Formula for Calculating the Wiener Index of Catacondensed Benzenoid Graphs

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The Wiener index is a topological index (graph invariant) defined as the sum of distances between all pairs of vertices in a chemical graph. This index is examined for molecular graphs of catacondensed benzenoid hydrocarbons. A simple method for the calculation of the Wiener index is put forward.

INTRODUCTION

The 50th anniversary of Wiener's paper[1] has stimulated new intensive investigations of distance-based topological indices and its applications in chemistry. First of all, many novel results have been discovered for the Wiener index. Some of these results can be found in the special issues of three international journals dedicated to this jubilee.[2−4] The previous results on the Wiener index are described in numerous articles in the chemical and mathematical literature (see monographs[5−8] and selected reviews[9−13]).

Recall that the Wiener index is a graph invariant introduced originally for molecular graphs of alkanes.[1] For an arbitrary graph H, the Wiener index is defined as the sum of distances between all unordered pairs of its vertices:[14]

$$W(H) = \sum_{\{u,v\} \subseteq V(H)} d(u, v),$$

where $d(u, v)$ is the standard distance of the simple graph H, i.e., the number of edges in a shortest path connecting the vertices u and v in H.

Many methods and algorithms for computing the Wiener index were proposed for various classes of graphs and, in particular, for molecular graphs of benzenoid hydrocarbons.[15−31] In many cases, chemists are often interested in elementary methods for the calculation of the Wiener index. An example of such a method is a combinatorial formula for the calculation W of trees in refs 23 and 24.

In this paper we derive a new formula for computing the Wiener index of molecular graphs of catacondensed benzenoid hydrocarbons. The obtained formula is based on examination the structure of branching in a benzenoid graph.

BENZENOID GRAPHS

In this section we define a class of graphs which include molecular graphs of catacondensed benzenoid hydrocarbons.[32] *Benzenoid graphs* are composed exclusively of six-membered cycles (hexagonal rings). We assume that a graph contains at least two hexagonal rings. Any two rings either have one common edge (and are then said to be adjacent) or have no common vertices. No three rings share a common vertex. Each hexagonal ring is adjacent to two or three other rings, with the exception of the *terminal rings* to which a single ring is adjacent. The *characteristic graph* of a given benzenoid graph consists of vertices corresponding to hexagonal rings of the graph; two vertices are adjacent if and only if the corresponding rings share an edge.[33] A benzenoid graph is called *catacondensed* if its characteristic graph is a tree. The characteristic graph of a *hexagonal chain* is isomorphic to the simple path. An example of a catacondensed benzenoid graph and its characteristic graph is shown in Figure 1.

The set of all catacondensed benzenoid graphs (or simply benzenoid graphs) with h rings is denoted by $\mathcal{H}_h$. Every graph H from $\mathcal{H}_h$ has $p_H = 4h + 2$ vertices.

Hexagonal rings of a benzenoid graph may be angularly or linearly connected. Each angularly connected ring is said to correspond to a "kink" in a graph. As an illustration consider the graph shown in Figure 1. Black vertices of its characteristic graph correspond to angularly connected rings. An angularly connected ring is called a *branching ring* of a graph. The set of all branching rings of a benzenoid graph is denoted by B.

BRANCHING IN A BENZENOID GRAPH

In this section we deal with two types of branching in a benzenoid graph. The first type of branching is determined by a single branching ring. The corresponding configuration may be described by three subgraphs G_1, G_2, and G_3 attached with the branching ring r as shown in Figure 2a (a subgraph in a benzenoid graph will be drawn as an eight-membered ring); in particular, any of these subgraphs may be empty. We associate with the ring r three quantities h_1, h_2, and h_3 that are the numbers of rings in the subgraphs G_1, G_2, and G_3, respectively. It is assumed that $h_i = 0$ for an empty subgraph G_i, $i = 1, 2, 3$.

The second type of branching is defined by two neighboring branching rings r and r' in a benzenoid graph. The corresponding configuration includes four subgraphs G_1, G_2, and G'_1, C'_2 as depicted in Figure 2b; any of these subgraphs may also be empty. In this case, we associate with the pair r, r' the numbers of rings h_1, h_2 and h'_1, h'_2 of these subgraphs. It should be noted that subgraphs G_1 and G'_1 lie on the same side of the line crossing the centers of rings between r and r'.

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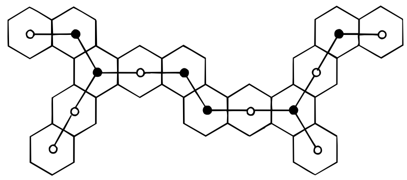

Figure 1. Benzenoid graph and its characteristic graph.

