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CONNECTIVITY INDICES OF DENDRIMERS

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ABSTRACT. Formulas for calculating connectivity-based indices Randi≡-type index calculated on vertices, χ, and on edges, ε, Zagreb index, M_2, and Bertz index, B in regular homogeneous dendrimers are established. Values of the above topological indices for families of dendrimers, with up to 10 orbits, are calculated. Mutual intercorrelation of these indices, in the considered dendrimers, is evaluated.

INTRODUCTION

Dendrimers are hyperbranched molecules, synthesised basically by two procedures: (i) by "divergent growth", [1-3] when branched blocks are added around a central *core*, thus obtaining a new, larger orbit or generation and (ii) or by "convergent growth" [4-7] when large branched blocks , previously built up starting from the periphery, are attached to the core. These structures show spherical shape, which can be functionalized [8-11] , thus modifying their physico-chemical or biological properties. Reviews in the field are available. [12-14]

Some particular definitions in dendrimers are needed :

Vertices in a dendrimer, except the external endpoints, are considered as branching points. The number of edges incident in a branching point is called degree, δ .

A regular dendrimer has all the branching points with the same degree, otherwise it is irregular [15-17].

A dendrimer is called *homogeneous* if all its radial chains (i.e., the chains starting from the core and ending in an external point) have the same length [12]. In graph theory, they correspond to the Bethe lattices [18] .

A tree has either a monocenter or a dicenter [19] (i.e. two points joined by an edge). Accordingly, a dendrimers is called *monocentric* and *dicentric*, respectively. Examples are given in the Figure. The numbering of orbits (generations [12]) starts with zero for the core and ends with **r,** which is the radius of the dendrimer (i.e., the number of edges along a radial chain, starting from the core and ending to an external node).

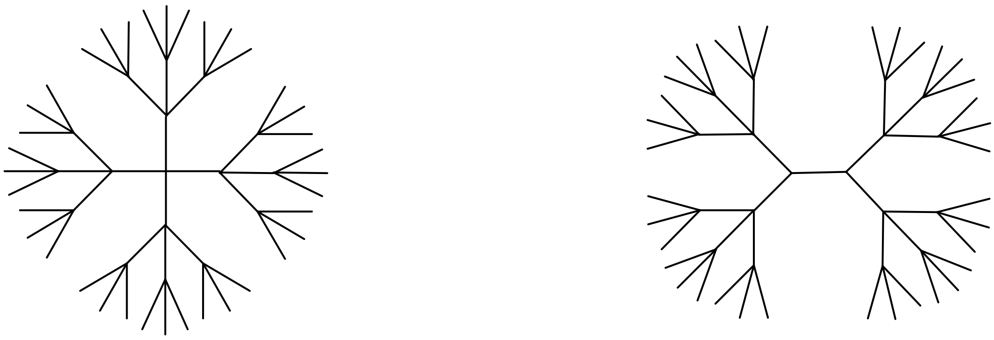

***Figure*.** Monocentric and dicentric regular dendrimers

ATOM (VERTEX) CONNECTIVITY INDEX

The atom (vertex) connectivity index was introduced by Randi≡ [20] as a measurement of the molecular branching in alkanes. It was subsequently extended by Kier and Hall to account for heteroatoms differentiation and it was renamed as molecular connectivity index [21]. The Randic original index is calculated from the following expression

$$\chi = \sum_{t=1}^{m} (\delta_i \delta_j)_t^{-0.5} \tag{1}$$

where the summation is carried out over all pairs of adjacent vertices, that is over all edges *m*, in the molecular graph. The index was later extended by Altenburg to include exponents other than -0.5 in the expression (1). The generalized vertex connectivity index is then calculated as

$$\chi = \sum_{t=1}^{m} (\delta_i \delta_j)_t^{g} \tag{2}$$

Several exponents have been investigated by Altenburg, Randic and very recently a mathematical justification of the necessity of use exponent different to -0.5 to avoid “accidental” degeneration of isomers was pointed out.

In order to calculate the vertex connectivity index for regular dendrimers we need to introduce some mathematical results that will be given below.

