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An algorithm for the calculation of the hyper-Wiener index of benzenoid hydrocarbons

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Abstract

An algorithm for the calculation of the hyper-Wiener index (WW) of benzenoid hydrocarbons (both cata- and pericondensed) is described, based on the consideration of pairs of elementary cuts of the corresponding benzenoid graph B. A pair of elementary cuts partitions the vertices of B into four classes. WW is expressed as a sum of terms of the form $n_{11}n_{22} + n_{12}n_{21}$, each associated with a pair of elementary cuts; n_{rs}, r, $s = 1, 2$ are the numbers of vertices in the respective four classes. The algorithm proposed enables a relatively easy calculation of WW, finding expressions for WW of homologous series of benzenoid hydrocarbons, and envisaging the relations between WW and molecular structure.

Keywords: Hyper-Wiener index; Benzenoid hydrocarbons; Topological index; Benzenoid graph; Elementary cut

1. Introduction

The hyper-Wiener index WW is one of the recently conceived distance-based graph invariants, used as a structure-descriptor for predicting physico–chemical properties of organic compounds (often those significant for pharmacology, agriculture, environment-protection etc.). The hyper-Wiener index was invented by Randić (1993) and was eventually extensively studied (Randić et al., 1993, 1994; Lukovits, 1994, 1995, 1996; Lukovits and Linert, 1994; Klein et al., 1995; Linert et al., 1995a,b; Diudea, 1996; Zhu et al., 1996; Gutman, 1997; Gutman et al., 1997; Linert and Lukovits, 1997; Diudea and Gutman, 1998; Klavžar, 1999). Randić's original definition of the hyper Wiener index (Randić, 1993, Randić et al., 1993, 1994) was applicable to trees, but not to cycle containing systems. The difficulty was overcome by Klein et al. (1995) who showed that for trees,

$$WW(G) = \frac{1}{2}\sum_{x<y} d(x, y; G)^2 + \frac{1}{2}\sum_{x<y} d(x, y; G) \qquad (1)$$

where $d(x, y; G)$ stands for the distance between the vertices x and y in the graph G. For some time the right-hand side of Eq. (1) is being used as the definition of the hyper–Wiener index of all, both acyclic and cycle-containing, (molecular) graphs (Linert et al., 1995a,b; Lukovits, 1995, 1996; Zhu et al., 1996; Gutman, 1997; Gutman et al., 1997; Linert and Lukovits, 1997; Diudea and Gutman, 1998; Klavžar, 1999). Recall that the Wiener index of G is given by

$$W(G) = \sum_{x<y} d(x, y; G)$$

In the case of polycyclic molecules the calculation of WW by means of Eq. (1) is not easy, especially if one is interested in finding general expressions for WW of homologous series (Linert et al., 1995a; Linert and

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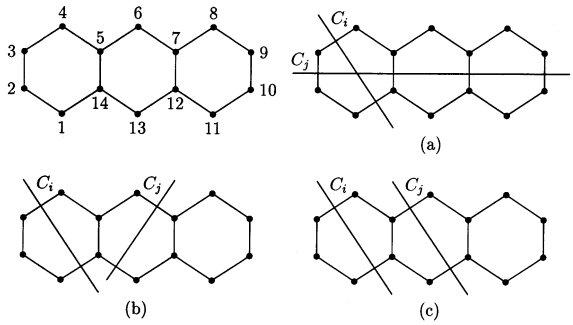

Fig. 1. The three possible arrangements of a pair of elementary cuts in a benzenoid system: (a) the cuts intersect inside the benzenoid system, (b) the cuts intersect outside the benzenoid system, (c) the cuts are parallel.

Lukovits, 1997). As a consequence, until now not a single such expression has been reported for any homologous series of benzenoid hydrocarbons.

We now contribute towards filling this gap, by describing a new method for the computation of the hyper Wiener index, applicable to benzenoid molecules, both catacondensed and pericondensed. In order to formulate our algorithm we need some preparations.

2. Benzenoid systems and their elementary cuts

Elementary cuts in benzenoid systems have been described and illustrated by numerous examples in several earlier articles (Sachs, 1984; Gutman and Klavžar, 1995, 1996, 1998; Gutman and Cyvin, 1997; Klavžar and Gutman, 1997; Klavžar, 1999). They found applications in the theoretical chemistry of benzenoid hydrocarbons, in studies concerned with Kekule structures, Wiener and Szeged indices. In view of this, here we only repeat the basic definitions.

