# Zhang – Zhang Polynomial of Multiple Linear Hexagonal Chains

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An explicit combinatorial expression is obtained for the Zhang-Zhang polynomial (also known as “Clar cover polynomial”) of a large class of pericondensed benzenoid systems, the multiple linear hexagonal chains $M_{n,m}$. By means of this result, various problems encountered in the Clar theory of $M_{n,m}$ are also resolved: counting of Clar and Kekulé structures, determining the Clar number, and calculating the sextet polynomial.

*Key words:* Clar Aromatic Sextet Theory; Zhang-Zhang Polynomial; Clar Cover Polynomial; Sextet Polynomial.

## 1. Introduction

In a series of papers [1 – 4] Heping Zhang and Fuji Zhang introduced a molecular-graph-based polynomial, pertaining to the Clar aromatic sextet theory of benzenoid hydrocarbons [5 – 7]. They named it “*Clar cover polynomial*”, but in our opinion it deserves to be called “*Zhang-Zhang polynomial*”. We denote it by $\zeta(B) = \zeta(B,\lambda)$, where $B$ stands for the underlying benzenoid system.

Let $B$ be a benzenoid system with $K = K\{B\} > 0$ Kekulé structures and $C = C\{B\} > 0$ Clar aromatic sextet formulas [6]. The Clar formulas possess a maximal possible number of aromatic sextets (denoted by $Cl = Cl\{B\} > 0$ and called the Clar number [8]). If the number of aromatic sextets is not required to be maximum ($= Cl\{B\}$), then one speaks of generalized Clar formulas; these were first considered by Hosoya and Yamaguchi [9]. Let their number be denoted by $\tilde{K} = \tilde{K}\{B\}$. For many benzenoid systems (including those that are studied in this paper), $\tilde{K} = K$.

Let $S_i$ ($i = 1,2,,\ldots,\tilde{K}\{B\}$), be the generalized Clar formulas of the benzenoid system $B$. Let $S_i$ possess $c_i$ aromatic sextets, $0 \le c_i \le Cl\{B\}$. Let the $\pi$-electrons of $B$, not included in the $c_i$ aromatic sextets of $S_i$ be arranged into $k_i$ distinct Kekulé structures.

The Zhang-Zhang polynomial may now be defined as

$$\zeta(B) = \zeta(B,\lambda) = \sum_{i=1}^{\tilde{K}\{B\}} k_i \lambda^{c_i}. \qquad (1)$$

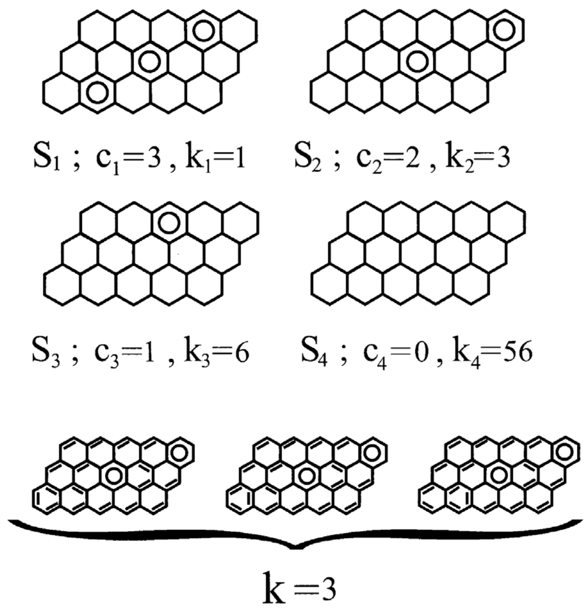


Fig. 1. There are 56 distinct generalized Clar formulas of the triple hexagonal chain $M_{3,5}$, of which four ($S_1, S_2, S_3$, and $S_4$) are shown. By $c_i$ and $k_i$ are denoted the number of aromatic sextets and Kekulé structures of $S_i$, ($i = 1,2,3,4$). In the case of $S_2$ the respective three Kekulé structures are shown.

The Zhang-Zhang polynomial of $M_{3,5}$ is $10\lambda^3 + 60\lambda^2 + 105\lambda + 56$, implying that $M_{3,5}$ has $K = 56$ Kekulé and $C = 10$ Clar structures, and that its Clar number is $Cl = 3$. Because $10\lambda^3 + 60\lambda^2 + 105\lambda + 56 = 10(\lambda+1)^3 + 30(\lambda+1)^2 + 15(\lambda+1) + 1$, the sextet polynomial of $M_{3,5}$ is equal to $10\lambda^3 + 30\lambda^2 + 15\lambda + 1$ and, consequently, $M_{3,5}$ has a total of $\tilde{K} = 10 + 30 + 15 + 1 = 56$ generalized Clar formulas.

