MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **60** (2008) 135-142

ISSN 0340 - 6253

ON THE PI INDEX OF PHENYLENES AND THEIR HEXAGONAL SQUEEZES

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(Received May 16, 2007)

Abstract

The PI indices of a phenylene PH with h hexagons, and its hexagonal squeeze HS (also with h hexagons) are related as $PI(PH) = 4\,PI(HS) - 36\,h^2 - 44\,h + 8$.

INTRODUCTION

Phenylenes are polycyclic conjugated molecules possessing both six– and four–membered rings. In view of the fact [1] that six–membered rings stabilize, whereas four–membered rings destabilize a conjugated molecule, phenylenes are of particular interest in theoretical organic chemistry. Needless to say that phenylenes were (and still are) subject of numerous both experimental and theoretical studies.

The formal definition of the molecular graph of a phenylene (which we also call "phenylene") is as follows. A phenylene (denoted by PH) is a 2-connected plane graph composed of mutually congruent regular hexagons and mutually congruent squares, both with edges of equal length. Each square is joined to exactly two hexagons, whereas all hexagons are mutually disjoint.

An example of a phenylene is found in Fig. 1.

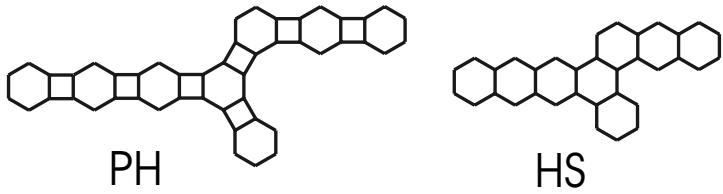

Fig. 1. A phenylene (PH) and its hexagonal squeeze (HS), both possessing $h = 8$ hexagons.

Each phenylene is in a one–to–one correspondence with a catacondensed benzenoid system called [2] "hexagonal squeeze", denoted by HS. The construction of the hexagonal squeezes should be evident from the example given in Fig. 1; for more details see [3].

Both the phenylene and its hexagonal squeeze have equal number of hexagons, which will be denoted by h.

The concept of hexagonal squeeze was introduced into the theory of phenylenes after the remarkable discovery [2] that the algebraic structure count of PH is equal to the Kekulé structure count of HS, which in turn is equivalent to the equality

$$\det \mathbf{A}(PH) = (-1)^{h+1} \det \mathbf{A}(HS)$$

where $\mathbf{A}$ denotes the adjacency matrix.

In the sequel many other relations were found to exist between a phenylene and its hexagonal squeeze: for the total π-electron energy [4], for the Wiener index [5–7] and other Wiener–index–type molecular structure descriptors [8], for the connectivity

index [9], for the energy–effect of cycles [10], and several other [11–13]. In this paper we report one more such relation — for the PI index.

THE PI INDEX

In year 2000 a molecular structure descriptor, named "the PI index" was put forward by Khadikar [14]. Eventually, in a series of papers [15-22] and a book [23] the main mathematical properties of the PI index were determined and examples were offered for its applicability in QSPR/QSAR studies.

The PI index is defined as follows.

Let G be a (molecular) graph with $m = m(G)$ edges. Let $e = (uv)$ be an edge of G, connecting the vertices u and v. Let $m_u(e|G)$ be the number of edges of the graph G whose distance to the vertex u is smaller than the distance to the vertex v. Analogously, let $m_v(e|G)$ be the number of edges of the graph G whose distance to the vertex v is smaller than the distance to the vertex u. Then [14]

$$PI = PI(G) = \sum_e [m_u(e|G) + m_v(e|G)] \tag{1}$$

with summation going over all edges of G.

If $m_{uv}(e|G)$ denotes the number of edges that are equidistant to the vertices u and v (including the edge e itself), then evidently

$$m_u(e|G) + m_v(e|G) + m_{uv}(e|G) = m(G) \ . \tag{2}$$

Combining Eqs. (1) and (2) we arrive at

$$PI(G) = m(G)^2 - \sum_e m_{uv}(e|G) \ . \tag{3}$$

In the subsequent section we show that in the case of phenylenes and benzenoid systems, the term $m_{uv}(e|G)$ in Eq. (3) is equal to the length of the elementary cut intersecting the edge e.

ELEMENTARY CUTS

In the theory of benzenoid systems elementary cuts (or, orthogonal cuts [22]) play a distinguished role. Details on elementary cuts and their various applications

can be found in [7,18,21,22,24–27], and especially in [28, 29]. The method of cuts is equally applicable to phenylenes [7, 21] and, more generally, to the so-called isometric subgraphs of hypercubes (see [30] and the references cited therein).

An elementary cut is a line segment that starts from the middle of a peripheral edge of a benzenoid system or phenylene, goes orthogonal to this edge and ends at the first next peripheral edge that it intersects. We denote elementary cuts by C. The number of edges intersected by C is the length of C, and will be denoted by $|C|$.

In Fig. 2 are shown six elementary cuts of a phenylene and four elementary cuts of the corresponding hexagonal squeeze.

