The evaluation of spectral moments for molecular graphs of phenylenes

Svetlana Marković, Aleksandra Stajković

Faculty of Science, University of Kragujevac, P.O. Box 60, Yu-34000 Kragujevac, Yugoslavia

Abstract. The evaluation of some spectral moments for phenylenes is considered. Explicit topological formulae for the fourth, sixth and eighth moments are derived. This was achieved by adopting the method of Hall [1], which was originally applied to benzenoid systems, and applying it to molecular graphs of phenylenes. It is shown that the moments considered in this paper can be expressed in terms of three mutually independent graphical invariants.

Key words: Phenylenes – Graphical invariants – Spectral moments

1 Introduction

Phenylenes are a group of conjugated hydrocarbons composed of six- and four-membered rings, where the six-membered rings (hexagons) are adjacent only to four-membered rings, and every four-membered ring is adjacent to a pair of hexagons. A phenylene containing hexagons is called an [h] phenylene. In Fig. 1 some examples of phenylenes are presented. It is assumed that the number of four-membered rings of an [h] phenylene amounts to h-1. It means that structures in which six- and four-membered rings are linked together in phenylenic super-rings are not considered in the present paper.

The chemistry of phenylenes is rapidly expanding, owing to the work of Peter Volhardt's research group. More information on the phenylenes can be found in the reviews [2–4], as well as in recent papers [5–8]. Recent developments in the experimental chemistry of phenylenes has challenged a great number of theoretical investigations [9–18].

One of the main aims of theoreticians is to analyse the dependence of various physico-chemical properties of molecules on their structure. The graph theory is often employed for this purpose [19, 20], because molecular graphs contain relevant information about the molecular structure. In Fig. 1 the phenylene examples are also presented by their corresponding molecular graphs. The adjacency matrix (A) of the molecular graph consists of zero diagonal elements and unit off-diagonal elements corresponding to the nearest neighbours. The eigenvalues of the adjacency matrix, $x_1, x_2, \ldots, x_n$, form the spectrum of the respective molecular graph.

The k-th spectral moment of a molecular graph (M_k) is defined as:

$$M_k = \sum_{i=1}^{n} x_i^k . \tag{1}$$

It is well known that M_k can be expressed as:

$$M_k = \mathrm{Tr}\left[A^k\right] \tag{2}$$

where an element $\left[A^k\right]_{ij}$ is equal to the number of walks of length k between the vertices i and j. Walks are an object of interest for many theoretical chemists [21, 22].

The spectral moments of molecular graphs have found a number of applications in the physical chemistry of solid state [23–26]. Namely, using a continued fraction technique, the normalized moments were used to obtain the HMO density of states and other useful properties for solids. The application of moments in the theoretical chemistry of conjugated molecules is also worth noting [1, 27–39].

In all applications of moments it is necessary to understand how they depend on the molecular structure. For these reasons an effort has been made to establish topological formulae for spectral moments. Particular attention has been devoted to benzenoid hydrocarbons [1, 29, 30, 40–42] and acyclic chains [28, 43]. Many of the topological formulae established in previous papers have been used in the theoretical chemistry of conjugated compounds. In a series of papers [1, 27–35] moments were used for the estimation of HMO total π-electron energy and examination of its dependence on molecular structure. A treatment based on the energy partitioning via spectral moments was proposed for dealing with aromaticity of conjugated systems [35, 36].
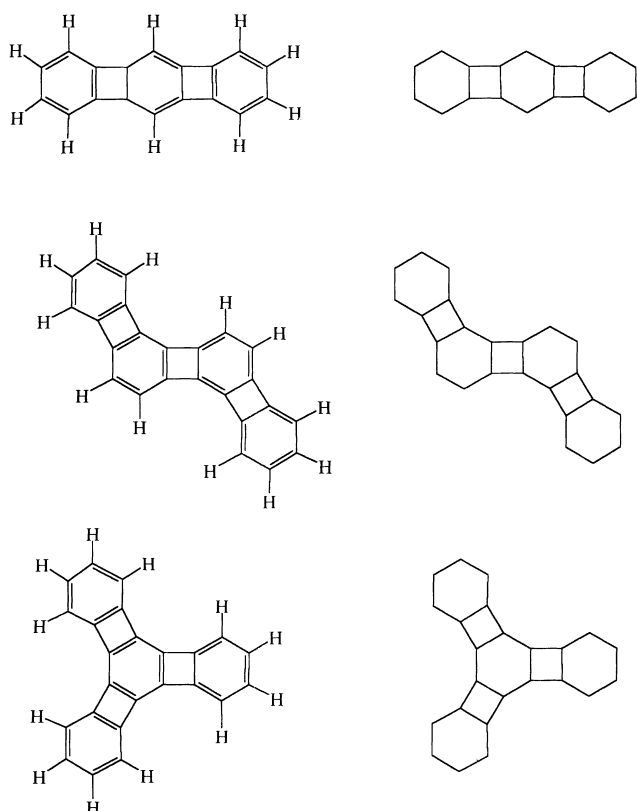
Correspondence to: S. Marković

