

Topological Properties of Benzenoid Systems. II. Hosoya Index of Molecules Containing a Polyacene Fragment

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Recursion relations and explicit formulas are obtained for the Hosoya index (Z) of molecules containing a linear chain of hexagons. Our main concern is the dependence of Z on h , the length of the linear chain. The asymptotic behaviour of Z for large values of h is established.

1. Introduction

The theory of the Hosoya topological index [1] is nowadays well elaborated. Numerous mathematical properties of Z have been established [2]; for recent work along these lines see [3–7]. Among the unsolved problems in this field one should mention that very little is known about the behaviour of Z in the case when the corresponding molecule is very large (or more precisely: when its size tends to infinity). In the present paper we arrive at an analytical solution of this problem for a certain class of benzenoid hydrocarbons.

Further, explicit combinatorial expressions for Z are known only for a limited number of homologous series of molecules (e.g. n -alkanes [1], cycloalkanes [8]). The results obtained in the present paper represent the first such formulas for homologous series of polycyclic hydrocarbons.

The Hosoya index is equal to the total number of ways in which one can choose non-touching carbon-carbon bonds in a hydrocarbon molecule. If $m(G, k)$ denotes the number of k -matchings (i.e. the selections of k independent edges) in the molecular graph G [1, 2, 9], then

$$Z = Z(G) = \sum_{k=0}^m m(G, k).$$

Conventionally, $m(G, 0) = 1$ for all graphs G , and $m(G, 1) = m$ = number of edges of G .

The basic properties of the Hosoya index are [2]:

$$Z(G) = Z(G - e_{pq}) + Z(G - p - q) \quad (1)$$

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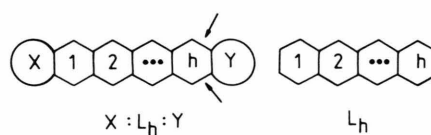
and

$$Z(G_1 \cup G_2) = Z(G_1) Z(G_2). \quad (2)$$

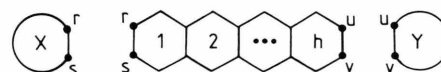
In the above formulas e_{pq} is an (arbitrary) edge of G , connecting the vertices p and q ; $G_1 \cup G_2$ symbolizes a graph composed of two disconnected components G_1 and G_2 .

The Main Results

In the present paper we examine the Hosoya index of the molecule $X : L_h : Y$ which is obtained by attaching two (arbitrary) terminal groups X and Y to the polyacene L_h containing h hexagons.



The system $X : L_h : Y$ can be viewed as being obtained from X , L_h and Y by coalescing the four pairs of equally labeled vertices:



Let an auxiliary topological function Z^* be defined as

$$Z^*(X : L_h : Y) = Z(X : L_h : Y) + F$$

where

$$F = 0.5 [Z(X - r) - Z(X - s)] \cdot [Z(Y - u) - Z(Y - v)]. \quad (3)$$

Here $X - r$ denotes the subgraph obtained by deletion of the vertex r from X ; the subgraphs $X - s$, $Y - u$, $Y - v$ are defined analogously.

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Then the following relation is obeyed:

$$Z^*(X:L_h:Y) = 9Z^*(X:L_{h-1}:Y) - 7Z^*(X:L_{h-2}:Y) + Z^*(X:L_{h-3}:Y). \quad (4)$$

If either $Z(X-r) = Z(X-s)$ or $Z(Y-u) = Z(Y-v)$ or both, then $F = 0$ and (4) reduces to

$$Z(X:L_h:Y) = 9Z(X:L_{h-1}:Y) - 7Z(X:L_{h-2}:Y) + Z(X:L_{h-3}:Y). \quad (5)$$

In particular, (5) holds if either X possesses a plane of symmetry going through the edge e_{rs} or Y has a plane of symmetry going through e_{uv} .

