MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **78** (2017) 121-132

ISSN 0340 - 6253

Hexagonal Chains with Segments of Equal Lengths Having Distinct Sizes and the Same Wiener Index*

Andrey A. Dobrynin

Sobolev Institute of Mathematics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia
dobr@math.nsc.ru

(Received July 15, 2016)

Abstract

Hexagonal chains consist of hexagonal rings connected with each other by edges. This class of graphs contains molecular graphs of unbranched cata-condensed benzenoid hydrocarbons. The Wiener index is a topological index of a molecule, defined as the sum of distances between all pairs of vertices in the chemical graph representing the non-hydrogen atoms in the molecule. A segment of length ℓ of a chain is its maximal subchain with ℓ linear annelated hexagons. The Wiener index for chains in which all segments have equal lengths is considered. Conditions for the existence of hexagonal chains of distinct sizes having the same Wiener index are formulated and examples of such chains are presented.

1 Introduction

Topological indices have been extensively used for the development of quantitative structure–property relationships in which the biological activity or other properties of molecules are correlated with their chemical structure [2, 4, 5, 17, 24, 25, 26]. A well-known distance-based topological index is the Wiener index, which was introduced as structural descriptor for acyclic organic molecules [27]. It is defined as the sum of distances between all unordered pairs of vertices of an undirected connected graph G with vertex set $V(G)$:

$$W(G) = \frac{1}{2} \sum_{u,v \in V(G)} d(u,v)$$

* This work is supported by the Russian Foundation for Basic Research (grant 16–01–00499).

where distance $d(u, v)$ is the number of edges in the shortest path connecting vertices u and v in G. The Wiener index and its numerous modifications are extensively studied in theoretical and mathematical chemistry. The bibliography on the Wiener index and its applications can be found in books [3, 17, 20, 21] and reviews [9, 10, 14, 18, 19, 22, 23].

In the present paper, we deal with the Wiener index for hexagonal chains that include molecular graphs of unbranched cata-condensed benzenoid hydrocarbons. Benzenoid hydrocarbons are important raw materials of the chemical industry (used, for instance, for the production of dyes and plastics) but are also dangerous pollutants [15]. A class of hexagonal chains with constant number of linear annelated hexagons ℓ is considered. Properties of the Wiener index of this class are reported in [10, 13]. Fibonacenes are examples of such graphs with $\ell = 2$ [1, 11, 12, 16].

In this paper, necessary conditions for the existence of hexagonal chains of different sizes having the same Wiener index are formulated and examples of such chains are presented.

2 Hexagonal chains

In this section, we describe a class of graphs that includes molecular graphs of unbranched polycyclic aromatic hydrocarbons. A hexagonal system is a connected plane graph in which every inner face is bounded by hexagon. An inner face with its hexagonal bound is called a hexagonal ring (or simply ring). We consider hexagonal systems in which two hexagonal rings are either disjoint or have exactly one common edge (adjacent rings), a hexagonal ring has at most two adjacent rings, and no three rings share a common vertex. A ring having exactly one adjacent ring is called terminal. A hexagonal system having exactly two terminal rings is called a hexagonal chain. Denote by $\mathcal{C}_h$ the set of all hexagonal chains with h hexagonal rings.

A segment of a hexagonal chain is its maximal subchain in which all rings are linearly annelated. A segment including a terminal hexagon is a terminal segment. The number of hexagons in a segment S is called its length and is denoted by $\ell(S)$. If S is a segment of a chain $G \in \mathcal{C}_h$ then $2 \leq \ell(S) \leq h$.

Denote by $\mathcal{G}_{n,\ell} \subset \mathcal{C}_h$ the set of all hexagonal chains having n segments of equal length ℓ. Since two neighboring segments of $G \in \mathcal{G}_{n,\ell}$ have always one hexagon in common, i.e. $h = n(\ell - 1) + 1$, the number of segments is $n = (h - 1)/(\ell - 1)$. We say that G consists of the set of segments $S_1, S_2, \ldots, S_n$ with lengths ℓ for some $n \geq 3$. As an illustration, all hexagonal chains having 5 segments of length 3 are shown in Fig. 1. Hexagonal chains of $\mathcal{G}_{n,2}$ with minimal length of segments $\ell = 2$ are known as fibonacenes [1]. The name of these chains comes from the fact that the number of perfect matchings of any fibonacene relates with the Fibonacci numbers. This class of hexagonal chains will be also denoted by $\mathcal{F}_n$. It is clear that the cardinality of $\mathcal{G}_{n,\ell}$ does not depend on ℓ and [1]

