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ELEMENTARY EDGE–CUTS IN THE THEORY OF BENZENOID HYDROCARBONS – AN APPLICATION

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Abstract

The method of elementary edge–cuts (outlined in the preceeding paper [?]) is applied to explain the finding that within families of isomeric phenylenes, the points obtained by plotting the Szeged numbers of phenylenes vs. the Szeged numbers of the corresponding hexagonal squeezes lie on several parallel straight lines, having slopes equal to 3.

Introduction

This paper reports some applications of the method of elementary edge cuts, whose theoretical details are outlined in the preceding paper [?].

In this paper we are concerned with *phenylenes* (PH) and their *hexagonal squeezes* (HS). The fact that a variety of topological properties of phenylenes and of the corresponding hexagonal squeezes is intimately related and/or correlated has been established in a number of previous investigations [1]–[10]. The quantities for which such connections have been established so far are the Kekulé structure count [1], total π-electron energy [2, 3], HOMO LUMO separation [3], cyclic conjugation [4], local aromaticity [5], Wiener number [6]–[9] and spectral moments [10].

In a recent work [6] we calculated the Wiener numbers (W) of sets of isomeric phenylenes and of the corresponding hexagonal squeezes, expecting to find some kind of correlation between them. Instead of this we noticed a remarkable mathematical regularity: the points obtained by plotting $W(PH)$ vs. $W(HS)$ lie on several parallel straight lines, all having slopes equal to 9/4. A detailed analysis of the calculated numerical values for $W(PH)$ and $W(HS)$ revealed that points pertaining to isomers with the same inner dual lie on the same line. Moreover, even if the inner duals are different, but have coinciding Wiener numbers, the corresponding points lie of the same line. This led to the relation [6]

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

the validity of which has eventually been verified in a mathematically satisfactory manner [7, 8].

We mention in passing that relations other than Eq. (1), involving Wiener numbers of PH and HS, have also been discovered recently [8, 9].

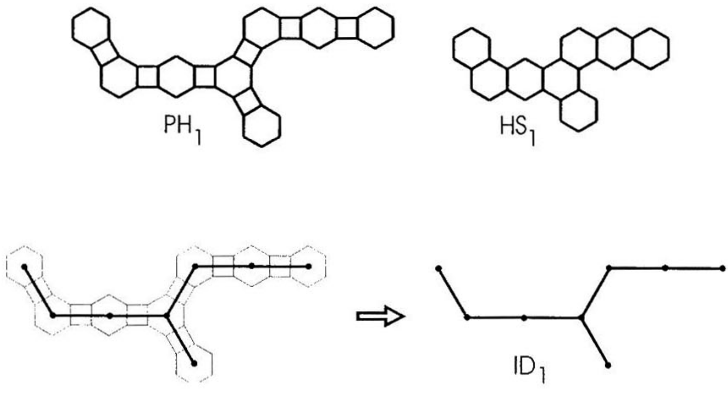

Fig. 1. A phenylene (PH_1), the corresponding hexagonal squeeze (HS_1) and the inner dual (ID_1); the construction of the inner dual is indicated

In formula (1) h is the number of hexagons of both PH and HS whereas ID stands for the respective *inner dual*. Because the formal definition and structural characterization of PH, HS and ID were given in many previous papers (see, for instance, [1, 2, 6, 7, 11]), we skip these details and give only a self-explanatory example, see Fig. 1. References to experimental chemistry of phenylenes and discussions on the chemical significance of the relations between properties of PH and HS are outlined in due detail elsewhere

[1]-[5],[11].

Motivated by the fortuitous finding of the identity (1), we have undertaken analogous studies of Szeged numbers (Sz) of PH and HS. Bearing in mind the numerous, previously established [?]-[?], similarities between Sz and W we hoped that it will be possible to establish a relation analogous to (1). Thus, we calculated the Sz-values for families of isomeric phenylenes (namely phenylenes having the same number of hexagons) and plotted them vs. the Sz-values of the respective hexagonal squeezes. Also in this case it was found that the points lie on several parallel straight lines which now have slopes equal to 3. A typical result of this kind is depicted in Fig. 2, with the structures of the respective hexagonal squeezes shown in Fig. 3.