Formula (1) should be compared with the analogous expression for the sextet polynomial [9 – 12]

$$\sigma(B) = \sigma(B,\lambda) = \sum_{i=1}^{\tilde{K}\{B\}} \lambda^{c_i}. \tag{2}$$

An example, illustrating the Clar theoretic concepts encountered in (1), is shown in Figure 1. As one may guess from this example, the calculation of $\zeta(x)$ directly from (1) would be a rather cumbersome and error-prone task.

In what follows it is convenient to write the Zhang-Zhang and the sextet polynomials in the form

$$\zeta(B,\lambda) = \sum_{k=0}^{Cl\{B\}} z(B,k)\lambda^k, \tag{3}$$

$$\sigma(B,\lambda) = \sum_{k=0}^{Cl\{B\}} s(B,k)\lambda^k. \tag{4}$$

The basic properties of the Zhang-Zhang polynomial are the following:

(a) The coefficient $z(B,0)$ is equal to the number of Kekulé structures, $K\{B\}$.
(b) The power of $\zeta(B,x)$ is equal to the Clar number, $Cl\{B\}$.
(c) The coefficient $z(B,Cl)$ is equal to the number of Clar aromatic sextet formulas, $C\{B\}$.

Thus, all the important mathematical features of the Clar aromatic sextet theory are contained in the Zhang-Zhang polynomial. If we calculate this polynomial, then we simultaneously determine $K$, $C$, $Cl$, and – as pointed out below – $\tilde{K}$ and $\sigma(x)$. It is worth mentioning that in the earlier chemical literature separate approaches were elaborated for counting the Kekulé structures [13], Clar formulas [14, 15], and generalized Clar formulas [16, 17], as well as for the determination of the Clar number [8, 16, 18, 19] and the sextet polynomial [10 – 12, 19, 20] of benzenoid molecules.

Now, the Zhang-Zhang polynomial can be computed recursively [2]: Let $e_{\mathrm{rs}}$ be an edge of the benzenoid system $B$, connecting the vertices $v_{\mathrm{r}}$ and $v_{\mathrm{s}}$. Let further $e_{\mathrm{rs}}$ lie on the perimeter of $B$ and thus belong to a unique hexagon $H$. (For an illustrative example see Fig. 2.) Then

$$\zeta(B,\lambda) = \zeta(B-e_{\mathrm{rs}},\lambda) + \zeta(B-v_{\mathrm{r}}-v_{\mathrm{s}},\lambda) + \lambda\zeta(B-H,\lambda). \tag{5}$$

The subgraphs occurring on the right-hand side of (5) may possess edges that do not belong to any cycle. If $B'$ is such a subgraph and $e'_{xy}$ such an edge (connecting the vertices $v_x$ and $v_y$), then

$$\zeta(B',\lambda) = \zeta(B'-e_{xy},\lambda) + \zeta(B'-v_x-v_y,\lambda). \tag{6}$$

A special case of (6) is obtained if the vertex $v_x$ is of degree 1. Then,

$$\zeta(B',\lambda) = \zeta(B'-v_x-v_y,\lambda). \tag{7}$$

Using formulas (5) – (7), Zhang and Zhang have obtained explicit combinatorial expressions for $\zeta(B)$ for a variety of homologous series of catacondensed benzenoid systems [2], but not for a single pericondensed benzenoid. In this paper we intend to contribute to filling this gap.

## 2. The Multiple Linear Hexagonal Chain Benzenoids

The structure of the multiple linear hexagonal chain benzenoid hydrocarbons, whose general representative is denoted by $M_{n,m}$, is depicted in Figure 2.

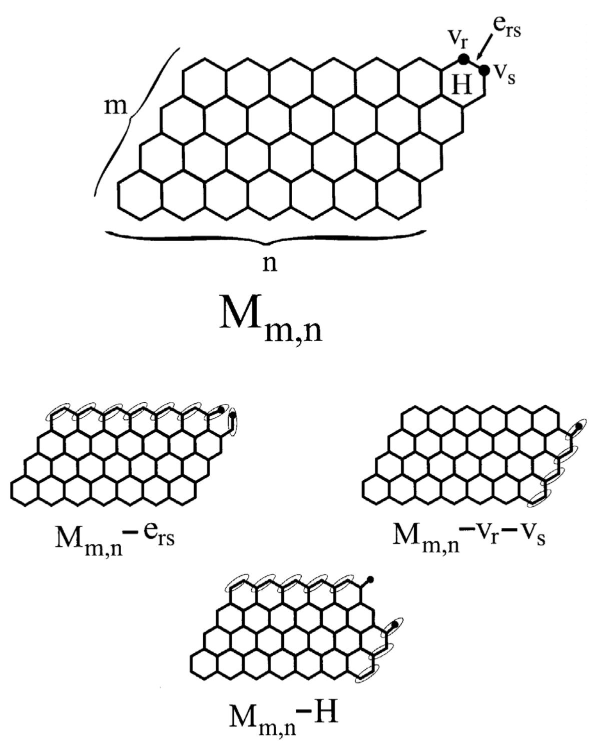


Fig. 2. The multiple linear hexagonal chain $M_{n,m}$ and its subgraphs needed for the calculation of the Zhang-Zhang polynomial; for details see text.