$$|\,\mathcal{G}_{n,\ell}\,| = \begin{cases} 2^{\,n-3} + 2^{\frac{n-4}{2}}, & \text{if } n \text{ is even} \\ 2^{\,n-3} + 2^{\frac{n-3}{2}}, & \text{if } n \text{ is odd} . \end{cases}$$

The set of graphs $\mathcal{G}_{n,\ell}$ can be divided into two disjoint subsets $\mathcal{G}_{n,\ell} = \mathcal{L}_{n,\ell} \cup \mathcal{N}_{n,\ell}$, where the set $\mathcal{L}_{n,\ell}$ is composed of chains which are embedded into a two-dimensional regular hexagonal lattice without vertex overlapping, while chains of the set $\mathcal{N}_{n,\ell}$ cannot be embedded into such a hexagonal lattice. For small hexagonal chains with $\ell = 2, n \leq 4$ and $\ell \geq 3, n \leq 5$, we have $\mathcal{N}_{n,\ell} = \emptyset$.

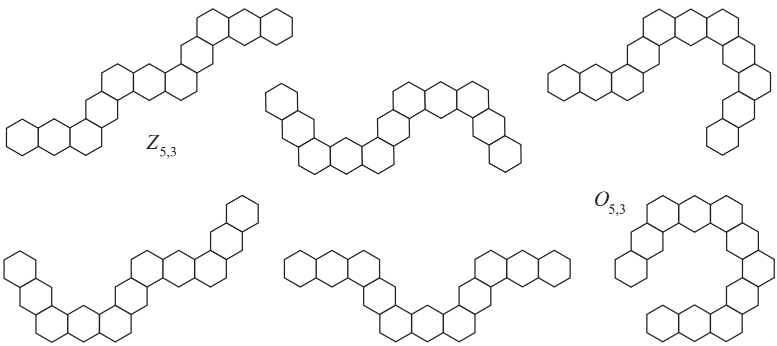

Figure 1. Hexagonal chains of $\mathcal{G}_{5,3}$ with 5 segments of length 3.

3 Representation of hexagonal chains

By construction of hexagonal chains, segments of $G \in \mathcal{G}_{n,\ell}$ can be of two kinds. Suppose that a nonterminal segment S with two neighboring segments embedded into a two-dimensional regular hexagonal lattice and draw a line through the centers of the hexagons of S. If the neighboring segments of S lie on different sides of the line, then S is called a zigzag segment. If these segments lie on the same side, then S is said to be a nonzigzag segment. It is convenient to consider that the terminal segments are zigzag segments.

The zigzag hexagonal chain $Z_{n,\ell} \in \mathcal{G}_{n,\ell}$ contains only zigzag segments. All segments of the spiral hexagonal chain $O_{n,\ell} \in \mathcal{G}_{n,\ell}$ are nonzigzag with the exception of the terminal segments. The zigzag and spiral hexagonal chains of $\mathcal{G}_{5,3}$ are shown in Fig. 1.

Since we have two types of segments, a hexagonal chain $G \in \mathcal{G}_{n,\ell}$ can be represented by its binary code $r(G)$. Every nonzigzag (zigzag) segment of chain G corresponds to 1 (0) in the code $r(G)$. We assume that all segments of a chain are sequentially numbered by $0, 1, ..., n-1$ beginning from a terminal segment. Then the structure of a hexagonal chain G with n segments is completely defined by code $r(G) = (r_1, r_2, ..., r_{n-2})$ of length $n-2$, $n \geq 3$. Note that a reverse code generates the same chain. A chain with nontrivial symmetry has symmetrical code. For instance, the central hexagonal chains in Fig. 1 have the following codes: (101) and (010). The zigzag and the spiral chains have codes (00..0) and (11..1), respectively. Denote by $\overline{r}_i$ the bitwise negation of component r_i of a code.

