Novel *PI* indices of hexagonal chains

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*Dedicated to Professor Ivan Gutman, teacher, inspirer, friend and proprietor of graph theory
and topology*

"Problems don't hung on trees. Formulation of a good problem is often the most
important part of a (theoretical) research. New problems usually arise when you try
to solve old problems."
Ivan Gutman, June 27, 1995.

The Padmakar–Ivan (*PI*) index of hexagonal chains (i.e., the molecular graphs of unbranched
catacondensed benzenoid hydrocarbons) is examined. The index *PI* is a graph invariant de-
fined as the summation of the sums of edges of n_{eu} and n_{ev} over all the edges of connected
graph G, where n_{eu} is the number of edges of G lying closer to u than to v and n_{ev} is the
number of edges of G lying closer to v than to u. An efficient calculation of formula for *PI*
for hexagonal chains are put forward.

KEY WORDS: *PI* index, hexagonal chains, unbranched catacondensed benzenoid, topologi-
cal indices, polyphenylenes, zig-zag polyacenes

1. Introduction

It is well known that the chemical behaviour of a compound is dependent upon
the structure of the molecule. Quantitative structure-activity relationships (QSAR) stud-
ies [1] and quantitative strucure-property (QSPR) relationships [2] are active areas of
chemical research that focus on the nature of this dependency [3]. Regression analysis
[2], expert system [4] and other techniques are used to model the prediction of property
(activity) of molecules from their structural parameters.

The structure of a molecule could be represented in a variety of ways [5]. The
information on the chemical constitution of a molecule is conventionally represented by
a molecular graph [2]. Usually hydrogen-suppressed graphs are used.

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A number that is mathematically derived in an unambiguous manner from the molecular graph is called topological index. Evidently, topological index must be a graph invariant [2]. The first reported use of a topological index in chemistry was by Wiener [6] in the study of paraffin boiling points. Since then, in order to model various molecular properties (activities), a plethora of topological indices have been designed [2]. Such a proliferation is still going on and is becoming counter productive [7].

Recently, Gutman [8] and coworkers [9] have introduced a generalization of the Wiener index (*W*) for cyclic graphs called Szeged index (*Sz*). The main advantage of the Szeged index is that it is a modification of *W* for cyclic graphs; otherwise, it coincides with Wiener index. In an attempt to remove this lacuna in *Sz* index we now introduced another topological index *PI*. This index was conceived through the prolonged academic interactions with Professor Ivan Gutman and thus this new index is named as Padmakar–Ivan index and abbreviated as *PI* in the honour of Ivan Gutman.

The primary aim of present investigation is to introduce the method for the calculation of *PI*-index for hexagonal chains.

It is known for some time [2] that topological indices reflect mainly molecular size and shape, and only in a less extent they are sensitive to other structural features of the molecules. Therefore, by inter-correlation of topological indices one should not be surprized to find that a plethora of topological indices could be reduced to a small numbers of independent, mutually orthogonal (or almost orthogonal) topological indices [10–14].

2. Hexagonal chains

Hexagonal chains are exclusively composed of hexagons. Two hexagons have either one common edge (and are then said to be adjacent) or have no common vertices. No three hexagons share a common vertex. Each hexagon is adjacent to other hexagons with the exception of the terminal hexagons to which a single hexagon is adjacent. The hexagonal chains have exactly two terminal hexagons. Hexagonal chains include the molecular graphs (*G*) of the unbranched catacondensed benzenoid hydrocarbons [14].

The set of all hexagonal chains with h hexagons is denoted by C_h. It is easy to see that every G from C_h has $pG = 4h + 2$ verites and $qG = 5h + 1$ edges.

Hexagonal chains are of great importance for theoretical chemistry because they are the natural graph representations of benzenoid hydrocarbons [15]. A considerable amount of research in mathematical chemistry has been developed to hexagonal chains (benzenoid hydrocarbons) [16–20]. A great deal of mathematical and mathematico-chemical results known in the theory of hexagonal systems apply, in fact, only to hexagonal chains [16–20]. In particular, the enumeration of hexagonal chains was accomplished by Balaban and Harary [21].

Benzenoid systems are divided [18,20] into catacondensed and pericondensed systems. In a pericondensed system there exist three hexagons share common vertex. In catacondensed systems no three hexagons share a common vertex. Catacondensed benzenoids are further classified into non-branched (in which no hexagon has more than two neighbors) and branched (in which at least one hexagon has three neighbors).

In the present paper we shall be mainly concerned with molecular graph G_h, whose general form is shown in figure 1. Here G_0 denotes an arbitrary, not necessarily benzenoid, terminal fragment, to which a chain of h linearly annelated hexagons is attached.

