communications in mathematical
match
and in computer chemistry

no. 35, March 1997

ISSN 0340-6253

MATCDY (35) 105-116 (1997)

WIENER AND SZEGED INDICES OF BENZENOID HYDROCARBONS CONTAINING A LINEAR POLYACENE FRAGMENT

Ivan GUTMAN[a,b], Padmakar V. KHADIKAR[c] and Tripti KHADDAR[d]

[a] *Institute of Physical Chemistry, Atilla József University, P. O. Box 105, H-6701 Szeged, Hungary*

[b] *Faculty of Science, University of Kragujevac, P. O. Box 60, YU-34000 Kragujevac, Yugoslavia*

[c] *Faculty of Sciences, D.A.V.V., 3 Khatipura, Indore 452007, India*

[d] *Chemistry Department, Islamia Karimia College, Chawani Chowk, Indore 452001, India*

(received: January 1996)

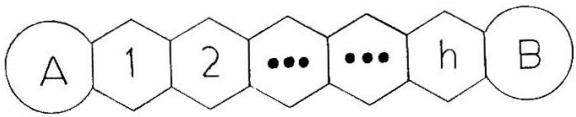
Abstract

Using recently developed methods for calculating the Szeged (Sz) and Wiener indices (W), we deduce general expressions for Sz and W of benzenoid hydrocarbons (X_h), containing a linear polyacene fragment. Both $Sz(X_h)$ and $W(X_h)$ are shown to be cubic polynomials in h, the number of hexagons in the polyacene fragment of X_h. Besides, the coefficient of h^3 is 44/3 for $Sz(X_h)$ and 16/3 for $W(X_h)$. These properties do not depend on the nature of the terminal groups in X_h. Other features of the dependence of Sz and W on the structure of X_h are also established.

Introduction

In this paper we are concerned with the Szeged and Wiener indices of benzenoid hydrocarbons containing a linear polyacene fragment. The basic terminology and notation used in this work is the same as in the preceding paper [1], and will not be specified here once again. In [1] the definitions of the Szeged index (Sz) and of the Wiener index (W) are given in due detail.

The general form of a benzenoid system [2] possessing a linear polyacene fragment is X_h:



X_h

Here A and B denote arbitrary (but benzenoid) terminal groups, and h is the number of hexagons in the polyacene fragment. Either A or B or both may be absent from X_h. If both A and B are absent, then X_h reduces to the polyacene L_h, which is one of the most extensively studied homologous series of conjugated molecules.

A plethora of works exists in chemical graph theory, devoted to systems of the form X_h or to their special case L_h. Of them we mention the early works on graph eigenvalues [3] – [6], on Kekulé structures [7], on resonance energy [8, 9], on characteristic and matching polynomials [10] – [12], on the Hosoya index [13], on the Merrifield Simmons index [14], on the Wiener index [15, 16], on cyclic conjugation [17, 18], on spectral moments [19, 20] and on the Szeged index [21]. In particular, expressions for the Wiener and Szeged indices of L_n are known for some time:

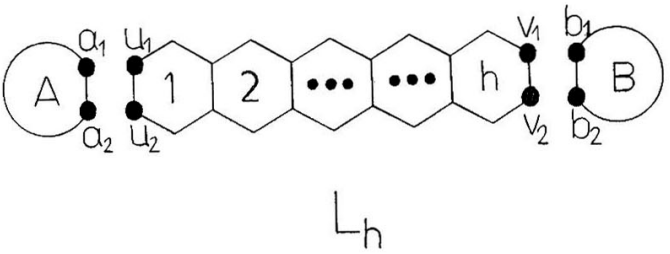
$$W(L_h) = \frac{16}{3}h^3 + 12h^2 + \frac{26}{3}h + 1 \qquad (1)$$

$$Sz(L_h) = \frac{44}{3}h^3 + 24h^2 + \frac{43}{3}h + 1 \qquad (2)$$

see [15] and [21], respectively.

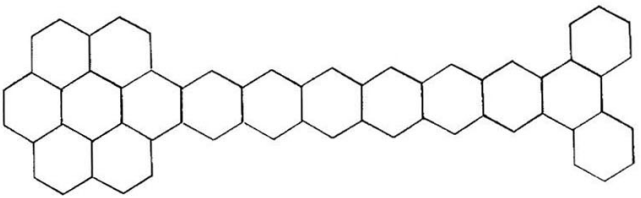
In this work we generalize Eqs. (1) and (2) to systems of the type X_h, in which A and B are arbitrary. It will be seen that some features of the polynomials on the right-hand side of (1) and (2) are maintained also in the most general case, whereas other depend on the actual form of the terminal fragments A and B.