In order to determine $\zeta(M_{n,m},\lambda)$ it is convenient to start the application of (5) by choosing the edge $e_{\mathrm{rs}}$ as indicated in Figure 2. If so, then the subgraphs $(M_{n,m}-e_{\mathrm{rs}})$, $(M_{n,m}-v_{\mathrm{r}}-v_{\mathrm{s}})$, and $(M_{n,m}-H)$ possess vertices of degree one, and to these subgraphs (7) is applicable. According to (7), by deleting a vertex of degree one and its (unique) first neighbor the Zhang-Zhang polynomial remains unchanged. If $(M_{n,m}-e_{\mathrm{rs}})$, $(M_{n,m}-v_{\mathrm{r}}-v_{\mathrm{s}})$, and $(M_{n,m}-H)$, such two-vertex deletions can be consecutively repeated several times, as indicated by the encircled pairs of vertices in the respective diagrams in Figure 2. Finally we arrive at

$$\zeta(M_{n,m}-e_{\mathrm{rs}})=\zeta(M_{n,m-1}),$$
$$\zeta(M_{n,m}-v_{\mathrm{r}}-v_{\mathrm{s}})=\zeta(M_{n-1,m}),$$
$$\zeta(M_{n,m}-H)=\zeta(M_{n-1,m-1}),$$

which combined with (5) yields the recurrence relation

$$\zeta(M_{n,m})=\zeta(M_{n,m-1})+\zeta(M_{n-1,m}) + \lambda\zeta(M_{n-1,m-1}). \tag{8}$$

## 3. Solving (8)

### 3.1. Single Linear Hexagonal Chains (Polyacenes); $m = 1$

In the case of linear polyacenes $M_{n,1}$, $n\geq 1$ [benzene ($n=1$), naphthalene ($n=2$), anthracene ($n=3$), …], the solution is immediate. For these benzenoids $Cl=1$, $K=n+1$, and $C=n$, which in view of the properties (a)–(c), results in

$$\zeta(M_{n,1})=n\lambda+(n+1). \tag{9}$$

Formula (9) has first been deduced in [2]. For reasons that will become clear below we rewrite (9) as

$$\zeta(M_{n,1})=\binom{n}{1}\lambda+\binom{n+1}{1},\quad n\geq 1. \tag{10}$$

### 3.2. Double Linear Hexagonal Chains; $m = 2$

In the case of double linear chain benzenoids $M_{n,2}$, $n\geq 2$ [pyrene ($n=2$), anthanthrene ($n=3$), …], (8) reduces to

$$\zeta(M_{n,2})=\zeta(M_{n,1})+\zeta(M_{n-1,2})+\lambda\zeta(M_{n-1,1}).$$

Substituting (9) we arrive at

$$\zeta(M_{n,2})=\zeta(M_{n-1,2})+\left[(n-1)\lambda^2+2n\lambda+(n+1)\right],$$

from which

$$\zeta(M_{n,2})=\zeta(M_{1,2})+\sum_{k=2}^{n}\left[(k-1)\lambda^2+2k\lambda+(k+1)\right]. \tag{11}$$

Bearing in mind that $M_{1,2}\equiv M_{2,1}=$ naphthalene, with $\zeta(M_{2,1})=2\lambda+3$, from (11) we directly compute

$$\zeta(M_{n,2})=\frac{1}{2}n(n-1)\lambda^2+n(n+1)\lambda+\frac{1}{2}(n+2)(n+1), \tag{12}$$

which may be written as

$$\zeta(M_{n,2})=\binom{n}{2}\lambda^2+2\binom{n+1}{2}\lambda+\binom{n+2}{2},\quad n\geq 2. \tag{13}$$

