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Randić Index of Benzenoid Systems and Phenylenes*

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A new parameter, related to and easily determined from the structure of a benzenoid system and that of a phenylene – the number of inlets (r) – is introduced. The connectivity (Randić) index of both benzenoid systems and phenylenes is then shown to depend solely on the number of vertices and on r. A simple relation is established between the connectivity index of a phenylene and of the corresponding hexagonal squeeze. Analogous relations are reported for the edge-connectivity indices.

Key words: connectivity index, benzenoid systems, phenylenes.

INTRODUCTION

The connectivity index, invented by Randić a quarter of century ago,[1] is the graph-based molecular structure descriptor that is most frequently applied in quantitative structure-property and structure-activity studies.[2–5] It is defined as the sum over all edges of the (molecular) graph of the terms $(\delta_u \delta_v)^{-1/2}$ where u and v are the vertices incident with the respective edge and δ_x denotes the degree (= number of first neighbors) of a vertex x.

In further text, a j-vertex denotes a vertex of degree j, and a (j, k)-edge stands for an edge connecting a j-vertex with a k-vertex. The number of

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j-vertieces and (*j, k*)-edges in the graph considered will be denoted by n_j and m_{jk}, respectively.

Then, the Randić index of any graph G is denoted by n_j and m_{jk}, respectively. Then, the Randić index of any graph G with n vertices conforms to the relation

$$\chi(G) = \sum_{1 \le j \le k \le n-1} \frac{m_{jk}}{\sqrt{jk}} .$$

Benzenoid systems (graph representations of benzenoid hydrocarbons) are defined as finite connected plane graphs with no cut-vertices, in which all interior regions are mutually congruent regular hexagons. More details on this important class of molecular graphs can be found in the book[6] and in the references cited therein.

In the case of a benzenoid system S, which possesses only (2,2)-, (2,3)-, and (3,3)- edges, the above formula reduces to

$$\chi(S) = \frac{m_{22}}{2} + \frac{m_{23}}{\sqrt{6}} + \frac{m_{33}}{3} \qquad (1)$$

Because of the simplicity of expression (1), the connectivity index of benzenoid systems has not attracted much attention of mathematical chemists so far. Some fundamental identities for m_{22}, m_{23}, and m_{33} have been reported[7] and the relations between the vertex-connectivity index (*i.e.*, the ordinary Randić index) and the edge-connectivity index (*i.e.*, the Randić index of the line graph) have been examined in some detail.[8]

The connectivity index of phenylenes has not been studied until now.

In this article we introduce the number of inlets, r, a novel parameter related in a simple manner to the structure of benzenoid systems and/or phenylenes, and show that the connectivity index is a simple function of r. As a consequence, some hitherto unnoticed regularities for the connectivity indices of benzenoids and phenylenes are revealed.

INLETS OF BENZENOID SYSTEMS AND THEIR COUNTS

Throughout this paper, the structural features of a benzenoid system are named and their counts denoted according to the terminology proposed by Cyvin *et al.*[6,9,10] Thus,

n = number of vertices

m = number of edges

h = number of hexagons

n_j = number of j-vertices; j = 2,3

m_{jk} = number of (j,k)-edges; j,k = 2,3

B = number of simple bays

C = number of coves

F = number of fjords

b = number of bay regions; $b = B + 2C + 3F$

Complete sets of relations between these (and other) structural invariants of benzenoid systems have been worked out.[6,10]

Bays, coves, and fjords are structural characteristics of the perimeter of the benzenoid systems playing some role in their theory.[6] In addition to them, fissures were introduced[6] just for the sake of completeness. The number of fissures will be denoted by f. An illustrative example is depicted in Figure 1.

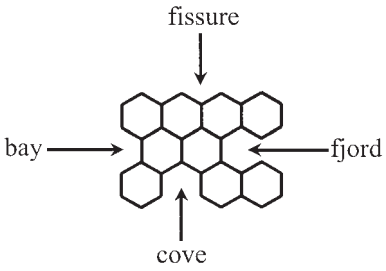

Figure 1. Types of inlets occurring on the perimeter of a benzenoid system.

