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Delta Number, D_Δ, of Dendrimers

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General formulas for the calculation of a novel Wiener-type number, D_Δ,[1] in regular dendrimers are proposed. They are derived on the basis of the novel matrix $\boldsymbol{D_\Delta}$,[1] by using progressive vertex degrees and orbit numbers[2] as parameters. Relations of D_Δ with the well known Wiener,[3] *W*, and hyper-Wiener,[4] *WW*, numbers, and a new relation (based on the $\boldsymbol{D_P}$ matrix[1]) for estimating *WW* in dendrimers are also given.

INTRODUCTION

Wiener[3] has defined his »path number« *W*, as »the sum of distances« between all pairs of vertices *i* and *j* in an acyclic graph G. He calculated *W* by summing up the »bond contribution« of all edges *e* in G. Randić[4] extended this definition to »path contributions«, resulting in the hyper-Wiener, *WW*, number. Condensing the two descriptors, one can write

$$I = I(\mathrm{G}) = \sum\nolimits_{e/p} I_{e/p} = \sum\nolimits_{e/p} N_{\mathrm{L},e/p} \cdot N_{\mathrm{R},e/p} \qquad (1)$$

with

$$N_{\mathrm{L},e} + N_{\mathrm{R},e} = N(\mathrm{G}) \qquad (2)$$

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In the above relations, N_L and N_R denote the number of vertices lying to the left and to the right of edge/path *e/p* and the summation runs over all edges/paths in the graph. The meaning of I, *cf.* Eq. (1), is the number of all »external« paths that include all the paths, of length *e/p*, in acyclic graphs.

Edge/path contributions $I_{e/p}$ are just the entries in the Wiener matrices, $\boldsymbol{W_e}$ and $\boldsymbol{W_p}$.[5,6] Thus, I is the half sum of entries in these matrices

$$I = (1/2)\sum_i \sum_j [\boldsymbol{W}_{e/p}]_{ij} \tag{3}$$

I being W for $\boldsymbol{W_e}$ and WW for $\boldsymbol{W_p}$. Lukovits *et al.*[7–9] derived formulas for calculating I in cycle-containing graphs.

A second main definition of I is based on the distance matrix, $\boldsymbol{D}$, as Hosoya[10] and Diudea[1] proposed

$$I = (1/2)\sum_i \sum_j [\boldsymbol{D}_{e/p}]_{ij} \tag{4}$$

where $\boldsymbol{D_e}$ is just the classical $\boldsymbol{D}$ matrix and $\boldsymbol{D_p}$ is the »distance path« matrix.[1] The meaning of I, *cf.* Eq. (4), is the number of all »internal« paths, of length *e/p*, included in all the shortest paths in the graph. Eq. (4) is valid both for acyclic and cyclic structures.

Another definition relates W to the eigenvalues of Laplace-Kirchhoff matrix, $\boldsymbol{x_i}$[11–14]

$$W = N\sum_{i=2}^{N} l/\boldsymbol{x_i} \tag{5}$$

a relation valid only for acyclic structures. For other definitions, modifications and computational methods of W, see Refs. 15,16.

Klein, Lukovits and Gutman[17] have decomposed WW by a relation equivalent to

$$WW = (\mathrm{Tr}(\boldsymbol{D_e}^2)/2 + W)/2 \tag{6}$$

where $\mathrm{Tr}(\boldsymbol{D_e}^2)$ is the trace of distance matrix raised to the second power. Relation (6) is valid for cycle-containing graphs when W is evaluated by the Hosoya[10] relation (4).

Wiener-type numbers are seen[17] as approximate measures of the expansiveness of graphs. They show good correlation with various physico-chemical and biological properties[18–21] of organic compounds.

In this paper, general formulas for evaluating the novel number D_Δ in dendrimers are derived and exemplified on several types of regular dendrimers. Relations of D_Δ with W and WW and a novel relation (based on the $\boldsymbol{D_P}$ matrix[1]) for calculating WW in dendrimers are also given.