Fig. 1. Some examples of phenylenes presented by their Kekulé structures and the corresponding molecular graphs
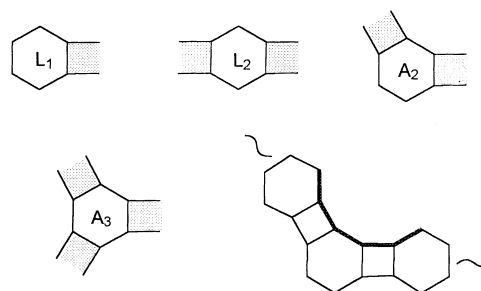

Fig. 2. Types of hexagons and a bay region of phenylenes

Because of the pairing theorem, all odd moments of bipartite graphs (and therefore of all phenylenes) are equal to zero.

$$M_{2k+1} = 0 \quad k = 0, 1, 2, \ldots \ .$$

For this reason, only the even moments of phenylenes $M_{2k}, k = 0, 1, 2, \ldots$ are considered in this paper.

The zeroth and the second moments of all graphs are given by long and well known formulae:

$$M_0 = n(= 6h \text{ for the graphs of phenylenes})$$

$$M_2 = 2m(= 16h - 4 \text{ in the same case}).$$

We have contributed the equations below:

$$M_4 = 80h - 44 , \tag{3}$$

$$M_6 = 484h - 352 + 6b , \tag{4}$$

$$M_8 = 3136h - 2636 + 128b + 16h_{A3} . \tag{5}$$

3 Method for deriving topological formulae for spectral moments of phenylenes

Equation (2) can obviously be put into the form:

$$M_{2k} = \mathrm{Tr}[B]^2 \tag{6}$$

where B denotes the symmetric matrix A^k. Since the trace of the square of a symmetric matrix is equal to the sum of the squares of all elements of that symmetric matrix, Eq. (6) can be expressed as:

$$M_{2k} = \sum_{i,j} (B_{ij})^2 . \tag{7}$$

On the basis of Eq. (7) the $2k$-the moment can be deduced from the matrix B (i.e. A^k) by squaring each element and adding them together. For such a calculation one has to know which numbers appear as the elements of the matrix B, and how many times. If $b_{k,w}$ denotes how many times a certain value w appears as an element of matrix B, then:

$$M_{2k} = \sum_{w=1}^{\infty} b_{k,w} \cdot w^2 . \tag{8}$$

Since an element B_{ij} is equal to the number of walks of length k between the vertices i and j, it follows that $b_{k,w}$ represents the number of structural fragments of phen-

2 Topological formulae for spectral moments of phenylenes

Before presenting our main results, we have to determine some structural details and to fix our notation. All symbols used in this paper refer to the graphs of phenylenes, although we follow the terminology suggested for benzenoid hydrocarbons [44]. Hence, h stands for the number of hexagons, n for the number of vertices ($n = 6h$ for the case presented, and m for the number of edges ($m = 8h - 2$ for the case presented).

