Relations between Wiener numbers of benzenoid hydrocarbons and phenylenes

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Using the method of elementary cuts [5], we deduce relations between the Wiener number of a phenylene (*PH*) and the catacondensed benzenoid hydrocarbon associated in a natural way to *PH*, called the hexagonal squeeze (*HS*). Similar relations are found also for the Szeged numbers of *PH* and *HS*.

Introduction

Although the research of the Wiener number (*W*) of benzenoid and other polycyclic hydrocarbons has a long history (for review and further references see [1–3]), the remarkably simple algorithm [4, 5] for the calculation of *W*, based on elementary edge-cuts, was not recognized until quite recently. Not only that this method of elementary cuts makes the evaluation of *W* quite easy, but it sheds light on the perplexed dependence of *W* on molecular structure [6].

By means of the method of elementary cuts we now establish relations between the Wiener numbers of two distinct, yet structurally related classes of polycyclic molecules: benzenoid hydrocarbons and phenylenes.

The name "phenylene" was coined by Vollhardt to specify conjugated molecules consisting of condensed 4-membered (cyclobutadiene) and 6-membered (benzene) rings, in which each cyclobutadiene unit is adjacent to two benzene rings, whereas benzene rings are not adjacent to each other. The structure of phenylenes should be evident from the examples depicted in Fig. 1. The chemistry of phenylenes is nowadays in great expansion, thanks to a recently discovered procedure for their synthesis (see [7–10] and the references quoted therein).
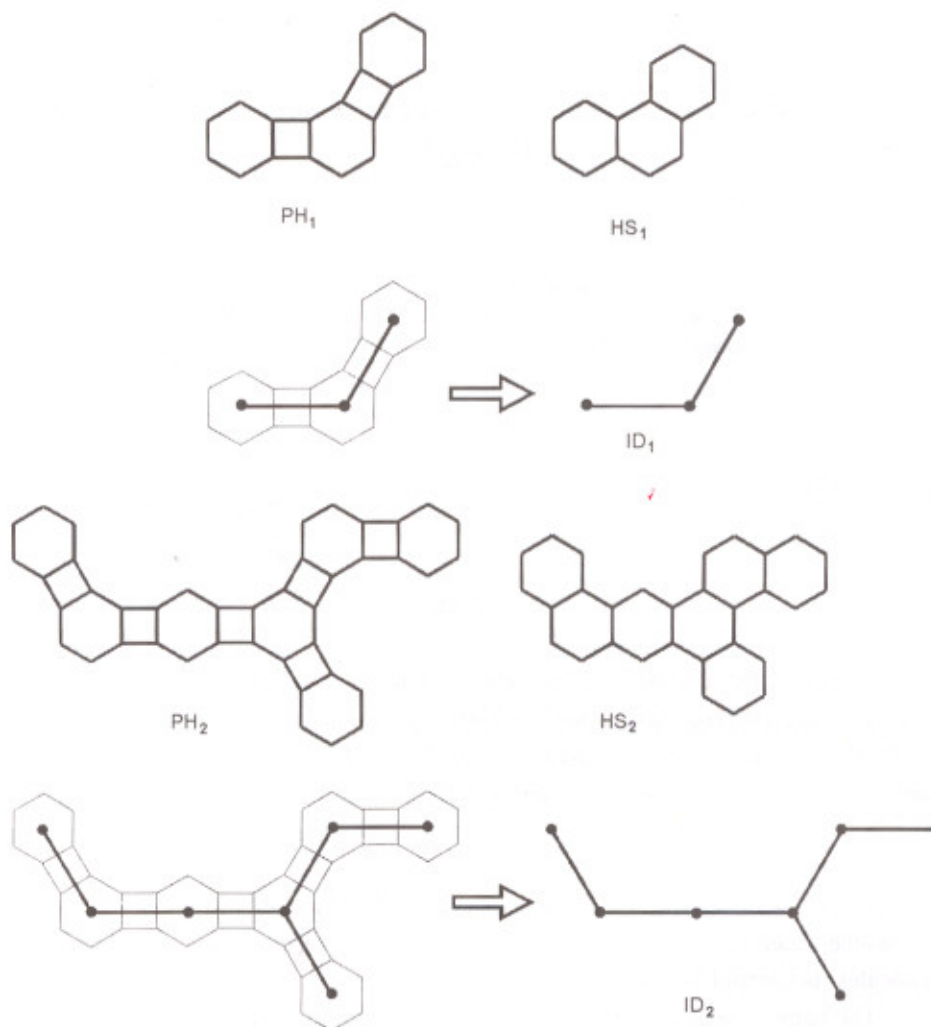
Fig. 1. Two phenylenes (PH_1 and PH_2), the corresponding hexagonal squeezes (HS_1 and HS_2) and the corresponding inner duals (ID_1 and ID_2); the construction of the inner duals is indicated