The benzenoid system X_h, the structure of which is depicted in the above diagram, can be considered as a graph [1, 2]. Then X_h can be viewed as being constructed from the graphs A, B and L_h, by identifying the vertices a_i of A with the vertices u_i of L_h, $i = 1, 2$, as well as by identifying the vertices b_i of B with the vertices v_i of L_h, $i = 1, 2$.



In harmony with the notation of [1], the number of vertices of a graph G will be denoted by $|G|$. As it is well known [2], $|L_h| = 4h + 2$. Then from the above described construction of X_h follows that this graph has $|A| + |B| + 4h - 2$ vertices.

As a concrete example of a benzenoid molecule of the type X_h may serve coroneno-phenanthreno-hexacene:



In this molecule A = coronene ($|A| = 24$), B = anthracene ($|B| = 14$) and $h = 6$. Coroneno-phenanthreno-hexacene possesses $24 + 14 + 4 \times 6 - 2 = 60$ carbon atoms.

Calculating the Wiener and Szeged indices of benzenoid molecules

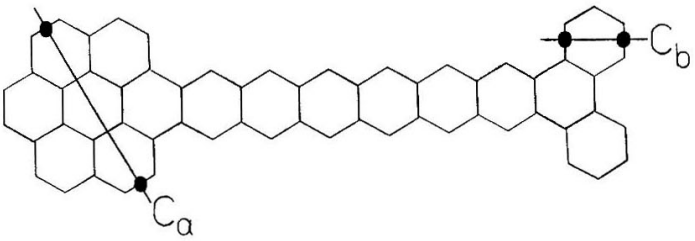
An efficient method for the calculation of the topological indices W and Sz of benzenoid molecules was recently put forward [22, 23], based on earlier research in the mathematical theory of Hamming graphs and its application to benzenoid systems (see [24] and the references cited therein). We now briefly outline this method.

Throughout the present considerations benzenoid systems are viewed as geometric figures in the plane [2]. Notice that these figures are composed of *regular* hexagons. Let B be such a benzenoid system.

Elementary cut

Choose an edge e of the benzenoid system B. Draw a straight line through the center of e, orthogonal on e. The straight line segment C, the end-points of which are at the perimeter of B, is an elementary cut induced by the edge e. Clearly, C intersects not only the edge e, but all edges lying between the two end-points (inclusive the two edges on the perimeter to which the end-points of C belong).

As examples we show the elementary cuts C_a and C_b of coroneno-phenanthreno-hexacene. On the below diagram the end-points of these elementary cuts are indicated by heavy dots.



If the above specified straight line intersects the perimeter in more than two points, then the end-points of the respective elementary cut are those points of intersection

with the perimeter, that lie nearest to the edge e. This, for instance, is the case with the cut C_b in the above example: By continuing the straight line pertaining to C_b, it would intersect also the coronene fragment; such an double–intersection is, however, not permitted.

Parameters of the elementary cut

If C is an elementary cut of the benzenoid system B, then the number of edges it intersects is denoted by $r(C|B)$. This cut divides B into two parts which we denote by B' and B''. These parts possess $n(B'|C)$ and $n(B''|C)$ vertices, respectively. Of course, for all elementary cuts C of B,

$$n(B'|C) + n(B''|C) = |B| \tag{3}$$

For the elementary cuts of coroneno–phenanthreno–hexacene, shown in the previous example, $r(C_a|B) = 4$, $n(B'|C_a) = 12$, $n(B''|C_a) = 48$, and $r(C_b|B) = 2$, $n(B'|C_b) = 3$, $n(B''|C_b) = 57$. Recall that $n(B''|C_a)$ needs not be obtained by independent counting, but by using the relation (3): $n(B''|C_a) = |B| - n(B'|C_a) = 60 - 12$. Similarly, $n(B''|C_b) = 60 - 3$.

Which part, obtained by intersecting B with C, is labeled by B' and which by B'' is immaterial. In what follows we use a labeling which is most convenient for the present purpose, i.e., by means of which our expressions get the simplest possible form.

