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The evaluation of the eighth moment for benzenoid graphs

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Summary. The evaluation of the eighth moment of the adjacency matrix of benzenoid graphs is considered. It is found that the eighth moment can be expressed in terms of 7 graphical invariants. By this we extend the recently obtained results of Hall [1] and Dias [2].

Key words: Graph theory – Graphical invariants – Eighth moment

1. Introduction

Conjugated hydrocarbons are a class of compounds where topological effects play a significant role in determination of their physico-chemical properties. So, they are of a great interest for theoretical chemistry. Very often a conjugated hydrocarbon is represented by a molecular graph [3]. The adjacency matrix of the molecular graph (A) contains relevant information about molecular topology. It 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 [4].

The kth spectral moment of a molecular graph (M_k) is defined as:

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

where summation runs over all eigenvalues.

It is well known that:

$$M_k = \mathrm{Tr}[A^k].$$

The element $[A^k]_{ij}$ represents the number of walks of length k between the vertices i and j. Walks of different lengths are an object of interest of many graph theoreticians. A concept of an atomic code, based on enumeration of self-returning walks of different lengths, was put forward by Randić [5]. Non-equivalent vertices that have the same atomic codes, so-called isocodal vertices, have been discovered [5, 6]. The ID number (molecular identification number), proposed also by Randić for identifying molecular graphs by a real number, is based on similar concepts [7, 8].

The spectral moments have been used in a topological theory of conjugated hydrocarbons already in the early seventies [9–11]. In the recent past they have been intensively examined and various applications in chemistry have been found. Being very closely connected with the coefficients of the characteristic polynomial, they were used for facile calculation of the characteristic polynomial of acyclic [12] and different small molecules with or without heteroatoms [13, 14]. In a series of papers [1, 9, 10, 12–19] spectral moments were used for the estimation of HMO total π-electron energy and the examination of its dependence on molecular structure. A treatment based on the energy partitioning via moments was proposed [19, 20] for dealing with aromaticity of conjugated systems. The moments also found remarkable applications in the solid-state physical chemistry [21–24]. Namely, it has been shown that, using a continued fraction technique, the normalized moments can be used for obtaining the HMO density of states and other useful properties for solids.

In all applications of moments it is important to know how the moments depend on molecular structure. For these reasons efforts have been made to establish explicit topological formulae for moments. In these works particular attention has been devoted to benzenoid hydrocarbons, but it is worth mentioning that a procedure for evaluation of moments for acyclic chains was also put forward [18]. This method was further elaborated and adapted to benzenoid systems [19].

Topological formulae for spectral moments

We first mention some topological invariants which will be needed in the text that follows. Note that all symbols refer to benzenoid graphs.

h – number of six-membered rings

n – number of vertices

m – number of edges

B – number of bays

C – number of coves

F – number of fjords

n_b – number of bay regions ($n_b = B + 2C + 3F$)

h_R – number of rings all of whose verticies are of degree 3

h_I – number of rings one of whose vertices is of degree 2

n_i – number of internal vertices.

Some of these structural details are illustrated in Fig. 1.

According to Eq. (1) the zeroth spectral moment of all graphs is in a trivial manner given by:

$$M_0 = n.$$

Because of the pairing theorem all odd moments of bipartite graphs (and therefore, of all benzenoid systems) are equal to zero:

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

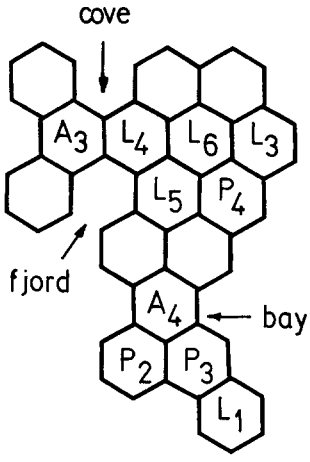


Fig. 1. Symbols used in this paper [25]. There are 5 types of rings all of whose vertices are of degree 3: L_4, L_5, L_6, A_3, and A_4; their total number is denoted by h_R. There are 2 types of rings one of whose vertices is of degree 2: P_3 and P_4; their total number is denoted by h_I

