and reactivity of the analyzed graphene flakes [23, 27, 28, 38].

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These concepts are also useful for studying whole families of benzenoids $\mathbf{B}(n), n = 1, 2, 3, \ldots$ with identical structure [1, 4, 8, 9, 11–13, 19, 21, 25, 33, 34, 39–41, 43, 45, 47]. Topological invariants associated with the Kekulé structures and Clar covers of $\mathbf{B}(n)$ often permit us to understand their limiting properties as $n \to \infty$ [42]. Various topological and graph-theoretical tools have been developed for this purpose. One of the most important concept here is the Clar covering polynomial $\mathrm{ZZ}(\mathbf{B}, x)$ (known also as the Zhang-Zhang polynomial or simply ZZ polynomial) [22, 46–49], which contains information about the most essential topological invariants of $\mathbf{B}$: the total number of Kekulé structures $\mathcal{K} \equiv \mathcal{K}(\mathbf{B}) = \mathrm{ZZ}(\mathbf{B}, 0)$, the total number of Clar covers $\mathcal{C} \equiv \mathcal{C}(\mathbf{B}) = \mathrm{ZZ}(\mathbf{B}, 1)$, and the Clar number $Cl \equiv Cl(\mathbf{B}) = \deg(\mathrm{ZZ}(\mathbf{B}, x))$, just to name a few. From a formal perspective, the ZZ polynomial of $\mathbf{B}$, $\mathrm{ZZ}(\mathbf{B}, x)$, is simply the generating function for the sequence $[c_0 \equiv \mathcal{K}, c_1, c_2, \ldots]$ of the numbers of Clar covers of $\mathbf{B}$ of a given order (where c_k is the number of Clar covers of order k; for more details, see the next Section). The most inviting property of $\mathrm{ZZ}(\mathbf{B}, x)$ is the set of recursive properties allowing to determine $\mathrm{ZZ}(\mathbf{B}, x)$ in a fast and robust manner [7, 10, 22]. Surprisingly, determination of the ZZ polynomial of $\mathbf{B}$ (i.e., the whole set of its topological invariants) turned out to be a much simpler (or comparable) task than the determination of a single invariant of $\mathbf{B}$ [7, 10, 37].

The Clar aromatic sextet [14] is the the smallest—and historically the only one—conjugated circuit that has been considered in the topological analysis of benzenoids. From the point view of graph theory, a benzenoid $\mathbf{B}$ is a finite connected subgraph of an infinite hexagonal lattice, a Kekulé dublet K_2 corresponds to any edge of $\mathbf{B}$ together with its endpoints, and a Clar sextet corresponds to a cycle C_6 embedded in $\mathbf{B}$. In general, a conjugated circuit R_n is a cycle C_{4n+2} embedded in $\mathbf{B}$. As already mentioned, the smallest conjugated circuit is the Clar sextet, $R_1 \equiv C_6$. The next smallest conjugated circuit is $R_2 \equiv C_{10}$. Stretching somewhat the definition of a conjugated circuit, we can identify a Kekulé structure (i.e., a double bond) with a conjugated circuit of length $n = 0$, $K_2 \equiv R_0$. Then, the concept of conjugated circuits allows us to introduce a uniform and compact representation of various types of benzenoid coverings. We say

that a Kekulé structure of **B** is a covering of **B** that involves only conjugated circuits R_0. We also say that a Clar cover of **B** is a covering of **B** that uses conjugated circuits R_0 and R_1. Similarly, we can say that a generalized Clar cover of **B** of circuit order m is a covering of **B** that uses the conjugated circuits R_0, R_1, ..., R_m in the construction process.

The current work follows the work of Žigert Pleteršek [51] and focuses on the simplest generalized Clar covers, which employ only the three smallest conjugated circuits (i.e., $R_0 \equiv K_2$, $R_1 \equiv C_6$, and $R_2 \equiv C_{10}$) in the construction process. For brevity, we simply refer to coverings constructed in this way as generalized Clar covers. Similarly, the bivariate generating function $\mathrm{GZZ}(\mathbf{B}, x, y) = \sum_{j,k} c_{jk} x^j y^k$ corresponding to the 2D sequence $[c_{jk} : j, k = 0, 1, 2, \ldots]$ is called the generalized Zhang-Zhang polynomial of **B**. Here, c_{jk} denotes the number of generalized Clar covers of **B** with exactly j cycles C_6 and k cycles C_{10}. Note that the information about the number of the K_2 components in a given covering is not included in the GZZ polynomial, as it can be always readily determined from the remaining data as $(|V(\mathbf{B})| - 6j - 10k)/2$ for any particular covering.

The generalized Zhang-Zhang polynomials $\mathrm{GZZ}(\mathbf{B}, x, y)$ were introduced in graph-theoretical analysis of benzenoids very recently by Žigert Pleteršek [51], who first gave their definition and demonstrated their equivalence to the generalized cube polynomial of the corresponding resonance graph, extending the previous results known for standard ZZ and cube polynomials [3, 50]. Basic properties of the GZZ polynomials were studied by Furtula *et al.* [17], who obtained recursive formulas for their explicit calculations, extending the previously known results for the standard ZZ polynomials [7, 22, 46], and proposed an algorithm for their determination for benzenoid chains. In addition, Furtula *et al.* employed the GZZ polynomials determined in this way to cross-correlation investigation of π-electron properties of benzenoid linear chains, such as the total π-electron energy (E), the Dewar resonance energy (DRE), and the topological resonance energy (TRE). In particular, it was discovered that the values of E, DRE, and TRE are determined not only by the Kekulé count $\mathcal{K}$ and Clar count $\mathcal{C}$, but also by the generalized Clar covers; the contributions from the generalized Clar covers with cycles C_{10} were found to have several

times smaller effect than that of the Clar covers using only cycles C_6 [17].