If one goes along the perimeter of a benzenoid system, then a fissure is a structural feature formed by a 2-vertex, followed by a 3-vertex, followed by a 2-vertex. A simple bay is formed by a 2-vertex, followed by two 3-vertices, followed by a 2-vertex. A cove and a fjord are features formed, respectively, by three and four consecutive 3-vertices, lying between 2-vertices.

The quantity $b = B + 2C + 3F$ plays a significant role in the spectral theory of benzenoid molecules.[6,11–15] It is easy to see that b is just the number of (3,3)-edges, lying on the perimeter.

The number of fissures will be denoted by f.

Fissures, bays, coves, and fjords are various types of inlets. The total number of inlets on the perimeter of a benzenoid system, $f + B + C + F$, will be denoted by r (for »rada«, which in Spanish means »bay«).

We define an additional type of inlet – the lagoon. This is a feature of the perimeter, formed by a 2–vertex, followed by five 3-vertices, followed by a 2-vertex, *cf*. Figure 2.

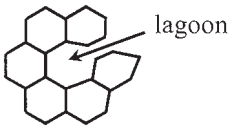

Figure 2. A lagoon – an inlet that is encountered only in helicenic species; *cf.* Figure 6.

If the number of lagoons is denoted by L, then the invariants b and r should be defined as

$$b = B + 2C + 3F + 4L$$

$$r = f + B + C + F + L \tag{2}$$

Evidently, lagoons cannot occur in (geometrically planar) benzenoids, but only in helicenic systems.

THE RANDIĆ INDEX OF BENZENOID SYSTEMS

Consider first the isomeric benzenoid systems with 18 vertices and 4 hexagons, depicted in Figure 3.

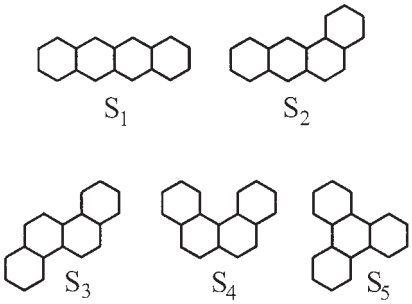

Figure 3. The five isomeric tetrycyclic catacondensed benzenoids; their inlet counts and Randić indices are given in Table I.

Table I shows the number of inlets of each type in the benzenoids from Figure 3, together with their total number of inlets and the Randić index.

We observe that the Randić index increases as the total number of inlets decreases. Moreover, S_3 and S_4 have equal number of inlets and $\chi(S_3) = \chi(S_4)$. We now prove that this behavior holds for benzenoid systems in general.

TABLE I

The number of fissures (f), simple bays (B), coves (C) and fjords (F), and the total number of inlets (r) and Randić indices (χ) of the isomeric benzenoids depicted in Figure 3

molecule	f	B	C	F	r	χ
S_1	6	0	0	0	6	8.89898
S_2	4	1	0	0	5	8.91582
S_3	2	2	0	0	4	8.93265
S_4	3	0	1	0	4	8.93265
S_5	0	3	0	0	3	8.94949

LEMMA 1. Let S be a benzenoid system with n vertices, h hexagons, and r inlets, Eq. (2). Then,

$$m_{22} = n - 2h - r + 2 \tag{3}$$

$$m_{23} = 2r \tag{4}$$

$$m_{33} = 3h - r - 3. \tag{5}$$

PROOF. Relation (4) follows directly from the definition of an inlet, namely an inlet corresponds to a sequence of vertices on the perimeter, of which the first and the last are 2-vertices and all other are 3-vertices.

From the fact[6] that the number of 3-vertices in S is

$$n_3 = 2(h - 1)$$

it follows

$$m_{23} + 2m_{33} = 3n_3 = 6h - 6$$

which combined with (4) results in Eq. (5).