The second spectral moment of all graphs is given by a long and well known formula:

$$M_2 = 2m$$

whereas the expressions below hold only for benzenoid systems:

$$M_4 = 18m - 12n$$

$$M_6 = 148m - 144n + 48 + 6n_b.$$

The result for the fourth moment seems to be first reported in Ref. [11], and was eventually rediscovered several times [1, 15, 16, 26]. Dias [2] and Hall [1] independently arrived at the result for M_6. Dias [2] gave also a formula for the eighth coefficient of the characteristic polynomial of catacondensed benzenoid systems. From it a topological expression for the eighth spectral moment of catacondensed benzenoids can easily be deduced. Jiang and Zhang [19] gave the formulae for benzenoid systems up to M_{12}. Although their method is very useful for acyclic chains [18], it becomes practically useless for calculation of moments of cyclic graphs. Moreover, formulae of Jiang and Zhang are of the form that cannot be compared with the formulae listed below in the present paper. Nevertheless, formulae from Ref. [19] show that the spectral moments can be expressed in terms of graph fragments.

In this paper we derive a topological formula for the eighth moment of all (catacondensed and pericondensed) benzenoid systems.

2. Evaluation of M_8

Since a benzenoid system is bipartite, its vertices can be separated into two groups (white and black), such that a white vertex has only black neighbours and vice versa. Then the adjacency matrix can be put into the form [27]:

$$A = \begin{bmatrix} 0 & B \\ B^T & 0 \end{bmatrix}$$

where B contains all the non-zero interactions, and B^T is the transpose of B.

In the case of M_8 we have:

$$M_8 = \mathrm{Tr}[A^8] = \mathrm{Tr}[C^2] + \mathrm{Tr}[C'^2], \tag{2}$$

where C and C' denote the symmetric matrices $[B \cdot B^T]^2$ and $[B^T \cdot B]^2$, respectively. Since the trace of the square of a symmetric matrix is the sum of the squares of all elements of the matrix, Eq. (2) can be put into the form:

$$M_8 = \sum_{i,j} C_{ij}^2 + \sum_{i,j} C_{ij}'^2.$$

It can be proved that:

$$\sum_{i,j} C_{ij}^2 = \sum_{i,j} C_{ij}'^2,$$

which implies:

$$M_8 = 2\sum_{i,j} C_{ij}^2 = 2\sum_{i,j} C_{ij}'^2. \tag{3}$$

Both matrices refer to only one group of vertices – either black or white. In the text that follows it will be considered that C reflects the interactions of black vertices, and C' that of white ones. In Fig. 2 we present as an example the matrices C and C' of perinaphthyl.

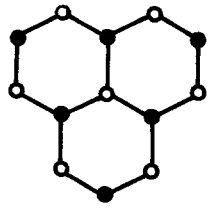
As a consequence of Eq. (3), the eighth moment can be deduced from the matrix C as well as from the matrix C' by squaring each element and adding. For such a calculation it is necessary to know which numbers appear in the matrices C and C' and how many times. If a_w and b_w show how many times a certain value w appears among the matrix elements of C and C', respectively, then M_8 can be expressed as follows:

$$M_8 = 2\sum_{w=1}^{\infty} a_w w^2 = 2\sum_{w=1}^{\infty} b_w w^2. \tag{4}$$

By elementary transformations of Eq. (4) the result:

$$M_8 = \sum_{w=1}^{\infty} (a_w + b_w) w^2 = \sum_{w=1}^{\infty} c_w w^2 \tag{5}$$

$$C = \begin{bmatrix} 6 & 6 & 6 & 2 & 1 & 1 \\ 6 & 13 & 8 & 8 & 2 & 6 \\ 6 & 8 & 13 & 8 & 6 & 2 \\ 2 & 8 & 8 & 13 & 6 & 6 \\ 1 & 2 & 6 & 6 & 6 & 1 \\ 1 & 6 & 2 & 6 & 1 & 6 \end{bmatrix}$$



$$C' = \begin{bmatrix} 7 & 7 & 5 & 5 & 2 & 1 & 2 \\ 7 & 15 & 7 & 7 & 7 & 7 & 7 \\ 5 & 7 & 7 & 2 & 1 & 2 & 5 \\ 5 & 7 & 2 & 7 & 5 & 2 & 1 \\ 2 & 7 & 1 & 5 & 7 & 5 & 2 \\ 1 & 7 & 2 & 2 & 5 & 7 & 5 \\ 2 & 7 & 5 & 1 & 2 & 5 & 7 \end{bmatrix}$$

Fig. 2. Matrices C and C' of perinaphthyl; C refers to black vertices, C' to white vertices

is obtained. In Eq. (5) c_w represents the total number of elements of C and C' taking the value w.

