Wiener Numbers of Phenylenes: An Exact Result

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An exact relation is established between the Wiener number (*W*) of a phenylene (*PH*), its hexagonal squeeze (*HS*), and inner dual (*ID*): $W(PH) = (9/4)[W(HS) + 16W(ID) - (2h+1)(4h+1)]$, where *h* stands for the number of hexagons. Various applications of this relation are pointed out.

1. INTRODUCTION

The rapid development of the experimental (mainly synthetic) chemistry of phenylenes (see, for instance refs 1−3 and the references quoted therein) motivated a number of recent theoretical studies of these conjugated π-electron systems[4−7] as well as of the more general case, namely of nonbenzenoid alternant catafusenes.[8−11] One remarkable result along these lines was the discovery[6] that the algebraic structure count of a phenylene *PH* is equal to the Kekulé structure count of a benzenoid molecule, the so-called "hexagonal squeeze" *HS*, which in a natural way is associated with *PH*.

Continuing the research on other possible connections between *PH* and *HS* we examined a number of their physicochemical and quantum-chemical characteristics as well as molecular-graph-based structure-descriptors,[12−16] among which was also the Wiener number *W*.[17] (For the definition of the Wiener number and its fundamental properties see, for instance, the recent reviews.[18,19] Numerical calculations revealed[16] that the correlation between *W*(*PH*) and *W*(*HS*) is linear (which was anticipated) but also that (surprisingly) the *W*(*PH*)/*W*(*HS*)-points lie on a number of parallel straight lines. This eventually enabled us to guess the formula[16]

$$W(PH) = \frac{9}{4}[W(HS) + 16W(ID) - (2h+1)(4h+1)] \qquad (1)$$

where *h* is the number of hexagons and *ID* the inner dual (see below). As we demonstrate in this paper, eq 1 is a mathematically exact relation.

2. PHENYLENES, HEXAGONAL SQUEEZES, INNER DUALS

Phenylenes (*PH*) are non-benzenoid conjugated π-electron systems composed of six-membered rings (hexagons) and four-membered rings, in which no two hexagons are adjacent, and each four-membered ring is adjacent to two hexagons. The number of hexagons is denoted by *h*. A characteristic representative of phenylenes, with $h = 6$, is depicted in Figure 1.

To every phenylene it is possible to associate a catacondensed benzenoid system, obtained so that the four-membered rings of the phenylene are "squeezed off". This benzenoid system was named[6] the hexagonal squeeze (*HS*) of the respective phenylene. The construction of the hexagonal squeeze should be evident from the example depicted in Figure 1. Clearly, each *PH* determines a unique *HS* and vice versa, and these two systems have an equal number of hexagons.

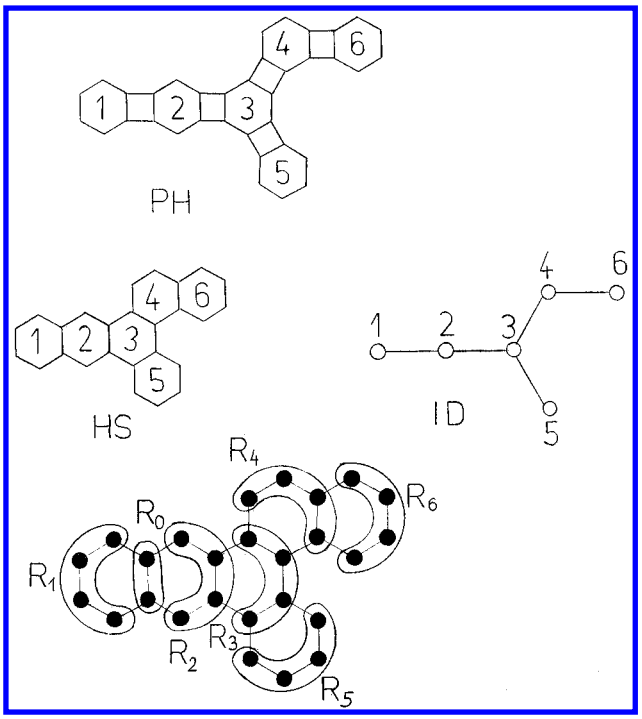

Figure 1. An example of a phenylene (*PH*), its hexagonal squeeze (*HS*), and its inner dual (*ID*); the vertex set of *HS* is partitioned into disjoint subsets $\mathbf{R}_i$, $i = 0,1,...,6$.

