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Hosoya Polynomials of Random Benzenoid Chains

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ABSTRACT Let G be a molecular graph with vertex set $V(G)$ and $d_G(u,v)$ be the topological distance between vertices u and v in G. The Hosoya polynomial $H(G,x)$ of G is a polynomial $\sum_{\{u,v\}\subseteq V(G)} x^{d_G(u,v)}$ in variable x. In this paper, we obtain an explicit analytical expression for the expected value of the Hosoya polynomial of a random benzenoid chain with n hexagons. Furthermore, as corollaries, the expected values of the well-known topological indices: Wiener index, hyper-Wiener index and Tratch–Stankevitch–Zefirov index of a random benzenoid chain with n hexagons can be obtained by simple mathematical calculations, which generates the results given by I. Gutman et al. [Wiener numbers of random benzenoid chains, *Chem. Phys. Lett.* **173** (1990) 403–408].

KEYWORDS Wiener index • random benzenoid chain • Hosoya polynomial • expected value • generating function.

1. INTRODUCTION

A molecular graph (or chemical graph) is a representation of the structural formula of a chemical compound in terms of graph theory. Specifically, a *molecular graph* is a simple graph whose vertices correspond to the atoms of the compound and edges correspond to chemical bonds. Note that hydrogen atoms are often omitted. For example, *benzenoid chains* are molecular graphs of unbranched catacondensed benzenoid hydrocarbons. *Molecular structure descriptors* (or *topological indices*) of molecular graphs are graph

invariants and are used for Quantitative Structure-Activity Relationship (QSAR) and Quantitative Structure-Property Relationship (QSPR) studies, which mainly focus on structure-dependent chemical behaviours of molecules [4, 18].

Let G be a molecular graph with vertex set $V(G)$, $d_G(u,v)$ be the *topological distance* (or *distance* for short) between vertices u and v in G, i.e., the length of a shortest path connecting u and v in G. The subscript is omitted when there is no risk of confusion. The *Hosoya polynomial*} in variable x of G, introduced by Hosoya [12], is defined as $H(G,x)=\sum_{\{u,v\}\subseteq V(G)} x^{d_G(u,v)}$, where the sum is taken over all unordered pairs of (not necessarily distinct) vertices in G. Hence the polynomial contains the number of vertices as the constant term.

The Hosoya polynomial not only contains more information concerning distance in the molecular graph than any of the hither to proposed distance-based molecular structure descriptors, which were extensively studied in chemical graph theory, see for instance the surveys [16, 17], but also deduces some of them. For example, Wiener index $W(G)$ of a molecular graph G [20], the oldest and most well-studied molecular structure descriptor so far, is equal to the first derivative of the Hosoya polynomial in $x=1$, i.e.,

$$W(G)=\frac{d}{d_x}H(G,x)\Big|_{x=1}. \tag{1}$$

The chemical applications and mathematical properties of $W(G)$ are well documented [5, 6, 9, 10]. Moreover, hyper-Wiener index $WW(G)$ [14], Tratch–Stankevitch–Zefirov index $TSZ(G)$ [19] can be deduced from $H(G,x)$ as follows:

$$WW(G)=\frac{1}{2}\frac{d^2}{dx^2}xH(G,x)\Big|_{x=1}, \tag{2}$$

$$TSZ(G)=\frac{1}{3!}\frac{d^3}{dx^3}x^2H(G,x)\Big|_{x=1}. \tag{3}$$

Two classes of general molecular structure descriptors

$$\frac{1}{k!}\frac{d^k}{dx^k}x^{k-1}H(G,x)\Big|_{x=1} \text{ and } \frac{1}{k!}\frac{d^k}{dx^k}H(G,x)\Big|_{x=1}$$

for positive integers k were also studied in Refs. [2, 15]. On the other hand, recently Brückler etc. [2] proposed a new class of distance-based molecular structure descriptors: Q-indices, which can reflect the fact that any kind of interaction between physical objects (in particular, between atoms in a molecule) decrease with increasing distance, and showed that Q-indices are equal to the Hosoya polynomial. So the Hosoya polynomial and the

quantities derived from it will play a significant role in QSAR and QSPR researches, and abundant literature appeared on this topic [3, 8,21, 22, 23].