A catacondensed benzenoid hydrocarbon [11] is associated to a phenylene in a natural manner, as illustrated in Fig. 1. This benzenoid system was named the "hexagonal squeeze" of the respective phenylene [12]. Evidently, there is a one-to-one correspondence between a phenylene (*PH*) and its hexagonal squeeze (*HS*), i.e., *PH* uniquely determines *HS* and *vice versa* [13].

The connection between phenylenes and their hexagonal squeezes is far from being formal. Numerous deep-lying parallelisms between the π-electron properties of phenylenes and the associated benzenoid hydrocarbons have been discovered. The first such result is the equality of the algebraic structure count of *PH* and the Kekulé structure count of *HS* [12]; a survey of the hitherto established relations together with a complete list of references is found in [14, 15].

Elementary cuts in phenylenes and their hexagonal squeezes

Because notation and terminology used in this paper is same as in our previous articles [5, 6], we do not repeat the definition of an elementary cut and the notions related to it. These will anyway become clear from the examples given below. Exceptionally, the elementary cuts of the phenylene are labeled by P_1, P_2, $\cdots$, P_{2h+1}, Q_1, Q_2, $\cdots$, Q_{h-1} while the elementary cuts of the hexagonal squeeze are S_1, S_2, $\ldots$, S_{2h+1}, see Fig. 2. Here and later h stands for the number of hexagons in both the phenylene and its hexagonal squeeze.

The number of edges intersected by an elementary cut C is denoted by $r(C)$.

The elementary cuts of a phenylene *PH* are divided into two groups: those intersecting hexagons and those intersecting just one cyclobutadiene unit. The former are denoted by P_i, $i = 1,2,\ldots$, the latter by Q_j, $j = 1,2,\ldots$. An illustrative example is given in Fig. 2. Notice that $r(Q_j) = 2$ for all phenylenes and for all values of j.

It is easy to prove, e.g., by mathematical induction, that a phenylene *PH* with h hexagons possesses $2h+1$ elementary cuts of type P and $h-1$ elementary cuts of type Q.

The hexagonal squeeze *HS* of *PH* possesses also h hexagons. It has $2h+1$ elementary cuts, denoted by S_i, $i = 1,2,\ldots, 2h+1$, see Fig. 2.

