The number of perfect matchings in random polyazulenoid chains

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Abstract: A perfect matching of a graph is a set of independent edges covering every vertex exactly once. A polyazulenoid structure is a kind of nonalternant conjugated hydrocarbon consisting of a series of alternatingly fused azulene units. In this paper, we give a simple counting formula for the expected value of the number of perfect matchings in random polyazulenoid chains. Furthermore, we obtain the average number of perfect matchings of the set of all polyazulenoid chains with n azulene units.

Key words: Random polyazulenoid chain, perfect matching, azulene unit, expected value.

1 Introduction

A *perfect matching* of a graph in mathematics is a set of independent edges covering every vertex exactly once, which is called *Kekulé*

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structure in organic chemistry and *closed-packed dimer* in statistical physics. Denote the number of perfect matchings of a graph G by $m(G)$. In organic chemistry, there are strong connections between the number of the Kekulé structures and chemical properties for benzenoid hydrocarbons and nonbenzenoid hydrocarbons such as azulenoid kekulene. For instance, those edges which are present in comparatively few of the Kekulé structures of a (molecule) graph turn out to correspond to the bonds which are least stable, and the more Kekulé structures a graph possesses the more stable the corresponding benzenoid molecule is [17]. Additionally, the number of Kekulé structures is an important topological index which had been applied for estimation of the resonant energy and total π-electron energy [6, 10]. In crystal physics, the perfect matching problem is closely related to the dimer problem [12, 13]. But the enumeration problem for perfect matchings in general graphs (even in bipartite graphs) is NP-hard [15, 18]. For a survey of results and further bibliography on the chemical applications of the perfect matching, see [6, 20] and the references cited therein.

Azulene [2] whose chemical formula is $C_{10}H_8$ (see Fig. 1) is an organic compound and an isomer of naphthalene, which has a long history dating back to the 15th century as the azure-blue chromophore

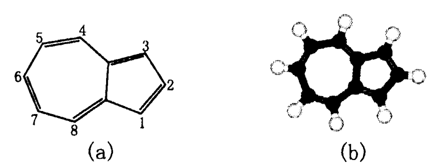

Figure 1: The chemical molecular structure of azulene.

obtained by steam distillation of German chamomile. The representation of the carbon skeleton (i.e. a five-membered ring together with one of its neighbored seven-membered ring) of an azulene is called an *azulene unit* in some literatures [14, 19].

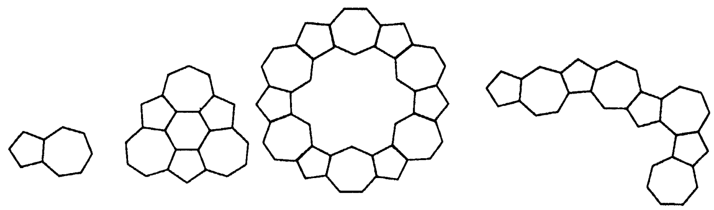

Figure 2: (a) The azulene unit; (b) isocoronene; (c) azulenoid kekulene; (d) a polyazulenoid structure consisting of four azulene units.

A *polyazulenoid structure* (or also called *azulenoid* [11]) is a kind of nonalternant conjugated hydrocarbon composed of two or more alternatingly fused azulene units. Fig. 2 shows the molecule graphs of the azulene unit, isocoronene [5] consisting of three azulene units, azulenoid kekulene [11] consisting of six azulene units and another polyazulenoid structure consisting of four azulene units, respectively. Polyazulenoid structures have been studied by chemists for many years. For example, azulenoid kekulene was firstly proposed by Hess et al. [11] in 1971, who calculated the resonance energies and resonance energies per π electron (REPE) of azulenoid kekulene and a series of other aromatic nonalternant hydrocarbons consisting of two or more fused azulene units. The superaromatic stabilization of azulenoid kekulene was estimated by a simple graph theoretical method [1] in 2008. The carbon skeleton of isocoronene has been considered as a possible native defect in carbon nanotubes [16]. Recently, Deng and Zhang [7, 21] gave an explicit counting formula for the number of the isomers in cyclic polyazulenoids and Möbius type cyclic polyazulenoids according to the number of azulene units, respectively.