Let B_{n+1} denote a benzenoid chain with n+1 hexagons ($n \geq 0$). There are obviously unique benzenoid chains B_{n+1} for $n = 0,1$. More generally, a benzenoid chain B_{n+1} can be regarded as a benzenoid chain B_n to which a new terminal hexagon u_n, y_1, y_2, y_3, y_4, v_n has been adjoined. However, when $n \geq 2$, the terminal hexagon can be attached in three ways, resulting in the local arrangements we describe as B^1_{n+1}, B^2_{n+1}, B^3_{n+1}, according to the related position of the terminal hexagon shown in Figure 1.

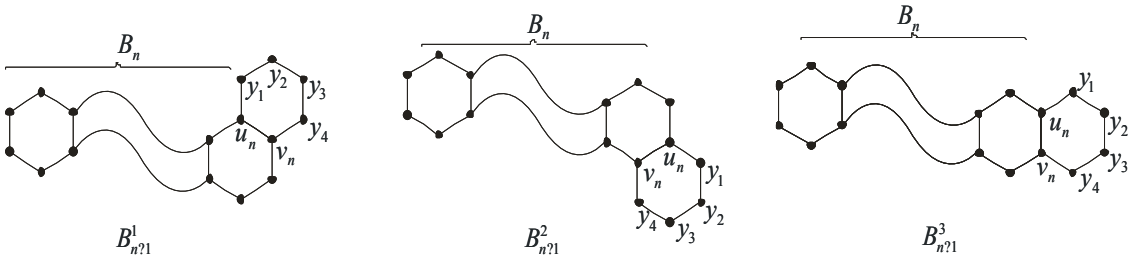

Figure 1. The three types of local arrangements in benzenoid chains B_{n+1}

A *random benzenoid chain*, R_{n+1} with $n+1$ hexagons, is a benzenoid chain obtained by stepwise additions of terminal hexagons. As the initial steps, $R_1 = B_1$, $R_2 = B_2$, and for each step k ($2 \leq k \leq n$) a random selection is made from one of the three possible constructions:

$B_k \rightarrow B^1_{k+1}$, with probability p_1,

$B_k \rightarrow B^2_{k+1}$, with probability p_2 or

$B_k \rightarrow B^3_{k+1}$, with probability q=1- p_1- p_2.

We assume the probabilities p_1 and p_2 are constants, invariant to the step parameter k. That is, the process described is a Markov chain of order zero with a state space consisting of three states [7].

In the present paper, we calculate the expected value of the Hosoya polynomial of a random benzenoid chain R_n and give an explicit analytical expression by using the mathematical method: generating function. As corollaries, formulae for the expected values of some topological indices deduced from the expression can be obtained by using simple mathematical operators.

2. RECURSION RELATIONS OF HOSOYA POLYNOMIALS OF RANDOM BENZENOID CHAINS

Let G be a connected graph with vertex set $V(G)$. For the simplicity, we define one notation as follows: for a vertex $u \in V(G)$,

$$H_G(u;x) = \sum_{v \in V(G)} x^{d(u,v)},$$

i.e., the contribution of the vertex u to the Hosoya polynomial $H(G,x)$ of G. As described above in the previous section, a benzenoid chain B_{n+1} is obtained by attaching to a benzenoid chain B_n a terminal hexagon consisting of vertices u_n, y_1, y_2, y_3, y_4, v_n (see Figure 1). For this construction the following relations are easily obtained [10]:

$$H_{B_{n+1}}(y_1;x) = xH_{B_n}(u_n;x) + x^3 + x^2 + x + 1 \quad (4a)$$

$$H_{B_{n+1}}(y_2;x) = x^2 H_{B_n}(u_n;x) + x^2 + 2x + 1, \quad (4b)$$

$$H_{B_{n+1}}(y_3;x) = x^2 H_{B_n}(v_n;x) + x^2 + 2x + 1, \quad (4c)$$

$$H_{B_{n+1}}(y_4;x) = xH_{B_n}(v_n;x) + x^3 + x^2 + x + 1, \quad (4d)$$

and

$$H(B_{n+1},x) = H(B_n,x) + \sum_{i=1}^{4} H_{B_{n+1}}(y_i;x) - (x^3 + 2x^2 + 3x). \quad (5)$$

Note that the last term on the right-hand side of Eq. (5) appears because the contribution of pairs of vertices y_i and y_j $(1 \le i < j \le 4)$ to $H(B_{n+1},x)$ are calculated twice in the second term on the right-hand side of Eq. (5). Substituting Eq. (4) for Eq.(5), we get

$$H(B_{n+1},x) = H(B_n,x) + x(x+1)(H_{B_n}(u_n;x) + H_{B_n}(v_n;x)) + x^3 + 2x^2 + 3x + 4. \quad (6)$$

In fact, the equations discussed above associated with a concrete benzenoid chain are valid for a random benzenoid chain, i.e., Eqs. (4)-(6) still hold when we simultaneously replace B_{n+1} for $R_{n+1}$and B_n for R_n.