4 Hexagonal chains with extremal Wiener index

The spiral and zigzag chains, $O_{n,\ell}$ and $Z_{n,\ell}$, are extremal hexagonal chains with regard to the Wiener index [10]. Their Wiener indices have the minimal $W(O_{n,\ell}) = W_{\min}(n,\ell)$ and the maximal $W(Z_{n,\ell}) = W_{\max}(n,\ell)$ values: $W(O_{n,\ell}) < W(G) < W(Z_{n,\ell})$ for all $G \in \mathcal{G}_{n,\ell} \setminus \{O_{n,\ell}, Z_{n,\ell}\}$, where

$$W_{\min}(n,\ell) = \frac{1}{3}\left(8n^3(\ell-1)^2(2\ell-3) + 96n^2(\ell-1)^2 - 2n(\ell-1)(2\ell-75) + 81\right),$$

$$W_{\max}(n,\ell) = \frac{1}{3}\left(16n^3(\ell-1)^3 + 72n^2(\ell-1)^2 + n(\ell-1)(12\ell+134) + 81\right).$$

For fibonacenes of $\mathcal{L}_{n,2}$ embedded into regular hexagonal lattice, the minimal value of the Wiener index is [6, 7, 8]

$$W_{\min}(n,2) = \frac{8}{9}\left[(n+1)^2(4n+25) + \phi(n)\right],$$

where

$$\phi(n) = \begin{cases} -6n+49, & \text{if } n = 3m, \quad m = 1,2,3,... \\ -54n+107, & \text{if } n = 3m+1, \quad m = 0,1,2,... \\ -6n+75, & \text{if } n = 3m+2, \quad m = 0,1,2,... \end{cases}$$

5 Values of the Wiener index

It is well-known that for hexagonal chains $G_1, G_2 \in \mathcal{C}_h$ the difference $W(G_1) - W(G_2)$ is divisible by 8, that is $W(G_1) \equiv W(G_2) \pmod 8$ [10]. For chains of $\mathcal{G}_{n,l}$, we have

Proposition 1. [13] *If* $G_1, G_2 \in \mathcal{G}_{n,\ell}$ *, then* $W(G_1) \equiv W(G_2) \pmod{16(\ell-1)^2}$.

Denote by $E_{n,\ell}$ the discrete interval of all possible values of the Wiener index for hexagonal chains of $\mathcal{G}_{n,\ell}$:

$$E_{n,\ell} = [\,W_{min}(n,\ell),\ W_{min}(n,\ell) + 16(\ell-1)^2,\ \ldots, W_{max}(n,\ell) - 16(\ell-1)^2,\ W_{max}(n,\ell)\,],$$

where $|E_{n,\ell}| = [\,W_{max}(n,\ell) - W_{min}(n,\ell)\,]/16(\ell-1)^2 + 1 = \binom{n}{3} + 1$.

Let $G_1 \in \mathcal{C}_{h_1}$, $G_2 \in \mathcal{C}_{h_2}$ and $h_1 \neq h_2$. If hexagonal chains G_1 and G_2 have equal Wiener indices, then $h_1 \equiv h_2 \pmod 4$ [7]. Such graphs may exist if intervals of the corresponding W-values have non-empty intersection. This implies that $h_1 \geq 23$ and $h_2 \geq 27$. Examples of such hexagonal chains with $h_1 = 25$ and $h_2 = 29$ were presented in [7, 8]. Here we construct similar examples for graphs of $\mathcal{G}_{n,\ell}$.

Case 1. Let $G_1 \in \mathcal{G}_{n,\ell_1}$, $G_2 \in \mathcal{G}_{n,\ell_2}$ and hexagonal chains have distinct segments' lengths, $\ell_1 < \ell_2$. Then the equality $W(G_1) = W(G_2)$ implies that $E_{n,\ell_1} \cap E_{n,\ell_2} \neq \emptyset$ or $W_{max}(n,\ell_1) - W_{min}(n,\ell_2) > 0$. Since the difference

$$\begin{aligned} &W_{max}(n,\ell-1) - W_{min}(n,\ell) = \\ &= \; -\frac{1}{3}\,n^3(40l^2 - 128l + 104) - n^2(8l^2 + 32l - 64) + \frac{1}{3}\,n(16l^2 - 56l - 94) \end{aligned}$$

is negative for $\ell > 2$, there are no such chains G_1 and G_2 with $W(G_1) = W(G_2)$.

