A method for calculating Wiener numbers of benzenoid hydrocarbons

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A method is elaborated for the calculation of the Wiener number W of benzenoid hydrocarbons, based on the examination of their elementary cuts. It requires the finding of all elementary cuts of a benzenoid system and counting the vertices lying on each side of these cuts. This is much easier than finding the distances between all pairs of vertices of the same system. By means of our approach is it quite simple to find combinatorial expressions for W of compact pericondensed benzenoid hydrocarbons, a task which hardly could have been accomplished by the hitherto existing calculation techniques.

Introduction

The topological index W, conceived by Wiener [1] almost half a century ago, is one of the most thoroughly studied, best understood and most frequently used molecular-shape descriptors in chemical graph theory. It found numerous applications in the modelling of a variety of physico-chemical, pharmacological and biological properties of organic molecules, and its theory is equally well developed; for recent reviews see [2, 3]. To illustrate the versatility of the practical applications of the Wiener number, we mention its use for predicting of ultrasonic sound velocities in alkanes and alcohols [4], of rates of electroreduction of chlorobenzenes [5], of cytostatic and antihistaminic activities of certain drugs [6], of protonation constants of derivatives of salicylhydroxamic acid and (in connection with this) of their fungicidal activities [7], and for distinguishing between fullerene isomers [8]. The success of W was long time sought in its (putative) capability of measuring molecular van der Waals volumes, surfaces and/or surface-to-volume ratios. It was shown quite recently [9] that, indeed, W is proportional to molecular surfaces. On the other hand, contrary to earlier expectations, no relation between W and molecular volumes could be established [9].

The Wiener number (or Wiener index) is defined as follows [2, 3].

Let u and v be two vertices of the molecular graph G [10]. The distance [10, 11] between u and v is equal to the length of a shortest path that connects u and v, i.e., to the number of edges in such a path. The distance between the vertices u and v in the graph G is denoted by $d(u, v \mid G)$.

The Wiener number is equal to the sum of the distances between all pairs of vertices of the respective molecular graph G,

$$W = W(G) = \sum_{u < v} d(u, v \mid G).$$ (1)

Recall that if G has n vertices, then the summation on the right-hand side of Eq. (1) embraces $n(n-1)/2$ terms.

Calculating the Wiener number

In view of the importance of the Wiener number, several methods have been developed for its efficient calculation. There exist fast algorithms for computer-aided numerical evaluation of $W(G)$ of a given molecular graph G [12–14]. Other methods enable the calculation of W by using its dependence on molecular structure (i.e., dependence on the structure of the molecular graph G) [1, 15–21]. Procedures of this kind were developed for alkanes [1, 15–19] and catacondensed benzenoid hydrocarbons [20, 21], resulting in combinatorial expressions for W for a large number of classes of such molecules. For other polycyclic systems of interest in chemistry, especially for compact pericondensed benzenoid molecules, no generally applicable structural method seems to have been reported in the literature.

In the present paper we offer a contribution towards filling this gap. We, namely, describe a structure-based algorithm which is applicable to all benzenoid systems (both cata- and pericondensed [22]), which is remarkably simple and, consequently, which is usable also in the case of very large molecules.

The mathematical background of our method was presented elsewhere [23], where it was demonstrated that the molecular graphs of benzenoid hydrocarbons are binary Hamming graphs [24, 25]. The readers interested in details of this kind should consult the works [23–25] and the references cited therein. For the present algorithm especially relevant is Proposition 3.1 of [23]. Note, however, that the algorithm itself is described in this paper for the first time.

The algorithm, in the form outlined in this paper, applies to benzenoid molecules, but its extension to other types of polycyclic systems would easily be possible.

Benzenoid systems and their normal cuts

Benzenoid systems (or benzenoid graphs) are graphs constructed in the following manner [22]. Let H be the hexagonal (graphite) lattice and let Z be a circuit on it. Then a benzenoid system is formed by the vertices and edges of H, lying on Z and in the interior of Z. The vertices and edges belonging to Z form the perimeter of the respective benzenoid system. The vertices of the benzenoid system (if any), not belonging to the perimeter are said to be the internal vertices.

The number of vertices, internal vertices, edges and hexagons of a benzenoid system B will be denoted by [22] $n = n(B)$, $n_i = n_i(B)$, $m = m(B)$ and $h = h(B)$, respectively. These parameters are known to be related as follows [22]:

$$n = 4h + 2 - n_i , \tag{2}$$
$$m = 5h + 1 - n_i . \tag{3}$$

In Fig. 1 the above definition is illustrated on the example of the pericondensed benzenoid molecule B_0 for which $h = 8$, $n_i = 6$, $n = 28$, $m = 35$.