To a hexagonal squeeze (or, what is the same: to a phenylene) one can associate a graph called the inner dual (*ID*).[20] The vertices of *ID* correspond to the hexagons of *HS*. Two vertices of *ID* are adjacent if the respective hexagons of *HS* are first neighbors. A self-explanatory example is found in Figure 1.

The inner duals of hexagonal squeezes (or phenylenes) are connected acyclic graphs (trees); the number of vertices of an *ID* is equal to the number of hexagons of *PH* or *HS*; the vertices of *ID* are of degree one, two, or three. Note that each *HS* (or *PH*) determines a unique *ID*, but (because *ID* is a graph and not a geometric object) the reverse is not true: the same *ID* may correspond to a whole family of *PH*/*HS*-pairs. According to eq 1 the *W*(*PH*)/*W*(*HS*)-points of all members of such a family lie on the same straight line.

3. PROOF OF EQ 1

In order to make our notation compact, it is convenient to number the hexagons of *PH* and *HS* 1,2,...,*h* according to

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the following procedure: Choose a terminal hexagon and label it 1. For $i = 2,...,h$ choose a hexagon whose neighbor has already been labeled and number it i.

Such a numbering of the hexagons of *PH* and *HS* as well as of the corresponding vertices of *ID* is indicated in Figure 1.

A Recursion Relation for the Wiener Number of Phenylenes. Consider the molecular graph of a phenylene *PH* with h hexagons and denote by $\mathbf{V}(PH)$ its vertex set. The number of vertices of *PH* is $6h$. Denote by $\mathbf{H}_i$ the set of (six) vertices belonging to the ith hexagon of *PH*. Then

$$\mathbf{V}(PH) = \bigcup_{i=1}^{h} \mathbf{H}_i$$

In the case of phenylenes, $\mathbf{H}_i \cap \mathbf{H}_j = \emptyset$ whenever $i \neq j$.

For $i \neq j$, let $x_{ij} \in \mathbf{H}_i$ and $x_{ji} \in \mathbf{H}_j$ be vertices of *PH*, such that for all $x_i \in \mathbf{H}_i$ and $x_j \in \mathbf{H}_j$

$$d(x_i,x_j) \geq d(x_{ij},x_{ji})$$

Here and later $d(p,q)$ denotes the distance[18,19] between the vertices p and q of the considered molecular graph. If we want to indicate that p and q are vertices of the graph G, then we will write $d(p,q|G)$.

Let $x'_{ij} \in \mathbf{H}_i$ be the vertex belonging to the same four-membered ring of *PH* as x_{ij}. Let $x'_{ji} \in \mathbf{H}_j$ be the vertex belonging to the same four-membered ring of *PH* as x_{ji}. Let the auxiliary quantity $L_{ij}(PH)$ be defined as

$$L_{ij}(PH) = d(x_{ij},x_{ji}) + d(x_{ij},x'_{ji}) + d(x'_{ij},x_{ji}) + d(x'_{ij},x'_{ji}) \quad (2)$$

Then for $i \neq j$,

$$\sum_{x \in \mathbf{H}_i} \sum_{x' \in \mathbf{H}_j} d(x,x') = 72 + 9L_{ij}(PH) \quad (3)$$

