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Wiener Index and Perfect Matchings in Random Phenylene Chains *

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Abstract. In this paper we obtain an explicit analytical expression for the expected value of the Wiener index of a random phenylene chain and a simple exact formula for the expected value of the number of perfect matchings in a random phenylene chain, respectively.

1 Introduction

In chemistry the topological indices of a molecular graph can provide some information on the chemical properties of the corresponding molecule. The first reported use of a topological index, the Wiener index, was by Wiener [1] in the study of paraffin boiling points. In the second half of the 20th century the Wiener index was found to be correlated to many physico-chemical properties and to have pharmacologic applications. The problem of the calculation of the Wiener index of phenylenes was solved by Gutman ([10]). The enumeration problem of Kekulé structure for linear phenylenes was solved by Gutman ([12, 13]). For the theory and applications of Kekulé structures of benzenoid hydrocarbons see the monograph ([11]) and the references cited therein.

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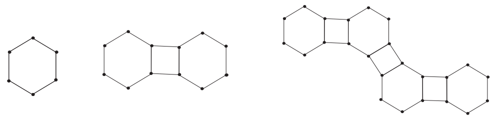

Fig. 1: Phenylene chains

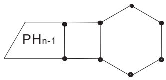

Fig. 2: A phenylene chain with n hexagons

Phenylenes are a class of conjugated hydrocarbons composed of six- and four-membered rings, where the six-membered rings (hexagons) are adjacent only to four-membered rings, and every four-membered ring is adjacent to a pair of non-adjacent hexagons. If each six-membered ring of a phenylene is adjacent only to two four-membered rings, we say that it is a phenylene chain. Due to their aromatic and antiaromatic rings, phenylenes exhibit unique physico-chemical properties. In Fig. 1 some examples of phenylene chains are presented. The unique phenylene chains for $n = 1$ and $n = 2$ are shown in Fig. 1. More generally, a phenylene chain with $n+1$ hexagons (see Fig. 2) can be regarded as a phenylene chain PH_n, with n hexagons to which a new terminal hexagon has been adjoined by a four-membered ring. But, for $n \geq 3$, the terminal hexagon can be attached in three ways, which results in the local arrangements we describe as PH^1_{n+1}, PH^2_{n+1}, and PH^3_{n+1} (see Fig. 3). A random phenylene chain $PH(n, p_1, p_2)$ with n hexagons is a phenylene chain obtained by stepwise addition of terminal hexagons. At each step k $(= 3, 4, ..., n)$ a random selection is made from one of the three possible constructions: (1) $PH_{k-1} \rightarrow PH^1_k$, with probability p_1, (2) $PH_{k-1} \rightarrow PH^2_k$, with probability p_2, or (3) $PH_{k-1} \rightarrow PH^3_k$, with probability $q = 1 - p_1 - p_2$. We assume that the probabilities p_1 and p_2 are constants, invariant to the step parameter k. That is, the process described is a zeroth-order Markov process.

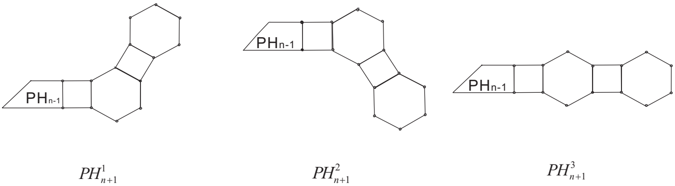

Fig. 3: The three types of local arrangements in phenylene chains

By eliminating, "squeezing out", the squares from a phenylene, a catacondensed hexagonal system (which may be jammed) is obtained, called the hexagonal squeeze of the respective phenylene (see Fig.4). Clearly, there is a one-to-one correspondence between a phenylene (PH) and its hexagonal squeeze (HS). Both possess the same number of hexagons. The respective hexagonal squeeze of a random phenylene chain $PH(n, p_1, p_2)$ is a random hexagonal chain, and we denote it by $HS(n, p_1, p_2)$.

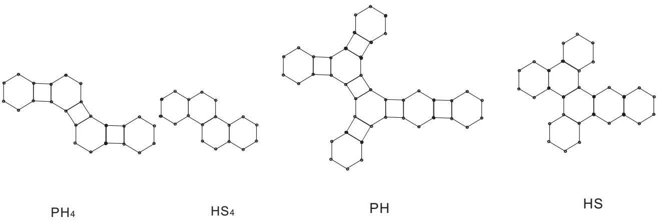

Fig. 4: Phenylenes and the corresponding hexagonal squeezes

In this paper we obtain an explicit analytical expression for the expected value of the Wiener index of a random phenylene chain $PH(n, p_1, p_2)$ and a simple exact formula for the expected value of the number of perfect matchings in a random phenylene chain $PH(n, p_1, p_2)$, respectively. Analogous results for a random hexagonal chain $HS(n, p_1, p_2)$ have been obtained by Gutman, Kennedy and Quintas in [3, 4, 6].

