Congruence Relations for the Wiener Index of Hexagonal Chains

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Received April 7, 1997⊗

The Wiener index (W) of certain classes of hexagonal chains is examined. Necessary and sufficient conditions for their W-values to be congruent modulo 16 are established. As a corollary, a necessary condition for the coincidence of Wiener indices of hexagonal chains is formulated.

The Wiener index (or Wiener number) is a well-known graph distance invariant introduced 50 years ago for acyclic molecules.[1] Wiener's concept was extended for cyclic graphs by Hosoya.[2] This index is defined as the half-sum of distances between all ordered pairs of vertices of the respective graph H,

$$W(H) = {}^1/_2 \sum_{u,v \in V(H)} d(u,v)$$

where $d(u,v)$ is the number of edges in a shortest path connecting the vertices u and v in H. Mathematical properties and chemical applications of the Wiener index are outlined in numerous reviews and books.[3−12] A well-known result from the theory of the Wiener index states that $W(H) \equiv W(H')$ (mod 8) for isomeric catacondensed benzenoid graphs H and H'; *i.e.*, the difference $W(H) - W(H')$ is divisible by 8.[13,14] Some necessary conditions for the congruence relation $W(H) \equiv W(H')$ (mod 16) have been recently established for hexagonal chains of certain classes.[16,17] In this paper we derive new necessary and sufficient conditions that provide the rule of modulo 16 for Wiener indices of hexagonal chains.

First we recall a definition of *hexagonal chains*. Hexagonal chains are exclusively composed of hexagons. Any two hexagons either have one common edge (and are then said to be adjacent) or have no common vertices. No three hexagons share a common vertex. Each hexagon is adjacent to two other hexagons, with the exception of the *terminal* hexagons to which a single hexagon is adjacent. A hexagonal chain has exactly two terminal hexagons. These graphs include molecular graphs of unbranched catacondensed benzenoid hydrocarbons.[15]

We define a *segment* of a hexagonal chain as its subgraph between neighboring kinks of the chain; *i.e.*, every segment is isomorphic to the linear polyacene. The hexagonal chain shown in Figure 1 has seven segments (every segment is marked by a straight line). The number of hexagons in a segment S is called its length and is denoted by $l(S)$. We assume that a hexagonal chain consists of a set of segments, $S_1, S_2, ..., S_n$ with lengths $l(S_i) = l_i$, where $n = n(H)$ is the number of all segments in a hexagonal chain H. The set of all hexagonal chains with h hexagons and n segments will be denoted by $C(h,n)$. It is clear that $2 \le l_i \le h$ for every segment. $n_o(H)$ and $n_e(H)$ denote the numbers of segments having odd and even lengths in H, respectively; $n(H) = n_o(H) + n_e(H)$. A segments' length of a chain forms an ordered sequence $\mathbf{L}(H) = (l_1, l_2, ..., l_n)$. For the graph H in Figure 1, $\mathbf{L}(H) = (2, 3, 2, 5, 2, 2, 3)$.

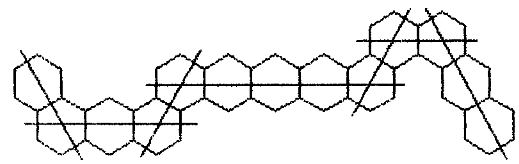

Figure 1. Segments of a hexagonal chain.

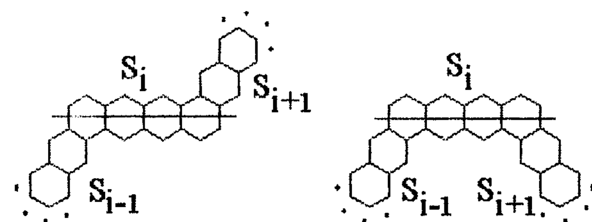

Figure 2. Mutual position of segments S_{i-1} and S_{i+1}.

In order to describe the mutual relation of segments, we define an additional vector $\mathbf{Z}(H) = (z_1, z_2, ..., z_n)$. An entry $z_i = z(S_i)$, either 0 or 1, is assigned to every segment S_i. We first choose $z_1 = z_n = 0$. Note that three segments S_{i-1}, S_i, S_{i+1}, $i = 2, ..., n - 1$, induce a hexagonal chain. Suppose that this chain is embedded into the regular hexagonal lattice in the plane. Consider the segment S_i and draw a line through the centers of the hexagons of S_i. Then $z_i = 0$ if S_{i-1} and S_{i+1} lie on the same side of the line, and $z_i = 1$ otherwise. In other words, if $z_i = 1$, then the segments S_{i-1}, S_i, S_{i+1} form a "zigzag fragment" in the corresponding graph. The graph in Figure 1 has three zigzag segments and $\mathbf{Z}(H) = (0, 0, 1, 1, 1, 0, 0)$.

Suppose now that $\mathbf{L}$ and $\mathbf{Z}$ are an arbitrary integer and an arbitrary binary n-dimensional vector, respectively, and let $l_i \ge 2$ for all i. It is clear that they uniquely determine a graph having n segments. Then the Wiener index of H may be calculated from the vectors $\mathbf{L}$ and $\mathbf{Z}$ by the following formula:[17]

$$W(H) = {}^1/_3 \sum_{i=1}^{n} (16l_i^3 + 36l_i^2 + 26l_i - 78) + 27 + 16\sum_{i=1}^{n}\Big((l_i - 1) \sum_{k=i+1}^{n} \Big[(l_i + l_k + 1)(l_k - 1) + (2l_k - 3 + z_k) \sum_{j=k+1}^{n} (l_j - 1)\Big]\Big) \quad (1)$$

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

This formula implies a simple condition for congruence relations of W-values of hexagonal chains.