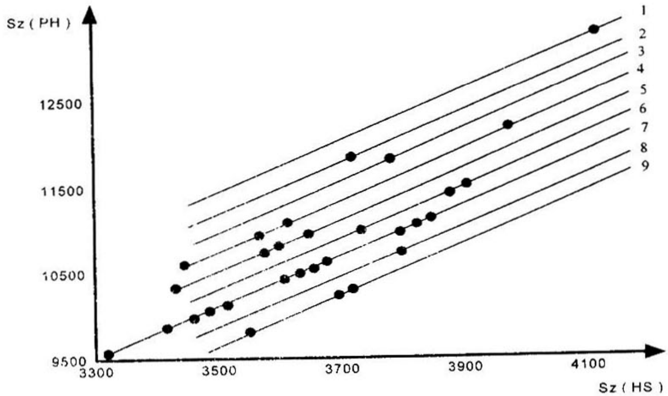

Fig. 2. Relation between the Szeged numbers of [6]phenylenes and their hexagonal squeezes (depicted in Fig. 3); the points lie on nine parallel lines, the equations of which read: $Sz(PH) = 3\ Sz(HS) - 12\ k - 693$ with $k = 0, 2, 3, 6, 8, 9, 10, 13$ and 14 for lines 1,2,3,4,5,6,7,8 and 9, respectively; in order to make these lines easier to distinguish, line 8 has been moved upwards by 200 units, line 7 by 400 units, line 6 by 600 units, etc; note that the systems 14 and 15 have equal $Sz(PH)$-values and also equal $Sz(HS)$-values, i.e., two points on line 6 coincide; the same is the case with systems 16 and 19, 17 and 23, 18 and 24, 21 and 26, 27 and 31, 29 and 32, so only 12 points appear on line 7

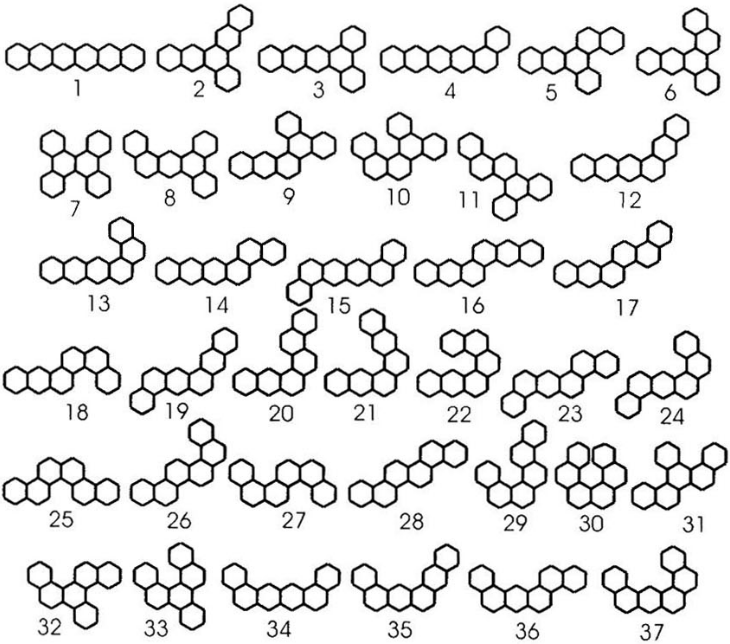

Fig. 3. The 37 hexagonal squeezes, corresponding to the 37 isomeric phenylenes with 6 hexagons [11]; the systems associated with the lines occurring in Fig. 2 are: 1 (line 1), 2 (line 2), 3 (line 3), 4,5,6,7 (line 4), 8,9,10,11 (line 5), 12,13,14,15 (line 6), 16, 17, ..., 33 (line 7), 34 (line 8) and 35,36,37 (line 9)

The analogy with the Wiener number ends here. For the Szeged number no relation of the kind (1) may exist, simply because there are isomeric structures possessing the same inner dual, but lying on different straight lines. [The smallest example of this kind is provided by the PH/HS-pairs in which the hexagonal squeezes are tetracene and tetraphene, namely four-cyclic ($h = 4$) unbranched catacondensed benzenoid systems. The inner duals of both tetracene and tetraphene are isomorphic to the 4-vertex path.] In the case of the Szeged number the structural details determining which isomers lie on the same straight line, and which do not are much less easy to recognize. In what follows we use the method of elementary edge–cuts [?] to shed some light on this problem.