There are four types of hexagons in phenylenes that are distinguishable with respect to their mutual positions. We use the notation from Gutman and Cyvin [44], and call the four types L_1, L_2, A_2 and A_3. Their definition is clear from Fig. 2. According to this notation h_{L1}, h_{L2}, h_{A2} and h_{A3} represent the numbers of hexagons of types L_1, L_2, A_2 and A_3, respectively.

In Fig. 2, a structural detail of the perimeter – a bay of phenylenes – is also depicted. In the following text this structural feature is simply called a bay. The number of bays is denoted by b.

Up to now, explicit topological formulae for spectral moments of phenylenes have not been communicated. In this paper the evaluation of M_4, M_6 and M_8 for phenylenes is considered.

ylenes enabling w distinct walks of length k. On this basis, the problem of deriving the $2k$-th spectral moments of phenylenes is reduced to recognition and enumeration of structural details that enable walks of length k.

We resolve this problem for $k = 2, 3$ and 4 in the following manner: all possible fragments of phenylenes that provide walks of length k (i.e. 2, 3 and 4) are considered, and classified according to their w values. Now w can assume only certain values (which, of course, differ for different values of k) so we have to determine the coefficients $b_{k,w}$. Here it turned out to be profitable to identify the vertices from which w distinct walks of length k started. Then the next part of the task involved enumeration of the vertices. We observed that particular attention should be paid to various types of hexagons and some structural details (Fig. 2).

4 Evaluation of M$_4$

Structural details enabling walks of length 2, classified according to their w values, are presented in Fig. 3. It is shown that w can only assume the values of 1, 2 and 3.

The structural detail that provides three distinct walks of length 2 is a vertex of degree 3. These are closed walks, the corresponding matrix elements of which lie on the diagonal of A^2. On the basis of this, $b_{2,3}$ is obviously given by the expression

$$b_{2,3} = 4(h-1) \ . \tag{9}$$

Every vertex of degree 2 enables two different closed walks of length 2. From the vertices of degree 3, two walks of length 2 also start. It is now clear that

$$b_{2,2} = n = 6h \ . \tag{10}$$

As for $b_{2,1}$, three types of vertices are distinguishable (Fig. 4). All designated vertices are the beginning parts of the fragments providing one walk of length 2, where
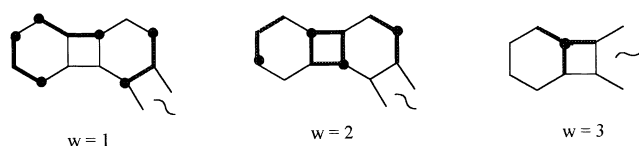

w = 1   w = 2   w = 3

Fig. 3. Structural fragments enabling walks of length 2. The vertices where a certain walk starts and ends are marked by *heavy dots*
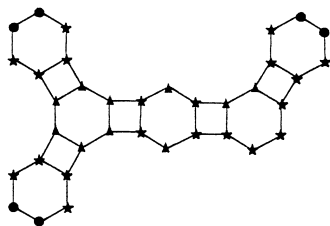

Fig. 4. An example for evaluation of M_4. *Heavy dots, asterisks* and *triangles* represent the vertices where one, two or three fragments enabling one walk of length 2 start.

vertices marked by heavy dots, asterisks and triangles are involved in one, two and three such fragments, respectively. (A similar convention is also used in Figs. 6 and 7, where heavy dots, asterisks and triangles represent the vertices where one, two or three fragments, enabling walks of length 3 and 4, start.) The hexagons of the L_1-type possess two vertices marked by heavy dots and four vertices marked by asterisks. Therefore, 16 distinct walks of length 2 start from the vertices of the L_1-type hexagons of phenylenes. Since the arrangement of the vertices of different types is clear from Fig. 4, we further conclude that 20, 20 and 24 walks of length 2 start from the vertices of types L_2, A_2 and A_3, respectively. It is obvious that $b_{2,1}$ can be expressed as:

$$b_{2,1} = 16h_{L1} + 20h_{L2} + 20h_{A2} + 2 + 24h_{A3} \ .$$

As $h_{L1} = h_{A3} + 2$ the formula above can be straightforwardly transformed into

$$b_{2,1} = 20h - 8 \ . \tag{11}$$

By substituting Eqs. (9–11) back into (8) we arrive at Eq. (3).