The complete sets of elementary cuts of *PH* and *HS* are thus

$$\mathbf{C}\,(PH) = \{P_1, P_2,.., P_{2h+1}, Q_1, Q_2,.., Q_{h-1}\}$$

and

$$\mathbf{C}\,(HS) = \{S_1, S_2,.., S_{2h+1}\},$$
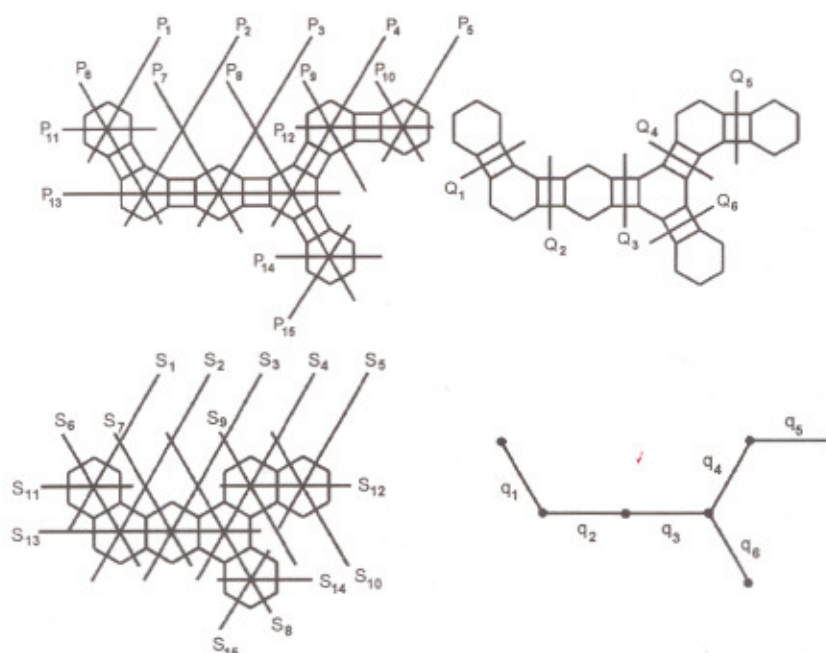
respectively.

Fig. 2. The elementary cuts of the phenylene PH_2 and its hexagonal squeeze HS_2, cf. Fig. 1; note the correspondence between the cuts P_i and S_i, $i = 1,2,\ldots, 15$, as well as between $Q_1, Q_2,\ldots, Q_6$ and the edges $q_1, q_2,\ldots, q_6$ of the inner dual ID_2

From the considerations in [5] it follows that the edge-cut formula for the calculation of the Wiener number (namely formula (5) in [5]), is applicable to both the phenylenes and their hexagonal squeezes. Thus, if C is an elementary cut of a phenylene PH, $C \in \mathbf{C}(PH)$, dissecting PH into fragments $PH'(C)$ and $PH''(C)$, then

$$W(PH) = \sum_{i=1}^{2h+1} n(PH')(P_i))n(PH''(P_i)) + \sum_{j=1}^{h-1} n(PH'(Q_j))n(PH''(Q_j)), \quad (1)$$

where $n(PH'(C))$ and $n(PH''(C))$ are the number of vertices of $PH'(C)$ and $PH''(C)$, respectively.

In a fully analogous manner, if C is an elementary cut of the hexagonal squeeze HS, $C \in \mathbf{C}(HS)$, dissecting HS into fragments $HS'(C)$ and $HS''(C)$, then

$$W(HS) = \sum_{i=1}^{2h+1} n(HS'(C_i))n(HS''(C_i)), \quad (2)$$

where $n(HS'(C))$ and $n(HS''(C))$ count the vertices of $HS'(C)$ and $HS''(C)$, respectively.

Now, there is an obvious one-to-one correspondence between the elementary cuts P_1, P_2,..., P_{2h+1} of a phenylene and the elementary cuts S_1, S_2,..., S_{2h+1} of the respective hexagonal squeeze. This is illustrated in Fig. 2, where the cuts of PH_2 and HS_2 are labeled so that P_i corresponds to S_i for $i = 1, 2,...,15$.

At this point it would be purposeful to look at the example given in Fig. 3, which is aimed at making easier to follow the proof of *Lemma 1* and the subsequent considerations.

Lemma 1

Let P be an elementary cut of a phenylene PH and S the corresponding elementary cut of the hexagonal squeeze HS. The cut P intersects $r(P)$ edges of PH and divides PH into fragments PH' and PH'' with $n(PH')$ and $n(PH'')$ vertices and $h(PH')$ and $h(PH'')$ hexagons, respectively. The cut S intersects $r(S)$ edges of HS and divides HS into fragments HS' and HS'' with $n(HS')$ and $n(HS'')$ vertices and $h(HS')$ and $h(HS'')$ hexagons, respectively. Then

$$r(P) = 2r(S)-2, \tag{3}$$
$$n(PH') = 6h(PH') + 3/2\, r(P); \quad n(PH'') = 6h(PH'') + 3/2\, r(P), \tag{4}$$
$$n(HS') = 4h(HS') + 2r(S)-1; \quad n(HS'') = 4h(HS'') + 2r(S)-1, \tag{5}$$
$$n(PH') = 3/2\, [n(HS')-1]; \quad n(PH'') = 3/2\, [n(HS'')-1]. \tag{6}$$