An Identity for the Szeged Numbers of PH and HS

In what follows we use the same notation and terminology and in [?], where the respective definitions can be found. Thus, bearing in mind that the hexagonal squeezes are catacondensed benzenoid systems [11], the Wiener and Szeged numbers of a hexagonal squeeze satisfy the relations

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

and

$$W(HS) = \sum_{i=1}^{2h+1} n'(C_i)\, n''(C_i) \tag{3}$$

in which C_i stands for the i-th elementary edge–cut, dividing HS into fragments with $n'(C_i)$ and $n''(C_i)$ vertices, and intersecting $r(C_i)$ edges; the summations go over all $2h+1$ elementary edge–cuts. (Recall [?] that the number of elementary edge cuts of a catacondensed system with h hexagons is equal to $2h+1$.)

Relations fully analogous to (2) and (3) hold also for phenylenes [?, ?]. It is easy to verify (for instance, by mathematical induction) that a phenylene with h hexagons has $3h$ elementary cuts. For reasons which will become clear below, we denote the elementary edge–cuts of PH by $D_1, D_2, \ldots, D_{2h+1}, E_1, E_2, \ldots, E_{h-1}$. The cuts D_i, $i = 1, 2, \ldots, 2h+1$ go through hexagons of PH, whereas each cut E_i intersects only a single 4-membered cycle of PH (and therefore $r(E_i) = 2$ for all $i = 1, 2, \ldots, h-1$). An illustrative example is given in Fig. 4.

With this notation, in parallel with Eqs. (2) and (3) we have

$$(4) \qquad Sz(PH) = \sum_{i=1}^{2h+1} r(D_i)\, n'(D_i)\, n''(D_i) + 2 \sum_{i=1}^{h-1} n'(E_i)\, n''(E_i)$$

and

$$(5) \qquad W(PH) = \sum_{i=1}^{2h+1} n'(D_i)\, n''(D_i) + \sum_{i=1}^{h-1} n'(E_i)\, n''(E_i) \ .$$

Combining (4) and (5) we readily obtain

$$(6) \qquad Sz(PH) - 2W(PH) = \sum_{i=1}^{2h+1} [r(D_i) - 2]\, n'(D_i)\, n''(D_i) \ .$$

Now, between the edge cuts $D_1, D_2, \ldots, D_{2h+1}$ of a phenylene and the edge cuts $C_1, C_2, \ldots, C_{2h+1}$ of the hexagonal squeeze there exists an obvious one–to–one correspondence, see Fig. 4. By elementary combinatorial reasoning we prove:

$$(7) \qquad r(D_i) = 2r(C_i) - 2$$

$$(8) \qquad n'(D_i) = \frac{3}{2}\, [n'(C_i) - 1] \quad ; \quad n''(D_i) = \frac{3}{2}\, [n''(C_i) - 1]$$

which substituted back into (6) yields

$$Sz(PH) - 2W(PH) = \frac{9}{2} \sum_{i=1}^{2h+1} [r(C_i) - 2][n'(C_i)\, n''(C_i) - n'(C_i) - n''(C_i) + 1] \ .$$

Taking into account that [?]

$$n'(C_i) + n''(C_i) = \text{number of vertices of } HS = 4h + 2$$

and

$$\sum_{i=1}^{2h+1} r(C_i) = \text{number of edges of } HS = 5h + 1$$

and bearing in mind the formulas (2) and (3) we arrive at the identity

$$(9) \qquad Sz(PH) - 2W(PH) = \frac{9}{2}\, [Sz(HS) - 2W(HS) - (4h^2 - 3h - 1)] \ .$$