If a benzenoid system B is viewed as a geometric figure in the plane [22] then an elementary cut is defined as follows. Choose an edge e of B and draw a straight line through the center of e, orthogonal on e. This line intersects the perimeter of B in two points P_1 and P_2. The straight line segment C, the end-points of which are P_1 and P_2, is the elementary cut pertaining to the edge e. Clearly, C intersects not only the edge e, but all edges lying between P_1 and P_2 (inclusive the two edges on the perimeter to which the points P_1 and P_2 belong).

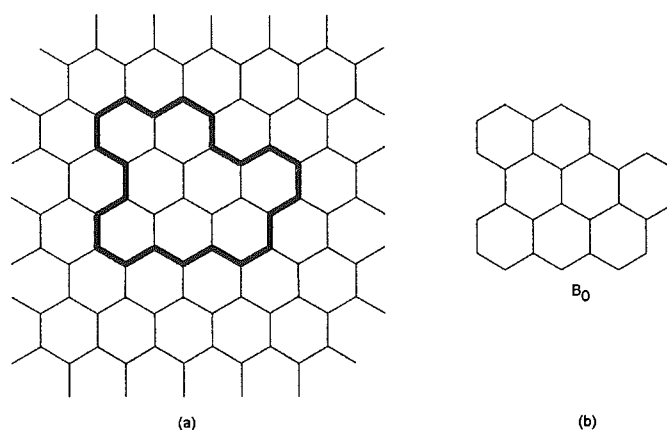(a)   (b)

Fig. 1. a) The hexagonal lattice and a circuit Z on it; b) The benzenoid system B_0 determined by the circuit Z; B_0 has six internal vertices and its perimeter is of size 22
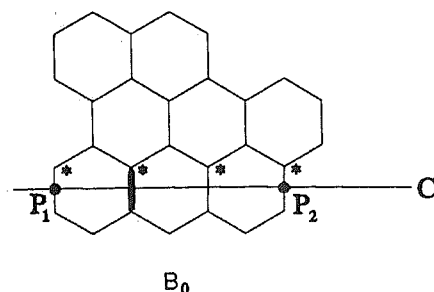
B_0

Fig. 2. The elementary cut C corresponding to an edge of the benzenoid system B_0, indicated by a heavy line; observe that C is an elementary cut intersecting the edges of B_0 marked by asterisk, hence $r(C) = 4$

It may, exceptionally, happen that the above specified straight line intersects the perimeter in more than two points. Then we choose as P_1 and P_2 the intersection points lying on opposite sides of, and being nearest to, the edge e.

Figure 2 provides an example of an elementary cut.

Elementary cuts are important concepts and are often encountered in the theory of benzenoid systems [22, 23, 26, 27].

The set of elementary cuts of a benzenoid system B, that involves all the edges of B is called the complete set of elementary cuts (CSEC) of B and is denoted by $C = C(B)$. The number of elementary cuts in the CSEC is denoted by $\gamma = \gamma(B)$. It should be noticed that γ is always much smaller than the number of vertex pairs in B. For instance, B_0 has 378 vertex pairs, but $\gamma(B_0) = 11$ (see Fig. 3).
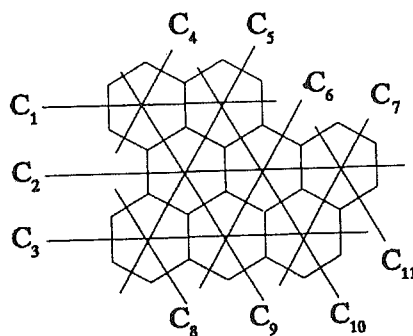

Fig. 3. All the 13 distinct elementary cuts of the benzenoid system B_0; $C(B_0) = \{C_1, C_2, \ldots C_{11}, \}$; $\gamma = 11$

The algorithm

Let C be an elementary cut of the benzenoid system B. Then C divides B into two parts, denoted by B' and B'' (see Fig. 4). The subgraphs B' and B'' may, but need not, be benzenoid systems themselves.