An element C_{ij} (as well as C'_{ij}) is equal to the number of walks of length 4 between the vertices i and j of the respective molecular graph. It means that a_w and b_w represent the numbers of structural fragments which enable w distinct walks of length 4. The quantities a_w and b_w count the fragments in which such walks start and end at black, respectively white vertices, and c_w is equal to the total number of the graph fragments which enable w walks of length 4. Hence our problem is reduced to the recognition and enumeration of structural fragments enabling walks of length 4.

3. Recognition and enumeration of structural fragments enabling walks of length 4

We consider all possible fragments of benzenoid systems which enable walks of length 4. They are classified according to their w value. They are depicted in Fig. 3. A systematic examination shows that w can assume only the values 1, 2, 5, 6, 7, 8, 13, 14, and 15.

We now have to determine the coefficients c_w. Since this requires a very detailed combinatorial consideration, we present here only the details for c_{13}.

Let t be the fragment that enables 13 walks of length 4. As shown in Fig. 3 it has a vertex of degree 3 (heavy dot) surrounded by two vertices of degree 2 and one vertex of degree 3. The vertex of t at which the walks start and end (heavy dot) will be called a vertex of type t. In linear polyacenes there are two fragments t between each pair of adjacent six-membered rings, therefore there are $(h-1)\cdot 2$ fragments t. Benzene has no fragments t, so that it, formally, satisfies the expression $(h-1)\cdot 2$.

Consider a graph R that consists of a certain (but arbitrary) number of (fused) hexagons lying along parallel lines. Each subgraph is a linear polyacene or benzene (Fig. 5). If the number of components of R is k, then the total number of its six-membered rings is:

$$h = h_1 + h_2 + \cdots + h_k$$

where h_i is the number of rings in the ith component. In such a system there are

$$2(h_1 - 1) + 2(h_2 - 1) + \cdots + 2(h_k - 1) = 2(h - k)$$

fragments t.

Imagine a condensation of the system R, forming the system S (Fig. 6). In the system S, five types of vertices can be observed:

– vertices which are of type t in the graph R and remain of the same type in the graph S (●);

– vertices which are of type t in the graph R, but not in the system S. They can be internal (○) or external (∗);

– vertices that become of type t by the condensation (□);

– vertices similar to those marked by □, but lying in bays, coves and fjords (■), that do not become of type t because of their position.

Obviously, there are n_i vertices marked by ○. If n_*, $n_\square$ and $n_\blacksquare$ represent numbers of vertices marked by ∗, □ and ■, respectively, then the expression

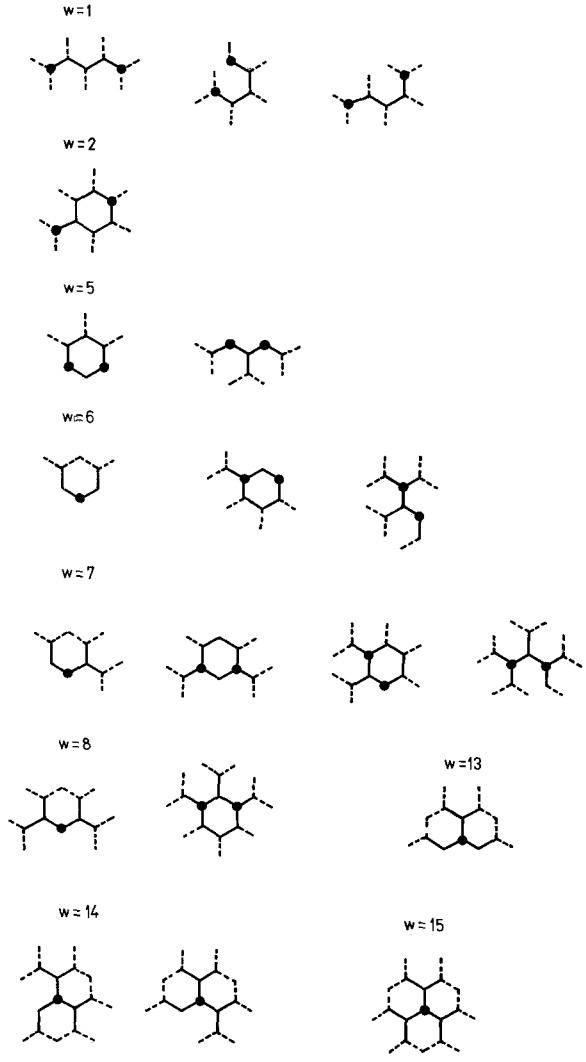


Fig. 3. Structural fragments in benzenoid systems enabling walks of length 4; the end vertices of the respective walks are marked by *heavy dots*; the edges which the fragment must possess are represented by *full lines*, the *dashed edges* may but need not exist