Proposition. Let H and H' be arbitrary hexagonal chains in $C(h,n)$. Then $W(H) \equiv W(H')$ (mod 16) if and only if $n_o(H) - n_o(H')$ is divisible by 4.

Proof. Let H, $H' \in C(h,n)$. We consider unordered families of segment lengths $F(H)$ and $F(H')$. Then they may be presented as follows:

$$F(H) = \{l_1, l_2, ..., l_m, l_{m+1}, l_{m+2}, ..., l_n\}$$
$$F(H') = \{l'_1, l'_2, ..., l'_m, l'_{m+1}, l'_{m+2}, ..., l'_n\}$$

where l_i and l'_i have the same parity, $l_i \equiv l'_i$ (mod 2), for every $i = 1, 2, ..., m$, and have distinct parity for every $i > m$. We assume without loss of generality that l_i is odd and l'_i is even for $i = m + 1, m + 2, ..., n$. $P(H)$ denotes the first sum in (1) for a hexagonal chain H. Then it suffices to prove that the difference $P(H) - P(H')$ is divisible by 16.

First we show that $P(H) \equiv 0$ (mod 3). Indeed, for all $i = 1, 2, ..., n$

$$16l_i^3 + 36l_i^2 + 26l_i - 78 \equiv l_i^3 + 2l_i = l_i(l_i^2 + 2) \equiv 0 \pmod 3$$

Next we can write that

$$\begin{aligned} W(H) - W(H') & \\ &\equiv P(H) - P(H') \equiv \sum_{i=1}^{n}[4(l_i^2 - (l'_i)^2) - 6(l_i - l'_i)] \\ &\equiv 4\sum_{i=1}^{n}(l_i^2 - (l'_i)^2) - 6\sum_{i=1}^{n}(l_i - l'_i) \pmod{16} \end{aligned}$$

Since H, H' belong to $C(h,n)$ and $\sum_{i=1}^{n} l_i = h + n - 1$ for every graph of $C(h,n)$, we have

$$W(H) - W(H') \equiv 4\sum_{i=1}^{n}(l_i^2 - (l'_i)^2) \equiv 4\sum_{i=m+1}^{n} 1 \pmod{16}$$

Therefore $P(H) - P(H')$ is divisible by 16 if and only if $n - m$ is divisible by 4. In conclusion we note that $n - m = |n_o(H) - n_o(H')|$.

The obtained result immediately leads to a necessary condition for the coincidence of W-values of hexagonal chains.

Corollary. Let H and H' be arbitrary hexagonal chains in $C(h,n)$. If $W(H) = W(H')$, then $n_o(H) \equiv n_o(H')$ (mod 4).

Since $|n_o(H) - n_o(H')| = |n_e(H) - n_e(H')|$, the proposition and corollary may be equivalently formulated in terms of segments having even lengths.

ACKNOWLEDGMENT

The author would like to thank the reviewers for helpful suggestions.

REFERENCES AND NOTES

(1) Wiener, H. Structural Determination of Paraffin Boiling Points. *J. Am. Chem. Soc.* **1947**, *69*, 17−20.
(2) Hosoya, H. Topological index. A newly proposed quantity characterizing the topological nature of structural isomers of saturated hydrocarbons. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332−2339.
(3) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983; 2nd ed., 1992.
(4) Balaban, A. T.; Motoc, I.; Bonchev, D.; Mekenyan, O. Topological Indices for Structure−Activity Correlations. *Top. Curr. Chem.* **1983**, *114*, 21−55.
(5) Bonchev, D. *Information Theoretic Indices for Characterization of Chemical Structure*; Research Studies Press: Chichester, U.K., 1983.
(6) Gutman, I.; Polansky, O. E. *Mathematical Concepts in Organic Chemistry*; Springer-Verlag: Berlin, 1986.
(7) Gutman, I.; Yeh, Y. N.; Lee, S. L.; Luo, Y. L. Some Recent Results in the Theory of the Wiener Number. *Indian J. Chem.* **1993**, *32a*, 651−661.
(8) Rouvray, D. H. The Topological Matrix in Quantum Chemistry. In *Chemical Applications of Graph Theory*; Balaban, A. T., Ed.; Academic Press: London, 1975; pp 175−222.
(9) Rouvray, D. H. Should We Have Designs on Topological Indices? In *Chemical Applications of Topology and Graph Theory*; King, R. B., Ed.; Elsevier: Amsterdam, 1983; pp 159−177.
(10) Canfield, E. R.; Robinson, R. W.; Rouvray, D. H. Determination of the Wiener Molecular Branching Index for the General Tree. *J. Comput. Chem.* **1985**, *6*, 598−609.
(11) Mihalić, Z.; Veljan, D.; Amić, D.; Nikolić, S.; Plavšić, D.; Trinajstić, N. The Distance Matrix in Chemistry. *J. Math. Chem.* **1992**, *11*, 223−258.
(12) Nikolić, S.; Trinajstić, N.; Mihalić, Z. The Wiener Index: Developments and Applications. *Croat. Chem. Acta* **1995**, *68*, 105−129.
(13) Gutman, I. Wiener Numbers of Benzenoid Hydrocarbons: Two Theorems. *Chem. Phys. Lett.* **1987**, *136*, 134−136.
(14) Gutman, I. On Distances in Some Bipartite Graphs. *Publ. Inst. Math. (Beograd)* **1988**, *43*, 3−8.
(15) Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1989.
(16) Dobrynin, A. A. On Congruence Relations for the Wiener Index of Hexagonal Chains. Submitted for publication.
(17) Dobrynin, A. A. A New Formula for the Calculation of the Wiener Index of Hexagonal Chains. *MATCH* **1997**, *35*, 75−90.

CI970445F