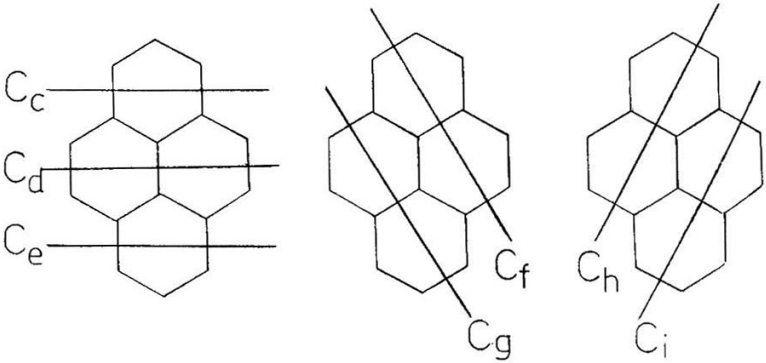
Complete set of elementary cuts

Every edge of B is intersected by just one elementary cut. The set of elementary cuts, intersecting all edges of B is called the complete set of elementary cuts (CSEC) of B.

The finding of the CSET of any given benzenoid molecule B is simple and straightforward. The number of elements of the CSET is usually not too large, and is certainly much smaller than the number of vertices or edges of B. If B is symmetric, then the construction of its CSET is further simplified by using symmetry–arguments.

For instance, the CSEC of pyrene has 7 members, namely the following seven elementary cuts C_c , C_d ,..., C_i. Notice that C_c and C_e, as well as C_f, C_g, C_h

and C_i are symmetry-equivalent. This, in particular, means that they have equal contributions to the right-hand sides of Eqs. (4) and (5).



Both the Wiener and the Szeged indices of benzenoid molecules can be computed from the CSEC. For the Wiener index [23]:

$$W(B) = \sum_{C} n(B'|C)\, n(B''|C) \tag{4}$$

whereas for the Szeged index [22]:

$$Sz(B) = \sum_{C} r(C|B)\, n(B'|C)\, n(B''|C) \tag{5}$$

In both Eqs. (4) and (5) the summation goes over all members of the CSEC of the respective benzenoid system B.

Application of Eqs. (4) and (5) to the benzenoid molecules containing a linear polyacene fragment

In order to apply Eqs. (4) and (5) to systems of the form X_h we must first determine the respective CSEC.

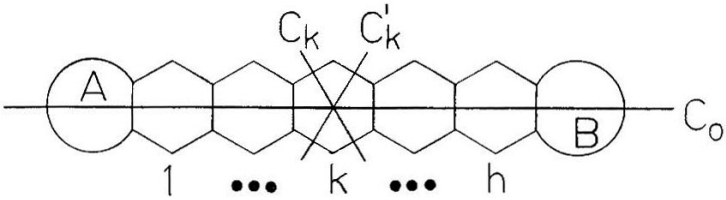
The members of the CSEC of X_h are classified into the following four groups:

(a) the elementary cuts of A, except C_0;

(b) the elementary cuts of B, except C_0;

(c) the elementary cut C_0 that goes through all h hexagons of the polyacene fragment, intersecting also some edges of A and B;

(d) the elementary cuts C_k and C'_k, each intersecting two edges of the k-th hexagon of the polyacene fragment, $k = 1, 2, \ldots, h$.



The sets of elementary cuts of type **(a)** and **(b)** will be denoted by **A** and **B**, respectively. For instance, for the above specified elementary cuts of coroneno–phenanthreno–hexacene, $C_a \in \mathbf{A}$ and $C_b \in \mathbf{B}$.

Bearing in mind the structure of X_h we immediately arrive at the following.

For the elementary cuts $C \in \mathbf{A}$:

$$n(L'_h|C) = n(A'|C)$$

$$n(L''_h|C) = n(A''|C) + |B| + 4h - 2$$

For the elementary cuts $C \in \mathbf{B}$:

$$n(L'_h|C) = n(B'|C)$$

$$n(L''_h|C) = n(B''|C) + |A| + 4h - 2$$

For the elementary cut C_0:

$$r(C_0|X_h) = r(C_0|A) + r(C_0|B) + k - 1$$

$$n(X'_h|C_0) = n(A'|C_0) + n(B'|C_0) + 2k - 1$$

$$n(X''_h|C_0) = n(A''|C_0) + n(B''|C_0) + 2k - 1$$

For the elementary cuts of the type **(d)**, $k = 1, 2, \ldots, h$:

$$r(C_k|L_h) = r(C'_k|L_h) = 2$$

$$n(L'_h|C_k) = n(L'_h|C'_k) = |A| + 4k - 3$$

$$n(L''_h|C_k) = n(L''_h|C'_k) = |B| + 4h - 4k + 1$$

Substitution of the above relations back into Eq. (4) yields

$$W(X_h) = \sum_{C \in \mathbf{A}} n(A'|C)\,[n(A''|C) + |B| + 4h - 2] + \sum_{C \in \mathbf{B}} n(B'|C)\,[n(B''|C)$$