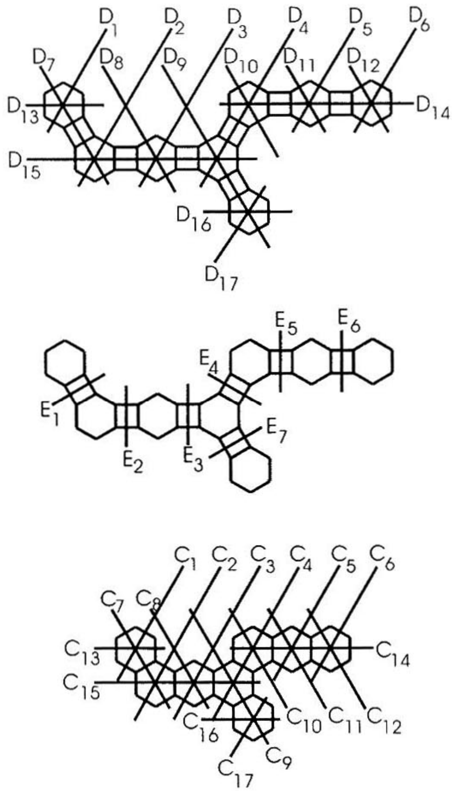

Fig. 4. The elementary edge-cuts of PH_1 and HS_1 from Fig. 1; notice the correspondence between the cuts C_i and D_i for all $i = 1, 2, \ldots, 17$

A Condition for Slope 3

Suppose that we have two isomeric phenylenes – PH_a and PH_b – and that the respective hexagonal squeezes are HS_a and HS_b. The slope of the $Sz(PH)/Sz(HS)$-line is then

$$\sigma = \frac{Sz(PH_a) - Sz(PH_b)}{Sz(HS_a) - Sz(HS_b)} \ . \tag{10}$$

Suppose further that the inner duals of PH_a and PH_b coincide. If so, then [6, 7] the slope of the $W(PH)/W(HS)$-line is equal to $9/4$, i.e.,

$$\frac{W(PH_a) - W(PH_b)}{W(HS_a) - W(HS_b)} = \frac{9}{4}$$

i.e.,

$$W(PH_a) - W(PH_b) = \frac{9}{4} \left[W(HS_a) - W(HS_b) \right] \ . \tag{11}$$

Combining Eq. (10) with the identity (9), and using relation (11), we obtain after simple calculation

$$\sigma = \frac{9}{2} \left[1 - \frac{W(HS_a) - W(HS_b)}{Sz(HS_a) - Sz(HS_b)} \right] \ . \tag{12}$$

The remarkable property of expression (12) is that its right–hand side is independent of the phenylene and is fully determined solely by the Sz- and W-values of the hexagonal squeezes. From (12) it immediately follows that the slope σ of the will be equal to 3 if the below condition is obeyed:

$$\frac{Sz(HS_a) - Sz(HS_b)}{W(HS_a) - W(HS_b)} = 3 \ . \tag{13}$$

It should be noted that not all PH/HS-pairs satisfy the condition that their Szeged numbers lie on slope–3 straight lines (i.e., that their hexagonal squeezes obey Eq. (13). The smallest example of the violation of the slope–3 rule is provided by the linear and angular [4]phenylenes, the hexagonal squeezes of which are tetracene and tetraphene, respectively. The corresponding $Sz(PH)/Sz(HS)$-line has slope $56/16 = 3.5$.

Slope–3 Relations between Szeged Numbers of Isomeric Phenylenes

In this section we demonstrate that condition (13) is satisfied for numerous pairs of isomeric phenylenes. Because of relation (12) it is enough to examine the hexagonal squeezes.

Rule 1. If the hexagonal squeezes of the phenylene isomers PH_a and PH_b have the structures shown in diagrams **1a** and **1b** in Fig. 5, where P, Q, R and S symbolize arbitrary fragments (not all four of which need to be present in the molecule), then the slope of the $Sz(PH)/Sz(HS)$-line is equal to 3.