In order to verify eq 3, denote $d(x_{ij},x_{ji})$, $d(x_{ij},x'_{ji})$, $d(x'_{ij},x_{ji})$, and $d(x'_{ij},x'_{ji})$ by d, d', $'d$, and $'d'$, respectively, and observe that the double sum, occurring on the right-hand side of eq 3, is equal to

$$[(d) + (d+1) + (d+2) + (d') + (d'+1) + (d'+2)] + [(d+1) + (d+2) + (d+3) + (d'+1) + (d'+2) + (d'+3)] + [(d+2) + (d+3) + (d+4) + (d'+2) + (d'+3) + (d'+4)] + [('d) + ('d+1) + ('d+2) + ('d') + ('d'+1) + ('d'+2)] + [('d+1) + ('d+2) + ('d+3) + ('d'+1) + ('d'+2) + ('d'+3)] + [('d+2) + ('d+3) + ('d+4) + ('d'+2) + ('d'+3) + ('d'+4)] = 4 \times 18 + 9(d+d'+'d+'d') = 72 + 9L_{ij}(PH)$$

Let *PH*′ be a phenylene obtained from *PH* by deleting from it the hexagon 1. Thus *PH*′ possesses $h - 1$ hexagons, labeled 2,3,...,h. Then bearing in mind that the Wiener index is equal to the sum of distances between all pairs of vertices,[18,19] we immediately have

$$W(PH) = \frac{1}{2}\sum_{x \in \mathbf{H}_1} \sum_{x' \in \mathbf{H}_1} d(x,x') + \sum_{x \in \mathbf{H}_1} \sum_{x' \in \mathbf{H}_2} d(x,x') + \sum_{x \in \mathbf{H}_1} \sum_{x' \in \mathbf{H}_3} d(x,x') + ... + \sum_{x \in \mathbf{H}_1} \sum_{x' \in \mathbf{H}_h} d(x,x') + W(PH') = 27 + \sum_{j=2}^{h} \sum_{x \in \mathbf{H}_1} \sum_{x' \in \mathbf{H}_j} d(x,x') + W(PH') \quad (4)$$

Taking into account eq 3 we now arrive at our first recursion relation:

$$W(PH) = W(PH') + 27 + \sum_{j=2}^{h} [72 + 9L_{1j}(PH)] \quad (5)$$

A Recursion Relation for the Wiener Number of Hexagonal Squeezes. Consider the molecular graph of the hexagonal squeeze *HS* associated with the above considered phenylene *PH*. Let the vertex set of this graph be $\mathbf{V}(HS)$. The number of vertices of *HS* is $4h + 2$. As before $\mathbf{H}_i$ is the set of (six) vertices belonging to the ith hexagon of *HS*. Then

$$\mathbf{V}(HS) = \bigcup_{i=1}^{h} \mathbf{H}_i$$

However, in the case of hexagonal squeezes, $\mathbf{H}_i \cap \mathbf{H}_j$ may be nonempty for some $i \neq j$. Because of this difficulty the calculation of $W(HS)$ is somewhat more complicated than the (above described) calculation of $W(PH)$.

In order to avoid the problem, we define mutually disjoint vertex sets $\mathbf{R}_0,\mathbf{R}_1,...,\mathbf{R}_h$ as follows:

$$\mathbf{R}_0 = \mathbf{H}_1 \cap \mathbf{H}_2$$

$$\mathbf{R}_1 = \mathbf{H}_1 \setminus \mathbf{R}_0$$

$$\mathbf{R}_2 = \mathbf{H}_2 \setminus (\mathbf{R}_0 \bigcup \mathbf{R}_1)$$

...

$$\mathbf{R}_h = \mathbf{H}_h \setminus (\mathbf{R}_0 \bigcup \mathbf{R}_1 \bigcup ... \bigcup \mathbf{R}_{h-1})$$

An illustrative example is found in Figure 1.