The current work is supposed to serve a number of purposes. First of all, we follow closely the approach presented by Furtula *et al.* [17] and develop a general algorithm for the determination of GZZ polynomials of arbitrary benzenoids following our earlier work on ZZ polynomials [7]. Subsequently, we extend the existing computer program (ZZCalculator) [7,10] to the GZZ polynomials. In this way, an arbitrary benzenoid can be conveniently drawn by choosing hexagons and edges of the underlying hexagonal lattice using ZZDecomposer [10] and the GZZ polynomial can be automatically computed by GZZCalculator integrated into the previously existing ZZDecomposer code [5, 6]. These results are presented in Section 3. In the subsequent part of the manuscript, we show how to use the developed software [35] to determine closed-form GZZ polynomial formulas for several families of benzenoids: polyacenes $L(m)$, single armchair chains $N(m)$, hammers $H(m)$, starphenes $St(n, m, l)$, and parallelograms $M(m, n)$, extending the body of previously available ZZ polynomial results [7, 8, 10, 12, 19, 21, 32, 46] for those structures. We hope that these results will motivate other groups to discover similar closed-form formulas also for other families of benzenoids in the spirit presented before for the regular ZZ polynomials.

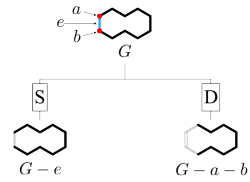
2 Generalized Zhang-Zhang polynomial and its properties

In this section, we review several properties that might be used in the computation of GZZ polynomials.

Property 1. [Theorem 3.2 of [17]] Let $e = ab$ be an edge not belonging to any hexagon or 10-cycle of G. Then

$$\mathrm{GZZ}(G) = \mathrm{GZZ}(G - e) + \mathrm{GZZ}(G - a - b)$$

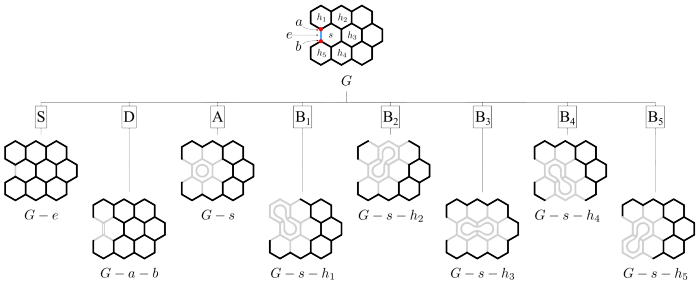
This particular situation is illustrated symbolically on the graph below



Property 2. [Theorem 3.3 of [17]] Let $e = ab$ be an edge of a hexagon s of G and let $r \leq 5$ be the number of hexagons $(h_1, h_2, \ldots, h_r)$ adjacent to s. Then

$$\begin{aligned} \mathrm{GZZ}(G) = \mathrm{GZZ}(G-e) + \mathrm{GZZ}(G-a-b) + x\ \mathrm{GZZ}(G-s) \\ + y \sum_{i=1}^{r} \mathrm{GZZ}(G-s-h_i) \end{aligned}$$

This particular situation is illustrated graphically below for $r = 5$

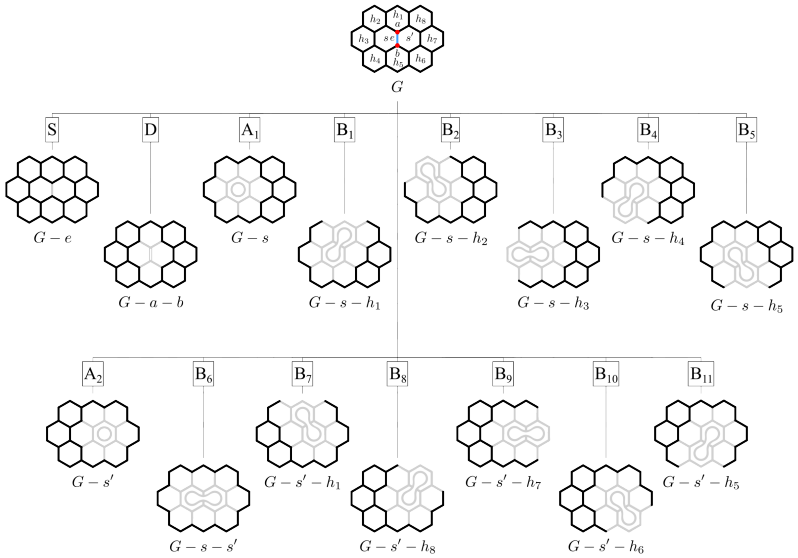


Property 3. [An extension of Theorem 3.3 of [17]] Let $e = ab$ be an edge belonging simultaneously to two hexagons s and s' of G. Let $h_1, h_2, \ldots, h_r$ be the hexagons adjacent to s (excluding s') and let $h'_1, h'_2, \ldots, h'_{r'}$ be the hexagons adjacent to s' (excluding s), where $r, r' \leq 5$. Then

$$\begin{aligned} \mathrm{GZZ}(G) = \mathrm{GZZ}(G-e) + \mathrm{GZZ}(G-a-b) + x\ \mathrm{GZZ}(G-s) \\ + x\ \mathrm{GZZ}(G-s') + y\ \mathrm{GZZ}(G-s-s') \\ + y \sum_{i=1}^{r} \mathrm{GZZ}(G-s-h_i) + y \sum_{i=1}^{r'} \mathrm{GZZ}(G-s'-h'_i) \end{aligned}$$

This particular situation is illustrated graphically below for $r, r' = 5$ and

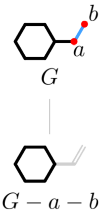
for $\{h'_1, h'_2, \ldots, h'_5\} = \{h_1, h_8, h_7, h_6, h_5\}$