Case 2. Let $G_1 \in \mathcal{G}_{n_1,\ell}$, $G_2 \in \mathcal{G}_{n_2,\ell}$ and hexagonal chains have distinct numbers of segments, $n_1 \neq n_2$. Then $h_1 - h_2 = (\ell-1)(n_1 - n_2) \equiv 0 \pmod 4$.

Proposition 2. *If* $W(G_1) = W(G_2)$ *then*

1. $\ell \equiv 1 \pmod 4$ *or*

2. $n_1 \equiv n_2 \pmod 4$ *or*

3. $\ell \equiv 3 \pmod 4$ *and* $n_1 \equiv n_2 \pmod 2$.

Proposition 2 gives some necessary conditions for chains with the same Wiener index in terms of number of segments and their lengths. For example, if n_1 and n_2 have distinct parity and $\ell \neq 5, 9, 13, \ldots$, then $W(G_1) \neq W(G_2)$.

We consider the case when $n_1 \equiv n_2 \pmod 4$. Since the Wiener index depends considerably on the number of vertices, the number of segments in a graph from $\mathcal{G}_{n,\ell}$ is compensated for by shorter distances between its vertices than in a graph from the class $\mathcal{G}_{n-4k,\ell}$. Thus, a graph from $\mathcal{G}_{n,\ell}$ is expected to be similar to a graph with the minimal value of the Wiener index in $\mathcal{G}_{n,\ell}$, while a graph from $\mathcal{G}_{n-4k,\ell}$ is expected to be similar to a graph with the maximal value of the Wiener index in $\mathcal{G}_{n-4k,\ell}$.

Proposition 3. *Let $G_1 \in \mathcal{G}_{n-4k,\ell}$ and $G_2 \in \mathcal{G}_{n,\ell}$ be hexagonal chains, $k \geq 1$ and $\ell \neq 74$. If $W(G_1) = W(G_2)$, then $n_1 \equiv n_2 \pmod{8(\ell-1)}$.*

Proof. Since $|E_{n-4k,\ell} \cap E_{n,\ell}| > 0$, the following expression has to be an integer

$$\frac{1}{16(\ell-1)^2}\Big(W_{max}(n-4k,\ell) - W_{min}(n,\ell)\Big) =$$

$$= \frac{1}{6}\Big(n^3 - 3n^2[\,8k(\ell-1)+1\,] + 2n[\,48k^2(\ell-1) - 36k + 1\,]$$

$$- 2k[\,64k^2(\ell-1) - 72k + 3\,] - \frac{73k}{(\ell-1)}\Big).$$

It is easy to see that the expression in the big brackets is an even integer if and only if $73k/(\ell-1)$ is an even integer. Then $k = 2m(\ell-1)$ or $k = 2m$ when $\ell = 74$, $m \geq 1$. ■

Values of the minimal numbers of segments n_1 and n_2 with nonempty intersections $E_{n_1,\ell} \cap E_{n_2,\ell}$ are shown in Table 1 for fibonacenes of $\mathcal{F}_{n_i}$ and $\mathcal{L}_{n_i,2}$, and hexagonal chains of $\mathcal{G}_{n_i,3}$, $i = 1, 2$.

Codes of several fibonacenes of $\mathcal{F}_{39}$ and $\mathcal{F}_{47}$ and their Wiener indices are presented in Table 2. Diagrams of six chains are shown in Fig. 2.

Codes of four fibonacenes of $\mathcal{L}_{63,2}$ and $\mathcal{L}_{71,2}$ are given Table 3. Diagrams of these graphs are depicted in Fig. 3.

Codes of hexagonal chains of $\mathcal{G}_{165,3}$ and $\mathcal{G}_{181,3}$ are shown in Table 4. Diagrams of two chains are presented in Fig. 4.

Table 1. Minimal numbers of segments with nonempty intersections of W-values.

