

Wiener Number of Polyphenyls and Phenylenes

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It is shown that the values which the Wiener numbers of isomeric polyphenyls may assume are all congruent modulo 36. Similarly, the Wiener numbers of isomeric phenylenes are always congruent modulo 18. These findings provide a rationalization for the known fact that the isomer-discriminating power of the Wiener number is rather weak. Extensions of the present results to more general classes of graphs are also pointed out.

Introduction

The fact that the Wiener number has a very poor isomer-discriminating power was noticed and investigated by several researchers [1–6]. This is especially the case within classes of structurally related molecules. One possible explanation of this phenomenon is that there are rigorous “selection rules” for the Wiener numbers, i.e., that the Wiener numbers of all members of a class of molecules must possess a common arithmetic property. The first hint for this came from the observation [7] that alternant hydrocarbons have odd-valued Wiener numbers if and only if both the number of starred and unstarred atoms is odd. Eventually a more powerful restriction for the Wiener numbers was discovered in the case of cata-condensed benzenoid hydrocarbons [3, 8]: the Wiener numbers of any two isomeric catacondensed species are congruent modulo 8. In other words, in the interval containing the Wiener numbers of isomeric cata-condensed benzenoids, among every eight consecutive integers seven are “forbidden”.

In this paper we demonstrate that similar, but even more restrictive, “selection rules” exist in the case of two further classes of molecules – polyphenyls and phenylenes. We also show that these results seem to represent only the tip of an iceberg, and that their various generalizations and extensions are possible.

If G is a molecular graph [9–11], then the Wiener number $W(G)$, associated with G , is equal to the sum of the distances between all pairs of vertices of G . The Wiener number is one of the most extensively studied topological indices; for some recent reviews see [9–16].

Let G be a connected graph, $V(G)$ its vertex set, and $d(u, v|G)$ the distance between the vertices u and v of G . Then the Wiener number $W(G)$ is given by

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

In the subsequent discussion we will often need the auxiliary quantity $d(v|G)$, called the distance of the vertex v , and defined as

$$d(v|G) = \sum_{u \in V(G)} d(u, v|G).$$

The Wiener Number of Polyphenyls

Polyphenyls are conjugated hydrocarbons consisting of benzene rings which are connected by essentially single bonds. It is required that polyphenyls do not possess rings other than six-membered.

The molecular graphs of polyphenyls are constructed from a certain number, say h , of disjoint six-membered circuits which are connected by means of $h-1$ edges; these latter edges must be bridges. (Recall that an edge e of the graph G is said to be a bridge if $G-e$ has more components than G [9].) The graphs $R_3(a)$, $R_3(b)$ and $R_3(c)$, depicted in Fig. 1 pertain to the three isomeric triphenyls. Our consideration applies also to graphs of the form $R_3(d)$.

It is clear that every polyphenyl graph R_h with h hexagons, $h > 1$, can be obtained from a polyphenyl graph R_{h-1} with $h-1$ hexagons, by attaching to it (via a bridge) a new hexagon. Hence, polyphenyl graphs have the structure shown in Figure 2. In Fig. 2 we also indicate the labeling of the vertices of R_h , referred to in the subsequent discussion.

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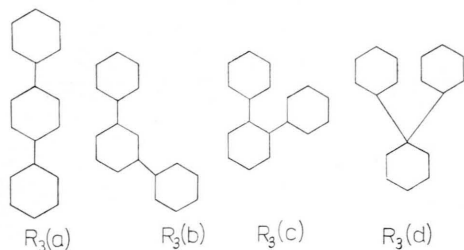


Fig. 1. Graphs obtained by connecting 3 hexagons by means of 2 bridges; $W(R_3(a)) = 657 = 549 + 3 \times 36$, $W(R_3(b)) = 621 = 549 + 2 \times 36$, $W(R_3(c)) = 585 = 549 + 36$, $W(R_3(d)) = 549$.