Let $n(B')$ and $n(B'')$ denote the number of vertices of the fragments B' and B'', respectively. Of course,

$$n(B') + n(B'') = n(B) . \qquad (4)$$

We are now prepared to formulate our method for calculating $W(B)$:

Let C be an elementary cut that divides the benzenoid system B into components $B'(C)$ and $B''(C)$. Then

$$W(B) = \sum_{C} n(B'(C))\, n(B''(C)) . \qquad (5)$$

The summation in Eq. (5) goes over the CSEC of B.

When applying formula (5) we need to count only the vertices of the smaller fragment, say B', because the number of vertices of B'' is determined via Eq. (4).

As an illustration of our algorithm we calculate $W(B_0)$ using the CSEC from Fig. 3. Recall that $n(B_0'') = n(B_0) - n(B_0') = 28 - n(B_0')$.

Elementary cut C	$n(B_0')$	$n(B_0'')$	$n(B') \times n(B'')$
C_1	5	23	$115 = 5 \times 23$
C_2	13	15	195
C_3	7	21	147
C_4	3	25	75
C_5	10	18	180
C_6	11	17	187
C_7	5	23	115
C_8	3	25	75
C_9	10	18	180
C_{10}	10	18	180
C_{11}	3	25	75
			Total: 1524

Hence, $W(B_0) = 1524$.

In large pericondensed benzenoid systems the counting of the vertices of the fragments B' and B'' may become somewhat tedious and error prone. In view of this, we further simplify formula (5): instead of counting the vertices of B' and B'' we may find it easier to count the hexagons and the internal vertices of B, lying in B' and B''. This is achieved by means of the following reasoning.
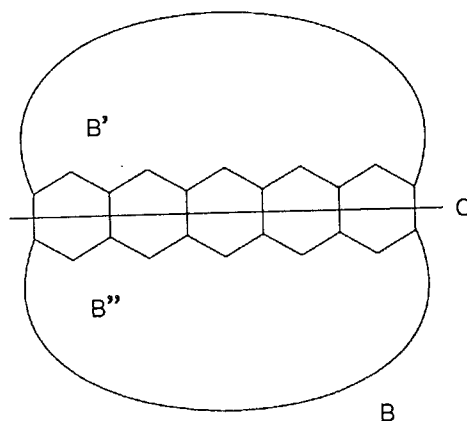
Fig. 4. Structural features used in the formulation of Eq. (5)

Denote the number of hexagons of B' and B'' by $h(B')$ and $h(B'')$, respectively. Let $n_i(B')$ and $n_i(B'')$ be the number of internal vertices of the benzenoid system B that belong to B' and B'', respectively. Then

$$h(B') + h(B'') + r - 1 = h, \tag{6}$$

$$n_i(B') + n_i(B'') = n_i. \tag{7}$$

In the above formulas h and n_i refer to the benzenoid system B and $r = r(C)$ is the number of edges intersected by the elementary cut C, i.e., the number of edges connecting B' and B''. Bearing in mind Eq. (2), we arrive at

$$n(B') = 4h(B') + 2r - 1 - n_i(B'), \tag{8}$$

$$n(B'') = 4h(B'') + 2r - 1 - n_i(B''). \tag{9}$$

In order to deduce Eq. (8) consider the (true) benzenoid system which embraces the hexagons of B' and the $r-1$ hexagons intersected by C. This benzenoid system has $h(B')+r-1$ hexagons, $n_i(B')$ internal vertices and $2r-1$ vertices more than B'. Eq. (2) has to be applied to it, and then the number of vertices has to be diminished by $2r-1$ in order to obtain $n(B')$.

Equation (9) is obtained in a fully analogous manner.

By substituting Eqs (8) and (9) back into Eq. (5), and by using Eqs (6) and (7), one obtains

$$W(B) = \sum \, [4h(B') - n_i(B')] \, [4h(B'') - n_i(B'')] - (4h - n_i + 3)\gamma \,+$$
$$+ 2(4h + 4 - n_i) \sum r - 4 \sum r^2 \, . \tag{10}$$

All the three summations on the right-hand side of Eq. (10) go over the CSEC of the benzenoid system B. Observing that $\sum r = m$, and using Eq. (3), we get

$$W(B) = \sum \, [4h(B') - n_i(B')] \, [4h(B'') - n_i(B'')] - (4h - n_i + 3)\gamma \,+$$
$$+ 2(4h + 4 - n_i) \, (5h + 1 - n_i) - 4 \sum r^2 \, . \tag{11}$$

Now, although Eqs (10) and (11) look more complicated than Eq. (5), the finding of $h(B')$ and $n_i(B')$ is a much easier task than the counting of the vertices of B'. As before, it is not necessary to independently search for $h(B'')$ and $n_i(B'')$, because these quantities are immediately calculated from Eqs (6) and (7).