5 Evaluation of M$_6$ and M$_8$

Following similar considerations, it was found that for $k = 3$ w assumes the values: 1, 2, 3, 4, 5 and 6, whereas for $k = 4$ w assumes the values: 1, 2, 3, 5, 6, 7, 8, 9, 14, 16 and 17. The corresponding coefficients $b_{3,w}$ and $b_{4,w}$ obey the formulae:

$$b_{3,1} = 12(h-1) + 2b \ , \tag{12}$$

$$b_{3,2} = 14h - 8 \ , \tag{13}$$

$$b_{3,3} = 6h_{L1} + 2h_{A2} \ , \tag{14}$$

$$b_{3,4} = 4(h - h_{A3}) + 4h_{L2} \ , \tag{15}$$

$$b_{3,5} = 2b \ , \tag{16}$$

$$b_{3,6} = 8(h-1) \ , \tag{17}$$

$$b_{4,1} = 12h - 16 + 4h_{A3} \ , \tag{18}$$

$$b_{4,2} = 4(h-1) + 4b \ , \tag{19}$$

$$b_{4,3} = 8(h-1) \ , \tag{20}$$

$$b_{4,5} = 4h_{L1} \ , \tag{21}$$

$$b_{4,6} = 6h_{L1} + 4h_{A2} \ , \tag{22}$$

$$b_{4,7} = 6h_{L1} + 12h_{L2} + 6h_{A2} \ , \tag{23}$$

$$b_{4,8} = 10h - 2b + 2h_{A3} - 12 \ , \tag{24}$$

$$b_{4,9} = 4b \ , \tag{25}$$

$$b_{4,14} = 4(h-1) \ , \tag{26}$$

$$b_{4,16} = 4(h-1) - 2b \ , \tag{27}$$

$$b_{4,17} = 2b \ . \tag{28}$$

By substituting Eqs. (12–17) as well as (18–28) into Eq. (8), topological formulae for M_6 and M_8 are obtained [Eqs. (4) and (5)].

As examples we present the details concerned with deriving $b_{3,2}, b_{3,5}$ and $b_{3,6}$, as well as $b_{4,2}, b_{4,6}$ and $b_{4,14}$. In Fig. 5 structural fragments of phenylenes that enable two, five and six walks of length 3, and two, six and 14 walks of length 4 are depicted. As an illustration we present the five walks of length 3, and the 14 walks of length 4.

$k = 3$ $w = 5$: 2-1-2-4, 2-3-2-4, 2-4-2-4, 2-4-5-4, 2-4-6-4,
$k = 4$ $w = 14$: 9-10-9-8-11, 9-10-9-13-11, 9-8-7-8-11, 9-8-11-8-11, 9-8-11-12-11, 9-8-11-13-11, 9-8-9-8-11, 9-8-9-13-11, 9-13-14-13-11, 9-13-11-13-11, 9-13-11-12-11, 9-13-9-13-11, 9-13-11-8-11, 9-13-9-8-11.

Structural fragments of phenylenes enabling five walks of length 3 are located at the bays, so that each bay provides two such fragments. On the basis of this, the dependence of $b_{3,5}$ on molecular structure is established by Eq. (16). A vertex of degree 3 is a starting point for two structural details enabling six walks of length 3. Therefore, the coefficient $b_{3,6}$ is equal to twice the number of vertices of degree 3, which is expressed by the Eq. (17).