In the following we consider contributions of u_{n+1} and v_{n+1} to $H(B_{n+1},x)$ according to the positions of u_{n+1} and v_{n+1}. There are three cases to consider:

Case 1. $B_{n+1} \rightarrow B_{n+2}^1$. In this case, $u_{n+1} = y_1$ and $v_{n+1}=y_2=$. Consequently, $H_{B_{n+1}}(u_{n+1};x) = H_{B_{n+1}}(y_1;x)$ and $H_{B_{n+1}}(v_{n+1};x) = H_{B_{n+1}}(y_2;x)$, which are given by Eqs. (4a) and (4b), respectively.

Case 2. $B_{n+1} \rightarrow B_{n+2}^2$. In this case, $u_{n+1} = y_3$ and $v_{n+1} = y_4$. Consequently, $H_{B_{n+1}}(u_{n+1};x) = H_{B_{n+1}}(y_3;x)$ and $H_{B_{n+1}}(v_{n+1};x) = H_{B_{n+1}}(y_4;x),$, which are given by Eqs. (4c) and (4d), respectively.

Case 3. $B_{n+1} \rightarrow B_{n+2}^3$. In this case, u_{n+1}=y_2 and $v_{n+1} = y_3$. Consequently, $H_{B_{n+1}}(u_{n+1};x) = H_{B_{n+1}}(y_2;x),$ and $H_{B_{n+1}}(v_{n+1};x) = H_{B_{n+1}}(y_3;x),$, which are given by Eqs. (4b) and (4c), respectively.

For a random benzenoid chain R_{n+1}, $H(R_{n+1},x)$, $H_{R_{n+1}}(u_{n+1};x)$ and $H_{R_{n+1}}(v_{n+1};x)$ are random variables and we denote their expected values by $H_{n+1}(x), U_{n+1}(x)$ and $V_{n+1}(x)$, respectively, i.e.,

$$H_{n+1}(x) = E(H(R_{n+1},x)), U_{n+1}(x) = E(H_{R_{n+1}}(u_{n+1};x)),$$
$$V_{n+1}(x) = E(H_{R_{n+1}}(v_{n+1};x)).$$

Since the above three cases occur in random benzenoid chains with probabilities p_1, p_2 and $1-p_1-p_2$, respectively, by the definition of the expected value we immediately obtain

$$U_{n+1}(x) = p_1 H_{R_{n+1}}(y_1;x) + p_2 H_{R_{n+1}}(y_3;x) + qH_{R_{n+1}}(y_2;x), \quad (7a)$$
$$V_{n+1}(x) = p_1 H_{R_{n+1}}(y_2;x) + p_2 H_{R_{n+1}}(y_4;x) + qH_{R_{n+1}}(y_3;x), \quad (7b)$$

Substituting the corresponding analogues associated with random benzenoid chains R_n and R_{n+1} to Eq. (4) for Eq. (7), we get

$$U_{n+1}(x) = (p_1 x + qx^2) H_{R_n}(u_n;x) + p_2 x^2 H_{R_n}(v_n;x) + (x^3 - x)p_1 + (x+1)^2, \quad (8a)$$
$$V_{n+1}(x) = (p_2 x + qx^2) H_{R_n}(v_n;x) + p_1 x^2 H_{R_n}(u_n;x) + (x^3 - x)p_2 + (x+1)^2, \quad (8b)$$

By applying the expectation operator to Eq. (8), and noting that $E(U_{n+1}(x)) = U_{n+1}(x)$ and $E(V_{n+1}(x)) = V_{n+1}(x)$, we obtain

$$U_{n+1}(x) = (p_1 x + qx^2) U_n(x) + p_2 x^2 V_n(x) + (x^3 - x)p_1 + (x+1)^2 , \quad (9a)$$
$$V_{n+1}(x) = (p_2 x + qx^2) V_n(x) + p_1 x^2 U_n(x) + (x^3 - x)P_2 + (x+1)^2 \quad (9b)$$