Benzenoid systems are plane graphs representing benzenoid hydrocarbons. They are always considered as embedded into the hexagonal (graphite) lattice. All their hexagons are regular, mutually congruent. A benzenoid system is always drawn so that some of its edges are vertical. For more details see Gutman and Klavžar (1995) and elsewhere (Sachs, 1984; Gutman and Cyvin, 1989, 1997; Gutman and Klavžar, 1996, 1998; Klavžar and Gutman, 1997).

Denote by B a benzenoid system and by n the number of its vertices. If all vertices of B lie on its perimeter (boundary), then B is said to be *catacondensed*; otherwise it is *pericondensed* (Gutman and Cyvin, 1989). In pericondensed benzenoid systems there exist vertices belonging to three hexagons.

An *elementary cut or elementary edge-cut* of B is a straight line segment, passing through the centers of some edges of B, being orthogonal to these edges, and intersecting the perimeter of B exactly two times, so that at least one hexagon lies between these two intersection points. (Examples of elementary cuts are given below.)

Let B be a benzenoid system, $V(B)$ its vertex set and C one of its elementary cuts. Then C partitions the vertices of B into two non-empty classes $V_1(C; B)$ and $V_2(C; B)$, such that

$$V_1(C; B) \cap V_2(C; B) = \phi$$

$$V_1(C; B) \cup V_2(C; B) = V(B)$$

The elements of $V_1(C; B)$ are the vertices of B lying on one side of C, the elements of $V_2(C; B)$ are the vertices of B lying on the other side of C. In what follows it makes no difference which side of C corresponds to $V_1(C; B)$ and which to $V_2(C; B)$.

As usual $|S|$ denotes the number of elements of the set S. Then, $|V(B)| = n$. Let $n_1(C)$ and $n_2(C)$ denote the numbers of vertices of B lying on the two sides of the elementary cut C, i.e.

$$\left.\begin{aligned} n_1 = n_1(C) = n_1(C; B) = |V_1(C; B)| \\ n_2 = n_2(C) = n_2(C; B) = |V_2(C; B)| \end{aligned}\right\} \tag{2}$$

Then the Wiener index of B can be calculated by means of the formula (Gutman and Klavžar, 1996):

$$W(B) = \sum_i n_1(C_i; B) n_2(C_i; B) \tag{3}$$

in which the summation embraces all elementary cuts of B. Recall that the Szeged index of B satisfies a similar, yet somewhat more complicated, expression (Gutman and Klavžar, 1995). Clearly, the sum $n_1 + n_2$ is independent of the elementary cut C and is equal to the number n of vertices of B.

Consider now two distinct (i.e. mutually non-identical) elementary cuts of B, say, C_i and C_j. They induce four vertex-classes: $V_1(C_i; B)$, $V_2(C_i; B)$, $V_1(C_j;$ B) and $V_2(C_j; B)$. Then we define:

$$\left.\begin{aligned} n_{11} = n_{11}(C_i, C_j) = n_{11}(C_i, C_j; B) = |V_1(C_i; B) \cap V_1(C_j; B)| \\ n_{12} = n_{12}(C_i, C_j) = n_{12}(C_i, C_j; B) = |V_1(C_i; B) \cap V_2(C_j; B)| \\ n_{21} = n_{21}(C_i, C_j) = n_{21}(C_i, C_j; B) = |V_2(C_i; B) \cap V_1(C_j; B)| \\ n_{22} = n_{22}(C_i, C_j) = n_{22}(C_i, C_j; B) = |V_2(C_i; B) \cap V_2(C_j; B)| \end{aligned}\right\} \tag{4}$$

Because the four quantities n_{rs}, $r, s = 1, 2$ play the central role in our algorithm, we illustrate their definition on the examples depicted in Fig. 1.

In the example (a), illustrating the case when the two elementary cuts intersect inside the benzenoid system,

$V_1(C_i) = \{1, 2, 3\}$

$V_2(C_i) = \{4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14\}$

$V_1(C_j) = \{3, 4, 5, 6, 7, 8, 9\}$

$V_2(C_j) = \{1, 2, 10, 11, 12, 13, 14\}$

Consequently,

$V_1(C_i) \cap V_1(C_j) = \{3\}$

$V_1(C_i) \cap V_2(C_j) = \{1, 2\}$

$V_2(C_i) \cap V_1(C_j) = \{4, 5, 6, 7, 8, 9\}$

$V_2(C_i) \cap V_2(C_j) = \{10, 11, 12, 13, 14\}$

and $n_{11} = 1$, $n_{12} = 2$, $n_{21} = 6$, $n_{22} = 5$.