In Fig. 6 the examples of phenylenes are given, illustrating the types of vertices that are distinguished in enumeration of structural details providing two walks of length 3 and 4. It is shown that 10, 14, 14 and 18 walks of length 3 (as well as two, four, eight and 18 walks of length 4) start from the vertices of the hexagons of L_1, L_2, A_2 and A_3 types, respectively. This provides a justification to express $b_{3,2}$ and $b_{4,2}$ in the form:

$$b_{3,2} = 10h_{L1} + 14(h_{L2} + h_{A2}) + 18h_{A3} = 14h - 8,$$
$$b_{4,2} = 2h_{L1} + 4h_{L2} + 8h_{A2} + 18h_{A3} = 4h + 4b - 4.$$

Fourteen walks of length 4 are accomplished between each pair of nonadjacent vertices of four membered rings (Eq. 26). Structural fragments providing six walks of length 4 can be found in hexagons of the type L_1 and A_2 (six and four such fragments), this is clearly demonstrated in Fig. 6.
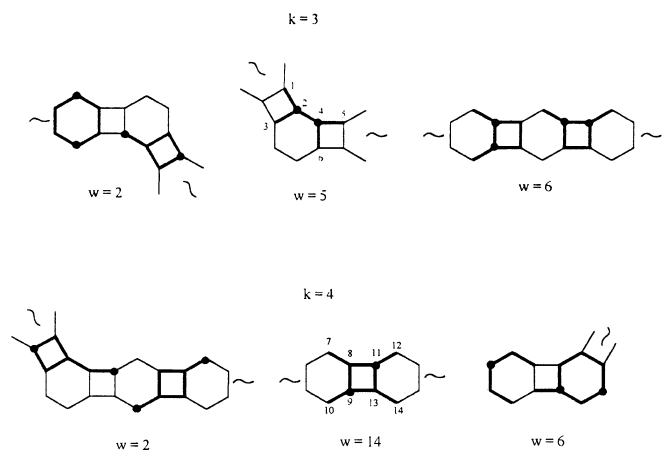
Fig. 5. Structural fragments providing walks of length 3 and 4. The start and end of walks are marked by *heavy dots*
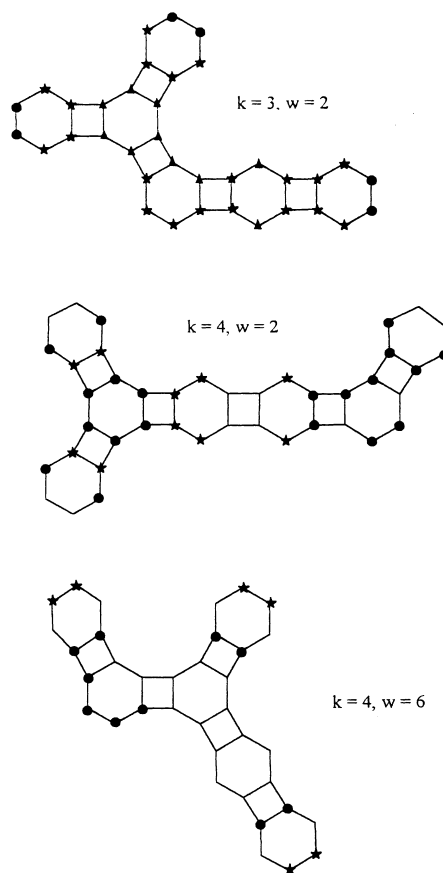
Fig. 6. Examples for evaluation of M_6 and M_8

6 Conclusions

Using the method of Hall [1], topological formulae for the fourth, sixth and eighth spectral moments of phenylenes are deduced in this paper. These formulae express the dependence of spectral moments on the molecular structure of phenylenes. The moments up to M_4 depend solely on the size of the molecule. The number of bays exerts influence both on M_6 and M_8. The number of hexagons of the A_3-type, i.e. the number of branchings in a molecule, is also a factor that plays a role in the structure dependence for M_8. All three of the mentioned graphical invariants can be easily deduced from molecular graphs of phenylenes.

It is worth noting that there is a remarkable similarity between the expressions for the moments of phenylenes and those for benzenoid systems [41, 42]. This is not the first resemblance observed between phenylenes and benzenoid hydrocarbons, in the study of the dependence of physico-chemical properties on molecular structure [17, 18].

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