Catacondensed benzenoid systems are characterized by the absence of internal vertices [22], i.e., they satisfy the condition $n_i = 0$. Bearing this in mind, formulas (10) and (11) are significantly simplified:

$$W(B) = 16 \sum h(B')h(B'') - (4h + 3)\gamma + 8(h + 1) \sum r - 4 \sum r^2 =$$
$$= 16 \sum h(B')h(B'') - (4h + 3)\gamma + 8(h + 1) \, (5h + 1) - 4 \sum r^2 \, .$$

Two more examples

To further illustrate the efficiency of our algorithm, we determine the general mathematical expressions for the Wiener numbers of the polyacenes (L_h) and of the members of the coronene/circumcoronene series (H_k). The respective structures and elementary cuts are depicted in Fig. 5.

Polyacenes

Using the notation from Fig. 5 we immediately see that the CSEC of the polyacenes is given by

$$C \, (L_h) = \{C_0 \, , \, C_{ia} \, , \, C_{ib} \mid i = 1, 2, \, ..., \, h\} \, .$$

For C_0

$$n(B') = n_i(B'') = 2h + 1 \, .$$

For both C_{ia} and C_{ib}, $i = 1, 2, \, ...h$:

$$n(B') = 4(i - 1) + 3 = 4i - 1 \, ,$$
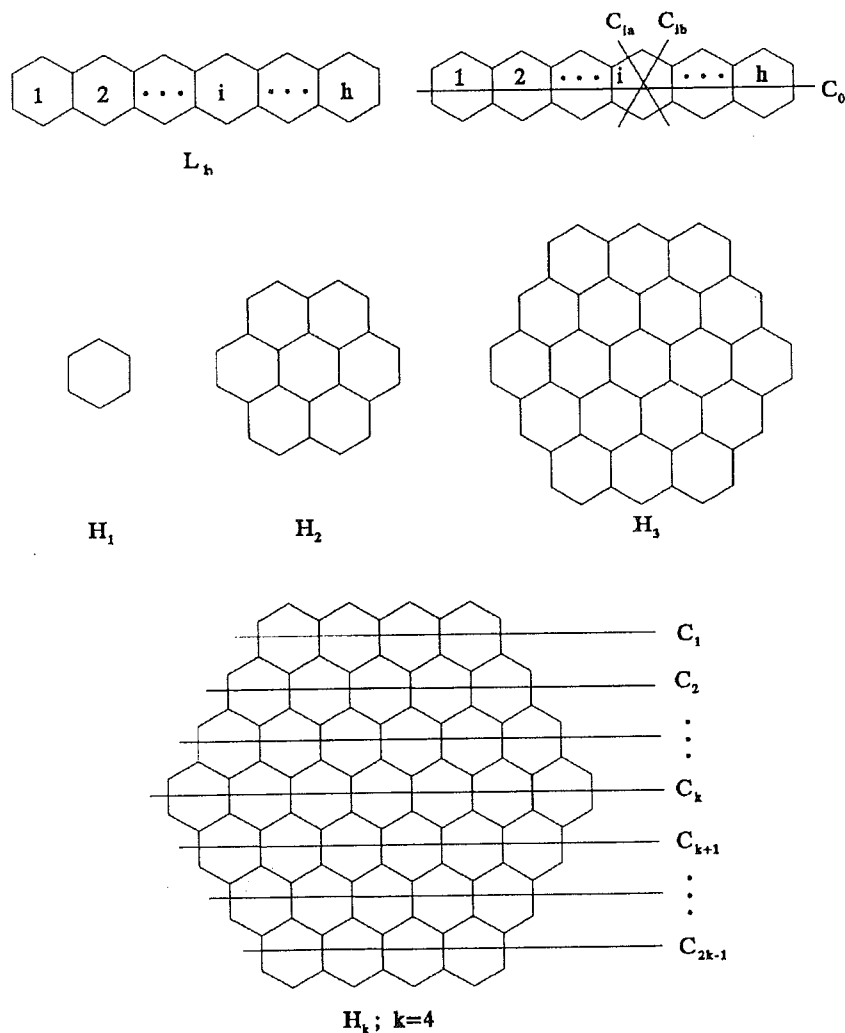$$n(B'') = 4h + 2 - (4i - 1) = 4h - 4i - 3 \, .$$