For an example illustrating the notation used in the above equations see Fig. 3.
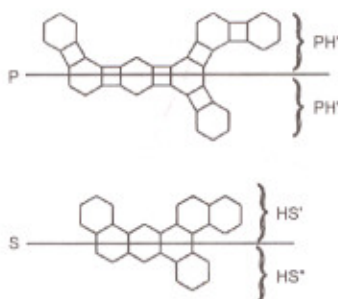

Fig. 3. An elementary cut P of $PH = PH_2$ and the corresponding elementary cut S of $HS = HS_2$; the cuts P and S intersect $r(P) = 6$ and $r(S) = 4$ edges of PH and HS, respectively; note that P and S intersect equal number ($=3$) of hexagons, and that $r(P) = 6 = 2\times3$, $r(S) = 4 = 3+1$; by deleting from PH the edges intersected by P we obtain the fragments PH' and PH'' with $n(PH') = 27$ and $n(PH'') = 15$ vertices, and with $h(PH') = 3$ and $h(PH'') = 1$ hexagons, respectively; by deleting from HS the edges intersected by S we obtain the fragments HS' and HS'' with $n(HS') = 19$ and $n(HS'') = 11$ vertices, and with $h(HS') = 3$ and $h(HS'') = 1$ hexagons, respectively; note that it necessarily must be $h(PH') = h(HS')$ and $h(PH'') = h(HS'')$

Proof

The cut P intersects $r(P)/2$ hexagons of PH. The cut S intersects $r(S)-1$ hexagons of HS. Since P and S intersect equal number of hexagons, Eq. (3) follows.

In order to count the vertices of PH' consider the phenylene $PH*$, consisting of the hexagons of PH' and the hexagons intersected by P. Because $PH*$ has $h(PH')+r(P)/2$ hexagons, it has $6[h(PH')+r(P)/2]$ vertices. Three vertices from each intersected hexagon do not belong to PH', therefore PH' has $6[h(PH')+r(P)/2]$ $-3[r(P)/2]$ vertices. This yields Eq. (4).

Formula (5) is deduced in a fully analogous manner, bearing in mind that a catacondensed benzenoid system with $h*$ hexagons has $4h*+2$ vertices.

In order to deduce Eq. (6) observe that $h(PH') = h(HS')$ and $h(PH'') = h(HS'')$. Then Eq. (6) is obtained by substituting relation (3) into (4), and combining this with Eq. (5).

A noteworthy property of Eq. (6) is that it is independent of $r(P)$ and $r(S)$. This implies that the size of the fragment PH' is completely determined (in a linear manner) by the size of the fragment HS' and *vice versa*. As a consequence, one arrives at remarkable relations between the Wiener and Szeged numbers of PH and HS. These are outlined in the subsequent section.

Relations between the Wiener and Szeged numbers of phenylenes and their hexagonal squeezes

The main results deduced in this section are summarized in the following:

Theorem 1

Let PH be a phenylene with h hexagons, HS its hexagonal squeeze and ID its inner dual. Then the Wiener (W) and Szeged numbers (Sz) of PH, HS and ID are related as

$$W(PH) = 9/4\ [W(HS)-(2h+1)(4h+1)+16W(ID)], \tag{7}$$
$$Sz(PH) = 9/2\ [Sz(HS)-W(HS)-3h(4h+1)+16W(ID)] \tag{8}$$

and

$$Sz(PH)-2W(PH) = 9/2\ [Sz(HS)-2W(HS)-(h-1)(4h+1)]. \tag{9}$$

The definition of the inner dual is given below.