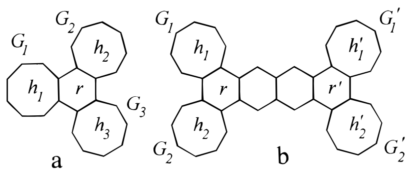

Figure 2. Two configurations of branching.

MAIN FORMULA

The linear polyacene L_h has a maximum Wiener index among all benzenoid graphs with h rings. The corresponding analytical expression for L_h was derived in many works as a cubic polynomial in h:[34−36]

$$W(L_h) = (16h^3 + 36h^2 + 26h + 3)/3$$

The following result shows that the Wiener index for every $H \in \mathcal{H}_h$ can be calculated from $W(L_h)$ and configurations of branching in H.

Theorem. *Let H be an arbitrary catacondensed benzenoid graph in $\mathcal{H}_h$. Then the Wiener index of H can be computed as follows:*

$$W(H) = W(L_h) - 8\Big[5\sum_{r\in B} h_1h_2h_3 - \sum_{r\in B}(h_1 - 1)(h_2 - 1) \times (h_3 - 1) + \sum_{r,r'\in B}(h_1 - h_2)(h_1' - h_2') + |B|(h - 2)\Big] \quad (1)$$

where the last summation goes over all neighboring branching rings of H.

Since branching rings can be easily recognized in a benzenoid graph, formula 1 provides a convenient paper-and-pencil method for the calculation of the Wiener index. For hexagonal chains, the above formula has a more simple form.

Corollary. *Let H be an arbitrary hexagonal chain in H_h. Then*

$$W(H) = W(L_h) - 8\Big[\sum_{r\in B} h_1h_2 + \sum_{r,r'\in B}(h_1 - h_2)(h_1' - h_2')\Big]$$

Other analytical formulas for computing the Wiener index of hexagonal chains have been derived in recent works.[25,31]

The proof of the theorem will be given in the last section.

EXAMPLE OF NUMERIC CALCULATION OF *W*

As an illustration consider the benzenoid graph $H \in \mathcal{H}_{16}$ shown in Figure 3. This graph has $|B| = 4$ branching rings marked by black balls. Configurations of all branchings and the numbers of rings in the corresponding subgraphs are also given in Figure 3. In order to obtain $W(H)$, we need to know $W(L_h)$. The Wiener index of the linear polyacene may be easily tabulated. Here several values are presented: $W(L_h) \in$ {279, 569, 1011, 1637, 2479, 3569, 4939, 6621, 8647, 11 049, 13 859, 17 109, 20 831, 25 057} for $h = 3, 4, 5, ...,$

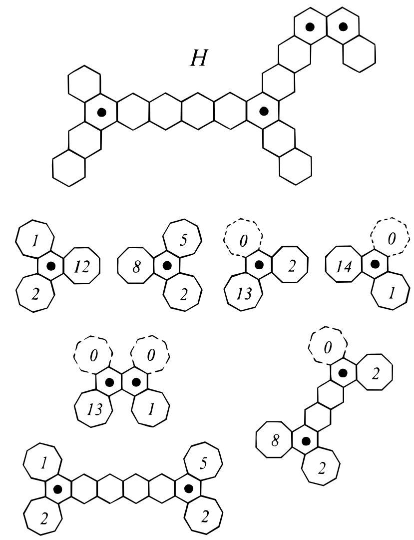

Figure 3. Benzenoid graph and its branchings.

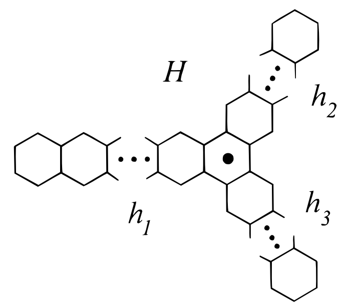

Figure 4. Benzenoid star.