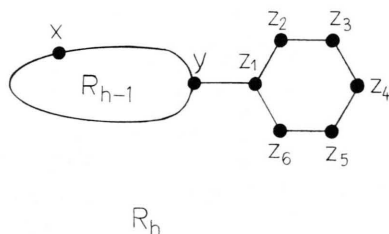


Fig. 2. The structure of the polyphenyl graph; h = number of hexagons.

Let x be an arbitrary vertex of R_h . Without loss of generality we may assume that x belongs to the fragment R_{h-1} , see Figure 2. Then by taking (1) into account, we conclude from Fig. 2 that

$$d(x|R_h) = d(x|R_{h-1}) + \sum_{i=1}^6 d(x, z_i|R_h) \quad (2)$$

as well as

$$d(x, z_1|R_h) = d(x, y|R_{h-1}) + 1 \quad (3a)$$

$$d(x, z_2|R_h) = d(x, z_6|R_h) = d(x, y|R_{h-1}) + 2, \quad (3b)$$

$$d(x, z_3|R_h) = d(x, z_5|R_h) = d(x, y|R_{h-1}) + 3, \quad (3c)$$

$$d(x, z_4|R_h) = d(x, y|R_{h-1}) + 4. \quad (3d)$$

Substituting (3) back into (2) we obtain

$$d(x|R_h) = d(x|R_{h-1}) + 6d(x, y|R_{h-1}) + 15. \quad (4)$$

Lemma 1. Let R_h and R'_h be two arbitrary polyphenyls with h hexagons. If x is an arbitrary vertex of R_h and x' an arbitrary vertex of R'_h , then

$$d(x|R_h) \equiv d(x'|R'_h) \pmod{6}. \quad (5)$$

Proof follows by induction on the number h of hexagons.

If $h = 1$, then there exists a unique R_1 (= the benzene graph), and its vertices are symmetry-equivalent. Hence, if $h = 1$, then (5) holds in a trivial manner.

Let $h > 1$. From (4),

$$d(x|R_h) - d(x'|R'_h) = d(x|R_{h-1}) - d(x'|R'_{h-1}) + 6[d(x, y|R_{h-1}) - d(x', y'|R'_{h-1})]. \quad (6)$$

Assume now that (5) holds for polyphenyls with $h-1$ hexagons. This implies that $d(x|R_{h-1}) - d(x'|R'_{h-1})$ is divisible by 6. If so, then by (6), $d(x|R_h) - d(x'|R'_h)$ is also divisible by 6, i.e., (5) holds for polyphenyls with h hexagons. ■

Note that in Lemma 1 the graphs R_h and R'_h need not be distinct. Also observe that the multiplier 6 in (6) is a proper consequence of the fact that polyphenyl graphs are composed of six-membered circuits.

Because $d(x|R_1) = 9$, from (4) and Lemma 1 one arrives at

Corollary: If h is odd, then $d(x|R_h) \equiv 3 \pmod{6}$, If h is even, then

$$d(x|R_h) \equiv 0 \pmod{6}.$$

We now proceed with the calculation of $W(R_h)$. Three types of vertex pairs u, v in R_h can be distinguished (see Figure 2):

(a) Both u and v belong to the R_{h-1} -fragment.

(b) Vertex u belongs to the R_{h-1} -fragment whereas v is one of the vertices z_i , $i = 1, 2, 3, 4, 5, 6$, or vice versa.

(c) Both u and v belong among the vertices z_i , $i = 1, 2, 3, 4, 5, 6$.

In case (a) the sum of distances between u and v is equal to $W(R_{h-1})$. In case (c) this is equal to $W(R_1) = 27$. In case (b) the respective sum is equal to

$$\sum_{u \in V(R_{h-1})} \sum_{i=1}^6 d(u, z_i|R_h). \text{ Therefore}$$

$$W(R_h) = W(R_{h-1}) + 27 + \sum_{u \in V(R_{h-1})} \sum_{i=1}^6 d(u, z_i|R_h). \quad (7)$$