Property 4. [Theorem 3.1 of [17]] Let G be a system consisting of m disconnected components: $G_1, G_2, \ldots, G_m$. Then, the GZZ polynomial of G is equal to the product of the GZZ polynomials of the disconnected components

$$\mathrm{GZZ}(G) = \prod_{i=1}^{m} \mathrm{GZZ}(G_i)$$

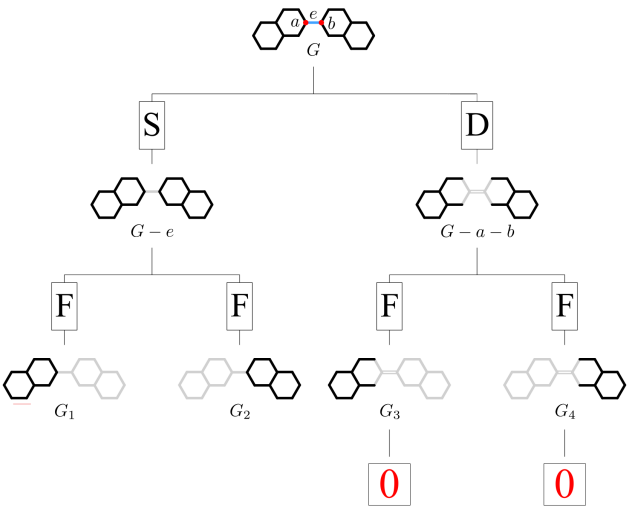
Property 5. [Theorem 3.4 of [17]] If $e = ab$ is a terminal bond, then it is obvious that e must be a double bond. Then, the GZZ polynomial of G is equal to the GZZ polynomial of G' with the atoms a and b removed.



Property 6. [Property 6 of [7]] The GZZ polynomial of a system G consisting of an odd number of carbon atoms is zero.

Property 7. [Property 7 of [7]] The GZZ polynomial of a system G consisting of zero atoms is equal to 1.

Example. Consider the benzenoid G (β, β'-binaphthyl) shown below. Consider further the recursive decomposition tree of G induced by selecting the bond



By **Property 1** we have

$$\mathrm{GZZ}(G) = \mathrm{GZZ}(G-e) + \mathrm{GZZ}(G-a-b)$$

Because both the structures $G-e$ and $G-a-b$ consist of two disconnected components, by **Property 4** we find that $\mathrm{GZZ}(G-e) = \mathrm{GZZ}(G_1) \cdot \mathrm{GZZ}(G_2)$ and $\mathrm{GZZ}(G-a-b) = \mathrm{GZZ}(G_3) \cdot \mathrm{GZZ}(G_4)$. Since further we have that $\mathrm{GZZ}(G_1) = \mathrm{GZZ}(G_2) = L_1 = 3+2x+y$ (by Eq. (3) below with $m=1$) and $\mathrm{GZZ}(G_3) = \mathrm{GZZ}(G_4) = 0$ (by **Property 6**), we find that

$$\mathrm{GZZ}(G) = \mathrm{GZZ}(G_1) \cdot \mathrm{GZZ}(G_2) = (3+2x+y)^2$$

3 Computer program for automatic computation of GZZ polynomials

The properties described above (**Properties 1–7**) can serve as a basis for an algorithm applicable for recursive computation of the GZZ polynomial

for an arbitrary benzenoid. The heart of the algorithm is the recursive procedure GZZ(G) whose flowchart is depicted in Fig. 1. This algorithm is a direct extension of the analogous recursive procedure that has been designed before (see Fig. 3 of [7]) for automatic computation of ZZ polynomials. Interestingly, the presented recursive procedure GZZ(G) computes

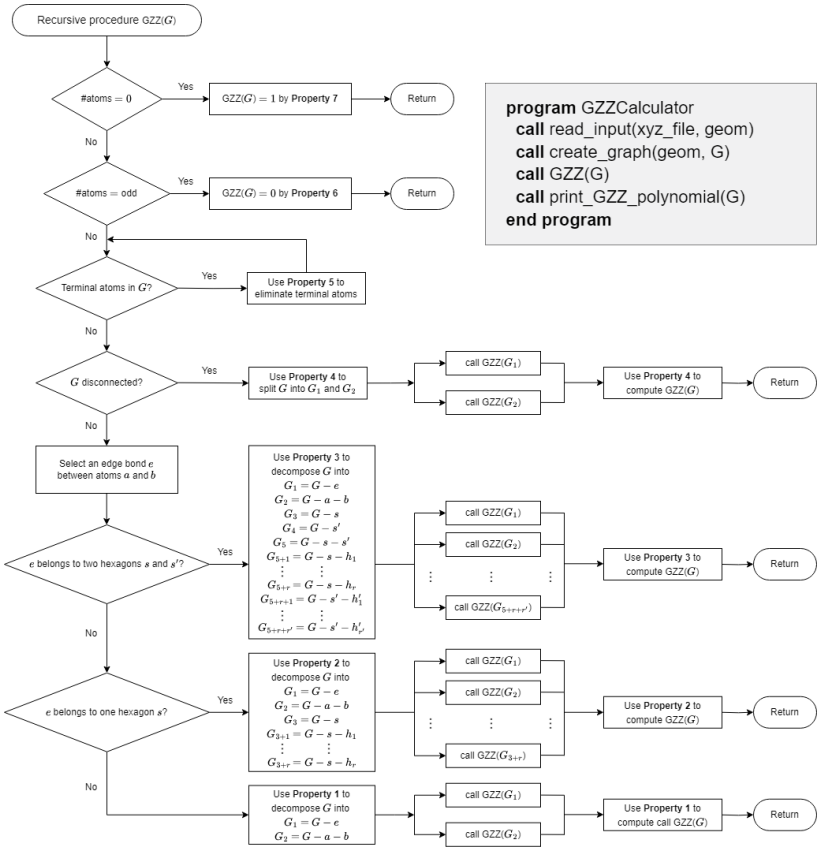


Figure 1. Flow chart for the recursive procedure GZZ constituting the most important ingredient of the GZZ polynomial calculator (see the inset).

directly a numerical value only in two cases: when G has no atoms (then GZZ(G) = 1 by **Property 7**) or when G has an odd number of atoms (then GZZ(G) = 0 by **Property 6**). In all the remaining cases, **Properties 1–5** are used to reduce the analyzed molecular graph into smaller

molecular graphs, to each of which the recursive procedure GZZ(G) is applied separately. In these cases, GZZ(G) is computed as a sum or as a product of GZZ polynomial of these smaller molecular graphs (subgraphs of G). Before splitting the molecular graphs G into its subgraphs, repeated application of **Property 5** is used to eliminate all the terminal atoms in G; this step substantially reduces the computational cost in the decomposition steps that follow. The recursive procedure GZZ(G) is then wrapped into a short Fortran 95 program (see the inset of Fig. 1), which reads the molecular graph of G in XYZ format, translates it to the adjacency matrix, calls GZZ(G), and prints out the result. Most of technical details of this approach were described previously for the ZZCalculator program [7].