$$+ |A| + 4h - 2] + [n(A'|C_0) + n(B'|C_0) + 2h - 1]\,[n(A''|C_0) + n(B''|C_0) + 2h - 1]$$

$$+ 2 \sum_{k=1}^{h} [|A| + 4k - 3]\,[|B| + 4h - 4k + 1]$$

After a lengthy, but elementary calculation, taking into account Eq. (3) and bearing in mind that

$$\sum_{C \in \mathbf{A}} n(A'|C)\,[n(A''|C) + |B| + 4h - 2] + n(A'|C_0)\,n(A''|C_0) = W(A)$$

$$\sum_{C \in \mathbf{B}} n(B'|C)\,[n(B''|C) + |A| + 4h - 2] + n(B'|C_0)\,n(B''|C_0) = W(B)$$

we finally arrive at

$$W(X_h) = a_3\,h^3 + a_2\,h^2 + a_1\,h + a_0 \tag{6}$$

where

$$a_0 = W(A) + W(B) + [|B| - 2] \sum_{C \in \mathbf{A}} n(A'|C) + [|A| - 2] \sum_{C \in \mathbf{B}} n(B'|C)$$

$$- |A| - |B| + n(A'|C_0)\,n(B''|C_0) + n(B'|C_0)\,n(A''|C_0) + 1$$

$$a_1 = 4 \sum_{C \in \mathbf{A}} n(A'|C) + 4 \sum_{C \in \mathbf{B}} n(B'|C) + 2\,|A|\,|B| + \frac{2}{3}$$

$$a_2 = 4(|A| + |B|) - 4 \quad ; \quad a_3 = \frac{16}{3}$$

By an analogous, but even more perplexed calculation based on Eq. (5) we obtain

$$Sz(X_h) = b_3\,h^3 + b_2\,h^2 + b_1\,h + b_0 \tag{7}$$

where

$$b_0 = Sz(A) + Sz(B) + [|B| - 2] \sum_{C \in \mathbf{A}} r(C|A)\, n(A'|C) + [|A| - 2] \sum_{C \in \mathbf{B}} r(C|B)\, n(B'|C)$$
$$+ [r(C_0|A) + r(C_0|B) - 1]\, [n(A'|C_0) + n(B'|C_0)]\, [n(A''|C_0) + n(B''|C_0)]$$
$$- r(C_0|A)\, n(A'|C_0)\, n(A''|C_0) - r(C_0|B)\, n(B'|C_0)\, n(B''|C_0)$$
$$- [r(C_0|A) + r(C_0|B) - 1]\, [|A| + |B| - 1]$$
$$b_1 = 4 \sum_{C \in \mathbf{A}} r(C|A)\, n(A'|C) + 4 \sum_{C \in \mathbf{B}} r(C|B)\, n(B'|C)$$
$$+ 2\, [r(C_0|A) + r(C_0|B)]\, [|A| + |B| - 2] + [n(A'|C_0) + n(B'|C_0)]\, [n(A''|C_0) + n(B''|C_0)]$$
$$+ 4\, |A|\, |B| - 7\, [|A| + |B|] + \frac{43}{3}$$
$$b_2 = 10\, (|A| + |B|) - 24 + 4\, [r(C_0|A) + r(C_0|B)] \quad ; \quad b_3 = \frac{44}{3}$$

Discussion

The special case L_h is (formally) obtained if both terminal fragments A and B in X_h are taken to be graphs with two vertices and an edge. Then for the elementary cut C_0, the subgraphs A', A'', B' and B'' have a single vertex each, $r(A|C_0) = r(B|C_0) = 1$, and the sets $\mathbf{A}$ and $\mathbf{B}$ are empty. By straightforward calculation it can be verified that in this case Eqs. (6) and (7) reduce to (1) and (2), respectively.

The Szeged index is necessarily greater than the Wiener index. From Eqs. (4) and (5) follows that $Sz(B) \geq W(B)$ holds for all benzenoid systems B, with equality only in the case of benzene. (To see this observe that for all elementary cuts, $r(C|B) \geq 2$).

We showed that irrespective of the nature of the terminal fragments A and B, both the Wiener and the Szeged indices of X_h are cubic polynomials in the variable h, Eqs. (6) and (7). The expressions obtained for the coefficients a_i and b_i , $i = 0, 1, 2, 3$, of these polynomials imply the following conclusions.