NOVEL WIENER-TYPE NUMBER, D_Δ

Diudea[1] has recently given a novel definition for WW. Accordingly, it can be calculated by using the $\boldsymbol{D_P}$ matrix[1]

$$WW = \sum_{i<j} [\boldsymbol{D_P}]_{ij} = \sum_{i<j} \binom{[\boldsymbol{D_e}]_{ij}+1}{2} \tag{7}$$

The expansion of the right member enabled decomposition of WW into two terms

$$WW = W + D_\Delta \tag{8}$$

where W is the Wiener number and the last term is the »non-Wiener« part of the hyper-Wiener number, denoted D_Δ

$$D_\Delta = \sum_{i<j} [\boldsymbol{D_\Delta}]_{ij} = \sum_{i<j} \binom{[\boldsymbol{D_e}]_{ij}}{2} \tag{9}$$

where $\boldsymbol{D_\Delta}$ is the »Delta« matrix, defined according to Eq. (9). D_Δ means the number of all paths (larger than unity) included into all the shortest paths in the graph.

In matrix form, WW can be written as

$$\sum_{i<j} [\boldsymbol{D_P}]_{ij} = \sum_{i<j} [\boldsymbol{D_e}]_{ij} + \sum_{i<j} [\boldsymbol{D_\Delta}]_{ij} \tag{10}$$

Relations (7) to (10) are valid for any graph, since they are based on $\boldsymbol{D}_\mathrm{e}$ matrix.

The number D_Δ can be related to the $\mathrm{Tr}(\boldsymbol{D_e}^2)$ by

$$D_\Delta = (\mathrm{Tr}(\boldsymbol{D_e}^2) - 2W) / 4 \tag{11}$$

Note that the subscript Δ does not refer to the »detour« matrix, Δ, of Amić and Trinajstić (Ref. 21a) but simply suggest the difference between WW and W.

W, D_{Δ} AND WW NUMBERS IN REGULAR DENDRIMERS

Dendrimers are hyperbranched macromolecules, synthesized by repeatable steps, either by » divergent growth « or »convergent growth« approaches (see Ref. 2). These rigorously tailored structures are mainly organic compounds but inorganic components can be also included.[22,23] They show a spherical shape, which can be functionalized,[24–28] for various purposes. Reviews in the field are available.[29–31]

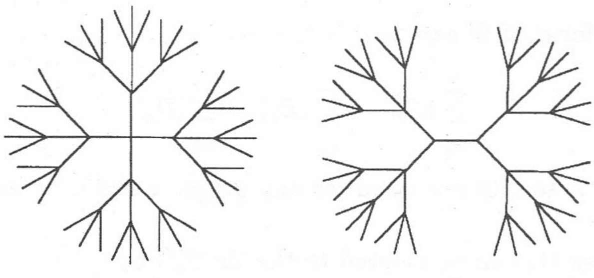
Some definitions in dendrimer topology are needed:

The vertices of a dendrimer, except for the external end points, are branching points. The number of edges emerging from each branching point is called[2] progressive degree, p (*i.e.* the edges that enlarge the number of points of a newly added orbit). It equals the classical degree, k, minus one: $p = k - 1$. If all the branching points have the same degree, the dendrimer is called regular. Otherwise, it is irregular.

A dendrimer is called homogeneous if all its radial chains (*i.e.* chains that start from the core and end in an external point) have the same length.[31] In graph theory, they correspond to the Bethe lattices.[32]

It is well known[33] that any tree has either a monocenter or a dicenter (*i.e.* two points joined by an edge). Accordingly, the dendrimers are called monocentric and dicentric, respectively. Examples are given in the Figure. The numbering of orbits (generations[2,31]) starts with zero for the core and ends with r (*i.e.* the radius of dendrimer, or the number of edges from the core to the external nodes).

A regular monocentric dendrimer, of progressive degree p and generation r is herein denoted by $D_{p,r}$ whereas the corresponding dicentric dendrimer by $DD_{p,r}$.



a b

Figure. Monocentric (a) and dicentric (b) regular dendrimers

In a previous work,[34] we reported the following relations for calculating WW in regular dendrimers

$$WW(\mathrm{D}_{p,r}) = \{2p^{2r}(p^2-1)^2r^2 + p^{2r}(p^2-1)(p^2-8p-5)r + (p+1)(p^r-1)[p^r(p^2+10p+3)-2]\} / 2(p-1)^4 \quad (12)$$

$$WW(\mathrm{DD}_{p,r}) = \{4p^{2r+2}(p-1)^2r^2 + 4p^{2r+2}(p-4)(p-1)r + p^{2r+2}(p^2-3p+16) - p^{r+1}(p^2+10p+5) + (p+1)\} / (p-1)^4 \quad (13)$$