For $i \neq j$, let $y_{ij} \in \mathbf{H}_i$ and $y_{ji} \in \mathbf{H}_j$ be vertices of *HS*, such that for all $y_i \in \mathbf{H}_i$ and $y_j \in \mathbf{H}_j$

$$d(y_i,y_j) \geq d(y_{ij},y_{ji})$$

Further, let $y'_{ij} \in \mathbf{H}_i$ be the vertex belonging to the same two hexagons of *HS* as y_{ij}. Let $y'_{ji} \in \mathbf{H}_j$ be the vertex belonging to the same two hexagons of *HS* as y_{ji}. Then in full analogy to eq 2 we define an auxiliary quantity $L_{ij}(HS)$ as

$$L_{ij}(HS) = d(y_{ij},y_{ji}) + d(y_{ij},y'_{ji}) + d(y'_{ij},y_{ji}) + d(y'_{ij},y'_{ji}) \quad (6)$$

and in analogy to eq 3 we prove

$$\sum_{y \in \mathbf{H}_i} \sum_{y' \in \mathbf{H}_j} d(y,y') = 48 + 4L_{ij}(HS) \quad (7)$$

Now, let *HS*′ be the hexagonal squeeze of the previously described phenylene *PH*′. Hence, *HS*′ embraces the hexa-

gons 2,3,...,h and the vertex sets $\mathbf{R}_0,\mathbf{R}_2,\mathbf{R}_3,...,\mathbf{R}_h$. Then in view of the fact that the vertex sets $\mathbf{R}_i$, $i = 0,1,2,...,h$ are all mutually disjoint, we can use the same argument as in the case of eq 4 to obtain

$$W(HS) = \frac{1}{2}\sum_{y\in\mathbf{R}_1}\sum_{y'\in\mathbf{R}_1} d(y,y') + \sum_{y\in\mathbf{R}_1}\sum_{y'\in\mathbf{R}_0} d(y,y') + \sum_{y\in\mathbf{R}_1}\sum_{y'\in\mathbf{R}_2} d(y,y') + ... + \sum_{y\in\mathbf{R}_1}\sum_{y'\in\mathbf{R}_h} d(y,y') + W(HS') = 10 + 16 + \sum_{j=2}^{h}\sum_{y\in\mathbf{R}_1}\sum_{y'\in\mathbf{R}_j} d(y,y') + W(HS')$$

which combined with eq 7 yields our second recursion relation

$$W(HS) = W(HS') + 26 + \sum_{j=2}^{h}[48 + 4L_{1j}(HS)] \quad (8)$$

A Relation between $L_{ij}(PH)$ and $L_{ij}(HS)$. By inspecting the structure of a phenylene and its hexagonal squeeze and by bearing in mind the definition of the vertices x_{ij}, x'_{ij} (of the phenylene) and y_{ij}, y'_{ij} (of the hexagonal squeeze), we conclude that distance between x_{ij} and x_{ji} (in the phenylene) and between y_{ij} and y_{ji} (in the hexagonal squeeze) differ by the number of four-membered rings between the ith and jth hexagon of the phenylene. This, however, is just the distance between the ith and jth vertices of the inner dual. In other words,

$$d(x_{ij},x_{ji}) = d(y_{ij},y_{ji}) + d(i,j|ID)$$

By the very same argument

$$d(x_{ij},x'_{ji}) = d(y_{ij},y'_{ji}) + d(i,j|ID)$$

$$d(x'_{ij},x_{ji}) = d(y'_{ij},y_{ji}) + d(i,j|ID)$$

$$d(x'_{ij},x'_{ji}) = d(y'_{ij},y'_{ji}) + d(i,j|ID)$$

which combined with eqs 2 and 6 results in

$$L_{ij}(PH) = L_{ij}(HS) + 4d(i,j|ID) \quad (9)$$

Completion of the Proof. The proof of eq 1 proceeds now by means of mathematical induction on the number h of hexagons.

The validity of eq 1 is directly checked for $h = 1, 2, 3$.

Suppose now that eq 1 is obeyed by all PH/HS with $h - 1$ hexagons. Any PH/HS with h hexagons can be obtained by taking an appropriate PH/HS with $h - 1$ hexagons and attaching to it a terminal hexagon. This corresponds to the transformations $PH' \rightarrow PH$ and $HS' \rightarrow HS$.

Thus, according to the induction hypothesis we will assume that

$$W(PH') = \frac{9}{4}[W(HS') + 36W(ID') - (2h-1)(4h-3)] \quad (10)$$

where ID' stands for the inner dual of HS'. Note that ID' is obtained from ID by deleting from it vertex 1.