In the example (b) the two elementary cuts intersect outside the benzenoid system. Then we have

$V_1(C_i) = \{1, 2, 3\}$

$V_2(C_i) = \{4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14\}$

$V_1(C_j) = \{1, 2, 3, 4, 5, 6, 14\}$

$V_2(C_j) = \{7, 8, 9, 10, 11, 12, 13\}$

implying

$V_1(C_i) \cap V_1(C_j) = \{1, 2, 3\}$

$V_1(C_i) \cap V_2(C_j) = \varnothing$

$V_2(C_i) \cap V_1(C_j) = \{4, 5, 6, 14\}$

$V_2(C_i) \cap V_2(C_j) = \{7, 8, 9, 10, 11, 12, 13\}$

and $n_{11} = 3$, $n_{12} = 0$, $n_{21} = 4$, $n_{22} = 7$.

The third example (c) illustrates the case when the two elementary cuts are parallel. Then

$V_1(C_i) = \{1, 2, 3\}$

$V_2(C_i) = \{4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14\}$

$V_1(C_j) = \{1, 2, 3, 4, 5, 13, 14\}$

$V_2(C_j) = \{6, 7, 8, 9, 10, 11, 12\}$

and

$V_1(C_i) \cap V_1(C_j) = \{1, 2, 3\}$

$V_1(C_i) \cap V_2(C_j) = \varnothing$

$V_2(C_i) \cap V_1(C_j) = \{4, 5, 13, 14\}$

$V_2(C_i) \cap V_2(C_j) = \{6, 7, 8, 9, 10, 11, 12\}$

resulting in $n_{11} = 3$, $n_{12} = 0$, $n_{21} = 4$, $n_{22} = 7$.Observe that

$$n_{11}(C_i, C_j) + n_{12}(C_i, C_j) + n_{21}(C_i, C_j) + n_{22}(C_i, C_j) = n \tag{5}$$

i.e. the sum of the quantities $n_{r,s}$, $r, s = 1, 2$ is independent of the elementary cuts C_i and C_j.

The definition (4) is, formally, applicable also in the case when the two elementary cuts coincide, $C_i \equiv C_j$. Then

$$\left.\begin{aligned} n_{11}(C_i, C_j; B) &= |V_1(C_i; B)| = n_1(C_i; B) \\ n_{12}(C_i, C_j; B) &= |V_1(C_i; B) \cap V_2(C_j; B)| = |\varnothing| = 0 \\ n_{21}(C_i, C_j; B) &= |V_2(C_i; B) \cap V_1(C_j; B)| = |\varnothing| = 0 \\ n_{22}(C_i, C_j; B) &= |V_2(C_i; B)| = n_2(C_i; B) \end{aligned}\right\} \tag{6}$$

3. The algorithm

The hyper–Wiener index of a benzenoid hydrocarbon whose molecular graph is B can be calculated by means of the formula

$$WW(B) = \sum_{i \le j} [n_{11}(C_i, C_j; B) n_{22}(C_i, C_j; B) + n_{12}(C_i, C_j; B) n_{21}(C_i, C_j; B)] \tag{7}$$

in which the summation goes over all pairs of (not necessarily distinct) elementary cuts of B. Bearing in mind the relations (3) and (6), formula (7) is rewritten as

$$WW(B) = \sum_i n_1(C_i; B) n_2(C_i; B) + WW^*(B) \tag{8}$$

or

$$WW(B) = W(B) + WW^*(B) \tag{9}$$

with $WW^*(B)$ being the abbreviation for the sum

$$\sum_{i < j} [n_{11}(C_i, C_j; B) n_{22}(C_i, C_j; B) + n_{12}(C_i, C_j; B) n_{21}(C_i, C_j; B)] \tag{10}$$

which embraces all pairs of (mutually distinct) elementary cuts of the benzenoid system B. Formulae (7)–(9) hold for all benzenoid systems, both cata- and pericondensed.