These relations were obtained according to Eq. (6), by using the ***LC*** (layer matrix of cardinality).[35] By the layer counter, $j = \mathrm{D}_{iu}$, the matrix ***LC*** is related to the distance matrix, their entries being the distance degrees and it itself a collection of distance degree sequences. The ***LC*** matrix (with the column $j = 0$ omitted) of a regular dendrimer, in the line form,[34] can be written as

$$A = (2-z)\{(p+1)p^{(j-1)}; (1-z)p^r\} \qquad j = 1,2,\ldots, r \quad (14)$$

$$B = (2-z)p^{(s-z)}(p+1)^z\{(p+1)p^{(j-1)}; E\} \qquad j = 1,2,\ldots, r-s \qquad s = 1,2,\ldots, r-2 \quad (15)$$

$$C = (2-z)p^{(s-z)}(p+1)^z\{(r-s)(p+1); E\} \qquad s = r-1, r \quad (16)$$

$$E = \{(p^{(r-s)})_j; (p^{(r-s+k)})_j; (p^{(r-s+k)})_j; (zp^r)_j\}$$
$$j = r-s+1 \quad j = r-s+2k \quad j = r-s+2k+1 \quad j = r+s$$
$$k = 1,2,\ldots, s-z \quad (17)$$

where A, B and C denote the type of rows (starting from the core) within the ***LC*** matrix of a dendrimer and E is a common part within several rows of ***LC***. Parameter z enables the use of Eqs. (14) to (17) (and the following ones) both for monocentric (z=1) and dicentric (z=0) dendrimers.

Thus, the ***LC*** matrix can serve as a basis for evaluating the Wiener-related numbers. By taking into account the layer counter j, expansion of the above ***LC*** matrix offers the parameters in Eq. (8): W, D_Δ and WW (denoted by I in Eq. (18))

$$I = (A_\mathrm{I} + B_\mathrm{I} + C_\mathrm{I}) / 2 \quad (18)$$

W number:

$$A_W = (2-z)\,[\sum_{j=1}^{r} (p+1)p^{(j-1)}j + (1-z)p^r(r+1)] \tag{19}$$

$$B_W = (2-z)(p+1)^z \sum_{s=1}^{r-2} [p^{(s-z)} (\sum_{j=1}^{r-s} (p+1)p^{(j-1)}j + E_W)] \tag{20}$$

$$C_W = (2-z)(p+1)^z \sum_{s=r-1}^{r} p^{(s-z)}\,[(r-s)(p+1) + E_W] \tag{21}$$

$$E_W = p^{(r-s)}\,(r-s+1) + zp^r(r+s)$$

$$+ \sum_{k=1}^{s-z} p^{(r-s+k)}\,[(r-s+2k) + (r-s+2k+1)] \tag{22}$$

Evaluation of sums in Eqs. (19) to (22) results in the following analytical relations for $D_{p,r}$ $(z = 1)$ and $DD_{p,r}$ $(z = 0)$, respectively

$$W(D_{p,r}) = (p+1)\,[p^{2r}(p^2-1)r - p^{2r}(2p+1) + 2p^r(p+1) - 1]\,/\,(p-1)^3 \tag{23}$$

$$W(DD_{p,r}) = \left[\begin{array}{c} 4p^{(2r+2)}\,(p-1)r + (4p^{(r+1)} - 1)\,(p+1) \\ + p^{(2r+2)}\,(p-7) \end{array}\right] \tag{24}$$