2 Wiener index of random phenylene chains

The Wiener index of a graph G, denoted by $W(G)$, is defined as the sum of distances between all pairs of vertices in G:

$$W(G) = \sum_{\{u,v\}\subseteq V(G)} d_G(u,v) = \frac{1}{2}\sum_{v\in V(G)} d_G(v),$$

where $d_G(u,v)$ is the distance between vertices u and v in graph G, and $d_G(v)$ is the sum of all the distances between vertex v and the other vertices in G. In [4], Gutman et al. obtained an explicit analytical expression for the expected value of the Wiener number of a random hexagonal chain with n hexagons (see also[5]).

Theorem 2.1[4] *If $n \geq 4$, then we have*

$$W(HS(n,p_1,p_2)) = 4n^3 + 16n^2 + 6n + 1 + \frac{4}{3}q(n^3 - 3n^2 + 2n) - \frac{4}{3}(p_1 - p_2)^2 F(n,q), \quad (1)$$

where $q = 1 - p_1 - p_2$ and

$$F(n,q) = \sum_{k=1}^{n-3} k(k+1)(k+2)q^{n-3-k}.$$

The inner dual ID of a phenylene (and of its hexagonal squeeze) is a tree, the vertices of which correspond to the hexagons, and two vertices are adjacent if the respective two hexagons in its hexagonal squeeze are first neighbors. The following theorem gives a relation between the W-values of a phenylene, its hexagonal squeeze and its inner dual.

Theorem 2.2[10] *Let PH be a phenylene containing n hexagons and let HS and ID be the hexagonal squeeze and inner dual corresponding to PH. Then their Wiener indices are related as*

$$W(PH) = \frac{9}{4}[W(HS) + 16W(ID) - (4n+1)(2n+1)]. \quad (2)$$

If PH is a phenylene chain with n hexagons, then ID is a path graph P_n with n vertices and it is not difficult to calculate that

$$W(P_n) = \frac{1}{6}n^3 - \frac{1}{6}n.$$

By Theorem 2.1 and 2.2, we obtain an expression for the Wiener index of a random phenylene chain $PH(n,p_1,p_2)$.

Theorem 2.3 *For $n \geq 4$, we have*

$$E(W(PH(n,p_1,p_2))) = 15n^3 + 18n^2 - 6n + 3q(n^3 - 3n^2 + 2n) - 3(p_1 - p_2)^2 F(n,q), \quad (3)$$

where $q = 1 - p_1 - p_2$ *and*

$$F(n,q) = \sum_{k=1}^{n-3} k(k+1)(k+2)q^{n-3-k}.$$

Just as discussed in [4], because $F(n,q)$ is not, in the general case, a polynomial in n, neither is $E(W(PH(n,p_1,p_2)))$. However, for some special cases $E(W(PH(n,p_1,p_2)))$ is a polynomial in n. If $p_1 = p_2$, for $n \geq 4$ we have

$$E(W(PH(n,p_1,p_2))) = 15n^3 + 18n^2 - 6n + 3q(n^3 - 3n^2 + 2n), \tag{4}$$

which is cubic in n and linear in q. Eq. (4) includes the case of linear chains, $p_1 = p_2 = 0$, $q = 1$: the Wiener numbers of the linear chain is $W(L_n) = 18n^3 + 9n^2$. If $p_1 = p_2 = 1/3$, for $n \geq 4$ we have $E(W(PH(n,p_1,p_2))) = 16n^3 + 15n^2 - 4n$, which is the average value of the Wiener indices of all the phenylene chains with n hexagons. If $p_1 + p_2 = 1$, then $q = 0$. Eq. (3) yields for $n \geq 4$

$$E(W(PH(n,p_1,p_2))) = 15n^3 + 18n^2 - 6n - 3(p_1 - p_2)^2(n-3)(n-2)(n-1), \tag{5}$$

which also is cubic in n. In the special case where either $p_1 = 1$ or $p_2 = 1$, eq. (5) yields the Wiener index of the helical chain:

$$W(H_n) = 12n^3 + 36n^2 - 39n + 18.$$

For if $q \neq 1$, then $\lim_{n\to\infty} F(n,q)/n^3 = 1/(1-q)$, so we have that

$$E(W(PH(n,p_1,p_2))) \sim [15 + 3q - 3(p_1 - p_2)^2/(1-q)]n^3,$$

as n tends to infinity. Hence, for $n \geq 4$, if either $p_1 = p_2$, then $E(W(PH(n,p_1,p_2)))$ is a cubic polynomial in n; while if (ii) $p_1 \neq p_2$, then $E(W(PH(n,p_1,p_2)))$ is not a cubic polynomial in n. However, in all cases, $E(W(PH(n,p_1,p_2)))$ is asymptotic to a cubic in n as $n \to \infty$.

3 Perfect matchings in random phenylene chains

A perfect matching or 1-factor of a graph G is a set of pairwise disjoint edges of G that cover all vertices of G. Let M_{n,p_1,p_2} be the number of perfect matchings of $PH(n,p_1,p_2)$. Then M_{n,p_1,p_2} is a random variable. Denote the expected value of M_{n,p_1,p_2} by $E(M_{n,p_1,p_2})$.