In benzenoid systems, $m_{22} + m_{23} + m_{33}$ is just the total number of edges, m, known to conform to the relation

$$m = n + h - 1.$$

Substituting relations (4) and (5) into

$$m_{22} + m_{23} + m_{33} = n + h - 1$$

one readily obtains Eq. (3).

We can now express the Randić index of S in terms of the numbers of vertices and inlets of S. Substituting relations (3)–(5) into Eq. (1), we directly arrive at:

THEOREM 2. Let S be a benzenoid systems with n vertices and r inlets. Then,

$$\chi(\mathrm{S}) = \frac{n}{2} - \frac{5-2\sqrt{6}}{6} r \,.$$

Note that $(5 - 2\sqrt{6})/6 = 0.016836752$.

Our next result classifies all benzenoid systems with an equal number of vertices that have an equal Randić index.

COROLLARY 3. Let S′ and S″ be benzenoid systems with an equal number of vertices. Then, $\chi(\mathrm{S}') = \chi(\mathrm{S}'')$ if an only if $r(\mathrm{S}') = r(\mathrm{S}'')$. Moreover, if $r(\mathrm{S}') \geq r(\mathrm{S}'')$, then $\chi(\mathrm{S}') \leq \chi(\mathrm{S}'')$.

In Theorem 2 we see that the Randić index of S is completely determined by the number of vertices and inlets, independently of the number of hexagons. The example depicted in Figure 4 illustrates this situation.

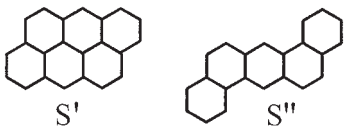

Figure 4. Both benzenoid systems S′ and S″ have 22 vertices and 6 inlets. Therefore, by Theorem 2, $\chi(\mathrm{S}') = \chi(\mathrm{S}'') = 10.89898$. However, S′ has 6 hexagons whereas S″ has 5.

THE RANDIĆ INDEX OF PHENYLENES

Phenylenes are polycyclic conjugated compounds composed of benzene rings that are fused *via* cyclobutadiene units. A number of such compounds has recently been synthesized[16,17] and, of course, they rapidly became the focus of interest of theoretical chemists (see, for instance Refs. 15, 18–25). An example of phenylene is found in Figure 5.

A benzenoid system, called hexagonal squeeze,[19] can in an obvious manner be associated to a phenylene, *cf.* Figure 5. Several properties of phenylene (PH) are found to be closely related to the analogous properties of the corresponding hexagonal squeeze (HS). For instance, the algebraic structure count of PH is equal to the Kekulé structure count of HS.[19] Exact relation between the Wiener indices of PH and HS was discovered.[25] Good correla-

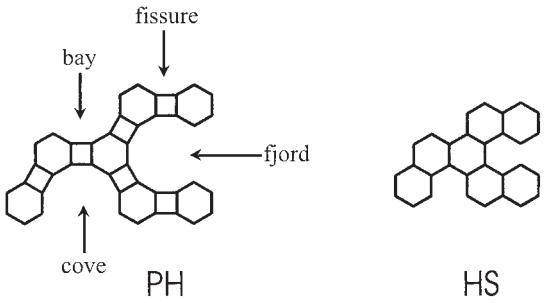

Figure 5. A phenylene (PH) and its hexagonal squeeze (HS).

tions (but not exact relations) were found between various π-electron properties of PH and HS,[23] including those pertaining to the total π-electron energy[22] and Clar aromatic sextets.[24] The spectral moments of PH and HS are also related.[15]

In view of these results, it may be of some interest to seek for relations between the connectivity indices of phenylenes and the corresponding hexagonal squeezes.

Before we establish such a relation, it should be mentioned that in certain cases a hexagonal squeeze is not a (geometrically planar) benzenoid system, but a helicenic species.[19,21] If so, then HS possesses lagoons. An illustrative example is given in Figure 6.