Because of (3) we have

$$\begin{aligned} & \sum_{u \in V(R_{h-1})} \left[\sum_{i=1}^6 d(u, z_i|R_h) \right] \\ &= \sum_{u \in V(R_{h-1})} [6d(u, y|R_{h-1}) + 15] \\ &= 6d(y|R_{h-1}) + 15|R_{h-1}| \\ &= 6d(y|R_{h-1}) + 90(h-1), \end{aligned}$$

where by $|G|$ we denote the number of vertices of the graph G . This yields

$$W(R_h) = W(R_{h-1}) + 27 + 6d(y|R_{h-1}) + 90(h-1), \quad (8)$$

from which it immediately follows

$$W(R_h) - W(R'_h) = W(R_{h-1}) - W(R'_{h-1}) + 6[d(y|R_{h-1}) - d(y'|R'_{h-1})]. \quad (9)$$

Observe that the multiplier 6 in (9) is again a consequence of the fact that we are dealing with six-membered circuits.

Because of Lemma 1, the last term on the right-hand side of (9) is divisible by 36. For $h=2$ and $h=3$ the graph R_{h-1} is unique and therefore $W(R_{h-1}) - W(R'_{h-1}) = 0$. Consequently, if $h=2$ and $h=3$, the right-hand side of (9) is divisible by 36. Induction on h leads now straightforwardly to the conclusion that the right-hand side of (9) is divisible by 36 for all $h > 1$. We thus arrived at

Theorem 1: Let R_h and R'_h be two arbitrary polyphenyls with h hexagons. Then $W(R_h) \equiv W(R'_h) \pmod{36}$.

Corollary: Let R_h be a polyphenyl with h hexagons. Chose the integer i , $i = 0, 1, 2$ or 3 , such that $h + i$ is divisible by 4. Then $W(R_h) \equiv 9i \pmod{36}$.

The Wiener Number of Phenylenes

Phenylenes represent another class of conjugated systems, obtained by joining six-membered rings. This time, however, six-membered rings are coupled via two bonds. As a consequence of this, a four-membered ring is formed between each pair of adjacent hexagons. The isomeric phenylenes with 4 hexagons are depicted in Figure 3.

Phenylenes are of outstanding interest in contemporary research in the chemistry of polycyclic aromatic compounds. For recent experimental and theoretical work on them see [17–21].

The molecular graphs of phenylenes are obtained from a certain number, say h , of disjoint hexagons. If two hexagons are adjacent, then they are joined by means of two edges. These edges involve adjacent vertices of each of the two hexagons, forming thus tetragons. Further, by deleting from a tetragon the two edges not belonging to hexagons, the resulting subgraph must become disconnected. The structure of a

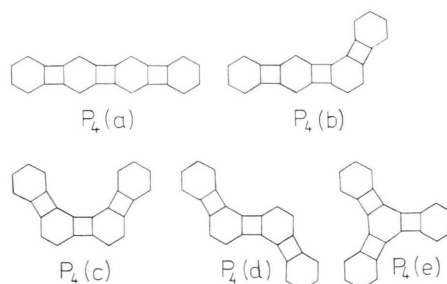


Fig. 3. The isomeric phenylenes with 4 hexagons; $W(P_4(a)) = 1296 = 1134 + 9 \times 18$, $W(P_4(b)) = W(P_4(c)) = W(P_4(d)) = 1260 = 1134 + 7 \times 18$, $W(P_4(e)) = 1134$; observe that three of the five isomers have equal W -values.

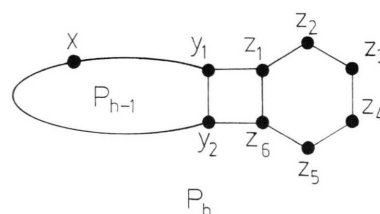


Fig. 4. The structure of the phenylene graph; h = number of hexagons

phenylene graph P_h , comprising h hexagons, and the labeling of some of its vertices is shown in Figure 4.

For phenylenes we establish results analogous as for polyphenyls, which we state in the form of a lemma and a theorem.