1. The coefficients a_3 and b_3 are constants, i.e., are independent of the terminal fragments A and B. Because these coefficients determine the gross value of Sz and

W, especially is h is large, we see that the terminal fragments have only a limited influence on the magnitude of Sz and W. Furthermore,

$$Sz(X_h) \approx \frac{11}{4} W(X_h)$$

holds as a good approximation for all benzenoid systems containing a linear polyacene fragment. Recall that $\frac{11}{4} = 2.75$, i.e., the ratio of Sz and W is only slightly greater than 2.

2. The other coefficients of Eqs. (6) and (7) depend on the structure of the terminal fragments. Even a superfluous inspection of the respective formulas suggests that the effect of terminal fragments is greater at the coefficients pertaining to lower powers of h. In particular, a_2 depends only on the number of vertices of A and B; this simple rule is *not* valid for b_2.

3. The structure-dependence of a_1 and b_1 is rather perplexed, the structure-dependence of a_0 and b_0 (although explicitly expressed by us) remains beyond comprehension.

4. The expressions for the coefficients b_i , $i = 0, 1, 2$ are significantly more complicated than the respective expressions for a_i. This feature is certainly caused by the fact that the right-hand side of Eq. (4) is simpler than the right-hand side of Eq. (5).

5. Irrespectively of the nature of the terminal fragments A and B, the coefficients a_i and b_i , $i = 0, 1, 2$, are positive-valued.

6. As a curiosity we mention that whereas a_0 , a_2 , b_0 and b_2 are integer-valued, the coefficients a_1, a_3, b_1 and b_3 are fractions (with nominator being equal to 3). This property is also independent of the choice of the terminal fragments.

Acknowledgement.

One author (I. G.) thanks the Mathematical Institute in Belgrade for financial support of this research.

References

[1] I. Gutman, L. Popović, P. V. Khadikar, S. Karmarkar, S. Joshi and M. Mandloi, *Commun. Math. Chem. (MATCH)*, preceding paper.

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

[3] D. E. Rutherford, *Proc. Roy. Soc. Edinburgh* **A62**, 229 (1947).

[4] C. A. Coulson, *Proc. Phys. Soc.* **60**, 257 (1948).

[5] E. Heilbronner, *Helv. Chim. Acta* **37**, 921 (1954).

[6] I. Gutman and O. E. Polansky, *Commun. Math. Chem. (MATCH)* **8**, 315 (1980).

[7] I. Gutman, *Croat. Chem. Acta* **55**, 371 (1982).

[8] I. Gutman and B. Mohar, *Croat. Chem. Acta* **55**, 375 (1982).

[9] I. Gutman, *Z. Naturforsch.* **37a**, 248 (1982).

[10] H. Hosoya and N. Ohkami, *J. Comput. Chem.* **4**, 585 (1983).

[11] E. J. Farrell and S. A. Wahid, *Discrete Appl. Math.* **7**, 45 (1984).

[12] M. Randić, H. Hosoya and O. E. Polansky, *J. Comput. Chem.* **10**, 683 (1989).

[13] I. Gutman, *Z. Naturforsch.* **43a**, 939 (1988).

[14] I. Gutman and N. Kolaković, *Bull. Acad. Serbe Sci. Arts.* **102**, 39 (1990).

[15] I. Gutman and O. E. Polansky, *Commun. Math. Chem. (MATCH)* **20**, 115 (1986).

[16] O. E. Polansky, H. Hosoya and M. Randić, *Commun. Math. Chem. (MATCH)* **24**, 3 (1989).

[17] I. Gutman and V. Petrović, *J. Serb. Chem. Soc.* **57**, 495 (1992).

[18] I. Gutman and V. Petrović, *Indian J. Chem.* **31A**, 647 (1992).

[19] P. V. Khadikar, N. V. Deshpande, P. P. Kale and I. Gutman, *J. Chem. Inf. Comput. Sci.* **34**, 1181 (1994).

[20] I. Gutman, N. Gavrilović, D. Banković, P. V. Khadikar, N. V. Deshpande and P. P. Kale, *J. Serb. Chem. Soc.* **59**, 579 (1994).

[21] I. Gutman, P. V. Khadikar, P. V. Rajput and S. Karmarkar, *J. Serb. Chem. Soc.* **60**, 759 (1995).

[22] I. Gutman and S. Klavžar, *J. Chem. Inf. Comput. Sci.* **35**, 1011 (1995).

[23] I. Gutman and S. Klavžar, *Acta Chim. Hung. (Models in Chemistry)*, submitted.

[24] S. Klavžar, I. Gutman and B. Mohar, *J. Chem. Inf. Comput. Sci.* **35**, 590 (1995).