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WIENER NUMBERS OF POLYACENES AND RELATED BENZENOID MOLECULES

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Abstract. A combinatorial formula for the Wiener number (W) of an arbitrary molecular graph containing a linear chain of hexagons is derived. It is shown that W is a cubic polynomial of the number of hexagons. Formulas for W of some other classes of benzenoid systems are also reported.

Since 1947, when Harry Wiener published the first paper[1] on the topological index which nowadays carries his name, a plethora of publications appeared, dealing with its various applications[2]. Bearing this in mind, it is somewhat surprising that there are quite a few general results about the Wiener number and its dependence on molecular structure[6]. Some elementary properties of the Wiener number are reported in[7]. Formulas for the calculation of the Wiener number of various polycyclic molecular graphs can be found in[8] whereas a general theory for acyclic graphs has been recently developed[5].

We shall use the following notation. Let G be a connected graph and $v_1, v_2, \ldots, v_n$ its vertices. The length of the shortest path which connects the vertices v_r and v_s is the distance between them and is denoted by $d(v_r, v_s)$. By definition, $d(v_r, v_r) = 0$.

The distance matrix $\mathcal{D}(G)$ is a square matrix of order n, whose element in the r-th row and the s-th column is equal to $d(v_r, v_s)$. This matrix is obviously symmetric and its diagonal elements are equal to zero.

The distance number $\mathcal{d}(v_r|G)$ of the vertex v_r of the graph G is just the sum of the elements of the r-th row of $\mathcal{D}(G)$:

$$\mathcal{d}(v_r|G) = \sum_{s=1}^{n} d(v_r, v_s) \quad . \tag{1}$$

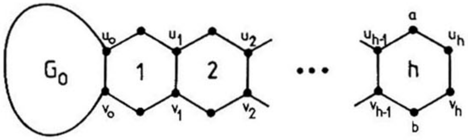
The Wiener number of the graph G is the sum of the elements of $\mathcal{D}(G)$ which lie below (or above) its diagonal:

$$W(G) = \sum_{r<s} d(v_r, v_s) \tag{2}$$

i.e.

$$W(G) = \frac{1}{2} \sum_{r=1}^{n} d(v_r|G) \quad . \qquad (3)$$

In the present paper we shall be mainly concerned with molecular graphs G_h, whose general form is given by



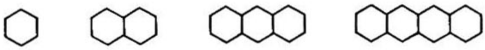
G_h

Here G_o denotes an arbitrary, not necessarily benzenoid, terminal fragment, to which a chain of h linearly annelated hexagons is attached.

In the simplest case when G_o is isomorphic to the path P_2, $G_o \simeq P_2$, i.e. when G_o consists of two, mutually connected vertices:

$G_0 \simeq P_2$

then G_h reduces to the molecular graph of linear polyacenes L_h, whose first four representatives are given as follows:



L_1 L_2 L_3 L_4

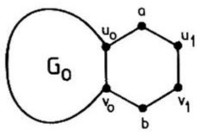
It has been established previously (see eq. (6) in ref.[8]) that

$$W(L_h) = (16h^3 + 36h^2 + 26h + 3)/3 \qquad (4)$$

Hence $W(L_h)$ is a cubic polynomial in the variable h, whose leading term is $(16/3)h^3$.

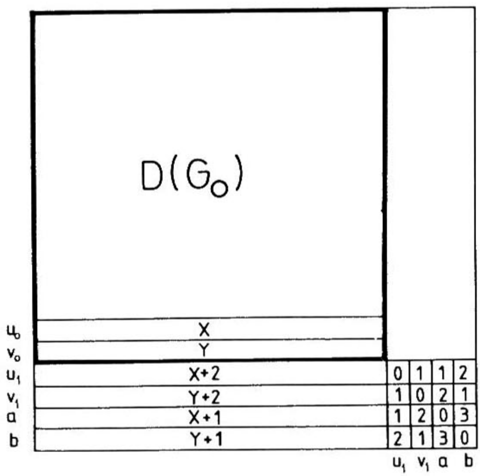
We show now that for an arbitrary terminal fragment G_o, $W(G_h)$ is a cubic polynomial in the variable h, whose leading term is $(16/3)h^3$.