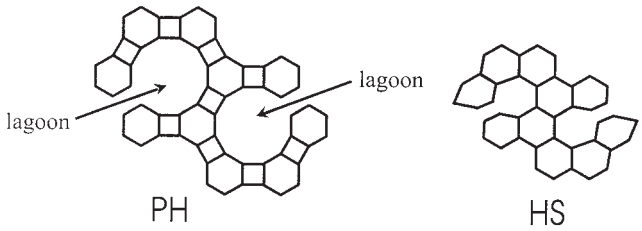

Figure 6. A phenylene (PH) whose hexagonal squeez (HS) is a helicenic species and which possesses lagoons; in this particular example, L(PH) = L(HS) = 2 whereas r(PH) = r(HS) = 8.

In the case of phenylenes, a fissure, bay, cove, fjord, and lagoon are defined in full analogy to the benzenoid systems: A fissure (resp. a bay, cove, fjord, or lagoon) corresponds to a sequence of four (resp. six, eight, ten, and twelve) consecutive vertices on the perimeter, of which the first and the last are 2-vertices and the rest are 3-vertices. For examples see Figures 5 and 6.

With the inlets defined as above, Eq. (2) remains applicable also in the case of phenylenes.

Instead of Lemma 1, we now have:

LEMMA 4. Let PH be a phenylene with h hexagons and r inlets, Eq. (2). Then,

$$m_{22} = 2h - r + 4 \tag{6}$$

$$m_{23} = 2r \tag{7}$$

$$m_{33} = 6h - r - 6 \tag{8}$$

The proof of Lemma 4 is fully analogous to the proof of Lemma 1. This time the number of 3-vertices is $n_3 = 4(h - 1)$, whereas the number of edges is $m = n + (2h - 1) - 1 = 8h - 2$.

One should note that a phenylene with h hexagons has $6h$ vertices. Bearing this in mind and inserting relations (6)–(8) back into Eq. (1), we readily arrive at:

THEOREM 5. Let PH be a phenylene with n vertices and r inlets. Then,

$$\chi(\mathrm{PH}) = \frac{n}{2} - \frac{5-2\sqrt{6}}{6} r \, .$$

This result should be compared with Theorem 2. Since a phenylene with n vertices has $n/6$ hexagons, its hexagonal squeeze has $4 \cdot n/6 + 2$ vertices. This implies

COROLLARY 6. The connectivity indices of a phenylene PH with h hexagons and its hexagonal squeeze HS are related as

$$\chi(\mathrm{PH}) = \chi(\mathrm{HS}) + h - 1.$$

THE EDGE-CONNECTIVITY INDICES OF BENZENOID SYSTEMS AND PHENYLENES

The concept of the edge-connectivity index was introduced by Estrada[26] and soon after that it was recognized[27] that this is just the ordinary connectivity index of a line graph. We denote the line graph of a graph G by L(G).

The basic properties of line graphs may be found in graph theory textbooks[28] and they were on several occasions outlined in chemical litera-

ture.[27,29,30] Paper[30] contains an extensive bibliography on the chemical applications of line graphs. As already mentioned, the connectivity index of the line graphs of benzenoid hydrocarbons (under the name edge-connectivity index) was examined by Nikolić, Trinajstić, and Baučić,[8] who compared it with the ordinary Randić index of the same molecules.

Two inlets of a benzenoid system or of a phenylene are said to be adjacent if they have a common 2-vertex. The number of adjacent inlets is denoted by a. Then, the following results hold.