The proof of formulae (7)–(9) proceeds via a graph theoretical technique called isometric embedding, and is based on the fact that benzenoid systems can be isometrically embedded into a hypercube; its details are given elsewhere (Klavžar, 1999).

The actual algorithm for the calculation of WW of a benzenoid hydrocarbon utilizes forrmulae (3) and (9). Its main steps are the following:

1. find all elementary cuts;
2. calculate n_r, $r = 1, 2$, Eq. (2), for each elementary cut;
3. calculate n_{rs}, $r, s = 1, 2$, Eq. (4), for each pair of elementary cuts;
4. apply Eq. (3) and calculate W;

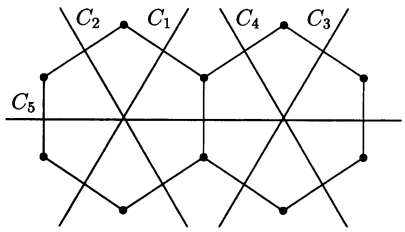

Fig. 2. The elementary cuts of naphthalene (L_2).

Table 1
The quantities n_r and n_{rs}, $r, s = 1, 2$ pertaining to the elementary cuts of naphthalene and pairs thereof; for labeling of the elementary cuts see Fig. 2

Cut		n_1	n_2	
C_1		3	7	
C_2		3	7	
C_3		7	3	
C_4		7	3	
C_1		5	5	
cuts	n_{11}	n_{12}	n_{21}	n_{22}
C_1, C_2	2	1	1	6
C_1, C_3	3	0	4	3
C_1, C_4	3	4	0	3
C_1, C_5	1	2	4	3
C_2, C_3	3	4	0	3
C_2, C_4	3	0	4	3
C_2, C_5	2	1	3	4
C_3, C_4	6	1	1	2
C_3, C_5	3	4	2	1
C_4, C_5	4	3	1	2

5. calculate WW^*, Eq. (10);
6. apply Eq. (9) and calculate WW.

Concerning step 1 it should be pointed out (Gutman and Klavžar, 1995, 1996) that the number of elementary cuts of a benzenoid system is significantly smaller than the number of vertex pairs. Therefore the number of terms in the summation (10) is much smaller than the number of terms on the right-hand side of (1). The calculations required in steps 2 and 3 are elementary and consist just of counting of vertices. In view of relation (5) it is sufficient to determine only three among the quantities n_{rs}, $r, s = 1, 2$, the fourth can then be computed from the (always known!) number of vertices of the benzenoid system considered.

In order to illustrate our algorithm we compute the hyper–Wiener index of naphthalene. The naphthalene graph L_2 has five elementary cuts C_1, C_2, C_3, C_4 and C_5, depicted in Fig. 2.

By direct counting we arrive at the numbers given in Table 1.

Using formula (3) and the data from Table 1 we have

$$W(L_2) = 3 \times 7 + 3 \times 7 + 7 \times 3 + 7 \times 3 + 5 \times 5 = 109$$

Next, we evaluate the sum (10), which in the case of $B = L_2$ is equal to

$$\begin{aligned} WW^* = {} & [2 \times 6 + 1 \times 1] + [3 \times 3 + 0 \times 4] \\ & + [3 \times 3 + 4 \times 0] + [1 \times 3 + 2 \times 4] \\ & + [3 \times 3 + 4 \times 0] + [3 \times 3 + 0 \times 4] \\ & + [2 \times 4 + 1 \times 3] + [6 \times 2 + 1 \times 1] \\ & + [3 \times 1 + 4 \times 2] + [4 \times 2 + 3 \times 1] = 106 \end{aligned}$$

Consequently, the hyper Wiener index of naphthalene is equal to $WW(L_2) = 109 + 106 = 215$.

The above calculation was performed without using the symmetry of the molecule considered. This symmetry causes that numerous summands are mutually equal. Needless to say that by taking into account molecular symmetry our algorithm would additionally gain on efficiency and simplicity.