Let G be a regular dendrimer graph, then if G is a monocentric tree, the number of vertices in the s^{th} orbit or generation n(s) is given by:

$$\mathbf{n(s) = \delta(\delta-1)^{s-1}} \quad ; \quad s \neq \mathbf{0} \tag{3}$$

In case that the dendrimer be dicentric n(s) is obtained as follows:

$$\mathbf{n(s) = 2(\delta-1)^{s}} \quad ; \quad s \neq \mathbf{0} \tag{4}$$

A general expression to calculate the number of vertices in the s*th* orbit of a regular dendrimer can be obtained from the combination of expressions (3) and (4):

$$\mathbf{n(s) = (k+1)\cdot(\delta-k)\cdot(\delta-1)^{s-1}} \quad ; \quad s \neq \mathbf{0} \tag{5}$$

where k = 0 for monocentric dendrimers and k = 1 for dicentric ones.

The total number of vertices, *N* , in the dendrimer can be obtained as follows:

$$\mathrm{N} = \mathbf{(}\mathrm{k}\mathbf{+1)+}\sum_{\mathrm{s}\mathbf{=1}}^{\mathrm{r}}\mathrm{n}\mathbf{(}\mathrm{s}\mathbf{)} \tag{6}$$

where r is the number of orbits in the dendrimer. By combining (5) and (6) we obtain the following expression for the total number of vertices in G:

$$\mathbf{N = (k+1)+(1+\sum_{s=1}^{r}(\delta-k)(\delta-1)^{s-1}} \tag{7}$$

and developing the geometrical progression given in (7) we have:

$$\mathbf{N = (k+1)\left[\frac{(\delta-1)^{k}(\delta-k)+k-2}{\delta-2}\right]} \tag{8}$$

In order to calculate the Randic χ index we can consider it as a combination of two χ indices, one of them χ_{ii} calculated from contributions coming from internal vertices in the dendrimer, i.e., those different from the end points, and the other χ_{ie} calculated from the end points contributions

$$\chi = \chi_{ii} + \chi_{ie} \tag{9}$$

The χ_{ii} index is calculated as:

$$\chi_{ii} = \sum_{t=1}^{m_i} (\delta_i \delta_i)^g = m_i \cdot \delta^{2g} \tag{10}$$

where m_i is the number of internal vertices, i.e. those inside the *r*-1 orbit, having degree δ. The number of internal vertices m_i is obtained from the total number of vertices and the number of end points in G:

$$m_i = N - n(r) - 1 \tag{11}$$

where n(r) is the number of vertices in the *rth* orbit, that is the number of end points. This number can be obtained from expression (5) to give:

$$m_i = N - (k+1) \cdot \delta^{1-k} \cdot (\delta - 1)^{r+k-1} - 1 \tag{12}$$

and the internal vertex connectivity index is obtained as follows:

$$\chi_{ii} = (N-1)\delta^{2g} - (k+1)(\delta-1)^{(r+k-1)}\delta^{(2g-k+1)} \tag{13}$$

Following a similar procedure for χ_{ie} we obtain:

$$\chi_{ie} = (k+1)(\delta-1)^{(r+k-1)}\delta^{(g-k+1)} \tag{14}$$

and

$$\chi = \delta^{2g}(N-1) + (k+1)(\delta-1)^{(r+k-1)}\delta^{(g-k+1)}(1-\delta^g) \tag{15}$$

When, as in the original definition of Randic, g = -1/2 , we have:

$$\chi_{-1/2} = \frac{N-1}{\delta} + \frac{(k+1)(\sqrt{\delta}-1)(\delta-1)^{(r+k-1)}}{\delta^k} \tag{16}$$

If we consider the case in which all the end points of a regular dendrimer are heteroatoms, i.e., atoms different from carbon and hydrogen, it is necessary to calculate a valence molecular connectivity index as defined by Kier and Hall [21]. This index will be obtained as follows:

$$\chi^{v}_{-1/2} = \frac{N-1}{\delta} + \frac{(k+1)(\delta-1)^{(r+k-1)}\left[(\delta^{v})^{-0.5}\delta^{0.5} - 1\right]}{\delta^k} \tag{17}$$

where δ^{v} is the valence degree for the heteroatom in the end point and δ is the degree of internal vertices in the dendrimer.