4 Applications

To demonstrate the capabilities of the GZZCalculator program described in the previous Section, we have applied it for calculation of the GZZ polynomials of various types of benzenoid systems. The results have close connection to the analogous ZZ polynomial results of the same structures announced earlier; one should remember that for an arbitrary benzenoid G one has

$$\mathrm{GZZ}(G,x,y)\Big|_{y=0} = \mathrm{ZZ}(G,x) \tag{1}$$

4.1 Polyacenes

We start our exposition by discussing the GZZ polynomials of polyacenes, the simplest class of benzenoids graphically defined in Fig. 2. The GZZ polynomials for the first several members of this class are given by

$$\begin{array}{lll} L_0 = 1 & L_2 = 3 + 2x + y & L_4 = 5 + 4x + 3y \\ L_1 = 2 + x & L_3 = 4 + 3x + 2y & L_5 = 6 + 5x + 4y \end{array} \tag{2}$$

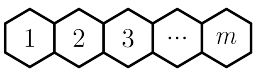
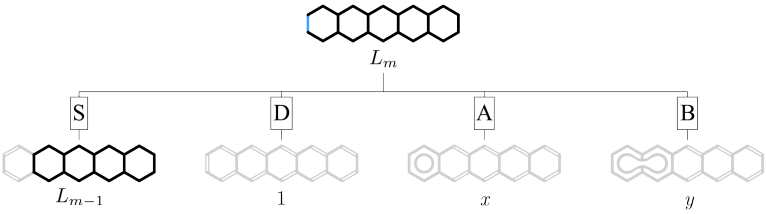


Figure 2. Graphical definition of polyacenes $L(m)$

where L_m is shorthand notation for $\mathrm{GZZ}(L(m), x, y)$. It is easy to see that for a polyacene $L(m)$ of an arbitrary length $m \geq 1$, its GZZ polynomial L_m is given by the following expression

$$L_m \equiv \mathrm{GZZ}(L(m), x, y) = (m-1)\,(1+x+y) + x + 2 \tag{3}$$

A formal derivation of Eq. (3) can proceed via the following recursive decomposition step



originating from **Property 2** with $r = 1$. Here, S assigns single character to the selected blue edge, D assigns double character, A assigns aromatic character, and B assigns biaromatic character to it. Consequently, the following recursive formula for L_m follows

$$L_m = L_{m-1} + 1 + x + y \tag{4}$$

which is valid for $m \geq 2$. Telescoping expansion of Eq. (4) with the boundary condition $L_1 = x + 2$ given by Eq. (2), furnishes a formal proof of Eq. (3). This somewhat exaggerated formal proof of a simple obvious fact (also given previously as **Preposition 2.2** of [17]) is supposed to serve here as a pedagogical introduction to the entire process, which is almost always based on a sequence of simple premises: a heuristic discovery of a general formula, a design of an appropriate recurrence relation, and a telescoping expansion of such a recurrence demonstrating the correctness of the previously discovered heuristic formula. Note that Eq. (3) correctly reduces by Eq. (1) to the ZZ polynomial of polyacenes reported previously in many various contexts (**Example 1** of [46], Eq. (8) of [7], Eq. (26) with $Cl = 1$ and $a_1 = a_2 = 0$ of [41], and entry $L(n)$ in **Table 1** of [31]).

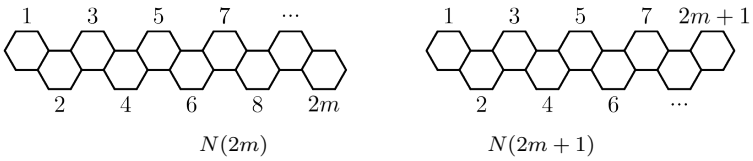


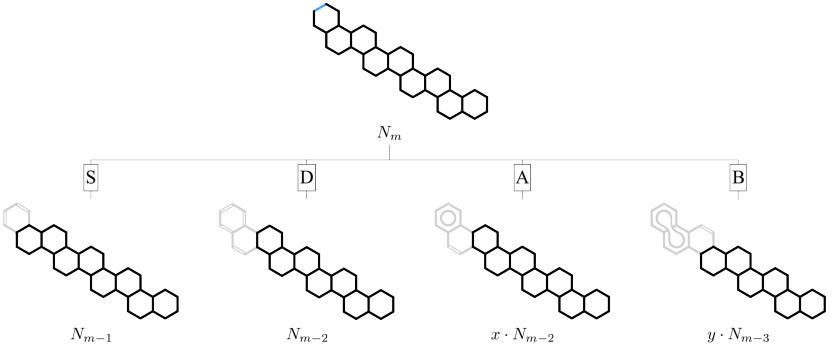
Figure 3. Graphical definition of single armchair chains of even and odd length. Note that $N(0) \equiv L(0)$ corresponds to ethylene, $N(1) \equiv L(1)$, to benzene, and $N(2) \equiv L(2)$, to naphthalene.