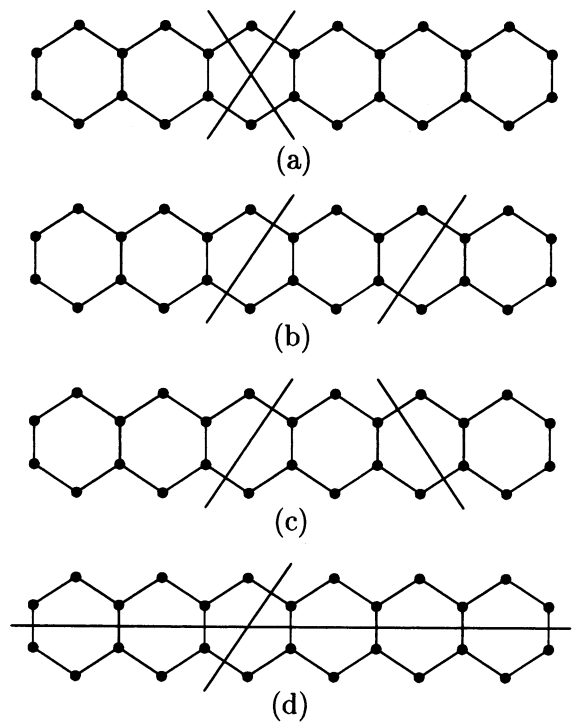

Fig. 3. Types of arrangements of a pair of elementary cuts in the linear polyacene L_h: (a) two slanted cuts in the p-th hexagon, $p = 1, 2, \ldots, h$; (b) two parallel slanted cuts in the p-th and q-th hexagons, $p = 1, 2, \ldots, h-1$, $q = p+1, \ldots, h$; (c) two nonparallel slanted cuts in the p-th and q-th hexagons, $p = 1, 2, \ldots, h-1$, $q = p+1, \ldots, h$; (d) the horizontal cut and a slanted cut in the p-th hexagon, $p = 1, 2, \ldots, h$; each arrangement of type (b), (c) and (d) exists in two symmetry-equivalent forms

Table 2
The quantities n_{rs}, $r, s = 1, 2$ pertaining to the four types of elementary cuts of the linear polyacene L_h, c.f. Fig. 3; n.s.e. = number of symmetry-equivalent forms

Type	n_{11}	n_{12}	n_{21}	n_{22}	n.s.e.
a	$4p-2$	1	1	$4(h-p)+2$	1
b	$4p-1$	$4(q-p)$	0	$4(h-q)+3$	2
c	$4p-1$	0	$4(q-p)$	$4(h-p)+3$	2
d	$2p$	$2p-1$	$2(h-p)+1$	$2(h-p)+2$	2

4. Hyper-Wiener index of linear polyacenes

In this section we deduce the expression for the hyper–Wiener index of the linear polyacene L_h, consisting of h hexagons, $h \geq 1$. Recall that for $h = 1, 2, 3, 4, 5, \ldots$ the graph L_h represents benzene, naphthalene, anthracene, naphthacene, pentacene,... (Gutman and Cyvin, 1989). A pair of elementary cuts of L_h can have the arrangements depicted in Fig. 3. The quantities n_{rs}, $r, s = 1, 2$, pertaining to these pairs are given in Table 2. Note that their sum is always equal to $n(L_h) = 4\ \mathrm{h} + 2$.

The calculation of the Wiener index of L_h by means of formula (3) was outlined in due detail in an earlier work (Gutman and Klavžar, 1996) and will not be reproduced here again. We have

$$W(L_h) = \frac{1}{3}(16h^3 + 36h^2 + 26h + 3)$$

In order to find the formula for $WW(L_h)$ we only need to the respective expression for the sum (10). Bearing in mind the data given in Table 2, we obtain

$$\begin{aligned} WW^*(L_h) = & \sum_{p=1}^{h} [(4p-2)(4h-4p+2) + 1 \cdot 1] \\ & + (2+2) \\ & \sum_{p=1}^{h-1} \sum_{q=p+1}^{h} [(4p-1)(4h-4q+3) \\ & + (4q-4p) \cdot 0] \\ & + 2 \sum_{p=1}^{h} [2p(2h-2p+2) \\ & + (2p-1)(2h-2p+1)] \end{aligned}$$

which after an elementary, but quite lengthy calculation yields

$$WW^*(L_h) = \frac{1}{3}(8h^4 + 16h^3 + 10h^2 + 11h)$$

Then by Eq. (9) we arrive at our final result:

$$WW^*(L_h) = \frac{1}{3}(8h^4 + 32h^3 + 46h^2 + 37h + 3)$$

which holds for all $h = 1, 2, \ldots$

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