$\mathcal{F}_{n_1}$ and $\mathcal{F}_{n_2}$			$\mathcal{L}_{n_1,2}$ and $\mathcal{L}_{n_2,2}$			$\mathcal{G}_{n_1,3}$ and $\mathcal{G}_{n_2,3}$		
n_1	n_2	$\lvert E_{n_1,2} \cap E_{n_2,2}\rvert$	n_1	n_2	$\lvert E_{n_1,2} \cap E_{n_2,2}\rvert$	n_1	n_2	$\lvert E_{n_1,3} \cap E_{n_2,3}\rvert$
39	47	323	62	70	24	164	180	206
40	48	684	63	71	523	165	181	5228
41	49	1076	64	72	1076	166	182	10366
42	50	1500	65	73	1684	167	183	15621
43	51	1957	66	74	2276	168	184	20994

Table 2. Fibonacenes of $\mathcal{F}_{39}$ and $\mathcal{F}_{47}$ with the same W.

chains	codes of lengths 37 and 45	W
G_1	0000000000000000000000000000001000100	349801
$O_{39,2}$	111111111111111111111111111111111111111111111	349801
G_3	0000000000000000000000000000010000001	350521
G_4	111111111111111111111111111111111111111111110	350521
G_5	1000000000000000000000000000000000011	352617
G_6	101111111111111111111111111111111111111111101	352617
G_7	0100000000000000000000000000000000010	352649
G_8	011111111111111111111111111111111111111111100	352649
G_9	0000000000000000000000000000000000011	353209
G_{10}	111111111111111111111111111111111111111110110	353209
G_{11}	0000000000000000000000000000000000100	353273
G_{12}	111111111111111111111111111111111111111111001	353273
G_{13}	0000000000000000000000000000000000010	353801
G_{14}	111111111111111111111111111111111111111101110	353801
G_{15}	0000000000000000000000000000000000001	354361
G_{16}	111111111111111111111111111111111111111011110	354361

Table 3. Fibonacenes of $\mathcal{L}_{63,2}$ and $\mathcal{L}_{71,2}$ with the same W.

chains	codes of lengths 61 and 69	W
G_1	000000000000000000 ... 00000000000000001	1431209
G_2	11011011011011011011011 ... 0110110110110100100	1431209
$Z_{63,2}$	000000000000000000 ... 000000000000000000	1432185
G_4	00011011011011011011011 ... 0110110110101101010	1432185

Table 4. Hexagonal chains of $\mathcal{G}_{165,3}$ and $\mathcal{G}_{181,3}$ with the same W.

chains	codes of lengths 163 and 179	W
G_1	101000000000000 ... 000000011101101	193961799
$O_{165,3}$	111111111111111111111 ... 1111111111111111111	193961799
G_3	000000000000000 ... 000000000010111	194183367
G_4	111111111111111111111 ... 1111111111100101111	194183367
G_5	000000000000000 ... 000000000100101	194194311
G_6	111111111111111111111 ... 1111111111010110110	194194311
G_7	000000000000000 ... 000000000001100	194224455
G_8	111011111011111111111 ... 1111111110111111111	194224455
G_9	000000000000000 ... 000000001000000	194225991
G_{10}	011111111111111111111 ... 1111111111001111010	194225991