4.2 Single armchair chains

The next class of benzenoids studied by us in this paper is the family of single armchair chains $N(m)$, defined graphically in Fig. 3. The GZZ polynomial for these structures can be computed as follows. The GZZ polynomials for the shortest few structures are given by

$$\begin{aligned} N_0 &= 1 & N_3 &= 5 + 5x + x^2 + 2y \\ N_1 &= 2 + x & N_4 &= 8 + 10x + 3x^2 + 5y + 2xy \\ N_2 &= 3 + 2x + y & N_5 &= 13 + 20x + 9x^2 + x^3 + 10y + 6xy + y^2 \end{aligned} \tag{5}$$

where we have adapted the shorthand notation $N_m \equiv \mathrm{GZZ}(N(m), x, y)$. It is difficult to anticipate the general form of the GZZ polynomial of $N(m)$ from this sequence. Instead, let us proceed directly to the following formal recursive decomposition of $N(m)$



which originates from **Property 2** with $r = 1$ and is valid for $m \geq 3$ with initial conditions $N_0 = 1$, $N_1 = 2 + x$, and $N_2 = 3 + 2x + y$ given

by Eq. (5). This recursive decomposition can be rewritten as a 4-term recursive formula for N_m

$$N_m = N_{m-1} + (1+x)\, N_{m-2} + y\, N_{m-3} \tag{6}$$

To solve this recurrence, we resort to the generating function methodology, defining the generating function for N_m

$$G = \sum_{m=0}^{\infty} N_m\, t^m \tag{7}$$

Multiplying Eq. (6) by t^m, summing over $m \geq 3$, accounting for the boundary conditions $N_0 = 1$, $N_1 = 2 + x$, and $N_2 = 3 + 2x + y$, and solving for G gives

$$G = \frac{1}{t}\left(\frac{1}{1 - t - (1+x)\, t^2 - y t^3} - 1\right) \tag{8}$$

Using the fact that

$$\begin{aligned}
\tfrac{1}{1-t-(1+x)t^2-yt^3} &= \sum_{m=0}^{\infty}\sum_{n=0}^{m}\sum_{j=0}^{n} \tbinom{m}{n}\tbinom{n}{j}\,(1+x)^{n-j}\, y^j\, t^{m+n+j} && (9)\\
&= \sum_{m=0}^{\infty}\sum_{n=0}^{\lceil\frac{m-2}{3}\rceil}\sum_{j=0}^{\lceil\frac{m-1-3n}{2}\rceil} \tbinom{m-2n-j}{n+j}\tbinom{n+j}{n}\,(1+x)^{j}\, y^n\, t^m && (10)\\
&= \sum_{m=0}^{\infty}\sum_{j=0}^{\lfloor\frac{m}{2}\rfloor}\sum_{n=0}^{\lfloor\frac{m-2j}{3}\rfloor} \tbinom{m-2n-j}{n+j}\tbinom{n+j}{n}\,(1+x)^{j}\, y^n\, t^m && (11)
\end{aligned}$$

where the first equality follows from three consecutive binomial expansions and the two latter follow from standard triple sum rotations, we arrive at two equivalent closed-form formulas for $N_m \equiv \mathrm{GZZ}(N(m), x, y)$

$$\begin{aligned}
\mathrm{GZZ}(N(m),x,y) &= \sum_{n=0}^{\lceil\frac{m-1}{3}\rceil}\sum_{j=0}^{\lceil\frac{m-3n}{2}\rceil} \tbinom{m+1-2n-j}{n+j}\tbinom{n+j}{n}\,(1+x)^{j}\, y^n && (12)\\
&= \sum_{j=0}^{\lfloor\frac{m+1}{2}\rfloor}\sum_{n=0}^{\lfloor\frac{m+1-2j}{3}\rfloor} \tbinom{m+1-2n-j}{n+j}\tbinom{n+j}{n}\,(1+x)^{j}\, y^n && (13)
\end{aligned}$$

Note that both these formulas correctly reduce by Eq. (1) (one should retain only terms with $n = 0$ in one of the sums and replace y^0 by 1) to the ZZ

polynomial of the single armchair chain $N(m)$

$$\mathrm{ZZ}(N(m),x) = \sum_{j=0}^{\lceil \frac{m}{2} \rceil} \binom{m+1-j}{j} (1+x)^j = \sum_{j=0}^{\lfloor \frac{m+1}{2} \rfloor} \binom{m+1-j}{j} (1+x)^j \qquad (14)$$

reported originally as the third equation in **Example 2** of [48] or as Eq. (9) of [10]. (Note that the minor discrepancy in the upper summation index can be safely ignored here owing to the properties of the binomial symbol.) Note also that various other expressions were discovered for the ZZ polynomial of the single armchair chain $N(m)$ including

$$\mathrm{ZZ}(N(m),x) = (2x+3)\sum_{j=0}^{\lfloor \frac{m-1}{2} \rfloor} \binom{m-1-j}{j} (1+x)^j + (x+2)\sum_{j=0}^{\lfloor \frac{m-2}{2} \rfloor} \binom{m-2-j}{j} (1+x)^{j+1} \qquad (15)$$

$$= \tfrac{1}{2}\left(1+\tfrac{2x+3}{\sqrt{4x+5}}\right)\left(\tfrac{1+\sqrt{4x+5}}{2}\right)^m + \tfrac{1}{2}\left(1-\tfrac{2x+3}{\sqrt{4x+5}}\right)\left(\tfrac{1-\sqrt{4x+5}}{2}\right)^m \qquad (16)$$

$$= \sum_{k=0}^{\lceil \frac{m}{2} \rceil} \sum_{j=0}^{\lceil \frac{m}{2} \rceil} \binom{m+1-j-k}{k+j} \binom{k+j}{j} x^k \qquad (17)$$

For the original source of these formulas, see Eq. (4.12) of [46], Eq. (11) of [7], and Eq. (16) of [32], respectively. We believe that for each of these formulations, there exists analogous expression for $\mathrm{GZZ}(N(m),x,y)$.