A recursion relation for the expected value of the Hosoya polynomial of a random benzenoid chain can be obtained from Eq. (6) by using R_k in place of B_k (k=n, n+1) and by using the expectation operator:

$$H_{n+1}(x) = H_n(x) + (x + x^2)(U_n(x) + V_n(x)) + x^3 + 2x^2 + 3x + 4. \quad (10)$$

The system of recursion equations (9) and (10) holds for $n \geq 0$, and has boundary conditions:

$$H_0(x) = x+2,\ U_0(x) = x+1,\ \ V_0(x) = x+1. \tag{11}$$

3. SOLUTION FOR THE SYSTEM OF RECURSION EQUATIONS

To solve the recursion equations (9) and (10), we use the method of the generating function [1]. First define the following generating functions in variable t. Let

$$U(t) = \sum_{n\geq 0} U_n(x)t^n\ ,\ \ V(t) = \sum_{n\geq 0} V_n(x)t^n\ ,\ \ H(t) = \sum_{n\geq 0} H_n(x)t^n\ ,\qquad 0 < t < 1.$$

From Eqs. (9)–(11), we get relations of their generating functions as follows:

$$U(t) = t(p_1 x + qx^2)U(t) + p_2 t x^2 V(t) + \frac{t(x^3 - x)p_1 + t(x+1)^2}{1-t} + x + 1 \tag{12a}$$

$$V(t) = t(p_2 x + qx^2)V(t) + p_1 t x^2 U(t) + \frac{t(x^3 - x)p_2 + t(x+1)^2}{1-t} + x + 1, \tag{12b}$$

$$H(t) = t\,H(t) + (x + x^2)t(U(t) + V(t)) + \frac{t(x^3 + 2x^2 + 3x + 4)}{1-t} + x + 2 \tag{12c}$$

As Eqs. (12a) and (12b) comprise a system of two linear equations in two variables $U(t)$ and $V(t)$, a straight forward calculation results in

$$U(t) = \frac{p_1 x(x+1)^2}{(x-1)(1-xt)} + \frac{(1-p_1)x(x+1)}{(x-1)(1-x^2 t)} + \frac{(p_1 x^2 + 1)(x+1)}{(1-x)(1-t)} + \frac{p_2(p_1 - p_2)t^2 x^3 (x+1)^2}{(1-t)(1-qt)}\left(\frac{1}{1-x^2 t} - \frac{1}{1-xt}\right), \tag{13a}$$

$$V(t) = \frac{p_2 x(x+1)^2}{(x-1)(1-xt)} + \frac{(1-p_2)x(x+1)}{(x-1)(1-x^2 t)} + \frac{(p_2 x^2 + 1)(x+1)}{(1-x)(1-t)} + \frac{p_1(p_2 - p_1)t^2 x^3 (x+1)^2}{(1-t)(1-qt)}\left(\frac{1}{1-x^2 t} - \frac{1}{1-xt}\right). \tag{13b}$$

Substituting Eq. (13) for Eq. (12) and then rearranging, we can easily get:

$$\begin{aligned} H(t) = {} & \frac{x+2}{1-t} + \frac{(x^3 + 2x^2 + 3x + 4)t}{(1-t)^2} + \frac{(1-q)x^2(x+1)^3 t}{(x-1)(1-t)(1-xt)} + \frac{(1+q)x^2(x+1)^2 t}{(x-1)(1-t)(1-x^2 t)} \\ & + \frac{(x+1)^2((1-q)x^3 + 2x)t}{(1-x)(1-t)^2} - \frac{(p_1 - p_2)^2 x^4 (x+1)^3 t^3}{(1-at)(1-t)^2}\left(\frac{1}{1-x^2 t} - \frac{1}{1-xt}\right). \end{aligned} \tag{14}$$