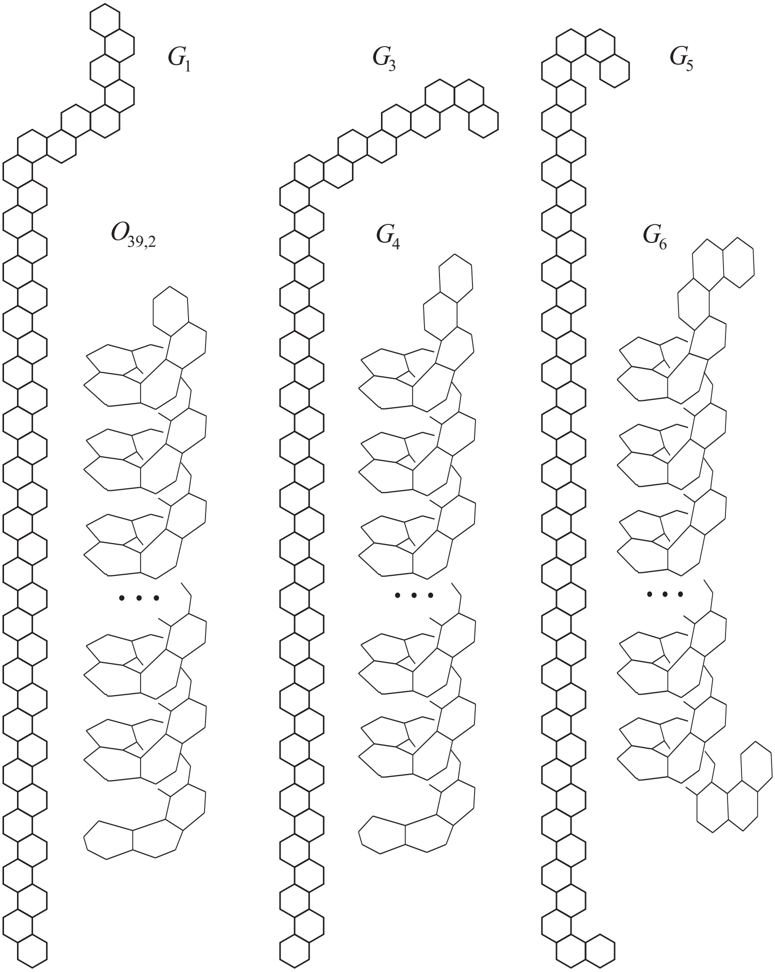

Figure 2. Fibonacenes of $\mathcal{F}_{39}$ and $\mathcal{F}_{47}$ with the same Wiener index.

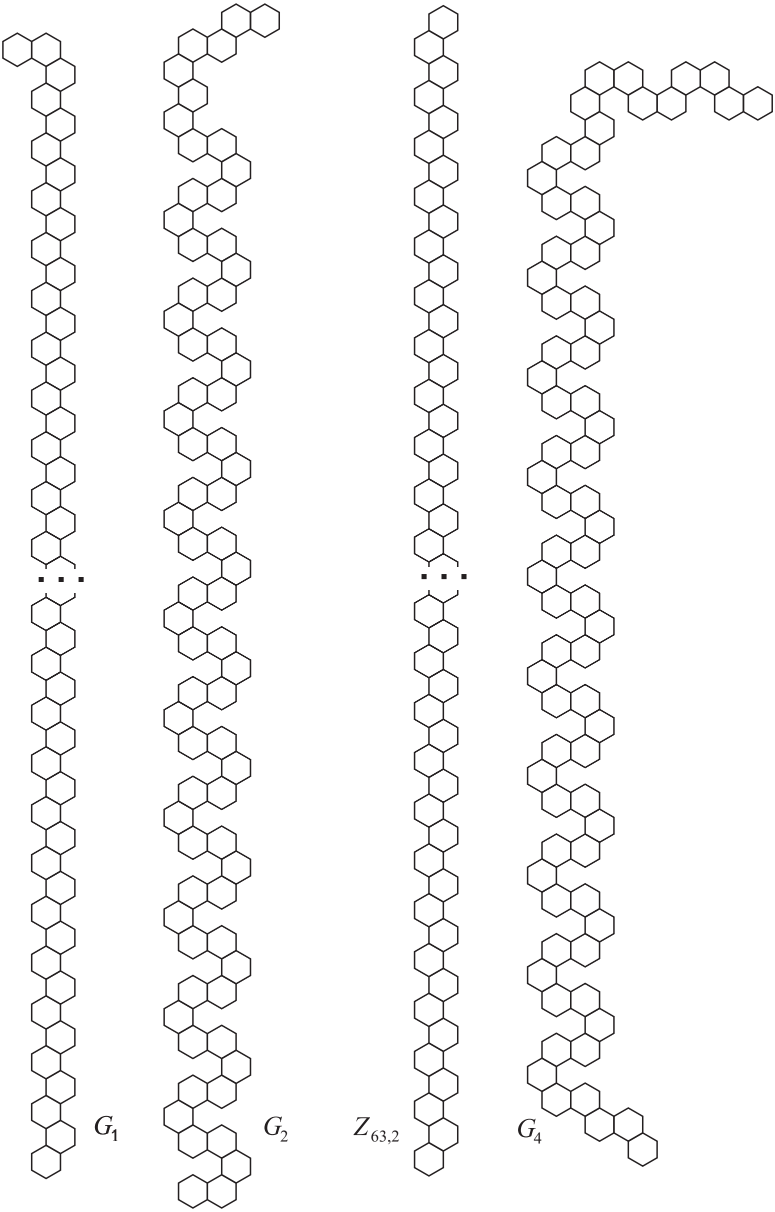

Figure 3. Fibonacenes of $\mathcal{L}_{63,2}$ and $\mathcal{L}_{71,2}$ with the same Wiener index.