A *polyazulenoid chain* is a polyazulenoid structure proved that each five-membered ring is always neighbored by a seven-membered ring by fusing one of the four HC-CH bonds of the seven-membered

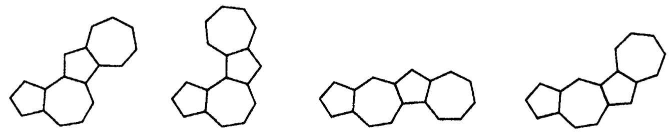

Figure 3: All polyazulenoid chains consisting of two azulene units.

ring to one of the two HC-CH bonds of the five-membered ring in the neighbored azulene units, which forms a 'chain of rings' or 'chain of azulenes'. That is, no azulene unit is adjacent to more than two other azulene units in the polyazulenoid chain (see Fig. 2(d) and Fig. 3). Fig. 2(a) and Fig. 3 show the unique polyazulenoid chains with 1 azulene unit and 2 azulene units.

Let P be a polyazulenoid chain with $n \geq 3$ azulene units labeled by $u_1, u_2, \ldots, u_n$ so that u_i and u_{i+1} are adjacent for each i, where $1 \leq i \leq n-1$. Both the first azulene unit u_1 and the last azulene unit u_n are called *terminal azulene unit*. And the remaining azulene units $u_2, u_3, \ldots, u_{n-1}$ are called *internal azulene unit*. Each internal azulene unit is of type-I, type-II, type-III or type-IV according to whether it separates its two adjacent azulene units by a distance of 3,4,5 or 6 from left to right as shown in Fig. 4, respectively. A *random polyazulenoid chain* of length n is a polyazulenoid chain with n azulene units in which each internal azulene unit is one of type-I with the probability q_1, type-II with the probability q_2, type-III with the probability q_3 or type-IV with the probability q_4, denoted by $P(n, q_1, q_2, q_3, q_4)$, where $\sum_{i=1}^{4} q_i = 1$. Gutman [8, 9] studied the perfect matchings about random benzenoid chain graphs. Chen and Zhang [4] obtained an expression for the expected value of perfect matchings in a random phenylene chain. Wei et al. [20] presented a simple formula for the expected value of perfect matchings in random polyomino chain graphs.

In the paper, simple formulae are given for the expected value of

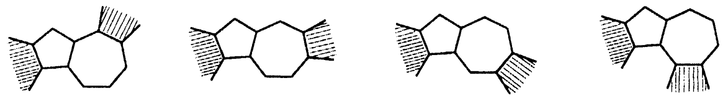

Figure 4: Four types of internal azulene units.

the number of perfect matchings in random polyazulenoid chains and for the asymptotic behavior of this expectation. Moreover, we obtain the average value of the number of perfect matchings with respect to the set of all polyazulenoid chains with n azulene units.

2 Main results

Recall that there is a recursive formula for the perfect matchings in a graph G [6], i.e.,

$$m(G) = m(G - u - v) + m(G - uv), \tag{1}$$

where uv denotes an edge of G incident with the vertices u and v. All notation not defined in this paper can be found in the book [3].

Lemma 2.1. *Let P_i be a polyazulenoid chain with i azulene units. Then the number of perfect matchings $m(P_i)$ of P_i can be obtained by the following recursive expression: $m(P_1) = 2, m(P_2) = 3$, and for $i \geq 3$,*

$$m(P_i) = \begin{cases} m(P_{i-1}) + m(P_{i-2}), & \text{if the } (i-1)\text{-st azulene unit is of type-I or type-III;} \\ 2m(P_{i-1}) - m(P_{i-2}), & \text{if the } (i-1)\text{-st azulene unit is of type-II or type-IV.} \end{cases}$$

Proof: Without loss of generality, let $e = uv$ be an edge in the polyazulenoid chain P_i shown in Fig. 5 and Fig. 6. There are four cases according to the type of the $(i-1)$-st azulene unit.