Substituting eq 10 back into (5) and using relation 9 we obtain

$$W(PH) = 72h - 45 + \frac{9}{4}[W(HS') + 4\sum_{j=2}^{h}L_{ij}(HS)] + 36[W(ID') + \sum_{j=2}^{h}d(1,j|ID)] - \frac{9}{4}(2h-1)(4h-3) \quad (11)$$

Now, $W(ID')$ is equal to the sum of distances of all pairs of vertices of ID, except those involving vertex 1. Therefore,

$$W(ID') + \sum_{j=2}^{h}d(1,j|ID) = W(ID) \quad (12)$$

From eq 8 we immediately see that

$$W(HS') + 4\sum_{j=2}^{h}L_{ij}(HS) = W(HS) - 26 - 48(h-1) \quad (13)$$

When eqs 12 and 13 are substituted back into (11), formula 1 is obtained by straightforward, yet somewhat tedious, calculation.

By this the proof of eq 1 has been completed.

4. APPLICATIONS

The Wiener numbers of catacondensed benzenoid molecules have been extensively studied, and many results for them are known. Formula 1 enables one to directly (and practically without any additional calculation) obtain analogous results for phenylenes. We mention here a few.

1. Among unbranched catacondensed benzenoids with a given number of hexagons (h), the linear polyacene (λ_h) has maximum and the helicene (χ_h) minimum Wiener number.[21] If we denote by λ_h^* and χ_h^* the respective phenylenes, then for any other phenylene PH with h hexagons,

$$W(\chi_h^*) \le W(PH) \le W(\lambda_h^*)$$

with the equality sign occurring only if $PH = \chi_h^*$ and $PH = \lambda_h^*$.

2. Because[21] $W(\chi_h) = (8h^3 + 72h^2 - 26h + 27)/3$ and $W(\lambda_h) = (16h^3 + 36h^2 + 26h + 3)/3$, we have

$$W(\chi_h^*) = 12h^3 + 36h^2 - 39h + 18$$

$$W(\lambda_h^*) = 18h^3 + 9h^2$$

3. Many other general expressions for the Wiener numbers of homologous series of benzenoid systems are known. From them, general expressions for W of homologous series of phenylenes are readily deduced. For instance, for ζ_h, the zigzag polyacene:[22] $W(\zeta_h) = (16h^3 + 24h^2 + 62h - 21)/3$. This yields

$$W(\zeta_h^*) = 18h^3 + 27h - 18$$

where ζ_h^* is the corresponding zigzag phenylene.

4. If HS^a and HS^b are two catacondensed benzenoids with an equal number of hexagons, then[21] $W(HS^a) - W(HS^b)$ is

divisible by eight. Therefore, if PH^a and PH^b are any two phenylenes with an equal number of hexagons, then

$$W(PH^a) \equiv W(PH^b) \pmod{18}$$

This latter is a previously known result.[23]

5. For a random hexagonal chain with h hexagons, in which the probability of linear annelation is q and the probabilities of angular annelations (in two directions) are p_1 and p_2, the expected value of the Wiener number is[24]

$$W_h = 4h^3 + 16h^2 + 6h + 1 + \frac{4}{3}q(h^3-3h^2+2h) - \frac{4}{3}(p_1-p_2)^2F(h,q)$$

where $p_1 + p_2 + q = 1$ and $F(h,q)$ is a function (which is not a polynomial!) given by

$$F(h,q) = \sum_{k=1}^{h-3} k(k+1)(k+2)q^{h-3-k}$$

The expected value of the respective random phenylene is then

$$W_h^* = 15h^3 + 18h^2 - 6h + 3q\,(h^3-3h^2+2h) - 3(p_1-p_2)^2F(h,q)$$

6. Catacondensed benzenoids with equal inner duals and equal Wiener numbers are frequently encountered.[22] The respective phenylenes have also equal W-values. Consequently, finding phenylenes with coinciding W is an easy task.

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