Lemma 2: Let P_h and P'_h be two arbitrary phenylenes with h hexagons. If x is an arbitrary vertex of P_h and x' an arbitrary vertex of P'_h , then $d(x|P_h) \equiv d(x'|P'_h) \pmod{6}$.

Theorem 2: Let P_h and P'_h be two arbitrary phenylenes with h hexagons. Then $W(P_h) \equiv W(P'_h) \pmod{18}$.

The proofs of Lemma 2 and Theorem 2 are based on reasoning similar to that used in the case of polyphenyls. We therefore sketch only the basic features of these proofs.

Proof of Lemma 2. We refer to the labeling of vertices of P_h as indicated in Figure 4. Without loss of generality consider a vertex x whose distance to y_1 is smaller than the distance to y_2 . [Recall that P_h is a bipartite graph. Therefore there cannot exist vertex x , for which

$d(x, y_1 | P_h) = d(x, y_2 | P_h)$. Then

$$d(x | P_h) = d(x | P_{h-1}) + \sum_{i=1}^6 d(x, z_i | P_h),$$

which combined with

$$d(x, z_1 | P_h) = d(x, y_1 | P_{h-1}) + 1,$$

$$d(x, z_2 | P_h) = d(x, z_6 | P_h) = d(x, y_1 | P_{h-1}) + 2,$$

$$d(x, z_3 | P_h) = d(x, z_5 | P_h) = d(x, y_1 | P_{h-1}) + 3,$$

$$d(x, z_4 | P_h) = d(x, y_1 | P_{h-1}) + 4$$

yields

$$d(x | P_h) = d(x | P_{h-1}) + 6d(x, y_1 | P_{h-1}) + 15. \quad (10)$$

Lemma 2 follows from (10) in the same way as Lemma 1 follows from (4). ■

Corollary: If h is odd, then $d(x | P_h) \equiv 3 \pmod{6}$. If h is even, then $d(x | P_h) \equiv 0 \pmod{6}$.

Proof of Theorem 2: In analogy to (7) we now have

$$W(P_h) = W(P_{h-1}) + 27 + \sum_{u \in V(P_{h-1})} \sum_{i=1}^6 d(u, z_i | P_h),$$

and in addition:

$$\sum_{u \in V(P_{h-1})} d(u, z_1 | P_h) = d(y_1 | P_{h-1}) + |P_{h-1}|,$$

$$\sum_{u \in V(P_{h-1})} d(u, z_2 | P_h) = d(y_1 | P_{h-1}) + 2|P_{h-1}|,$$

$$\sum_{u \in V(P_{h-1})} d(u, z_3 | P_h) = d(y_1 | P_{h-1}) + 3|P_{h-1}|,$$

$$\sum_{u \in V(P_{h-1})} d(u, z_4 | P_h) = d(y_2 | P_{h-1}) + 3|P_{h-1}|,$$

$$\sum_{u \in V(P_{h-1})} d(u, z_5 | P_h) = d(y_2 | P_{h-1}) + 2|P_{h-1}|,$$

$$\sum_{u \in V(P_{h-1})} d(u, z_6 | P_h) = d(y_2 | P_{h-1}) + |P_{h-1}|,$$

where $|P_{h-1}| = 6(h-1)$. This results in

$$W(P_h) = W(P_{h-1}) + 27 + 3[d(y_1 | P_{h-1}) + d(y_2 | P_{h-1})] + 72(h-1). \quad (11)$$

Theorem 2 follows now from (11) in the same manner as Theorem 1 is deduced from (8). ■

Corollary: If h is odd, then $W(P_h) \equiv 9 \pmod{18}$. If h is even, then $W(P_h) \equiv 0 \pmod{18}$.

Some Generalizations

From the proofs of the Lemmas 1 and 2, as well as Theorems 1 and 2 it is easily seen that the numbers 6, $36 = 6^2$ and $18 = \frac{1}{2} 6^2$ have their origins in the fact that both the polyphenyl and phenylene graphs are formed by joining 6-membered circuits. The following generalizations are thus straightforward. Because they involve molecular graphs of lesser chemical importance, or graphs which are not molecular at all, we state them just for the sake of completeness and without proof.