Let further

$$x = (1/3) \arccos [(7803/8000)^{1/2}]$$

and

$$\begin{aligned} t_1 &= 3 + (80/3)^{1/2} \cos x, \\ t_2 &= 3 + (80/3)^{1/2} \cos(x - 2\pi/3), \\ t_3 &= 3 + (80/3)^{1/2} \cos(x + 2\pi/3). \end{aligned}$$

Then

$$Z(X:L_h:Y) = a_1 t_1^h + a_2 t_2^h + a_3 t_3^h - F, \quad (6)$$

where a_1 , a_2 and a_3 are constants depending on the nature of X and Y (see Table 1). A special case of (6) is

$$Z(L_h) = 2.23 t_1^h - 0.24 t_2^h + 0.02 t_3^h.$$

From (6) it is evident that $Z(X:L_h:Y)$ exponentially increases with increasing h . In particular,

$$\lim_{h \rightarrow \infty} h^{-1} \log Z(X:L_h:Y) = \log t_1$$

irrespective of the nature of the terminal groups X and Y . Thus for the class of polycyclic hydrocarbons considered we have an analytical expression for the asymptotic behaviour of Z in the case of very large molecules.

Auxiliary Results

In order to deduce the results formulated in the preceding section we shall first examine the molecular graph $X:L_{h+1}$, having only one terminal fragment:

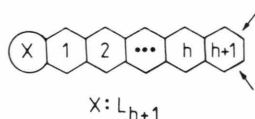
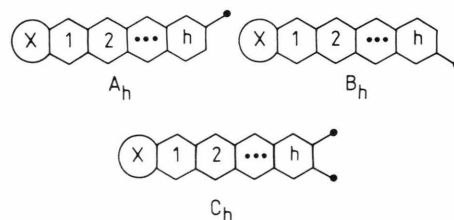


Table 1. Numerical data for (6).

Molecules	a_1	a_2	a_3	F
I	2.22599	-0.24463	0.01864	0
II	18.56504	-5.09578	-0.46926	0
III	154.61433	-41.83931	-3.77502	0
IV	151.69470	-43.53523	-4.15946	0
V	156.31304	-62.71583	-4.59721	0
VI	154.83468	-106.14609	11.81167	12.5
VII	154.83468	-106.14609	11.81167	-12.5
VIII	10976.58083	-16078.19855	1133.63561	0

Three additional auxiliary systems will be needed, namely A_h , B_h and C_h :



Now, pursuing an idea from [10, 11] we apply (1) to the edges of $X:L_{h+1}$, indicated by arrows, and then use (2). This straightforwardly results in

$$Z(X:L_{h+1}) = Z(X:L_h) + Z(A_h) + Z(B_h) + 2Z(C_h). \quad (7)$$

In a fully analogous manner,

$$Z(A_{h+1}) = Z(X:L_h) + Z(A_h) + 2Z(B_h) + 3Z(C_h), \quad (8)$$

$$Z(B_{h+1}) = Z(X:L_h) + 2Z(A_h) + Z(B_h) + 3Z(C_h), \quad (9)$$

$$Z(C_{h+1}) = Z(X:L_h) + 2Z(A_h) + 2Z(B_h) + 5Z(C_h), \quad (10)$$

The multipliers 2, 3, and 5 in (7)–(10) are, in fact, the Hosoya indices of the paths with 2, 3, and 4 vertices, respectively.

Whence we arrived at a system of four coupled recurrence relations in four unknowns. It can be solved according to the following reasoning. From $3 \times (7) - (8) - (9)$,

$$Z(A_h) + Z(B_h) = 3Z(X:L_h) - Z(X:L_{h-1}). \quad (11)$$

$$\text{From (8) + (9) and (11),} \quad (12)$$

$$Z(C_h) = 0.5[Z(X:L_{h+1}) - 4Z(X:L_h) + Z(X:L_{h-1})].$$

Substituting (11) and (12) back into (10) one obtains

$$Z(X:L_h) = 9Z(X:L_{h-1}) - 7Z(X:L_{h-2}) + Z(X:L_{h-3}). \quad (13)$$

Bearing in mind that the r.h.s. of (12) is a linear combination of $Z(L_i)$'s, (13) implies