4.3 Hammers

The next class of benzenoids analyzed here is usually referred to as hammers and denoted by a symbol $H(m)$ (see p. 100 of [15]). Its symbolic graphical definition is given in Fig. 4. A careful reader will recognize that a hammer $H(m)$ is equivalent to the benzenoid $G_1 \cdot L(m) \cdot G_2$ with $G_1 = G_1 = N(3)$, whose GZZ polynomial was reported previously by Furtula *et al.* in **Corollary 3.8** of [17]

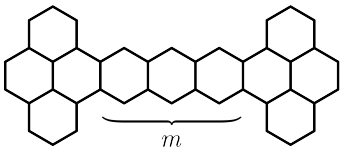


Figure 4. Hammers $H(m)$

The GZZ polynomials of the first five of the $H(m)$ structures are given by

$$\begin{cases} H_0 = N_3\,(\ 7 + \ \ 7x + \ \ \ x^2 + 6y) + \ \ \ y \\ H_1 = N_3\,(12 + 17x + \ \ 7x^2 + \ \ x^3 + 10y + \ \ 2xy) \\ H_2 = N_3\,(17 + 27x + 13x^2 + 2x^3 + 17y + \ \ 9xy + \ \ x^2y + 2y^2) \\ H_3 = N_3\,(22 + 37x + 19x^2 + 3x^3 + 24y + 16xy + 2x^2y + 4y^2) \\ H_4 = N_3\,(27 + 47x + 25x^2 + 4x^3 + 31y + 23xy + 3x^2y + 6y^2) \end{cases} \tag{18}$$

where we have introduced the shorthand notation $H_m \equiv \mathrm{GZZ}(H(m), x, y)$ and $N_3 \equiv \mathrm{GZZ}(N(3), x, y) = 5 + 5x + x^2 + 2y$ has been defined in Eq. (5). The intrinsic meaning of the multiplier N_3 becomes apparent later when we study decomposition pathways of $H(m)$. The coefficients of the observed progression pattern in Eq. 18 can be immediately generalized to

$$\begin{aligned} H_m = N_3\,\big[&(5m+7) + (10m+7)\,x + (6m+1)\,x^2 + m\,x^3 \\ &+ (7m+3)\,y + (7m-5)\,xy + (m-1)\,x^2y + 2\,(m-1)\,y^2\big] \end{aligned} \tag{19}$$

valid for any $m \geq 1$. Much more information—and a formal proof of Eq. (19)—can be obtained via the following decomposition pathways corresponding to the application of **Corollary 3.8** of [17] with $G_1 = G_2 = N(3)$

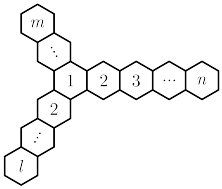


Figure 5. Starphene $St(n, m, l)$

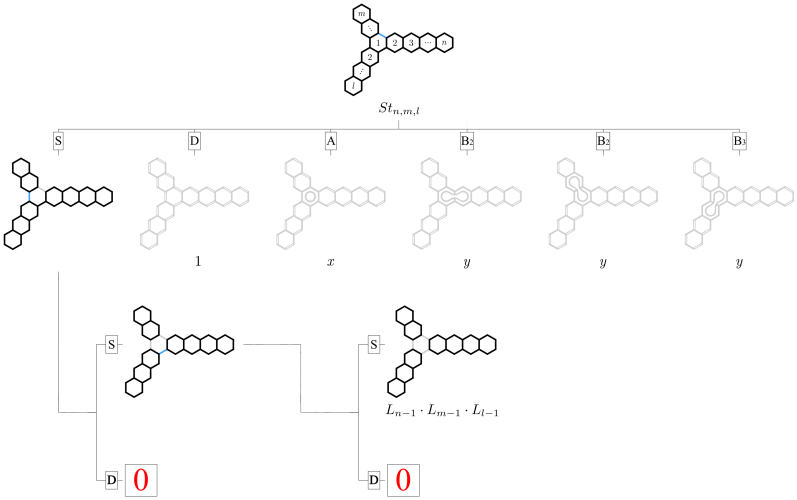
whose analysis effectively leads to the following formula for $\mathrm{GZZ}(H(m), x, y)$

$$H_m = N_3^2 \cdot L_m + 2\, N_3\, (1 + x + 3y) \tag{20}$$

with N_3 given by Eq. (5) and $L_m \equiv \mathrm{GZZ}(L(m), x, y)$ given by Eq. (3). Note that the substitution of the explicit formulas for N_3 and L_m into Eq. (20) and expanding it reproduces Eq. (19). Note also that evaluation of Eq. (20) at $y = 0$ correctly reproduces the ZZ polynomial of $H(m)$ given by Eq. (15) of [7].

4.4 Starphenes

Starphene $St(n, m, l)$ with $n, m, l \geq 2$, formally obtained by fusing three polyacenes with lengths n, m, and l, is graphically defined in Fig. 5. The following decomposition pathway of starphene



equivalent to **Theorem 3.9** of [17] for $St(n,m,l) = L(n-1)\cdot L(m-1)\cdot L(l-1)$, produces a compact, closed-form formula for the GZZ polynomial of $St(n,m,l)$

$$St_{n,m,l} \equiv \mathrm{GZZ}(St(n,m,l),x,y) = L_{n-1}\cdot L_{m-1}\cdot L_{l-1} + 1 + x + 3y \qquad (21)$$

with $L_k \equiv \mathrm{GZZ}(L(k),x,y)$ defined by Eq. (3).

It is instructive to consider yet another method of deriving $St_{n,m,l}$. (For more details, see Sections 2c and 2d of [8].) Geometrical invariance of $St(n,m,l)$ under the operations of permutation of its indices ensures that six starphene structures: $St(n,m,l)$, $St(n,l,m)$, $St(m,l,n)$, $St(l,m,n)$, $St(m,n,l)$, and $St(l,n,m)$ must have identical GZZ polynomials, as the number of generalized Clar covers of each type is not altered by these geometrical manipulations. Consequently, the GZZ polynomial of the six distinct starphenes sharing the same set of indices, $\{n,m,l\}$, must be a function of only symmetric polynomials of these indices: 1, $n+m+l$, $n^2+m^2+l^2$, $nm+nl+lm$, etc. Empirical analysis shows that

$$St_{n,m,l} = \sum_{j=0}^{3}\sum_{k=0}^{3} f_{k,j}\,(n,m,l)\,x^k y^j \qquad (22)$$

with the unknown coefficients $f_{k,j}\,(n,m,l)$ being linear combinations of symmetric polynomials in $\{n,m,l\}$. The linear combination coefficients can be found by solving a set of linear equations for a finite (and rather small) set of starphenes: $St(2,2,2)$, $St(2,3,3)$, $St(2,3,4)$, $St(2,3,5)$, $St(3,3,5)$, etc. We have discovered that a particularly compact expression for $St_{n,m,l}$ can be obtained in this way by using slightly modified structural parameters $N = n-2$, $M = m-2$ and $L = l-2$, and by introducing the following shorthand notation $z = 1+x$ and $w = 1+x+y$

$$St_{n,m,l} = \begin{bmatrix} 1 \\ z \\ z^2 \\ z^3 \\ w \\ wz \\ wz^2 \\ w^2 \\ w^2 z \\ w^3 \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ L+M+N \\ LM+LN+MN \\ LMN \end{bmatrix} + 3w - 2z \qquad (23)$$