In the simplest case G_0 is isomorphic to the path P_2, i.e., when G_0 consists of two, mutually connected vertices, the G_h reduces to the molecular graph of linear polyacenes L_h (figure 2). In addition to L_h, we have also considered two additional classes of non-branched catacondensed benzenoid system viz. zig-zag polyacene called fibonacenes F_h and helicenes H_h as shown in figures 3 and 4, respectively.

The primary aim of the present investigation is to introduce a method for the calculation of *PI* indices for the aforementioned benzenoid chains.
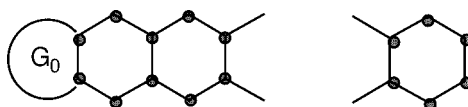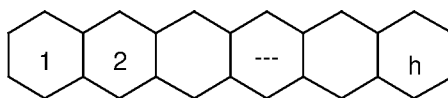
Figure 1. Molecular graph G_h.

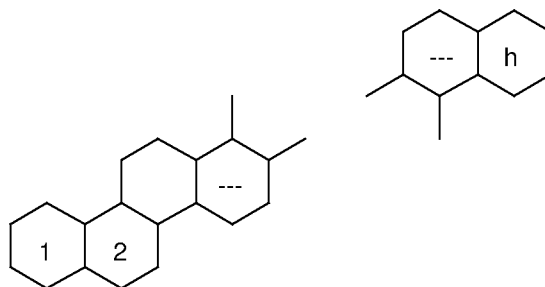Figure 2. Molecular graph for linear polyacenes L_h.

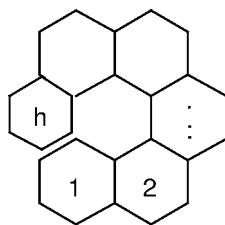Figure 3. Molecular graph for Fibonacenes F_h.

Figure 4. Molecular graph for helicenes H_h.

3.   Definition of *PI*-index

In order to propose the methods for the calculation of *PI*-index, we first need to specify our notations and terminology, in particular, to define *PI*.

Let G be the usual, hydrogen-atom depleted, graph representation of the molecule under consideration [10,11]. Hence, G is a connected graph without directed and multiple edges and without loops. By $V(G)$ and $E(G)$ we denote the vertex and edge sets, respectively, of G. If e is an edge of G, connecting the vertices u and v then we write $e = uv$. The number of vertices of G is denoted by $|G|$.

Let U be the subset of vertices of $V(G)$ which are closer to u than v and V be the subset of vertices of $V(G)$ which are closer to v than u:

$$U = \{u_i \mid u_i \in V(G),\ d(u, u_i) < d(u_i, v)\}, \tag{1}$$
$$V = \{v_i \mid v_i \in V(G),\ d(v, v_i) < d(v_i, v)\}. \tag{2}$$

Let

$$\langle U \rangle = (U, E_1), \qquad \langle V \rangle = (V, E_2), \tag{3}$$

$$n_1(e) = |E_1| \quad \text{and} \quad n_1(e) = |E_2|. \tag{4}$$

Here, $n_1(e) = |E_1|$ are the number of edges nearer to u than v and $n_2(e) = |E_2|$ are the number of edges nearer to v than u.

In all case of cyclic graphs there are edges equidistant to the both ends of the edges. Such edge are not taken into account.

Then, the *PI* index is defined as:

$$PI = PI(G) = \sum_{e \in E} \left[n_1(e) + n_2(e) \right]. \tag{5}$$

4.   Calculation of *PI*-index for polyacenes

Consider a polyacene having h hexagons as shown in figure 5.

From the definition of *PI* (5) and from the figure 5, we observe that for any edge like $a_i b_i$, $a_i b_{i+1}$, $c_i d_i$, $d_i c_{i+1}$, $i = 1, 2, 3, \ldots, h$, we have:

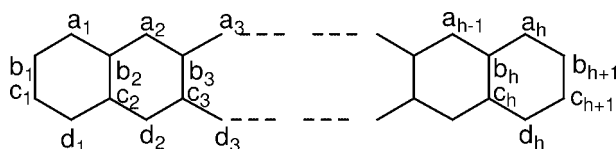$$n_1(e) = |E_1| = 5i - 3 \tag{6}$$

Figure 5. Case of polyacenes.

and

$$n_2(e) = |E_2| = 5h - (5i - 2), \tag{7}$$

thus giving

$$n_1(e) + n_2(e) = |E_1| + |E_2| = 5h - 1. \tag{8}$$

Similarly, for any edge like $b_i c_i$, $i = 1, 2, 3, \ldots, h + 1$, we have

$$n_1(e) = n_2(e) = |E_1| = |E_2| = 4h. \tag{9}$$

Hence, *PI* index of the polyacene will be given by

$$PI(L_h) = 4h(5h - 1) + 4h(h + 1) = 24h^2. \tag{10}$$

Recall that L_h has $2(2h + 1) = n$ vertices. In view of this $PI(L_h)$ in terms of vertices n is given by the following expression:

$$PI(L_h) = \frac{3}{2}(n - 2)^2. \tag{11}$$

5. Calculation of *PI* index for zig-zag polyacenes (Fibonacenes)

Consider the zig-zag polyacene (Fibonacenes) as given in figure 6. Consider the edge of the type e and $e^|$. Such edges will be $2h + 4$ in number. The contribution of such edges to *PI* will be $5h - 1$.