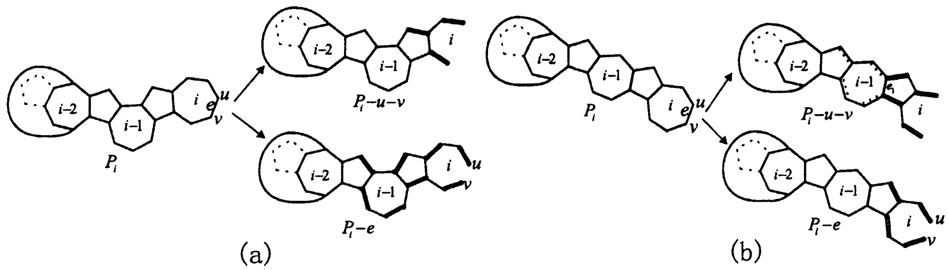

Figure 5: (a)Illustration of type-I; (b)Illustration of type-II.

Case 1. Suppose the $(i-1)$-st azulene unit is of type-I. It is easy to see from Fig. 5(a) that

$$m(P_i - u - v) = m(P_{i-1}) \text{ and } m(P_i - e) = m(P_{i-2}).$$

Therefore, by the formula (1), we have the conclusion, i.e.,

$$m(P_i) = m(P_{i-1}) + m(P_{i-2}).$$

Case 2. Suppose the $(i-1)$-st azulene unit is of type-II. It is easy to see from Fig. 5(b) that

$$m(P_i - u - v) = m(P_{i-1}) - m(P_{i-1} - e_1) = m(P_{i-1}) - m(P_{i-2})$$

and $m(P_i - e) = m(P_{i-1})$. So we obtain the result by the formula (1), i.e.,

$$m(P_i) = 2m(P_{i-1}) - m(P_{i-2}).$$

Case 3. Suppose the $(i-1)$-st azulene unit is of type-III. It is easy to see from Fig. 6(a) that

$$m(P_i - u - v) = m(P_{i-2}) \text{ and } m(P_i - e) = m(P_{i-1}).$$

Hence, by the formula (1) we get the result, i.e.,

$$m(P_i) = m(P_{i-1}) + m(P_{i-2}).$$

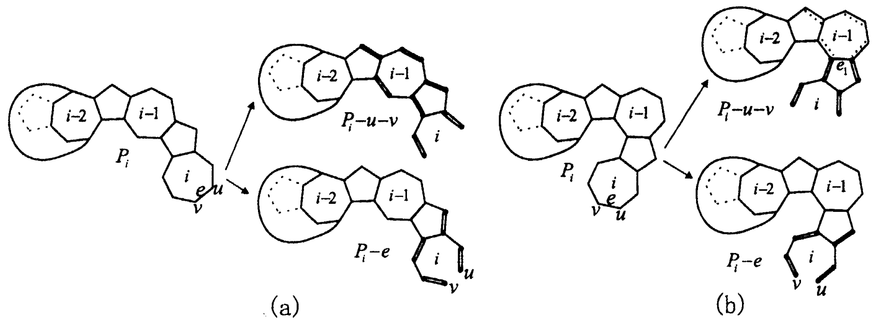

Figure 6: (a)Illustration of type-III; (b)Illustration of type-IV.

Case 4. Suppose the $(i-1)$-st azulene unit is of type-IV. It is easy to see from Fig. 6(b) that

$$m(P_i - u - v) = m(P_{i-1}) - m(P_{i-1} - e_1) = m(P_{i-1}) - m(P_{i-2})$$

and $m(P_i - e) = m(P_{i-1})$. So we have the result by the formula (1), i.e.,

$$m(P_i) = 2m(P_{i-1}) - m(P_{i-2}).$$

This completes the proof. $\square$

Here $m(P(n, q_1, q_2, q_3, q_4))$ is a random variable. Let $E[m(P(n, q_1, q_2, q_3, q_4))]$ denote the expected value of $m(P(n, q_1, q_2, q_3, q_4))$.