Proof of identity (7)

Using the relations from *Lemma 1* we can straightforwardly deduce a connection between the first summation on the right-hand side of Eq. (1) and the Wiener number of *HS*, Eq. (2). Indeed, assuming that the elementary cuts of *PH* and *HS* are labeled so that P_i corresponds to S_i for all $i = 1, 2, \ldots, 2h+1$, and by means of Eq. (6),

$$\sum_{i=1}^{2h+1} n(PH'(P_i))n(PH''(P_i)) = \sum_{i=1}^{2h+1} \left[\frac{3}{2}[n(HS'(S_i)) - 1]\right]\left[\frac{3}{2}[n(HS''(S_i)) - 1]\right] =$$

$$\frac{9}{2}\sum_{i=1}^{2h+1}[n(HS'(S_i))n(HS''(S_i)) - n(HS'(S_i)) - n(HS''(S_i)) + 1] =$$

$$\frac{9}{4}\left[\sum_{i=1}^{2h+1} n(HS')S_i))n(HS''(S_i)) - (2h+1)(4h+1)\right].$$

Above we employed the fact that for any cut C of the hexagonal squeeze, $HS'(C) + HS''(C)$ = number of vertices of $HS = 4h+2$. Taking into account Eq. (2) we then obtain

$$\sum_{i=1}^{2h+1} n(PH'(P_i))n(PH''(P_i)) = \frac{9}{4}[W(HS) - (2h+1)(4h+1)]. \tag{10}$$

It remains to find an appropriate expression for the second summation on the right-hand side of Eq. (1). For this notice a one-to-one correspondence between the elementary cuts $Q_1, Q_2, \ldots, Q_{h-1}$ of *PH* and the edges $q_1, q_2, \ldots, q_{h-1}$ of the inner dual of *PH*. (For a self explanatory illustration see Fig. 2.)

The inner dual *ID* of a phenylene *PH* is a tree (=connected acyclic graph) whose vertices represent benzene rings of *PH*, such that neighboring benzene rings (i.e., those separated by one cyclobutadiene unit) correspond to adjacent vertices of *ID*. Consequently, *ID* has h vertices and $h-1$ edges. Two examples of how inner duals are constructed are found in Fig. 1.

The number of edges of *ID* is equal to the number of cyclobutadiene units of *PH*. The elementary cuts $Q_1, Q_2, \ldots, Q_{h-1}$ of *PH* can be labeled so that Q_i corresponds to the edge q_i of *ID* for $i = 1, 2, \ldots, h-1$.

Let T be an arbitrary tree and q its arbitrary edge. Denote by $n_1(q|T)$ and $n_2(q|T)$ the number of vertices of T, lying on the two sides of the edge q. Then,

according to a classical result found in the very first paper [16] on (what we nowadays call) the Wiener number,

$$W(T) = \sum_q n_1(q|T) n_2(q|T),$$
(11)

with summation going over all edges of T.

Now, bearing in mind the above described correspondence between the edges of the inner dual and the elementary cuts of the phenylene, we see that

$$n(PH'(Q_i)) = 6n_1(q_i|ID) \quad ; \quad n(PH''(Q_i)) = 6n_2(q_i|ID),$$

which oombined with Eq. (11) yields

$$\sum_{j=1}^{h-1} n(PH'(Q_j)) n(PH''(Q_j)) = 36 W(ID).$$
(12)

Substituting relations (10) and (12) back into Eq. (l) we arrive at Eq. (7).

Formula (7) was recently noticed [15] within a systematic empirical study [17] of the correlation between physico-chemical properties of phenylenes and their hexagonal squeezes. An inductive proof of Eq. (7) was designed [18], different and much more complicated than what we presented above.

Proof of identity (8)

A consideration similar to what was used in the previous proof leads to a connection between the Szeged numbers of phenylenes and their hexagonal squeezes. It has been shown [19] that the Szeged number of phenylenes and their hexagonal squeezes conforms to relations fully analogous to Eqs (1) and (2), namely,

$$Sz(PH) = \sum_{i=1}^{2h+1} r(P_i) n(PH'(P_i)) n(PH''(P_i)) + \sum_{j=1}^{h-1} r(Q_i) n(PH'(Q_j)) n(PH''(Q_j))$$

$$Sz(HS) = \sum_{i=1}^{2h+1} r(S_i) n(HS'(C_i)) n(HS''(C_i)),$$
(13)

where, as before, $r(C)$ is the number of edges intersected by the cut C. (More details on the theory of the Szeged numbers can be found in [19] and the references cited therein.)