D_Δ number:

$$A_{D_\Delta} = (2-z)\,[\sum_{j=1}^{r} (p+1)p^{(j-1)}j(j-1)\,/\,2 + (1-z)p^r(r+1)r\,/\,2] \tag{25}$$

$$B_{D_\Delta} = (2-z)\,(p+1)^z \sum_{s=1}^{r-2} [p^{(s-z)}\,(\sum_{j=1}^{r-s} (p+1)p^{(j-1)}j(j-1)\,/\,2 + E_{D_\Delta})] \tag{26}$$

$$C_{D_\Delta} = (2-z)\,(p+1)^z \sum_{s=r-1}^{r} p^{(s-z)}\,E_{D_\Delta} \tag{27}$$

$$E_{D_\Delta} = p^{(r-s)}\,(r-s+1)\,(r-s)\,/\,2 + zp^r(r+s)\,(r+s-1)\,/\,2 +$$

Evaluation of sums in Eqs. (25) to (28) results in the following analytical relations:

$$D_\Delta(\mathrm{D}_{p,r}) = \{2p^{2r}(p^2-1)^2r^2 - p^{2r}(p^2-1)(p^2+8p+3)r + (p+1)(p^r-1)[p^r(5p^2+8p+1)-2p]\} / 2(p-1)^4 \quad (29)$$

$$D_\Delta(\mathrm{DD}_{p,r}) = \{4p^{2r+2}(p-1)^2r^2 - 12p^{2r+2}(p-1)r + p^{2r+2}(5p+9) - p^{r+1}(5p^2+10p+1) + p(p+1)\} / (p-1)^4 \quad (30)$$

WW number:

$$A_{WW} = (2-z)\,[\sum_{j=1}^{r}(p+1)p^{(j-1)}j(j+1)/2 + (1-z)p^r(r+1)(r+2)/2] \quad (31)$$

$$B_{WW} = (2-z)(p+1)^z\sum_{s=1}^{r-2}[p^{(s-z)}(\sum_{j=1}^{r-s}(p+1)p^{(j-1)}j(j+1)/2 + E_{WW})] \quad (32)$$

$$C_{WW} = (2-z)(p+1)^z\sum_{s=r-1}^{r}p^{(s-z)}[(r-s)(p+1) + E_{WW}] \quad (33)$$

TABLE

Topological Data for Regular Dendrimers

p	*r*	*W*		D_Δ		WW	
		z = 0	z = 1	z = 0	z = 1	z = 0	z = 1
1	1	10	4	5	1	15	5
	2	35	20	35	15	70	35
	3	84	56	126	70	210	126
	4	165	120	330	210	495	330
	5	286	220	715	495	1001	715
2	1	29	9	18	3	47	12
	2	285	117	382	120	667	237
	3	1981	909	4214	1626	6195	2535
	4	11645	5661	34534	14766	46179	20427
	5	62205	31293	239046	108630	301251	139923
3	1	58	16	39	6	97	22
	2	1147	400	1695	462	2842	862
	3	16564	6304	38982	12684	55546	18988
	4	207157	82336	677910	240348	885067	322684
	5	2392942	975280	10093917	3762066	12486859	4737346

$$E_{WW} = p^{(r-s)}(r-s+1)(r-s+2)/2 + zp^{r}(r+s)(r+s+1)/2 +$$

$$\sum_{k=1}^{s-z} p^{(r-s+k)} [(r-s+2k)(r-s+2k+1)/2 + (r-s+2k+1)(r-s+2k+2)/2] \quad (34)$$

Evaluation of sums in Eqs. (31) to (34) leads to Eqs. (12) and (13) presented above, thus proving that the two ways for calculating the number *WW* are correct. Values for the three numbers in regular dendrimers with $p = 1-3$ and $r = 1-5$ are listed in the Table.

Note that the relations for *W* (Eqs. (23) and (24)) are equivalent to the relations reported by Gutman *et al.*[36] and Diudea[37] and give identical numerical values. For $p = 1$, dendrimers reduce to line graphs (*i.e.* normal alkanes)

Analytical relations and their numerical evaluation were made using the MAPLE V Computer Algebra System (Release 2).

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SAŽETAK

Delta broj, D_{Δ}, dendrimera

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Predložene su formule za račun novog indeksa, D_{Δ}, Wienerova tipa, koje su izvedene uz pomoć pripadne matrice uporabom progresivnih stupnjeva čvorova i brojeva orbita kao parametara. Izvedena je veza indeksa D_{Δ} s poznatim Wienerovim, W, i hiper-Wienerovim, WW, indeksima, te jedna nova relacija za procjenu indeksa u dendrimerima.