Similarly consider the edge of the type $e^{||}$ and $e^{|||}$. Such edges will be $3h - 3$ in numbers and the contribution of such edges to *PI* will be $5h - 3$.
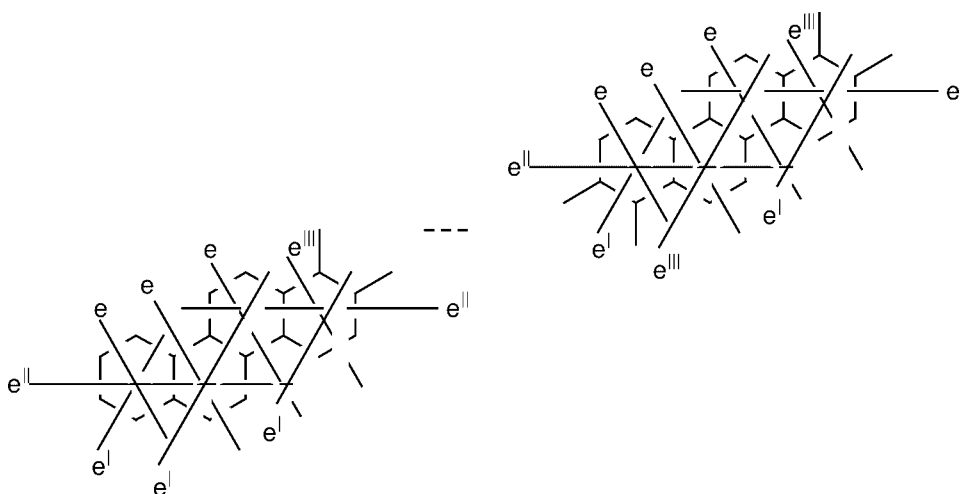

Figure 6. Case of zig-zag polyacenes (Fibonacenes).

Therefore, the sum of the contributions of edges e, $e^|$, $e^{||}$, and $e^{|||}$ will give the *PI* index for the zig-zag polyacenes (Fibonacenes)

$$PI = (2h + 4)(5h - 1) + (5h - 2)(3h - 3) = 25h^2 - 3h + 2.$$

6. Calculation of *PI*-index for helicenes (H_h)

Note that *PI* for the helicenes of the type figure 7 is also given by the same formula as above:

$$PI = 25h^2 - 3h + 2.$$

7. Calculation of *PI*-index for phynalenes

Now, consider the phynalenes of the type figure 8. The total number of edges $q = 8h - 2$.

The contribution of the edges of the type e, $e^|$ and $e^{||}$ can be calculated as described above and added together to give *PI*-index of phenalenes as under

$$
\begin{aligned}
PI &= 4h(q - 2) + (6h - 2) + (2h - 2)(q - 2) \\
&= 4h(8h - 4) + (6h - 2) + 2h(6h - 2) \\
&= (6h - 2)(8h - 4 + 2h) \\
&= 4(3h - 1)(5h - 2) \\
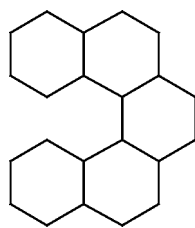&= 60h^2 - 44h + 8.
\end{aligned}
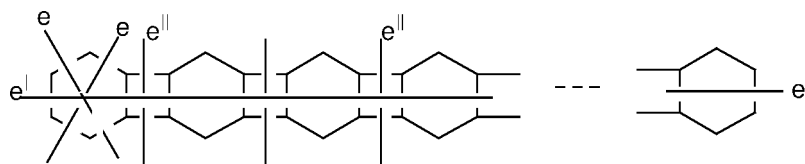$$

Figure 7. Case of helicenes (H_h).
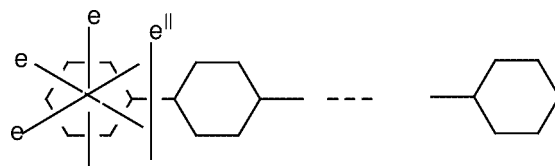

Figure 8. Case of phynalenes.

Figure 9. Case of polyphenylenes.

8. Calculation of *PI*-index for polyphenylenes

Consider the polyphenylenes of the type figure 9. The total number of edges, $q = 7h - 1$.

The contributions of edges e and $e^{\|}$ towards *PI* once again can be calculated as above and added together to give *PI* for polyphenylenes.

$$PI = 6h(q-2) + (h-1)(q-1) = 6h(7h-3) + (h-1) + (7h-2) = 49h^2 - 27h + 2.$$

Acknowledgement

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