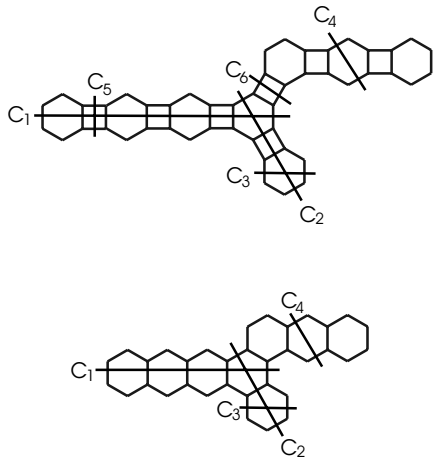

Fig. 2. Some elementary cuts of the phenylene PH and its hexagonal squeeze HS, depicted in Fig. 1. Observe the evident correspondence between the elementary cuts C_i of PH and C_i of HS, $i = 1, 2, 3, 4$. On the other hand, the elementary cuts C_5 and C_6 of PH have no counterparts in HS. In PH the lengths of the indicated elementary cuts are $|C_1| = 8$, $|C_2| = 4$, $|C_3| = |C_4| = |C_5| = |C_6| = 2$. In HS the respective lengths are $|C_1| = 5$, $|C_2| = 3$, $|C_3| = |C_4| = 2$.

Let PH be a phenylene and HS its hexagonal squeeze, both having h hexagons. It is known [28] that a catacondensed benzenoid system with h hexagons has a total of $2h + 1$ elementary cuts. Therefore HS has $2h + 1$ elementary cuts. Each of these elementary cuts corresponds to an elementary cut of the associated phenylene PH.

However, PH has additional $h-1$ elementary cuts, that intersect the squares (two of these are C_5 and C_6 in Fig. 2). Therefore the total number of elementary cuts of PH is $(2h+1)+(h-1)=3h$.

For the following considerations it is purposeful to classify the elementary cuts into "short" and "long". Short cuts are those for which $|C| = 2$, whereas long cuts are those for which $|C| > 2$. This division is motivated by the fact that if $C(HS)$ is a short (resp. long) elementary cut of HS, then it corresponds to a short (resp. long) elementary cut $C(PH)$ of PH. Therefore, for short elementary cuts, $|C(PH)| = |C(HS)| = 2$. It is easy to verify (cf. Fig. 2) that for long elementary cuts,

$$|C(PH)| = 2\,|C(HS)| - 2\ . \tag{4}$$

Let G be a molecular graph that is either a benzenoid system or a phenylene. Let $e=(uv)$ be an edge of G. Let C be the elementary cut intersecting the edge e. Then C intersects a few other edges of G. The edges intersected by C are precisely those that are equidistant to the vertices u and v. Furthermore, all edges equidistant to both end vertices of e lie on the elementary cut C. Bearing this in mind, arrive at the noteworthy equality:

$$m_{uv}(e|G) = |C|\ . \tag{5}$$

Substituting (5) back into (3) and observing that there are exactly $|C|$ edges in G to which the relation (5) is applicable, we obtain

$$PI(G) = m(G)^2 - \sum_C |C|^2 \tag{6}$$

with the summation going over all elementary cuts of the molecular graph G.

Formula (6) seems to be first reported by John et al. [22]. This formula will serve as the starting point for the subsequent considerations.

RELATING $PI(PH)$ AND $PI(HS)$

Let, as before, PH be a phenylene with h hexagons, and HS its hexagons squeeze. Denote by $\lambda = \lambda(PH) = \lambda(HS)$ the number of long elementary cuts in either PH or HS. Then PH and HS have $3h-\lambda$ and $2h+1-\lambda$ short cuts, respectively.

Because a phenylene PH with h hexagons has $8h-2$ edges, from Eq. (6) we get

$$PI(PH) = (8h-2)^2 - 4\,(3h-\lambda) - \sum_{long} |C(PH)|^2 \tag{7}$$

with the right–hand side summation going over long elementary cuts. Now, in view of Eq. (4), and the fact that there is a one–to–one correspondence between the long elementary cuts of PH and HS, we have

$$\begin{aligned} \sum_{long} |C(PH)|^2 &= \sum_{long} [|2\,|C(HS)| - 2]^2 \\ &= 4 \sum_{long} |C(HS)|^2 - 8 \sum_{long} |C(HS)| + 4\,\lambda\ . \end{aligned}$$

Further,

$$\sum_{long} |C(HS)| = \sum_{C} |C(HS)| - \sum_{short} |C(HS)| = m(HS) - 2\,(2h+1-\lambda) = h - 1 + 2\,\lambda$$

because $m(HS) = 5h+1$.

When all these relations are substituted back into (7) the parameter λ cancels out and we get

$$PI(PH) = 64\,h^2 - 4h + 12 - 4 \sum_{C} |C(HS)|^2\ . \tag{8}$$

From (6),

$$PI(HS) = (5h+1)^2 - \sum_{C} |C(HS)|^2$$

i. e.,

$$-4 \sum_{C} |C(HS)|^2 = 4\,PI(HS) - 4\,(5h+1)^2$$

which combined with (8) yields our final result:

Theorem. *Let PH be phenylene and HS its hexagonal squeeze, both having h hexagons. Then their PI indices are related as*

$$PI(PH) = 4\,PI(HS) - 36\,h^2 - 44\,h + 8\ .$$

Acknowledgement. This research was in part supported by a grant from the Center of Excellence of Algebraic Methods and Applications of Isfahan University of Technology.

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