Theorem 3: Let $R_{n,h}$ be a graph obtained by connecting h disjoint n -membered circuits by means of $h-1$ bridges. Let $R'_{n,h}$ be another graph of the same type. Let x and x' be vertices of $R_{n,h}$ and $R'_{n,h}$, respectively. Then $d(x | R_{n,h}) \equiv d(x' | R'_{n,h}) \pmod{n}$ and $W(R_{n,h}) \equiv W(R'_{n,h}) \pmod{n^2}$.

Theorem 4: Let $P_{n,h}$ be a graph obtained by connecting h disjoint n -membered circuits by means of $h-1$ pairs of edges, in the manner described in the case of phenylenes. Let $P'_{n,h}$ be another graph of the same type. Let x and x' be vertices of $P_{n,h}$ and $P'_{n,h}$, respectively. If n is even, then $d(x | P_{n,h}) \equiv d(x' | P'_{n,h}) \pmod{n}$ and $W(P_{n,h}) \equiv W(P'_{n,h}) \pmod{\frac{1}{2}n^2}$.

If $n = 6$, then $R_{n,h}$ and $P_{n,h}$ reduce to the previously studied polyphenyl and phenylene graphs, R_h and P_h , respectively. Notice that whereas Theorem 3 holds for both even and odd values of n , in Theorem 4 it is required that n is even-valued. The extension of this latter result to odd n is not known to us.

Theorem 3 can be further generalized. Let G be a connected n -vertex graph whose all vertices are symmetry-equivalent. (Recall that the circuit is such a graph, but that there are many other graphs of this kind.)

Theorem 5: Let G_h be a graph obtained by connecting h disjoint copies of G by means of $h-1$ bridges. Let G'_h be another graph of the same type. Let x and x' be vertices of G_h and G'_h , respectively. Then $d(x | G_h) \equiv d(x' | G'_h) \pmod{n}$ and $W(G_h) \equiv W(G'_h) \pmod{n^2}$.

Of several other modulo-type relations for the Wiener number which we discovered during the present study, we wish to mention only the following. Let $C_n(1), C_n(2), \dots, C_n(h)$ be disjoint copies of the n -mem-

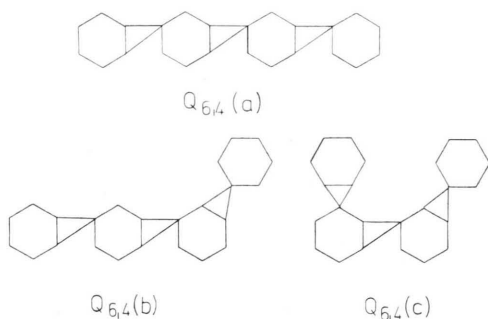


Fig. 5. Three representatives of graphs $Q_{6,4}$; $W(Q_{6,4}(a)) = 1296 = 1152 + 4 \times 36$, $W(Q_{6,4}(b)) = 1224 = 1152 + 2 \times 36$, $W(Q_{6,4}(c)) = 1152$.

bered circuit. Construct a graph $Q_{n,h}$ by joining (via two new edges) two adjacent vertices of $C_n(i)$ to a vertex $C_n(i+1)$, and by performing this procedure for

$i = 1, 2, \dots, h-1$. Three examples of graphs of the type $Q_{n,h}$ are depicted in Figure 5.

Theorem 6: Let $Q_{n,h}$ and $Q'_{n,h}$ be two graphs of the above described type. Then for $n \geq 3$, $h \geq 1$, $W(Q_{n,h}) \equiv W(Q'_{n,h}) \pmod{n^2}$.

Notice that, in a certain loosely defined way, the structure of $Q_{n,h}$ lies on the half way between $P_{n,h}$ and $R_{n,h}$. Also notice that an n -membered circuit in $C_{n,h}$ must not have more than two neighbors (in contrast with $P_{n,h}$ and $R_{n,h}$).

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