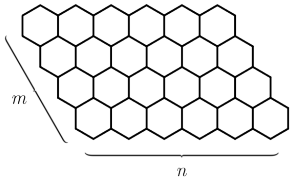


Figure 6. Parallelograms $M(m,n)$

which can be written in a more compact way as

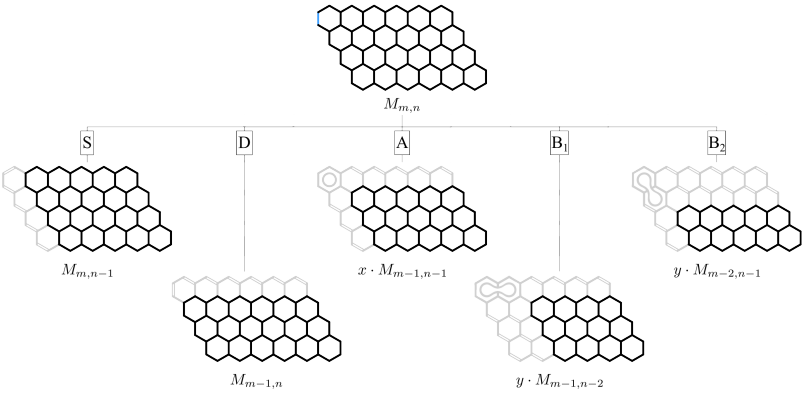
$$St_{n,m,l} = \begin{bmatrix} w^0\,(1+z)^3 \\ w^1\,(1+z)^2 \\ w^2\,(1+z)^1 \\ w^3\,(1+z)^0 \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} 1 \\ L+M+N \\ LM+LN+MN \\ LMN \end{bmatrix} + 3w - 2z \tag{24}$$

$$= (1+z+Lw)(1+z+Mw)(1+z+Nw) + 3w - 2z \tag{25}$$

Note that the last equation reproduces Eq. (21) once we recognize $1+z+Kw$ as L_{K+1} using Eq. (3) with $K = L, M, N$. Note also that evaluation of Eq. (25) at $y = 0$ reproduces the ZZ polynomial of $St(n,m,l)$ given originally by Eq. (4.17) of [46] and Eq. (22) of [8].

4.5 Parallelograms

The most complicated structures considered in the current work are parallelograms $M(m,n)$ of height m and length n as defined schematically in Fig. 6. Let us consider the following decomposition pathway of $M(m,n)$



which leads to a 5-term recursive formula for $M_{m,n} \equiv \mathrm{GZZ}(M(m,n),x,y)$

$$M_{m,n} = M_{m,n-1} + M_{m-1,n} + x\,M_{m-1,n-1} + y\,(M_{m-1,n-2} + M_{m-2,n-1}) \tag{26}$$

Solving this two-dimensional recurrence can pose considerable problems. Therefore, for purely pedagogical reasons, we resort here to an intermediate solution, where we demonstrate how to guess the solution to the recurrence given by Eq. (26). Formal check of correctness of a solution discovered in this way can be performed by mathematical induction.

We start our considerations by listing the GZZ polynomials of parallelograms $M_{2,n}$ with a constant width $n = 2$

$$\begin{cases} M_{2,0} = & 1 \\ M_{2,1} = & 3 + & 2x + & y \\ M_{2,2} = & 6 + & 6x + & x^2 + & 4y \\ M_{2,3} = & 10 + & 12x + & 3x^2 + & 9y + & 2xy \\ M_{2,4} = & 15 + & 20x + & 6x^2 + & 16y + & 6xy + & y^2 \\ M_{2,5} = & 21 + & 30x + & 10x^2 + & 25y + & 12xy + & 3y^2 \\ M_{2,6} = & 28 + & 42x + & 15x^2 + & 36y + & 20xy + & 6y^2 \\ M_{2,7} = & 36 + & 56x + & 21x^2 + & 49y + & 30xy + & 10y^2 \\ M_{2,8} = & 45 + & 72x + & 28x^2 + & 64y + & 42xy + & 15y^2 \end{cases} \tag{27}$$

It is obvious that the coefficients in front of each of the $x^j y^k$ monomials are simple, binomial-like functions of n. This leads to the following equation valid for $n \geq 2$

$$M_{2,n} = \tbinom{n+2}{2} + 2\tbinom{n+1}{2}\,x + \tbinom{n}{2}\,x^2 + n^2\,y + (n-1)\,(n-2)\,xy + \tbinom{n-2}{2}\,y^2 \tag{28}$$

In the next step, we perform similar analysis for $m = 3$. We have

$$\begin{cases} M_{3,0} = & 1 \\ M_{3,1} = & 4 + & 3x + & 2y \\ M_{3,2} = & 10 + & 12x + & 3x^2 + & 9y & + & 2xy \\ M_{3,3} = & 20 + & 30x + & 12x^2 + & x^3 + & 24y + & 12xy + & 2y^2 \\ M_{3,4} = & 35 + & 60x + & 30x^2 + & 4x^3 + & 50y + & 36xy + & 3x^2y + & 9y^2 \\ M_{3,5} = & 56 + & 105x + & 60x^2 + & 10x^3 + & 90y + & 80xy + & 12x^2y + & 24y^2 + & 3xy^2 \\ M_{3,6} = & 84 + & 168x + & 105x^2 + & 20x^3 + & 147y + & 150xy + & 30x^2y + & 50y^2 + & 12xy^2 + & y^3 \\ M_{3,7} = & 120 + & 252x + & 168x^2 + & 35x^3 + & 224y + & 252xy + & 60x^2y + & 90y^2 + & 30xy^2 + & 4y^3 \\ M_{3,8} = & 165 + & 360x + & 252x^2 + & 56x^3 + & 324y + & 392xy + & 105x^2y + & 147y^2 + & 60xy^2 + & 10y^3 \end{cases} \tag{29}$$