Consider for the beginning the case h = 1, i.e. the molecular graph G_1:



G_1

If v is an arbitrary vertex of G_o with the distances $d(v,u_o)=x$ and $d(v,v_o)=y$ then the distance between the vertices v and a in G_1 is equal to $d(v,u_o)+d(u_o,a)=x+1$. Similarly, $d(u,v_1)=x+2$, $d(v,b)=y+1$, $d(v,v_1)=y+2$. Consequently, the distance matrix of G_1 has the following form (wherein x and y stay for the respective matrix elements):



$D(G_1)$

Summing the elements of the above matrix which lie below its diagonal we easily see that

$$W(G_1) = W(G_o) + [d(u_o|G_o) + 2\ n_o] + [d(v_o|G_o) + 2\ n_o] +$$

$$+ [d(u_o|G_o) + n_o] + [d(v_o|G_o) + n_o] + (1+1+2+2+1+3) =$$

$$= W(G_o) + 2[d(u_o|G_o) + d(v_o|G_o)] + 6\ n_o + 10 \quad , \qquad (5)$$

where n_o stands for the number of vertices of G_o. It is also evident from the above scheme that

$$d(x_1|G_1) = d(x_o|G_o) + 2\ n_o + 4 \quad ; \quad x = u,v \quad . \qquad (6)$$

The relations (5) and (6) are immediately generalized to the graphs G_h, $h > 1$. Let n_h denote the number of vertices of G_h. Then

$$W(G_h) = W(G_{h-1}) + 2[d(u_{h-1}|G_{h-1}) + d(v_{h-1}|G_{h-1})] + 6\ n_{h-1} + 10 \qquad (7)$$

and

$$d(x_h|G_h) = d(x_{h-1}|G_{h-1}) + 2\ n_{h-1} + 4 \quad ; \quad x = u,v \qquad (8)$$

Since G_h has $n_o + 4h$ vertices, we further have

$$W(G_h) = W(G_{h-1}) + 2[d(u_{h-1}|G_{h-1}) + d(v_{h-1}|G_{h-1})] +$$

$$+ 24\ h + 6\ n_o - 14 \quad , \qquad (9)$$

$$d(x_h|G_h) = d(x_{h-1}|G_{h-1}) + 8\ h + 2\ n_o - 4 \quad ; \quad x = u,v \quad . \qquad (10)$$

We first solve the recurrence relation (10). Applying it repeatedly for $h = 1,2,3,...$ we arrive at eq. (6) and further at

$$d(x_2|G_2) = d(x_o|G_o) + 4\ n_o + 8(1 + 2) - 2 \cdot 4 \qquad (11)$$

$$d(x_3|G_3) = d(x_o|G_o) + 6\ n_o + 8(1 + 2 + 3) - 3 \cdot 4 \qquad (12)$$

...

...

$$d(x_h|G_h) = d(x_o|G_o) + 2\,h\,n_o + 8\sum_{i=1}^{h} i - 4\,h \quad . \tag{13}$$

Thus,

$$d(x_h|G_h) = d(x_o|G_o) + 2\,h\,n_o + 4\,h^2 \quad ; \quad x = u,v \quad . \tag{14}$$

Substituting (14) back into (9) we obtain

$$W(G_h) = W(G_{h-1}) + 2[d(u_o|G_o) + d(v_o|G_o)] + 16h^2 + 8h(n_o-1) - 2(n_o-1) \tag{15}$$

which for h = 1,2,3,... gives eq. (5) and

$$W(G_2) = W(G_o) + 4[d(u_o|G_o) + d(v_o|G_o)] + 16(1^2+2^2) + 8(1+2)(n_o-1) - 4(n_o-1) \tag{16}$$

$$W(G_3) = W(G_o) + 6[d(u_o|G_o) + d(v_o|G_o)] + 16(1^2+2^2+3^2) + 8(1+2+3)(n_o-1) - 6(n_o-1) \tag{17}$$