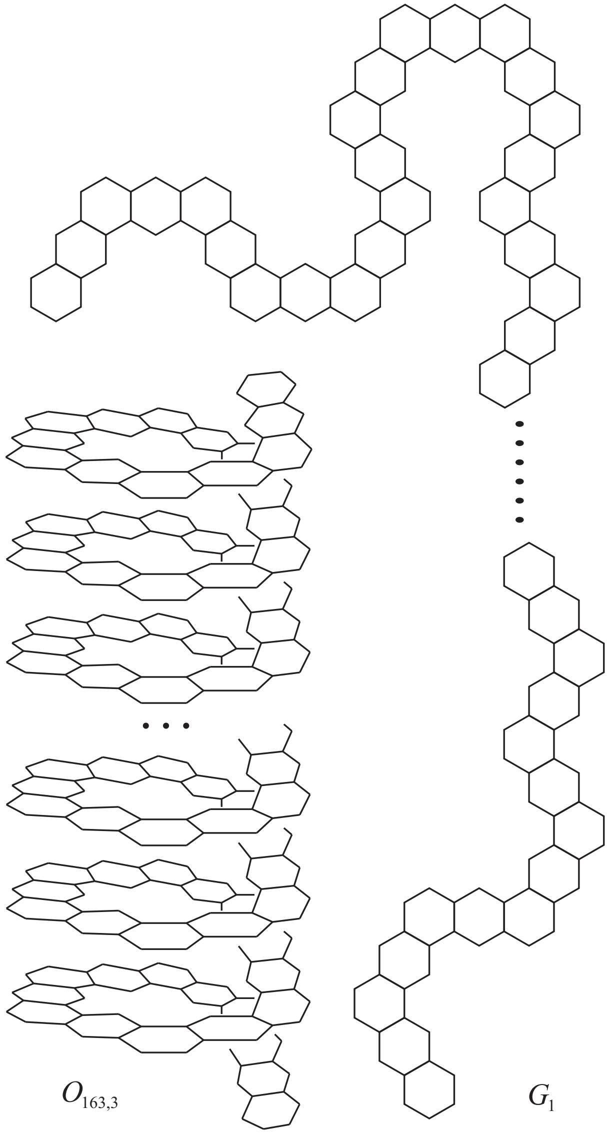

Figure 4. Hexagonal chains of $\mathcal{G}_{163,3}$ and $\mathcal{G}_{179,3}$ with the same Wiener index.

There is a method for constructing new hexagonal chains with the same Wiener indices by switching of two symmetrical components of codes of asymmetrical chains.

Proposition 4. [11] *Let* $G_1, G_2 \in \mathcal{G}_{n,\ell}$ *and* $r(G_1) = (\ldots r_i \ldots r_{n-i-1} \ldots)$*, where* $r_i \neq r_{n-i-1}$ *for fixed* $i \in \{1, 2, \ldots, n-2\}$*. Suppose that code* $r(G_2)$ *coincide with* $r(G_1)$ *except for two components,* $r(G_2) = (\ldots \overline{r}_i \ldots \overline{r}_{n-i-1} \ldots)$*. Then* $W(G_1) = W(G_2)$*.*

By Proposition 4, it is possible to obtain a new hexagonal chain from every chain G_1, G_3, G_9, G_{10}, G_{12}, G_{14}, or G_{16} of Table 2. Several chains with the same Wiener index can be constructed, for example, from every chain G_1 or G_6 of Table 4.

References

[1] A. T. Balaban, Chemical graphs. L. Symmetry and enumeration of fibonacenes (unbranched catacondensed benzenoids isoarithmic with helicenes and zigzag catafusenes, *MATCH Commun. Math. Comput. Chem.* **24** (1989) 9–38.