### 3.3. Triple Linear Hexagonal Chains; $m = 3$

The starting recurrence relation now reads

$$\zeta(M_{n,3})=\zeta(M_{n,2})+\zeta(M_{n-1,3})+\lambda\zeta(M_{n-1,2}).$$

Combining the above expression with (12) yields

$$\zeta(M_{n,3})=\zeta(M_{n-1,3})+\left[\frac{1}{2}(n-1)(n-2)\lambda^3+\frac{3}{2}n(n-1)\lambda^2+\frac{3}{2}n(n+1)\lambda+\frac{1}{2}(n+1)(n+2)\right],$$

from which

$$\zeta(M_{n,3})=\zeta(M_{2,3})+\sum_{k=3}^{n}\left[\frac{1}{2}(k-1)(k-2)\lambda^3+\frac{3}{2}k(k-1)\lambda^2+\frac{3}{2}k(k+1)\lambda+\frac{1}{2}(k+1)(k+2)\right].$$

Bearing in mind that $\zeta(M_{2,3})\equiv\zeta(M_{3,2})=3\lambda^2+12\lambda+10$, after a lengthy calculation we arrive at

$$\zeta(M_{n,3})=\frac{1}{6}n(n-1)(n-2)\lambda^3+\frac{1}{2}n(n-1)(n+1)\lambda^2+\frac{1}{2}n(n+1)(n+2)\lambda+\frac{1}{6}(n+1)(n+2)(n+3),$$

i. e.,

$$\zeta(M_{n,3}) = \binom{n}{3}\lambda^3 + 3\binom{n+1}{3}\lambda^2 + 3\binom{n+2}{3}\lambda + \binom{n+3}{3}, \quad n \geq 3. \tag{14}$$

*3.4. The General Case; $M_{n,m}$, $n \geq 3$*

A calculation analogous to what was described above, but significantly more cumbersome, leads to the following expression for the quadruple linear chains:

$$\zeta(M_{n,4}) = \binom{n}{4}\lambda^4 + 4\binom{n+1}{4}\lambda^3 + 6\binom{n+2}{4}\lambda^2 + 4\binom{n+3}{4}\lambda + \binom{n+4}{4}, \quad n \geq 4. \tag{15}$$

Comparing (15) with (10), (13), and (14) suggests that the general solution of the recurrence relation (8) is of the form

$$\zeta(M_{n,m},\lambda) = \sum_{k=0}^{m} \binom{m}{k}\binom{n+k}{m}\lambda^{m-k}, \quad n \geq m. \tag{16}$$

Indeed, the validity of (16) could be proven by mathematical induction on the parameter $m$; details of this proof are omitted.

In the notation defined by (3), the coefficients of the Zhang-Zhang polynomial of $M_{n,m}$ satisfy the relation

$$z(M_{n,m},k) = \binom{m}{m-k}\binom{n+m-k}{m} \tag{17}$$

for $k = 0, 1, \ldots, m$.

## 4. Applications

Bearing in mind the properties (a)–(c) of the Zhang-Zhang polynomial, from formula (16) we readily deduce the following three properties of the multiple linear hexagonal chains:

1. The number of Kekulé structures of $M_{n,m}$ is $\binom{n+m}{m}$, a long time known result [13,21].
2. Provided $n \geq m$, the Clar number of $M_{n,m}$ is $m$. If $n \leq m$, then $Cl\{M_{n,m}\} = n$.
3. Provided $n \geq m$, the number of Clar resonance sextet formulas of $M_{n,m}$ is $\binom{n}{m}$. If $n \leq m$, then $C\{M_{n,m}\} = \binom{m}{n}$. This result has been reported in [14]. It is worth noting that in the case $n = m$ the Clar formula of $M_{n,m}$ is unique, i.e., $C\{M_{n,n}\} = 1$.

Zhang and Zhang proved in [3, 4] a remarkable identity, relating their polynomial with the sextet polynomial of Hosoya and Yamaguchi:

$$\sigma(B,\lambda) = \zeta(B,\lambda-1), \tag{18}$$

cf. (1)–(4). Formula (18) holds if no coronene fragment can be deleted from $B$, so that the resulting subgraph is Kekuléan. The multiple linear chains considered in this paper obey this condition. Therefore (18) holds for $M_{n,m}$.

From (18) immediately follows that

$$s(B,k) = \sum_{j \geq k} (-1)^j \binom{j}{k} z(B,j)$$

for $j = 0, 1, 2, \ldots, Cl\{B\}$. Combined with (17), this gives for the coefficients of the sextet polynomial of the multiple linear benzenoid chains

$$s(M_{n,m},k) = \sum_{j \geq k} (-1)^j \binom{j}{k}\binom{m}{m-j}\binom{n+m-j}{m},$$

and for the entire sextet polynomial

$$\sigma(M_{n,m},\lambda) = \sum_{k=0}^{m} \left[\sum_{j \geq k} (-1)^j \binom{j}{k}\binom{m}{m-j}\binom{n+m-j}{m}\right]\lambda^k.$$


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