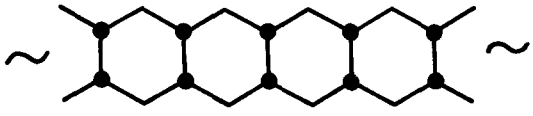


Fig. 4. Vertices of type t are indicated by *heavy dots*

$2h - 2k - n_i - n_* + n_\square$ represents the number of fragments t in the system S. Since $n_\square + n_\blacksquare = 2(k-1)$ we further have:

$$c_{13} = 2h - 2 - n_i - (n_\blacksquare + n_*).$$

Vertices marked by ■ and $*$ lie on bays, coves and fjords, so that a bay has 2, a cove 3 and a fjord 4 of them. Finally, the formula:

$$c_{13} = 2(h-1) - n_i - 2B - 3C - 4F \tag{6}$$

is obtained.

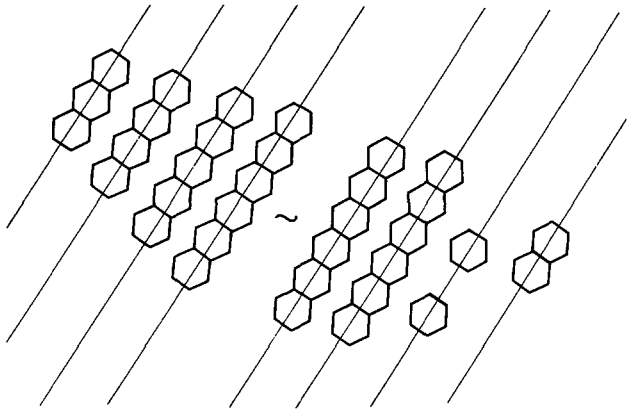


Fig. 5. Example of a graph R

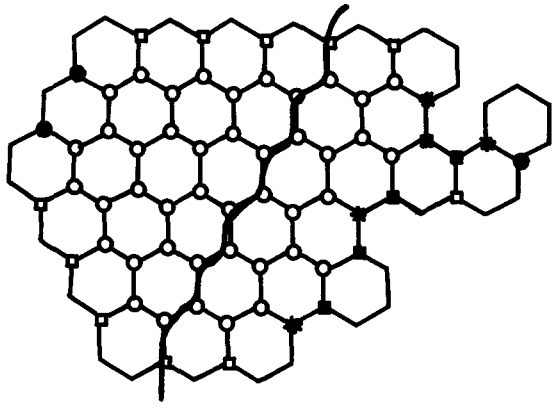


Fig. 6. Examples of a system S

Following similar considerations it can be shown that:

$$c_1 = 8(h-2) + 4 + 4B + 10C + 16F + 4h_R + 2h_I \tag{7}$$

$$c_2 = 8(h-1) + 2n_i \tag{8}$$

$$c_5 = 4(h+1) - 4B - 6C - 8F + 4h_R + 2h_I - 4n_i \tag{9}$$

$$c_6 = 6(2-h_R) + 8B + 12C + 16F + 3n_i - 3h_I \tag{10}$$

$$c_7 = 12(h-1) - 6B - 10C - 14F - 6n_i \tag{11}$$

$$c_8 = 2(h-2) + 2B + 4C + 6F + 2h_R + 4n_i + h_I \tag{12}$$

$$c_{14} = 2(B + C + F) \tag{13}$$

$$c_{15} = C + 2F + n_i. \tag{14}$$

By substituting Eqs. (6)–(14) back into Eq. (5) we arrive at:

$$M_8 = 1194h - 694 + 80B + 168C + 256F + 16h_R + 18h_I + 34n_i \tag{15}$$

which is easily transformed into:

$$M_8 = 1330m - 1364n + 704 + 80B + 168C + 256F + 16h_R + 8h_I. \tag{16}$$

Both Eqs. (15) and (16) show that M_8 can be expressed in terms of 7 mutually independent topological factors. These formulae are valid for all benzenoid systems, except benzene. The special case for catacondensed benzenoids agrees with the previous result of Dias [2].

It is worth noting that the present result has already been exploited in [28] for obtaining McClelland-type approximations for total π-electron energies of benzenoid hydrocarbons.

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