BOND (EDGE) ADJACENCY INDEX

The bond (edge) connectivity ε index [22] was introduced by Estrada as a measurement of molecular volume in alkanes. It was subsequently extended to molecules containing heteroatoms [23] and to account for spatial (3D) features [24] of organic molecules. The ε index is calculated by using the Randic graph theoretical invariant in which the vertex degrees is substituted by edge degrees. Mathematically, the index is obtained as follows

$$\varepsilon = \sum_{l=1}^{S} (\delta e_i \delta e_j)_l^g \tag{18}$$

where δe_i is the degree of edge *i*, *S* is the number of pairs of adjacent edges in the graph and *g* is an exponent which generally takes the value of -0.5. It has been pointed out elsewhere that the edge degree can be expressed in terms of vertex degrees through the following expression:

$$\delta e_p = \delta_i + \delta_j - 2 \tag{19}$$

in which δ_i and δ_j are the degrees of vertices *i* and *j* incident to the edge e_p.

In regular dendrimers we can consider the ε index as the sum of three index accounting for contributions coming from pairs internal-internal adjacent edges ε_{ii}, pairs of internal-external adjacent edges ε_{ie}, and pairs of external-external adjacent edges ε_{ee}. One edge will be called internal if it is inside the (*r*-2)*th* orbit or generation and external if it is outside this orbit, that is if it is incident to an external vertex (end point). It is straightforward to realize that the internal edges of the regular dendrimer have the same degree, $\delta e_i = 2\delta - 2$, and the external ones have degree $\delta e_e = \delta - 1$. Now, the expression for edge connectivity index can be written as:

$$\varepsilon = \varepsilon_{ii} + \varepsilon_{ie} + \varepsilon_{ee} \tag{20}$$

The ε_{ii} index can be calculated by adapting the expression (18) to consider internal edges only:

$$\varepsilon_{ii} = \sum_{l=1}^{S_{ii}} (\delta e_i)_k^{2g} = S_{ii}(2\delta - 2)^{2g} \tag{21}$$

where S_{ii} is the number of pairs of internal-internal edges, which can be obtained as follows:

$$\mathbf{S_{ii}} = \binom{\delta}{2}\mathbf{N(r-2)} \qquad r \geq 2 \tag{22}$$

where $N(r-2)$ is the total number of vertices inside the (r-2)th orbit (including it):

$$\mathbf{S_{ii}} = \frac{\delta(\delta-1)}{2}\left\{(k+1)+(k+1)\delta^{1-k}\left[\frac{(\delta-1)^{k}-(\delta-1)^{r+k-2}}{2-\delta}\right]\right\};\ r \geq 2 \tag{23}$$

The internal edge connectivity index is then calculated as follows:

$$\varepsilon_{ii} = \frac{\delta}{4}(k+1)(2\delta-2)^{2g+1}\left\{1+\delta^{1-k}\left[\frac{(\delta-1)^{k}-(\delta-1)^{r+k-2}}{2-\delta}\right]\right\};\ r \geq 2 \tag{24}$$

The internal-external edge connectivity index ε_{ie} can be calculated from the expression (18) by considering the number of pairs of internal-external adjacent edges S_{ie} in the dendrimer:

$$\varepsilon_{ie} = S_{ie}\left[(\delta-1)(2\delta-2)\right]^{g} \tag{25}$$

$$S_{ie} = (\delta-1)\left[(k+1)\delta^{1-k}(\delta-1)^{r+k-2}\right]; \qquad r \geq 2 \tag{26}$$

The ε_{ie} index is then obtained from the following expression:

$$\varepsilon_{ie} = (k+1)(2\delta-2)^{g}\delta^{1-k}(\delta-1)^{g+r+k-1}; \qquad r \geq 2 \tag{27}$$

In order to calculate the external-external edge connectivity index ε_{ee} we use the number of pairs of external-external adjacent edges S_{ee}, which is calculated as:

$$S_{ee} = \binom{\delta-1}{2}\left[(k+1)\delta^{1-k}(\delta-1)^{r+k-2}\right] \qquad ; r \geq 2 \tag{28}$$

The ε_{ee} index is calculated as follows

$$\varepsilon_{ee} = S_{ee}(\delta-1)^{2g} \tag{29}$$

$$\varepsilon_{ee} = \frac{\delta - 2}{2}(\delta - 1)^{2g+r+k-1}(k+1)\delta^{1-k} \qquad r \geq 2 \tag{30}$$

The edge connectivity index of regular dendrimers can be obtained by combining expressions (24), (27) and (30) in expression (20).