Identification of the coefficient sequences appearing here is more complicated, but again, they turn out to be relatively simple functions of n. The identification leads to the following equation valid for $n \geq 3$

$$\begin{aligned} M_{3,n} = & \binom{3}{0}\binom{n+3}{3}\binom{n+3}{0} + \binom{3}{1}\binom{n+2}{3}\binom{n+1}{0}x + \binom{3}{2}\binom{n+1}{3}\binom{n-1}{0}x^2 + \binom{3}{3}\binom{n}{3}\binom{n-3}{0}x^3 \\ & + \binom{2}{0}\binom{n+1}{2}\binom{n+1}{1}y + \binom{2}{1}\binom{n}{2}\binom{n-1}{1}xy + \binom{2}{2}\binom{n-1}{2}\binom{n-3}{1}x^2y \\ & + \binom{1}{0}\binom{n-1}{1}\binom{n-1}{2}y^2 + \binom{1}{1}\binom{n-2}{1}\binom{n-3}{2}xy^2 \\ & + \binom{0}{0}\binom{n-3}{0}\binom{n-3}{3}y^3 \end{aligned} \tag{30}$$

which can be further expressed in closed, binomial-like form as

$$M_{3,n} = \sum_{i=0}^{\min(3,n)} \sum_{j=0}^{\min(3,n)} \binom{3-i}{j}\binom{n+3-2i-j}{3-i}\binom{n+3-2i-2j}{i} x^j y^i \tag{31}$$

which suggests more compact way of expressing Eq. (28) derived earlier as

$$M_{2,n} = \sum_{i=0}^{\min(2,n)} \sum_{j=0}^{\min(2,n)} \binom{2-i}{j}\binom{n+2-2i-j}{2-i}\binom{n+2-2i-2j}{i} x^j y^i \tag{32}$$

Eqs. (32) and (31) reproduce the GZZ polynomials of $M(2,n)$ and $M(3,n)$ given by Eqs. (27) and (29), respectively. They can also be readily generalized to an arbitrary value of m; the resulting equation has the analogous familiar form

$$M_{m,n} = \sum_{i=0}^{\min(m,n)} \sum_{j=0}^{\min(m,n)} \binom{m-i}{j}\binom{m+n-2i-j}{m-i}\binom{m+n-2i-2j}{i} x^j y^i \tag{33}$$

The main problem associated with Eq. (33) is the lack of the $m \leftrightarrow n$ interchange symmetry obvious from Fig. 6. Clearly $M_{m,n} = M_{n,m}$, because the collections of generalized Clar covers of $M(m,n)$ and $M(n,m)$ are identical, differing only in their geometrical orientations. To solve this shortcoming, we note that Eq. (33) can be rearranged in various ways manifestly accentuating the $m \leftrightarrow n$ interchange symmetry, e.g.

$$M_{m,n} = \sum_{i=0}^{\min(m,n)} \sum_{j=0}^{\min(m,n)} \binom{\min(m,n)-i}{j}\binom{m+n-2i-j}{\min(m,n)-i}\binom{m+n-2i-2j}{i} x^j y^i \tag{34}$$

$$= \sum_{i=0}^{\min(m,n)} \sum_{j=0}^{i} \binom{\max(m,n)-j}{\min(m,n)-i}\binom{\max(m,n)+i-2j}{i-j} \cdot \binom{\max(m,n)-\min(m,n)+2(i-j)}{j} x^{\min(m,n)-i} y^j \tag{35}$$

The last equation has an additional advantage: all the binomials coefficients con-

tain only non-negative entries, so one can use the usual factorial expansion of the binomial coefficients without the necessity of taking limits. Formal correctness of Eqs. (34) and (35) can be demonstrated using mathematical induction, but the proof is very lengthy and therefore it is omitted here.

Despite discovering an apparently correct formula for $\mathrm{GZZ}(M(m,n),x,y)$, there remains certain resentment associated with the fact that the corresponding ZZ polynomial formulas for the parallelogram $M(m,n)$ show much higher degree of symmetry

$$\mathrm{ZZ}(M(m,n),x) = \sum_{i=0}^{\min(m,n)} \frac{(m+n-i)!}{(m-i)!\,(n-i)!\,i!}\,x^i = \sum_{i=0}^{\min(m,n)} \frac{\binom{m+n}{m}\binom{m}{i}\binom{n}{i}}{\binom{m+n}{i}}\,x^i \quad (36)$$

$$= \sum_{i=0}^{\min(m,n)} \binom{m}{i}\binom{n}{i}(1+x)^i = {}_2F_1\left[\begin{matrix}-m,-n\\1\end{matrix};1+x\right] \quad (37)$$

(Eq. (3) of [12], Eq. (19) of [7], and Eqs. (4) and (5) of [12], respectively) than the current formulation of GZZ polynomials for $M(m,n)$ given by Eqs. (33), (34) and (35). Note that the situation was similar for the ZZ polynomials in the beginning: The first formula for $\mathrm{ZZ}(M(m,n),x)$ discovered by Gutman and Borovićanin (Eq. (16) of [21])

$$\mathrm{ZZ}(M(m,n),x) = \sum_{i=0}^{m} \binom{m}{i}\binom{n+m-i}{m}\,x^i \quad (38)$$

despite of its correctness missed the obvious $m \leftrightarrow n$ interchange symmetry too. We signalize this problem here (perhaps in a somewhat too obnoxious manner) to encourage others to discover such a symmetric formulation.

5 Conclusion

We have presented an algorithm designed for an automatic computation of the generalized Zhang-Zhang (GZZ) polynomials of arbitrary benzenoids. The algorithm has been implemented in Fortran 95 as GZZCalculator, freely available for download [35]. The developed computer code has been used for finding closed-form expressions of the GZZ polynomials for five families of benzenoids. Several interesting features of the presented results have been discussed in detail, mainly to stimulate other groups to participate in solving the remaining problems.

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