16, respectively. Since $W(L_{16}) = 25\,057$, we immediately arrive at

$$\begin{aligned} W(H) = {} & W(L_{16}) - 8\,[5(1{\cdot}2{\cdot}12 + 2{\cdot}5{\cdot}8) - (1{\cdot}4{\cdot}7 + (-1){\cdot}1{\cdot}12) + (1 - 2)(5 - 2) + (0 - 2) \times (8 - 2) + (13 - 0)(1 - 0) + 4{\cdot}14] \\ & = 25057 - 8[520 - 16 - 3 - 12 + 13 + 56] \\ & = 20593 \end{aligned}$$

EXAMPLE OF ANALYTICAL CALCULATION OF *W*

As another illustration of the application of the new formula we compute the Wiener index of certain benzenoid graphs. Consider a hexagonal star shown in Figure 4. This graph has the unique branching ring with exactly three branches; i.e., $h = h_1 + h_2 + h_2 + 1$. From formula 1, we have

$$\begin{aligned} W(H) &= W(L_h) - 8[5h_1h_2h_3 - (h_1 - 1)(h_2 - 1) \times (h_3 - 1) + (h - 2)] \\ &= W(L_h) - 32h_1h_2h_3 - 8(h_1h_2 + h_1h_3 + h_2h_3) \end{aligned}$$

If all h_i are considered as parameters depending on h, then explicit analytical expressions may be derived. For example, suppose that all branches of the star have the same size; i.e., $h_1 = h_2 = h_3 = (h - 1)/3$. Then we obtain after simple calculation

$$W(H) = (112h^3 + 348h^2 + 282h - 13)/27$$

If $h_2 = h_3 = 1$, then $h_1 = h - 3$ and H has maximum W among all nonchain benzenoid graphs in $\mathcal{H}_h$

$$W(H) = W(L_h) - 8(6h + 17) = (16h^3 + 36h^2 - 118h + 411)/3$$

Let $h_3 = 0$; i.e., H is a hexagonal chain with the unique branching ring. Then

$$W(H) = W(L_h) - 8h_1h_2$$

The last equality also follows from the corollary.

EXAMPLE OF COINCIDENCE OF W

In this section we apply formula 1 to obtain conditions for the coincidence of the Wiener index of two similar benzenoid graphs. Consider graphs H_1 and H_2 shown in Figure 5 ($a \neq b$). These graphs have the same structure except the size of two subgraphs between the branching rings x, y and y, z. Therefore

$$\begin{aligned} W(H_1) - W(H_2) = {} & 8[5(h_1 + h_2 + b + 1) \times (h_3 + h_4 + a + 1) + (h_1 - h_2)(h_3 + h_4 + a) + (h_3 - h_4)(h_1 + h_2 + b)] - 8[5(h_1 + h_2 + a + 1) \times \\ & (h_3 + h_4 + b + 1) + (h_1 - h_2)(h_3 + h_4 + b) + (h_3 - h_4)(h_1 + h_2 + a)] \\ = {} & 16(a - b)[3(h_1 - h_3) + 2(h_2 - h_4)] \end{aligned}$$

Then we can conclude that $W(H_1) = W(H_2)$ if and only if

$$3(h_1 - h_3) = 2(h_4 - h_2)$$

The obtained nonobvious condition does not include quantities a and b. The smallest graphs with this property are shown in Figure 6. Here $a = 0$, $b = 1$, $h_2 = h_3 = 0$, $h_1 = 2$, and $h_4 = 3$. These graphs have $h = 10$ rings, and $W(H_1) = W(H_2) = 5573$.

PROOF OF THE THEOREM

For an arbitrary edge $e = (v, u)$ of a benzenoid graph H, we define two disjoint vertex subsets $V_u(H) = \{w|d(w, u) < d(w, u)\}$ and $V_v(H) = \{w|d(w, v) < d(w, u)\}$. It is clear that $V_u(H) \cup V_v(H) = V(H)$ and $V_u(H) \cap V_v(H) = \emptyset$. Let $n_u(H) = |V_u(H)|$ and $n_v(H) = |V_v(H)|$. By $d(v|H)$ we denote the *distance* of a vertex v, $d(v|H) = \Sigma_u\, d(u, v)$. It is easy to verify that the equality $d(u|H) - d(v|H) = n_v(H) - n_u(H)$ holds for arbitrary adjacent vertices $u, v \in V(H)$.

Let G and F be benzenoid graphs. Suppose that a new benzenoid graph H is obtained from these graphs by identifying the edges (u, u_1) in G and (v, v_1) in F (see Figure 7). Then the Wiener index of the graph H can be expressed using the indices of its subgraphs G and F as follows:[37]

$$W(H) = W(G) + W(F) + h_G d(v|F) + h_F d(u|G) + 2[n_{u1}(G) + n_{v1}(F) - n_{u1}(G)\, n_{v1}(F)] - 4(h_G + h_F) - 3 \quad (2)$$

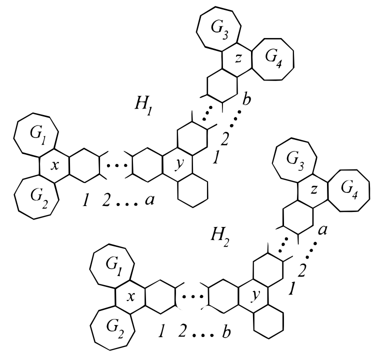

Figure 5. Two similar benzenoid graphs.