Substituting the identities (3) and (6) back into Eq. (13) and repeating the reasoning used in connection with the derivation of Eqs (10) and (12) we get:

$$\sum_{i=1}^{2h+1} r(P_i) n(PH'(P_i)) n(PH''(P_i)) = \frac{9}{2}[Sz(HS) - W(HS) - 3h(4h+1)],$$
(14)

where we used the fact that the sum of the r-values of all elementary cuts of HS is just the number of edges of HS, which is known [11] to be equal to $5h+1$, and

$$\sum_{j=1}^{h-1} r(Q_i)n(PH'(Q_j))n(PH''(Q_j)) = 72\,W(ID)\,, \tag{15}$$

where we used the fact that $r(Q_i) = 2$. Combining Eqs (14) and (15) with Eq. (13) we arrive at formula (8).

The identity (9) is an immediate consequence of Eqs (7) and (8). By this the proof of *Theorem 1* has been completed.

More relations for the Wiener number

Another relation between the Wiener numbers of phenylenes and their hexagonal squeezes was recently established [20]. To formulate it we have to introduce the concept of weighted graphs.

The degree of a vertex is the number of the first neighbors of this vertex. Recall that in graphs representing phenylenes and their hexagonal squeezes all vertices have degrees two or three.

Let G be an arbitrary graph and let $G[w]$ be the weighted graph, obtained from G by associating to its vertices certain weights. The weight of the vertex u is denoted by $w(u)$. Here $w(u)$ is set to be equal to the degree of the vertex u minus one. Hence, in the graphs considered in this paper, the vertex weights are either 1 or 2. Now the identity obtained in [20] reads:

$$W(PH) = W(HS[w]) + 36\,W(ID), \tag{16}$$

a result that should be compared with those stated in *Theorem 1*. Recall that in $W(G[w])$ the distance between the vertices u and v is counted $w(u)\cdot w(v)$ times.

Combining Eqs (7) and (16) we get

$$W(HS) = 4/9\,W(HS[w]) + (2h+1)(4h+1)$$

a relation which does not contain terms depending on the inner dual.

Since any catacondensed benzenoid molecule [11] can be viewed as the hexagonal squeeze of some phenylene, the above result can be re-stated as follows:

Theorem 2.

If H is the molecular graph of a catacondensed benzenoid hydrocarbon with h hexagons, and if $H[w]$ is its weighted variant (as specified above), then

$$W(H) = 4/9 \; W(H[w]) + (2h+1)(4h+1). \tag{17}$$

Let, as usual [2]–[5], $d(u, v \,|\, G)$ denote the distance between the vertices u and v of the graph G. Then we define

$$D_{ij}(G) = \sum d(u,v \,|\, G) \,,$$

with the summation going over all vertices u of degree i and all vertices v of degree j. In the case of phenylenes and their hexagonal squeezes, i.e., if $G = PH$ or $G = HS$, the vertex degrees are either 2 or 3, and we have the following decompositions of the Wiener number [21]

$$W(G) = 1/2 \; [D_{22}(G)+2D_{23}(G)+D_{33}(G)]. \tag{18}$$

The analogous relation for the graph G with vertices weighted in the above described manner reads

$$W(G[w]) = 1/2 \; (D_{22}(G)+4D_{23}(G)+4D_{33}(G)]. \tag{19}$$

Formulas (18) and (19), combined with Eq. (17), imply:

Corollary 2.1

Let H and h have the same meaning as in *Theorem 2*. Then

$$W(H) = 4D_{33}(H)-2D_{22}(H)+9(2h+1)(4h+1) \tag{20}$$

and

$$h = \frac{1}{24}\left[\sqrt{20D_{22}(H)+8D_{23}(H)-28D_{33}(H)+9}-9\right]. \tag{21}$$

Proof

Choose $G = H$ and insert the relations (18) and (19) into Eq. (17). This yields

$$5D_{22}(H)+2D_{23}(H)-7D_{33}(H) = 18(2h+1)(4h+1) \tag{22}$$

from which D_{23} can be expressed and substituted back into Eq. (17), resulting in Eq. (20).

Identity Eq. (22) can be viewed as a quadratic equation in the variable h. By solving this equation we get Eq. (21).

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