...

$$W(G_h) = W(G_o) + 2h[d(u_o|G_o) + d(v_o|G_o)] + 16\sum_{i=1}^{h} i^2 + 8(n_o-1)\sum_{i=1}^{h} i - 2(n_o-1)h \quad . \tag{18}$$

After an appropriate calculation we reach our final result

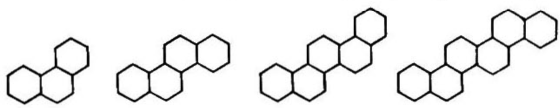
$$W(G_h) = (16/3)h^3 + (4n_o + 4)h^2 + [2d(u_o|G_o) + 2d(v_o|G_o) + 2\,n_o + 2/3]h + W(G_o) \quad . \tag{19}$$

From (19) we see that for all molecular graphs of the from G_h the Wiener number is a cubic polynomial of the number of linearly annelated hexagons. In the case when the terminal fragment is the path P_o (which corresponds to the choice $n_o = 2$, $d(u_o|G_o) = d(v_o|G_o) = 1$, $W(G_o) = 1$), then eq. (19) reduces to the previousknown formula (4).

It is interesting that the leading term in the polynomial (19), i.e. $(16/3)h^3$, is independent of the choice of the terminal fragment G_o. This, in particular, implies that the expression $h^{-3}W(G_h)$ becomes independent of G_o as h tends to infinity.

We have examined some additional classes of non-branched cata-condensed benzenoid systems and found that their Wiener numbers also conform to cubic polynomials of the number h of hexagons.

First of all, for the zig-zag polyacenes A_h, whose first six representatives are $A_1 \simeq L_1$, $A_2 \simeq L_2$, A_3, A_4, A_5 and A_6,



A_3 A_4 A_5 A_6

it was previously established that[8]

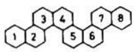
$$W(A_h) = (16h^3 + 24h^2 + 62h - 21)/3 \quad . \qquad (20)$$

For the helicenes H_h, whose first six members are $H_1 \simeq L_1$, $H_2 \simeq L_2$, $H_3 \simeq A_3$, H_4, H_5 and H_6 ,

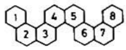
H_4 H_5 H_6

$$W(H_h) = (8h^3 + 72h^2 - 26h + 27)/3 \qquad (21)$$

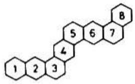
Further seven series for which polynomial expressions for W could be determined are B_h, C_h, D_h, E_h, F_h, J_h and K_h. Their structure is clear from the following examples (in which h = 8). The labels in the hexagons indicate the mode in which the chain increases.



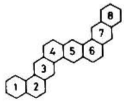
B_h



C_h



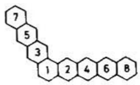
D_h



E_h

F_h

J_h



K_h

One should observe that for odd h, $B_h \simeq C_h$ whereas for even h, $D_h \simeq E_h$ and $F_h \simeq J_h$.

The formulas found read:

$$W(B_h) = 4h^3 + 16h^2 + 8h - 3 + (-1)^h(2h - 4) \qquad (22)$$

$$W(C_h) = 4h^3 + 16h^2 + 4h + 5 - (-1)^h(2h - 4) \qquad (23)$$

$$W(D_h) = (16h^3 + 24h^2 + 74h - 39)/3 - 2(-1)^h \qquad (24)$$

$$W(E_h) = (16h^3 + 24h^2 + 74h - 51)/3 + 6(-1)^h \; ; \; h>1 \qquad (25)$$

$$W(F_h) = 4h^3 + 20h^2 - 8h + 13 - (-1)^h(2h - 4) \qquad (26)$$

$$W(J_h) = 4h^3 + 20h^2 - 12h + 21 + (-1)^h(2h - 4) \; ; \quad h>1 \tag{27}$$

$$W(K_h) = (16h^3 + 30h^2 + 38h)/3 + (-1)^h \tag{28}$$

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