[2] A. T. Balaban, I. Motoc, D. Bonchev, O. Mekenyan, Topological indices for structure–activity correlations, *Topics Curr. Chem.* **114** (1983) 21–55.

[3] M. Dehmer, F. Emmert–Streib (Eds.), *Quantitative Graph Theory – Mathematical Foundations and Applications*, CRC Press, Boca Raton, 2014.

[4] J. Devillers, A. T. Balaban (Eds.), *Topological Indices and Related Descriptors in QSAR and QSPR*, Gordon & Breach, Reading, 2000.

[5] M. V. Diudea (Ed.), *QSPR/QSAR Studies by Molecular Descriptors*, Nova, Huntington, 2001.

[6] A. A. Dobrynin, Distribution of the distance numbers of unbranched hexagonal system graphs, *Vychisl. Sist.* **136** (1990) 61–140 (in Russian).

[7] A. A. Dobrynin, Graphs of unbranched hexagonal systems with equal values of Wiener index and different numbers of rings, *J. Math. Chem.* **9** (1992) 239–252.

[8] A. A. Dobrynin, Graph distance numbers of nonbranched hexagonal systems, *Siber. Adv. Math.* **2** (1992) 121–134.

[9] A. A. Dobrynin, R. Entringer, I. Gutman, Wiener index for trees: theory and applications, *Acta Appl. Math.* **66** (2001) 211–249.

[10] A. A. Dobrynin, I. Gutman, S. Klavžar, P. Žigert, Wiener index of hexagonal systems, *Acta Appl. Math.* **72** (2002) 247–294.

[11] A. A. Dobrynin, On the Wiener index of fibonacenes, *MATCH Commun. Math. Comput. Chem.* **64** (2010) 707–726.

[12] A. A. Dobrynin, On the Wiener index of certain families of fibonacenes, *MATCH Commun. Math. Comput. Chem.* **70** (2013) 565–574.

[13] A. A. Dobrynin, Wiener index of hexagonal chains with segments of equal length, in: M. Dehmer, F. Emmert–Streib (Eds.), *Quantitative Graph Theory – Mathematical Foundations and Applications*, CRC Press, Boca Raton, 2014, pp. 81–109.

[14] R. C. Entringer, Distance in graphs: trees, *J. Comb. Math. Comb. Comput.* **24** (1997) 65–84.

[15] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer–Verlag, Berlin, 1989.

[16] I. Gutman, S. Klavžar, Chemical graph theory of fibonacenes, *MATCH Commun. Math. Comput. Chem.* **55** (2006) 39–54.

[17] I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer–Verlag, Berlin, 1986.

[18] I. Gutman, J. H. Potgieter, Wiener index and intermolecular forces, *J. Serb. Chem. Soc.* **62** (1997) 185–192.

[19] I. Gutman, Y. N. Yeh, S. L. Lee, Y. L. Luo, Some recent results in the theory of the Wiener number, *Indian J. Chem.* **32A** (1993) 651–661.

[20] I. Gutman, B. Furtula (Eds.), *Distance in Molecular Graphs – Theory*, Univ. Kragujevac, Kragujevac, 2012.

[21] I. Gutman, B. Furtula (Eds.), *Distance in Molecular Graphs – Applications*, Univ. Kragujevac, Kragujevac, 2012.

[22] M. Knor, R. Škrekovski, A. Tepeh, Mathematical aspects of Wiener index, *Ars Math. Contemp.* **11** (2016) 327–352.

[23] S. Nikolić, N. Trinajstić, Z. Mihalić, The Wiener index: developments and applications, *Croat. Chem. Acta* **68** (1995) 105–129.

[24] D. H. Rouvray, The modelling of chemical phenomena using topological indices, *J. Comput. Chem.* **8** (1987) 470–480.

[25] R. Todeschini, V. Consonni, *Handbook of Molecular Descriptors*, Wiley–VCH, Weinheim, 2000.

[26] N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, 1983.

[27] H. Wiener, Structural determination of paraffin boiling points, *J. Amer. Chem. Soc.* **69** (1947) 17–20.