Applying two special cases of Newton's generalized binomial theorem

$$\frac{1}{1-y}=\sum_{n=0}^{+\infty}y^n \quad \text{and} \quad \frac{1}{(1-y)^2}=\sum_{n=0}^{+\infty}(n+1)\,y^n$$

to Eq. (14) and then rearranging it, we get

$$\begin{aligned}H(t)&=x+2+3(x^3+2x^2+2x+2)t+(2x^5+6x^4+12x^3+14x^2+11x+10)t^2+\\&\sum_{n=3}^{+\infty}[x+2+n(x^3+2x^2+3x+4)+\frac{n(x+1)^2((1-q)x^3+2x)}{1-x}+\frac{(1-q)x^2(x+1)^3(x^n-1)}{(x-1)^2}\\&+\frac{(1+q)x^2(x+1)(x^{2n}-1)}{(x-1)^2}-(p_1-p_2)^2x^4(x+1)^3\sum_{l=0}^{n-3}q^l(\sum_{k=0}^{n-3-l}(n-l-k-2)(x^{2k}-x^k))]t^n.\end{aligned} \quad .. \quad (15)$$

4. RESULTS AND DISCUSSION

From Eq. (15), we have the following main theorem.

Theorem 4.1. Let $H_n(x)$ be the expected value of the Hosoya polynomial of a random benzenoid chain with n hexagons. Then

$$H_1(x)=3x^3+6x^2+6x+6;$$

$$H_2(x)=2x^5+6x^4+12x^3+14x^2+11x+10;$$

and when and $n\geq 3$,

$$\begin{aligned}H_n(x)&=x+2+n(x^3+2x^2+3x+4)+\frac{n(x+1)^2((1-q)x^3+2x)}{1-x}+\\&\frac{(1-q)x^2(x+1)(x^{2n}-1)}{(x-1)^2}-(p_1-p_2)^2x^4(x+1)^3\sum_{l=0}^{n-3}q^l(\sum_{k=0}^{n-3-l}(n-l-k-2)(x^{2k}-x^k)).\end{aligned}$$

We can obtain some corollaries by taking parameters as special values or Eqs. (1)–(3). When q =1 (in this case p_1 = p_2 = 0), a random benezoid chain is definitely a linear benzenoid chain, i.e., a benzoid chain without no turns. So from Theorem 4.1 we have

Corollary 4.2. [21] Let G be a benzenoid chain with n hexagons. If G has no turns, then the Hosoya polynomial of G is

$$H(G,x)=x+2+\frac{n(x^2-x-4)(x^2+1)}{x-1}+\frac{2x^2(x+1)(x^{2n}-1)}{(x-1)^2}.$$

If p_1=1 or p_2=2, a random benzenoid chain with n hexagons is definitely a helicene with n hexagons, then we get

Corollary 4.3. [21] Let G be a helicene with n hexagons. Then the Hosoya polynomial of G is

$$H(G,x) = x+2+\frac{x^2(x+1)((x+1)^3x^n-(n-1)x^5-x^4+(n-3)x^3-x^2-2x-2)}{(x-1)^2} + \frac{n(x^5+x^4+2x^3+3x^2+x+4)}{1-x}$$

In addition, from Eqs. (1)–(3), we can obtain the expected values of some molecular structure descriptors from Theorem 4.1.

Corollary 4.4. [13] The expected value W_n of the Wiener index of a random benzenoid chain with n hexagons is

$$W_n = 4n^3+16n^2+6n+1+\frac{4}{3}q(n^3-3n^2+2n)-\frac{4}{3}(p_1-p_2)^2\sum_{l=0}^{n-3}l(l+1)(l+2)q^{n-3-l}$$

Corollary 4.5. The expected value WW_n of the hyper-Wiener index of a random benzenoid chain with n hexagons is

$$WW_n = \frac{1}{3}[3+(11+26q)n+(79-33q)n^2+(28+4q)n^3+(5+3q)n^4]- (p_1-p_2)^2\sum_{l=0}^{n-3}l(l+1)(l+2)(l+9)q^{n-3-l}$$

Corollary 4.6. The expected value TSZ_n of the Tratch-Stankevitch-Zefirov index of a random benzenoid chain with n hexagons is

$$TSZ_n = \frac{1}{30}[30+(-58+566q)n+(1185-635q)n^2+(490-10q)n^3+(135+65q)n^4 + (18+14q)n^5-(p_1-p_2)^2\sum_{l=0}^{n-3}l(l+1)(l+2)(14(l+3)^2+139(l+3)+510)q^{n-3-l}$$

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