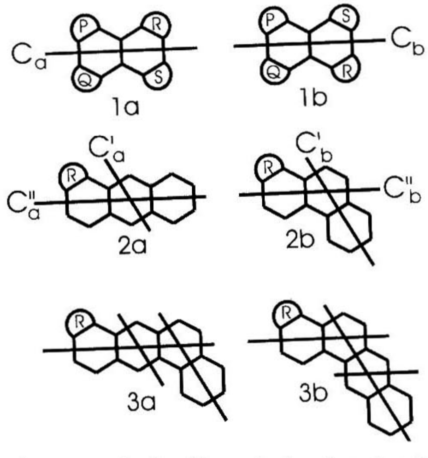

Fig. 5. Hexagonal squeezes of pairs of isomeric phenylenes for which the $Sz(PH)/Sz(HS)$-line has slope equal to 3

Proof. With a single exception, to each elementary edge cut of **1a** there corresponds a cut of **1b** with the same value of the parameters r, n', n''. The only cuts which differ in **1a** and **1b** are those indicated in Fig. 5 by C_a and C_b.

Formulas (2) and (3) show that every elementary edge–cut has a distinct contribution to the Szeged and Wiener numbers. Now, in the case of the isomeric pair **1a**, **1b** all such contributions are equal, except for the cuts C_a and C_b. Consequently, the differences

$$Sz(HS_a) - Sz(HS_b) \quad \text{and} \quad W(HS_a) - W(HS_b)$$

depend solely on C_a and C_b. Because of $r(C_a) = r(C_b) = 3$,

$$Sz(HS_a) - Sz(HS_b) = 3\, n'(C_a)\, n''(C_a) - 3\, n'(C_b)\, n''(C_b)$$

$$W(HS_a) - W(HS_b) = n'(C_a)\, n''(C_a) - n'(C_b)\, n''(C_b)$$

and we readily see that condition (3) is satisfied. □

Rule 1 is immediately generalized: If the two phenylene isomers differ in only one elementary edge–cut, and if this cut intersects r edges of the hexagonal squeeze, then the slope of the $Sz(PH)/Sz(HS)$-line is equal to

$$\sigma = \frac{9}{2}\left(1 - \frac{1}{r}\right) .$$

Rule 2. If the hexagonal squeezes of the phenylene isomers PH_a and PH_b have the structures shown in diagrams **2a** and **2b** in Fig. 5, where R symbolizes and arbitrary fragment, then the slope of the $Sz(PH)/Sz(HS)$-line is equal to 3.

Proof. The isomers **2a** and **2b** differ in two elementary edge–cuts, indicated in Fig. 5 as $C'_a, C'''_a, C'_b, C''_b$. If the number of vertices of the fragment R is denoted by n_R, then by direct counting we obtain:

$$r(C''_a) = 2 \quad ; \quad n'(C'_a) = n_R + 5 \quad ; \quad n''(C'_a) = 7$$

$$r(C'''_a) = 4 \quad ; \quad n'(C'''_a) = n_R + 5 \quad ; \quad n''(C'''_a) = 7$$

$$r(C'_b) = 3 \quad ; \quad n'(C'_b) = n_R + 7 \quad ; \quad n''(C'_b) = 5$$

$$r(C''_b) = 3 \quad ; \quad n'(C''_b) = n_R + 3 \quad ; \quad n''(C''_b) = 9 \, .$$

When these relations are substituted back into the the expressions

$$Sz(HS_a) - Sz(HS_b) = r(C'_a)\, n'(C'_a)\, n''(C'_a) + r(C'''_a)\, n'(C'''_a)\, n''(C'''_a) -$$

$$r(C'_b)\, n'(C'_b)\, n''(C'_b) - r(C''_b)\, n'(C''_b)\, n''(C''_b)$$

and

$$W(HS_a) - W(HS_b) = n'(C_a'') \, n''(C_a'') + n'(C_a''') \, n''(C_a''') -$$

$$n'(C_b'') \, n''(C_b'') - n'(C_b''') \, n''(C_b''')$$

the validity of condition (13) is verified after a tedious calculation. □

Rule 3. The statement of Rule 2 holds also for the isomers **3a** and **3b** from Fig. 5.