Lemma 3.1 *For* $n \geq 3$, *we have*

$$E(M_{n,p_1,p_2}) = (3-q)E(M_{n-1,p_1,p_2}) + (-1+2q)E(M_{n-2,p_1,p_2}). \tag{6}$$

Proof: It is not difficult to check that

$$M(PH_n^2) = M(PH_n^3) = 3M(PH_{n-1}) - M(PH_{n-2}), \tag{7}$$

$$M(PH_n^1)) = 2M(PH_{n-1}) + M(PH_{n-2}). \tag{8}$$

So

$$\begin{aligned} E(M_{n,p_1,p_2}) &= (1-q)\,(3E(M_{n-1,p_1,p_2}) - E(M_{n-2,p_1,p_2})) \\ &+ \; q\,(2E(M_{n-1,p_1,p_2}) + E(M_{n-2,p_1,p_2})) \\ &= (3-q)E(M_{n-1,p_1,p_2}) + (-1+2q)E(M_{n-2,p_1,p_2}). \end{aligned}$$

Thus, we have

$$E(M_{n,p_1,p_2}) = (3-q)E(M_{n-1,p_1,p_2}) + (-1+2q)E(M_{n-2,p_1,p_2}). \qquad \square$$

Eq. (6) or Eqs. (7) and (8) imply that M_{n,p_1,p_2} just depends on $q = 1 - p_1 - p_2$. In [3, 7, 8], it is suggested that the function $E(M_{n,p_1,p_2})$ has interest in chemistry, especially concerning its asymptotic behavior with respect to n. The recurrence relation obtained in Lemma 3.1 enables us to derive an explicit expression for this function. This is given in the following theorem.

Theorem 3.2 *For each $n \geq 0$, we have*

$$E(M_{n+1,p_1,p_2}) = \frac{5-2s}{r-s}r^n + \frac{2r-5}{r-s}s^n,$$

where $r = (3 - q + \sqrt{q^2+2q+5})/2,\ s = (3 - q - \sqrt{q^2+2q+5})/2.$

Proof: Let $a_n = E(M_{n+1,p_1,p_2})$, with $n > 0$, so that $a_0 = 2,\ a_1 = 5$, and by Lemma 3.1, we have that for $n \geq 2$,

$$a_n = (3-q)a_{n-1} + (-1+2q)a_{n-2}.$$

The characteristic equation of the recurrence relation is

$$x^2 - (3-q)x - (-1+2q) = 0,$$

and the characteristic roots are

$$r = (3 - q + \sqrt{q^2+2q+5})/2,\ s = (3 - q - \sqrt{q^2+2q+5})/2.$$

For the two roots are distinct, so we have that

$$a_n = \alpha r^n + \beta s^n.$$

The boundary conditions $a_0 = 2$ and $a_1 = 5$ imply that

$$\alpha + \beta = 2, \ \alpha r + \beta s = 5.$$

So that

$$\alpha = \frac{5-2s}{r-s}, \ \beta = \frac{2r-5}{r-s}.$$

We complete the proof of the theorem. □

The following corollary to Theorem 3.2 gives the values of the limit of $E(M_{n,p_1,p_2})/E(M_{n-1,p_1,p_2})$ and the limit of $\sqrt[n]{E(M_{n,p_1,p_2})}$, as $n \to \infty$.

Corollary 3.3 $\lim_{n\to\infty} E(M_{n+1,p_1,p_2})/E(M_{n,p_1,p_2}) = \lim_{n\to\infty} \sqrt[n]{E(M_{n,p_1,p_2})} = (3-q+\sqrt{q^2+2q+5})/2$.

Proof: For $r > s$, so we have that

$$\begin{aligned} & \lim_{n\to\infty} E(M_{n+1,p_1,p_2})/E(M_{n,p_1,p_2}) \\ = & \lim_{n\to\infty} \left(\frac{5-2s}{r-s}r^n + \frac{2r-5}{r-s}s^n\right) / \left(\frac{5-2s}{r-s}r^{n-1} + \frac{2r-5}{r-s}s^{n-1}\right) \\ = & \lim_{n\to\infty} \left(\frac{5-2s}{r-s}r + \frac{2r-5}{r-s}s(s/r)^{n-1}\right) / \left(\frac{5-2s}{r-s} + \frac{2r-5}{r-s}(s/r)^{n-1}\right) \\ = & (3-q+\sqrt{q^2+2q+5})/2. \end{aligned}$$

$$\begin{aligned} & \lim_{n\to\infty} \sqrt[n]{E(M_{n,p_1,p_2})} \\ = & \lim_{n\to\infty} r^{\frac{n-1}{n}} \sqrt[n]{\frac{5-2s}{r-s} + \frac{2r-5}{r-s}(s/r)^{n-1}} \\ = & (3-q+\sqrt{q^2+2q+5})/2. \end{aligned}$$

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