OTHER VERTEX CONNECTIVITY INDICES

As the equations for calculating the Rand≡ vertex index were established, it is easily to derive formulas for other two indices based on the connectivity in graph:

Zagreb Group index, $\mathbf{M_2}$ [25]

$$\mathbf{M}_2 = (\mathbf{N} - \mathbf{n}_r - 1)\delta^2 + \mathbf{n}_r\delta \tag{31}$$

$$\mathbf{M}_2 = \frac{\delta}{(\delta - 2)}[4(\delta - 1)^{(r+1)} - \delta^2 + k(k-3)(\delta - 1)^r(\delta - 2)] \tag{32}$$

Bertz index, **B** [26]

$$\mathbf{B} = (\mathbf{N} - \mathbf{n}_r)\binom{\delta}{2} \tag{33}$$

$$\mathbf{B} = \left[\frac{2(\delta - 1)^{(r+1)} - 1)}{(\delta - 2)} - (\delta - 1)^r k - (2-k)(\delta - 1 + k)(\delta - 1)^{(r-1)}\right]\frac{(\delta - 1)\delta}{2} \tag{34}$$

Bertz index equals the number of connected pairs of edges in a regular dendrimer. Values of the above discussed indices are listed in Tables 1 and 2, for dendrimers having δ = 3 and 4 and generations up to ten.

Table 1.

Vertex and Edge Connectivity Indices for Regular Dendrimers
Having δ = 3 and 4, and generations up to 10 Orbits

	N	$\chi_{-1/2}$	$\varepsilon_{-1/2}$	N	$\chi_{-1/2}$	$\varepsilon_{-1/2}$
r		k = 0			k = 1	
		δ = 3				
1	4	1.732	1.500	6	2.643	2.414
2	10	4.464	4.371	14	6.285	6.328
3	22	9.928	10.243	30	13.571	14.157
4	46	20.856	21.985	62	28.142	29.814
5	94	42.713	45.471	126	57.284	61.127
6	190	86.426	92.441	254	115.568	123.755
7	382	173.851	186.382	510	232.135	249.010

8	766	348.703	374.265	1022	465.270	499.519
9	1534	698.405	750.029	2046	931.540	1000.539
10	3070	1397.810	1501.558	4094	1864.080	2002.577
$\delta = 4$						
1	5	2	2.000	8	3.25	3.414
2	17	7	7.828	26	10.75	12.243
3	53	22	25.485	80	33.25	38.728
4	161	67	78.456	242	100.75	118.184
5	485	202	235.368	728	303.25	356.551
6	1457	607	714.103	2186	910.75	1071.654
7	4373	1822	2144.308	6560	2733.25	3216.962
8	13120	5467	6434.923	19680	8200.75	9652.885
9	39370	16400	19306.770	59050	24603.25	28960.655
10	118100	49210	57922.310	177100	73810.75	86883.966

Table 2.

Bertz and Zagreb Group Indices for Regular Dendrimers
Having $\delta = 3$ and 4, and generations up to 10 Orbits.

	N	B	M_2	N	B	M_2
r		k = 0			k = 1	
$\delta = 3$						
1	4	3	9	6	6	21
2	10	12	45	14	18	69
3	22	30	117	30	42	165
4	46	66	261	62	90	357
5	94	138	549	126	186	741
6	190	282	1125	254	378	1509
7	382	570	2277	510	762	3045
8	766	1146	4581	1022	1530	6117
9	1534	2298	9189	2046	3066	12261
10	3070	4602	18405	4094	6138	24549
$\delta = 4$						
1	5	6	16	8	12	40
2	17	30	112	26	48	184
3	53	102	400	80	156	616
4	161	318	1264	242	480	1912
5	485	966	3856	728	1452	5800
6	1457	2910	11632	2186	4368	17464
7	4373	8742	34960	6560	13116	52456
8	13120	26238	104944	19680	39360	157432
9	39370	78726	314896	59050	118092	472360
10	118100	236190	944752	177100	354288	1417144

Connectivity-type indices are highly intercorelated (correlating coefficient, r> 0.9999) in the set of homogeneous dendrimers with the degree 3 and 4 and generation up to ten.

The same correlation is shown vs. the number of vertices (i.e., the number of carbon atoms) in the dendrimer. It suggests that the connectivity-based indices are quite “amorphous” descriptors.

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