THEOREM 7. Let S be a benzenoid system with n vertices, h hexagons, r inlets, f fissures, and a adjacent inlets. Then,

$$\chi(\mathrm{L(S)}) = \frac{n}{2} + \frac{h}{2} + \frac{2\sqrt{6} + 4\sqrt{3} - 12}{6} r + \frac{7 - 4\sqrt{3}}{12} f + \frac{5 - 2\sqrt{6}}{6} a - \frac{1}{2} .$$

THEOREM 8. Let PH be a phenylene with h hexagons, r inlets, and a adjacent inlets. Then,

$$\chi(\mathrm{L(PH)}) = 4h + \frac{\sqrt{6} + 2\sqrt{3} - 6}{3} r + \frac{5 - 2\sqrt{6}}{6} a - 1 .$$

PROOF. Consider the class of graphs possessing only 2- and 3-vertices (to which benzenoid systems and phenylenes belong). Let G be such a graph and let L(G) be its line graph. Then, L(G) may possess only 2-, 3-, and 4-vertices and, consequently, only (2,2)-, (2,3)-, (3,3)-, (3,4)-, and (4,4)-edges. It is easy to see that L(G) cannot possess (2,4)-edges.

Using the relations

$$2m_{22}(\mathrm{L(G)}) + m_{23}(\mathrm{L(G)}) = 2n_2(\mathrm{L(G)})$$

$$m_{23}(\mathrm{L(G)}) + 2m_{33}(\mathrm{L(G)}) + m_{34}(\mathrm{L(G)}) = 3n_3(\mathrm{L(G)})$$

$$m_{34}(\mathrm{L(G)}) + 2m_{44}(\mathrm{L(G)}) = 4n_4(\mathrm{L(G)})$$

and

$$n_2(\mathrm{L(G)}) + n_3(\mathrm{L(G)}) + n_4(\mathrm{L(G)}) = m(\mathrm{G})$$

it can be shown that

$$\chi(\mathrm{L(G)}) = \frac{m(\mathrm{G})}{2} - \frac{1}{2}\left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{3}}\right)^2 m_{23}(\mathrm{L(G)}) - \frac{1}{2}\left(\frac{1}{\sqrt{3}} - \frac{1}{2}\right)^2 m_{34}(\mathrm{L(G)}) . \quad (9)$$

By means of reasoning analogous to that used in the proofs of Theorems 2 and 5, we conclude that for a benzenoid system S,

$$m_{23}(\mathrm{L(S)}) = 2(r - a) \quad \text{and} \quad m_{34}(\mathrm{L(S)}) = 4r - 2f$$

whereas for a phenylene PH,

$$m_{23}(\mathrm{L(PH)}) = 2(r - a) \quad \text{and} \quad m_{34}(\mathrm{L(PH)}) = 4r\ .$$

Theorems 7 and 8 are obtained by substituting these relations back into Eq. (9).

CONCLUSIONS

In the authors' opinion, the main result of this paper is the identity $\chi(\mathrm{PH}) = \chi(\mathrm{HS}) + h - 1$, relating the Randić indices of a phenylene and the corresponding hexagonal squeeze. This happens to be the third exact relation between topological properties of phenylenes and their hexagonal squeezes (the first pertains to the algebraic structure count,[19] the second to the Wiener number[25]). We believe we have thereby shed some more light on the presently not fully understood kinship between these two classes of molecular graphs.

For the first time, a simple and easy-to-count invariant of benzenoid systems (and phenylenes), the number of inlets r, was shown to play some role in the topological theory of conjugated molecules. Thus, our study of the structure dependence of the Randić index of benzenoids and phenylenes resulted in the introduction of a novel structure-descriptor. It may well be that the quantity r will eventually find other applications in the chemical graph theory.

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SAŽETAK

Randićev indeks benzenoidnih sustava i fenilena

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Za benzenoidne sustave i fenilene definiran je novi strukturni parametar – broj zaljeva (r) – koji se određuje izravno i jednostavno. Indeks povezanosti (Randićev indeks) kako benzenoidnih sustava tako i fenilena ovisi isključivo o broju vrhova i o r. Nađena je jednostavna veza između indeksa povezanosti fenilena i odgovarajuće heksagonske osnove. Analogne relacije postoje i u slučaju indeksa povezanosti linijskog grafa.