Lemma 2.2. *Let $P(i, q_1, q_2, q_3, q_4)$ be a random polyazulenoid chain with i azulene units. Then*

$$\begin{aligned} E[m(P(i, q_1, q_2, q_3, q_4))] &= (1 + q_2 + q_4)E[m(P(i-1, q_1, q_2, q_3, q_4))] \\ &\quad + (1 - 2q_2 - 2q_4)E[m(P(i-2, q_1, q_2, q_3, q_4))], \end{aligned}$$

where $i \geq 3$.

Proof: Since the $(i-1)$-st azulene unit of $P(i, q_1, q_2, q_3, q_4)$ is one of type-I with probability q_1, of type-II with probability q_2, of type-III with probability q_3 and of type-IV with probability q_4, by Lemma 2.1 we have

$$\begin{aligned}
&E[m(P(i, q_1, q_2, q_3, q_4))] \\
&\quad = q_1[m(P(i-1, q_1, q_2, q_3, q_4)) + m(P(i-2, q_1, q_2, q_3, q_4))] \\
&\qquad + q_2[2m(P(i-1, q_1, q_2, q_3, q_4)) - m(P(i-2, q_1, q_2, q_3, q_4))] \\
&\qquad + q_3[m(P(i-1, q_1, q_2, q_3, q_4)) + m(P(i-2, q_1, q_2, q_3, q_4))] \\
&\qquad + q_4[2m(P(i-1, q_1, q_2, q_3, q_4)) - m(P(i-2, q_1, q_2, q_3, q_4))] \\
&\quad = (q_1 + 2q_2 + q_3 + 2q_4)m(P(i-1, q_1, q_2, q_3, q_4)) \\
&\qquad + (q_1 - q_2 + q_3 - q_4)m(P(i-2, q_1, q_2, q_3, q_4)) \\
&\quad = (1 + q_2 + q_4)m(P(i-1, q_1, q_2, q_3, q_4)) \\
&\qquad + (1 - 2q_2 - 2q_4)m(P(i-2, q_1, q_2, q_3, q_4)).
\end{aligned}$$

Recall that $E[E[m(P(i, q_1, q_2, q_3, q_4))]] = E[m(P(i, q_1, q_2, q_3, q_4))]$. Since $E[m(P(i, q_1, q_2, q_3, q_4))]$ is a sum of random variables,

$$\begin{aligned}
E[m(P(i, q_1, q_2, q_3, q_4))] &= (1 + q_2 + q_4)E[m(P(i-1, q_1, q_2, q_3, q_4))] \\
&\quad + (1 - 2q_2 - 2q_4)E[m(P(i-2, q_1, q_2, q_3, q_4))]. \qquad \square
\end{aligned}$$

Theorem 2.3. *Let $P(n, q_1, q_2, q_3, q_4)$ be a random polyazulenoid chain with n azulene units, $n \geq 1$. 1. If $q_2 + q_4 < 1$, then*

$$E[m(P(n, q_1, q_2, q_3, q_4))] = \frac{2r-3}{r-t}t^{n-1} - \frac{2t-3}{r-t}r^{n-1}, \tag{2}$$

where $r = \frac{1+q_2+q_4+\sqrt{(3-q_2-q_4)^2-4}}{2}$ and $t = \frac{1+q_2+q_4-\sqrt{(3-q_2-q_4)^2-4}}{2}$.
2. If $q_2 + q_4 = 1$, then $E[m(P(n, q_1, q_2, q_3, q_4))] = 1 + n$.

Proof: Let $y_n = E[m(P(n+1, q_1, q_2, q_3, q_4))]$ with $n \geq 0$. Since $m(P_1) = 2$ and $m(P_2) = 3$, we have the initial conditions $y_0 = 2$, $y_1 = 3$. By Lemma 2.2, it follows that for $n \geq 0$