Proof. In the case of the isomers **3a**, **3b** we have to consider the (different) contributions of three pairs of elementary edge–cuts, indicated in Fig. 5. Otherwise the proof of Rule 3 is analogous to the proof of Rule 2. □

An Example

By means of Rules 1–3 it is possible to explain why some phenylenes belong to the same slope–3 family (cf. Fig. 2). This will be illustrated on the phenylenes whose hexagonal squeezes are depicted in Fig. 3 as diagrams $16, 17, \ldots, 33$. For these molecules the relation

$$Sz(PH) = 3 \, Sz(HS) - 813$$

was found to hold.

The systems 16–30 are unbranched catacondensed benzenoids. Therefore their inner duals coincide. It will be assumed that their hexagons are labeled consecutively by 1,2,3,4,5,6, starting with the left–hand side terminal hexagon. Further, the transformations **1a** → **1b** , **2a** → **2b** and **3a** → **3b** , occurring in Rules 1, 2 and 3 (cf. Fig. 5) will be abbreviated by R_1 , R_2 and R_3 , respectively. Clearly, if two hexagonal squeezes are interconverted by either R_1 or R_2 or R_3 , then they pertain to the same slope–3 line.

Now, the hexagonal squeezes 16–30 are all related by the transformations R_1 , R_2 and/or R_3 . To see this, start with the molecule 19:

Application of R_3 to the hexagons 1,2,3,4 of 19 results in 16.
Application of R_1 to the hexagons 3,4 of 16 results in 21.
Application of R_2 to the hexagons 4,5,6 of 19 results in 23.
Application of R_3 to the hexagons 1,2,3,4 of 23 results in 17.
Application of R_1 to the hexagons 4,5 of 17 results in 18.

Application of R_1 to the hexagons 3,4 of 18 results in 22.
Application of R_2 to the hexagons 1,2,3 of 22 results in 29.
Application of R_2 to the hexagons 1,2,3 of 18 results in 26.
Application of R_1 to the hexagons 3,4 of 26 results in 27.
Application of R_1 to the hexagons 3,4 of 27 results in 30.
Application of R_1 to the hexagons 3,4 of 17 results in 20.
Application of R_2 to the hexagons 1,2,3 of 20 results in 15.
Application of R_2 to the hexagons 1,2,3 of 17 results in 28.
Application of R_1 to the hexagons 4,5 of 23 results in 24.

Therefore, by Rules 1, 2 and 3 the $Sz(PH)/Sz(HS)$-points of the phenylenes whose hexagonal squeezes are 16–30 all lie on the same slope 3 line.

The hexagonal squeezes 31–33 are branched benzenoids; their inner duals are isomorphic and, of course, different from the inner duals of systems 16–30. The molecule 32 possesses two structural features to which the transformation R_1 is applicable. One R_1 transforms 32 into 31, the other transforms 32 into 33. Consequently, the $Sz(PH)/Sz(HS)$-points pertaining to molecules 31,32,33 lie on the same slope-3 line.

Concluding Remarks

Rules 1–3 suffice to recognize almost all members of families of phenylenes whose $Sz(PH)/Sz(HS)$-points lie on the same straight line, and in the same time prove a structural characterization of these families. However, Rules 1–3 are not complete.

For instance, the fact that the points corresponding to both the unbranched molecules 16–30 and the branched molecules 31–33 lie on one and the same slope 3 line cannot be deduced by means of the present rules. The finding that phenylenes with non-isomorphic inner duals may belong to the same family has, so far, found no satisfactory explanation. Whereas the analogous $W(PH)/W(HS)$ problem has been completely solved by the discovery of Eq. (1), no generally valid mathematical relation between the Szeged numbers of phenylenes and their hexagonal squeezes is known. Therefore further research in this direction is desirable.

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