Fig. 5. The polyacene (L_h) and the coronene / circumcoronene (H_k) series and their elementary cuts

Substituting these relations back into Eq. (5) we get

$$W(L_h) = (2h+1)^2 + 2\sum_{i=1}^{h}(4i-1)(4h-4i+3) .$$ (12)

Equation (12) yields by direct calculation:

$$W(L_h) = \frac{1}{3}(16h^3 + 36h^2 + 26h + 3) ,$$ (13)

which is a previously known result [20]. Of course, formula (13) was formerly obtained by a completely different way of reasoning, applicable only to unbranched catacondensed benzenoid molecules.

The coronene/circumcoronene series

These species represent the most compact pericondensed benzenoid molecules. They are also characterized by the highest possible symmetry (D_{6h}) that a benzenoid hydrocarbon can possess [22]. The finding of a general expression for $W(H_k)$ is, for a long time, considered as a special challenge in the theory of the Wiener number.

In Fig. 5 are indicated only the $2k+1$ horizontal elementary cuts of H_k. There exist two additional groups of $2k+1$ symmetry-equivalent elementary cuts, obtained by rotating the former group by $+60°$ and by $-60°$. Therefore, if one applies Eq. (5) to only the horizontal elementary cuts, the result will be just one third of the Wiener number of H_k.

It is also evident that, because of symmetry, the elementary cuts C_1 and C_{2k-1} have equal contributions to the right-hand side of Eq. (5). The same is true for the cuts C_2 and C_{2k-2}, for C_3 and C_{2k-3}, ... for C_{k-1} and C_{k+1}. The only elementary cut which is not paired in the above sense is C_k; its contribution to the right-hand side of Eq. (5) is equal to $[1/2 n(H_k)]^2$.

It has been previously established [27] that $n(H_k) = 6k^2$, and that for the elementary cut C_i :

$$n(B') = i(2k + i) , i = 1, 2, ..., k .$$

Taking into account all these properties of the elementary cuts of H_k and using Eq. (5) we obtain

$$\frac{1}{3} W(H_k) = [3k^2]^2 + 2 \sum_{i=1}^{k-1} i(2k+i)[6k^2 - i(2k+i)] ,$$

which after an elementary, but quite tedious calculation is reduced to

$$W(H_k) = \frac{1}{5}(164k_5 - 30k^3 + k) .$$

Formula (14) has, so far, not been reported in the chemical literature.

A note on the Szeged index

The Szeged index is another, recently introduced, distance-based topological index [28, 29]. It is defined as follows.

Let e be an edge of the molecular graph G, connecting the vertices x and y. Let $n_1(e \mid G)$ be the number of vertices of the graph G, having the property $d(u, x, \mid G,) < d(u, y, \mid G,)$. Let $n_2(e \mid G)$ be the number of vertices of the graph G, having the property $d(u, x, \mid G,) > d(u, y, \mid G,)$. In other words, $n_1(e \mid G)$ counts the vertices of G, lying closer to one end (namely x) of the edge e than to its other end (namely y). The meaning of $n_2(e \mid G)$ is analogous.

The Szeged index of the graph G is

$$Sz(G) = \sum_e n_1(e \mid G)\, n_2(e \mid G), \tag{15}$$

where the summation goes over all edges of G.

By comparing the definitions (1) and (15), little resemblance can be envisaged between the Wiener and the Szeged indices. Yet, these two quantities are intimately related [28, 29]. In particular, for benzenoid systems the following formula has been shown to be satisfied [27]:

$$Sz(B) = \sum_C r(C)\, n(B'(C))\, n(B''(C)). \tag{16}$$

The analogy between Eqs (5) and (16) is evident. As before, $r(C)$ denotes the number of edges intersected by the elementary cut C.

In benzenoid systems every elementary cut intersects at least two edges, $r(C) \geq 2$. Therefore, Eqs (5) and (16) imply that the following inequality

$$SZ(B) \geq 2\,W(B) \tag{17}$$

is obeyed by all benzenoid molecules. Equality in (17) occurs only if B is benzene.

For the members of the coronene/circumcoronene series (see Fig. 5), $r(C) \geq k+1$. For these benzenoid systems the inequality (17) can be improved as: $SZ(H_k) \geq (k+1)\, W(H_k)$. Again, equality will occur only in the case of benzene.

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