$$Z(C_h) = 9Z(C_{h-1}) - 7Z(C_{h-2}) + Z(C_{h-3}). \quad (14)$$

From (8)–(9),

$$Z(A_h) - Z(B_h) = Z(A_{h-1}) - Z(B_{h-1})$$

and, consequently, $Z(A_h) - Z(B_h)$ is independent of h . It is now easy to show that

$$Z(A_h) - Z(B_h) = Z(X-r) - Z(X-s). \quad (15)$$

From (11) and (15),

$$Z(A_h) = [3Z(X:L_h) - Z(X:L_{h-1})]/2 + [Z(X-r) - Z(X-s)]/2, \quad (16)$$

$$Z(B_h) = [3Z(X:L_h) - Z(X:L_{h-1})]/2 - [Z(X-r) - Z(X-s)]/2. \quad (17)$$

Using (12), (15) and (16) one can directly check that the below two relations hold:

$$Z(A_h) = 9Z(A_{h-1}) - 7Z(A_{h-2}) + Z(A_{h-3}) - [Z(X-r) - Z(X-s)], \quad (18)$$

$$Z(B_h) = 9Z(B_{h-1}) - 7Z(B_{h-2}) + Z(B_{h-3}) + [Z(X-r) - Z(X-s)]. \quad (19)$$

Hence $Z(A_h)$ and $Z(B_h)$ conform to a recurrence relation of the type (13) only if $Z(X-r) = Z(X-s)$.

Proof of Formulas (4) and (6)

We are now prepared to deduce (4). In order to do this, apply (1) to the edges of $X:L_h:Y$ indicated by arrows and use (2). It immediately follows

$$\begin{aligned} Z(X:L_h:Y) &= Z(Y-u-v)Z(X:L_{h-1}) \\ &\quad + Z(Y-v)Z(A_{h-1}) + Z(Y-u) \\ &\quad \cdot Z(B_{h-1}) + Z(Y)Z(C_{h-1}). \end{aligned}$$

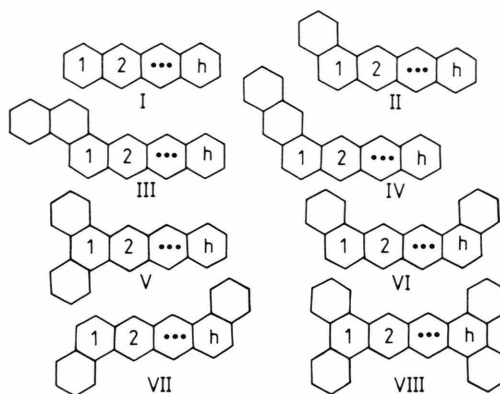


Fig. 1. Benzenoid systems for which explicit formulas for the Hosoya index are obtained (see Table 1).

Taking into account (13), (14), (18) and (19) one can verify the validity of

$$Z(X:L_h:Y) = 9Z(X:L_{h-1}:Y) - 7Z(X:L_{h-2}:Y) + Z(X:L_{h-3}:Y) + 2F,$$

where F is given by (3). The above relation is now easily transformed into (4).

Formula (6) is an immediate consequence of the recurrence relation (4) if one has in mind that t_1 , t_2 and t_3 are the solutions of the equation $t^3 = 9t^2 - 7t + 1$. Then (6) is just the general solution of (4) [12].

Numerical Work

The equation $t^3 = 9t^2 - 7t + 1$, associated with the recurrence relation $Z_h = 9Z_{h-1} - 7Z_{h-2} + Z_{h-3}$ has three real-valued solutions, viz.,

$$t_1 = 8.15685606, \quad t_2 = 0.65636267, \quad t_3 = 0.18678127.$$

The multipliers a_1 , a_2 and a_3 in (3) have been calculated for a number of homologous series of benzenoid systems, using the known values of the Hosoya index [13–15] for the three lowest members of each series. The homologous series considered are presented in Fig. 1 and the results obtained in Table 1. One should note that in Fig. 1 the hexagons are labeled in a somewhat different manner than in $X:L_h:Y$. This change in labeling, which is mathematically fully irrelevant, is convenient since then the multipliers a_1 , a_2 and a_3 attain smaller numerical values.

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