$$y_{n+2} = (1 + q_2 + q_4)y_{n+1} + (1 - 2q_2 - 2q_4)y_n. \tag{3}$$

Note that the characteristic equation of formula (3) is

$$\lambda^2 - (1 + q_2 + q_4)\lambda - (1 - 2q_2 - 2q_4) = 0$$

and the characteristic roots are

$$r = \frac{1 + q_2 + q_4 + \sqrt{(3 - q_2 - q_4)^2 - 4}}{2}$$

and

$$t = \frac{1 + q_2 + q_4 - \sqrt{(3 - q_2 - q_4)^2 - 4}}{2}.$$

Case 1. If $q_2 + q_4 < 1$, then the two roots are distinct. In this case,

$$y_n = k_1 r^n + k_2 t^n.$$

Substituting the initial conditions $y_0 = 2$ and $y_1 = 3$, we obtain

$$\begin{cases} k_1 + k_2 & = 2, \\ k_1 r + k_2 t & = 3. \end{cases}$$

The solution of the equations above is

$$k_1 = -\frac{2t - 3}{r - t} \text{ and } k_2 = \frac{2r - 3}{r - t}.$$

Therefore

$$y_n = E[m(P(n + 1, q_1, q_2, q_3, q_4))] = -\frac{2t - 3}{r - t} r^n + \frac{2r - 3}{r - t} t^n,$$

which proves the first statement of the theorem.
Case 2. If $q_2 + q_4 = 1$, then $r = t = 1$. In this case, $y_n = k_1 + k_2 n$. Substituting the initial conditions $y_0 = 2$ and $y_1 = 3$, we have

$$k_1 = 2 \text{ and } k_2 = 1,$$

which means that $y_n = E[m(P(n + 1, q_1, q_2, q_3, q_4))] = 2 + n$. $\square$

Corollary 2.4. *Let $P(n, q_1, q_2, q_3, q_4)$ be a random polyazulenoid chain with n azulene units. If $q_2 + q_4 < 1$, then*

$$\lim_{n\to\infty} \frac{E[m(P(n, q_1, q_2, q_3, q_4))]}{E[m(P(n-1, q_1, q_2, q_3, q_4))]} = \frac{1 + q_2 + q_4 + \sqrt{(3 - q_2 - q_4)^2 - 4}}{2}.$$

Proof: Keeping the notation defined in Theorem 2.3, we obtain that

$$\frac{E[m(P(n, q_1, q_2, q_3, q_4))]}{E[m(P(n-1, q_1, q_2, q_3, q_4))]} = \frac{k_1 r^{n-1} + k_2 t^{n-1}}{k_1 r^{n-2} + k_2 t^{n-2}} = \frac{r + t\frac{k_2}{k_1}\left(\frac{t}{r}\right)^{n-2}}{1 + \frac{k_2}{k_1}\left(\frac{t}{r}\right)^{n-2}}.$$

Since $r > t$, it follows that

$$\lim_{n\to\infty} \frac{E[m(P(n, q_1, q_2, q_3, q_4))]}{E[m(P(n-1, q_1, q_2, q_3, q_4))]} = r. \qquad \square$$

Let $\mathscr{M}_n$ be the set of all polyazulenoid chains with n azulene units. The average number of perfect matchings of $\mathscr{M}_n$ is defined by

$$m_{avr}(\mathscr{M}_n) = \frac{1}{|\mathscr{M}_n|} \sum_{G \in \mathscr{M}_n} m(G).$$

Actually, this is the population mean of the number of perfect matchings of all elements in $\mathscr{M}_n$. Since every element occurring in $\mathscr{M}_n$ has the same probability, we have $q_1 = q_2 = q_3 = q_4$. Thus, we may apply Theorem 2.3 by putting $q_1 = q_2 = q_3 = q_4 = \frac{1}{4}$ and obtain the following result.

Theorem 2.5. *The average value of the number of perfect matchings with respect to $\mathscr{M}_n$ is*

$$m_{avr}(\mathscr{M}_n) = 2\left(\frac{3}{2}\right)^{n-1}.$$

Proof: From Theorem 2.3 we get $r = \frac{3}{2}$ and $t = 0$. Hence we have

$$m_{avr}(\mathscr{M}_n) = -\left(\frac{0-3}{\frac{3}{2}-0}\right)\left(\frac{3}{2}\right)^{n-1} = 2\left(\frac{3}{2}\right)^{n-1}.$$

$\square$

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