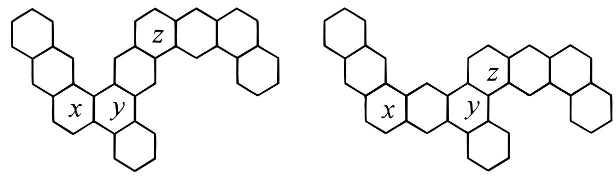

Figure 6.

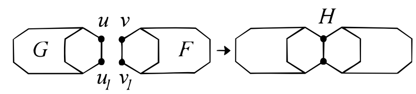

Figure 7.

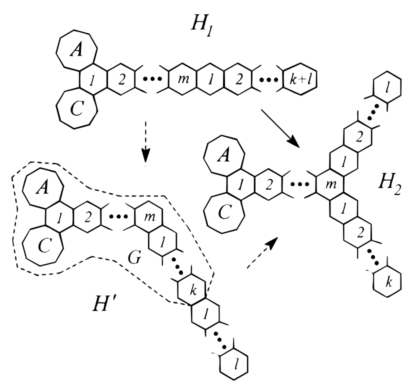

Figure 8. Graph operation of benzenoid graphs.

Let us consider a graph operation of a benzenoid graph H_1 that consists of decomposition of a terminal part of H_1 into two new terminal parts of H_2, as shown in Figure 8. In other words, a terminal part of H_1 is displaced from its initial location to another one, making a new branching ring in the resulting graph H_2. Here A and C stand for arbitrary fragments; in particular, they may be absent. In order to calculate the change in the Wiener index, we consider the intermediate graph H' (see Figure 8). If $l = 0$, then H' and H_2 coincide. Applying formula 2 to H_1, H' and H', H_2, we have

$$W(H_1) - W(H') = 16(k + l)h_C + 8(k + l)(m - 1)$$

$$W(H') - W(H_2) = 16l[2k(h_G - k - 1) + h_A - h_C] + 8kl$$

Summing the corresponding parts of the above equations, we obtain

$$W(H_1) - W(H_2) = 32kl(h_A + h_C + m - 1) + 8k(h_C + m - 1) + 8l(h_A + m - 1) + 8lh_A + 8kh_C + 8kl \quad (3)$$

The second and the third summands of eq 3 may be presented as follows:

$$8k(h_A + h_C + m - 1) - 8kh_A \quad \text{and} \quad 8l(h_A + h_C + m - 1) - 8lh_C$$

Then

$$W(H_1) - W(H_2) = 32kl(h_A + h_C + m - 1) + 8k(h_A + h_C + m - 1) + 8l(h_A + h_C + m - 1) + 8kl + 8(l - k)(h_A - h_C) \quad (4)$$

Consider the new branching ring marked by m in H_2 and the corresponding configuration of branching (see Figure 8). Let $h_1 = h_A + h_C + m - 1$, $h_2 = l$, and $h_3 = k$. For the new pair of neighboring branching rings marked by 1 and m in H_2, denote $h_1 = h_A$, $h_2 = h_C$ and $h'_1 = l$, $h'_2 = k$. Then we can rewrite eq 4 in the form

$$W(H_1) - W(H_2) = 32h_1h_2h_3 + 8(h_1h_2 + h_1h_3 + h_2h_3) + 8(h_1 - h_2)(h'_1 - h'_2) \quad (5)$$

It is not hard to verify that every benzenoid graph H can be obtained from the linear polyacene L_h by a sequence of the graph operation shown in Figure 8. Applying (*5*) for all operations transferring L_h to H, we arrive at

$$W(L_h) - W(H) = 32\sum_{r\in B} h_1h_2h_3 + 8\sum_{r\in B}(h_1h_2 + h_1h_3 + h_2h_3) + 8\sum_{r,r'\in B}(h_1 - h_2)(h'_1 - h'_2)$$

The proof is complete.

In conclusion we note that the Wiener index of the linear polyacene L_h with $p = 4h + 2$ vertices may be presented as follows

$$W(L_h) = \frac{1}{2}\binom{4h+4}{3} - 1 = \frac{1}{2}\binom{p+2}{3} - 1 = \frac{1}{2}\left[\binom{p}{3} + 2\binom{p}{2} + \binom{p}{1}\right] - 1$$

This implies some analogy between formula 1 of benzenoid graphs and a combinatorial formula for calculating W of trees in refs 24 and 23.

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