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MOLECULAR TOPOLOGY.19. ORBITAL AND WEDGEAL SUBGRAPH ENUMERATION IN DENDRIMERS

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Abstract: *Subgraph enumeration of orbital and wedgeal population in irregular dendrimers is given, and some properties such as molecular weight and volume are evaluated and examplified. On this basis, a congesting criterion for families of isodiametric dendrimers is proposed.*

Introduction

Dendrimers are hyperbranched macromolecules which, in the last years, particularly attracted the interest of chemists.[1-15] Such structures, with tailored interior, can be functionalized[5-10,14,15] at exterior spherical surface, which may result in new interesting properties, e.g. high solubility[5,7] and particular reactivity *vis a vis* to host-guest interactions.[1,6] In this respest the reader can consult the excellent review of Tomalia *et al.*[1]

A binary dendrimer, A_xB_y, consists of a branching core $(r=0)$ which is surrounded of branching atoms, A, at progressive radii, r (orbits, generations). The external chains are ended by nonbranching atoms B, which can be chemical functional groups. If all radial chains have the same length, it is referred to as a homogeneous dendrimer.

Since all branching atoms A have the same valence (kv) and graph theoretical degree (k), it is called a regular dendrimer. In a previuos paper[11] we stated for a binary dendrimer, A_xB_y, the general formula:

$$[AB_{(kv-k)}]_x \, B_{(k-2)x+2} \qquad (1)$$

which takes into account the possibility of attaching the nonbranching atoms B (e.g. hydrogen atoms) both at the inner and external orbits. When $kv = k$, it is obvious that all B atoms are external. The total number of B atoms, $y = (kv - 2)x + 2$, does not depend on the graph theoretical degree, k. The formula (1) holds for alkane trees and also for noncarbon branching compounds.

It is known[16] that a tree possesses either a monocenter or a dicenter, so one has to take into account both monocentric and dicentric dendrimers (see Fig.1). In a tree the edge diameter $ed = 2r+i$ and the combinatorial diameter[17] $cd = 2(r+1)-i$, with $i=0$ for even- and $i=1$ for odd-diameter, respectively.

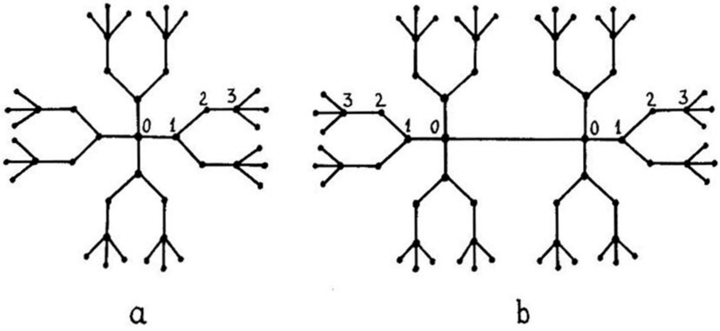

Fig. 1. Monocentric (a) and dicentric (b) irregular dendrimers

If the branching atoms differ in identity as change the orbits, the orbital formula of an ***irregular homogeneous dendrimer***[18] can be written as $A^r_{xr}B^r_{yr}$, with the superscript r as a label for the identity of branching atoms. Such a structure can be described by a radial sequence of vertices and their degrees:

$$A^0(k0);\ A^1(k1);\dots A^{rmax}(kmax);\ B \qquad (2)$$

with the nonbranching vertices B in the external shell. Fig. 1 shows a monocentric and a dicentric irregular dendrimer. By extension, one can consider the A^r vertices as subgraphs consisting of more than one atom. In the present paper, we present the orbital and wedgeal enumeration of subgraphs in irregular homogeneous dendrimers and a congesting criterion for families of isodiametric dendrimers (see below).

Orbital subgraph enumeration

A monomer which contributes to the growth of a dendrimer (a "dendritic" monomer[5]) can be regarded as a subgraph whose progressive degree is given by:

$$ps = \prod_{j\in s} p_j \qquad (3)$$

where $\mathbf{p}_j$ denotes the vertex progressive degree[18] ($p_j = k - (\pi+1)$ with π being the number of π bonds around the vertex j) and the product runs over all j branching vertices belonging to the subgraph **s**.

The orbital subgraph population, xs_r , can be counted by :

$$xs_r(ts_r) = (1+z) * (ps_0 + 1 - z) * ts_r * \prod_{1}^{r-1} ps_r \qquad (4)$$

where: r - is the subgraph radius (in a reduced graph of dendrimer, where each subgraph is replaced by a point of the corresponding progressive degree)

$z = i$, for edge diameter and $z = 1-i$, for combinatorial diameter

$r-1 \geq 1$; when $r-1 < 1$, the product equals unity, by definition

ts_r - is a weighting factor: 1 (for the counter);

vs_r (for a volume parameter[19]); ms_r (for a mass parameter);

$\Delta ps_r = kv - (p + 1)$ (for the counter of attached B groups).

The recurrence for the next subgraph orbit will be :

$$xs_{r+1}(ts_{r+1}) = xs_r * ps_r * ts_{r+1} \qquad (5)$$

and the total number of branching subgraphs, except the core:

$$xs = \sum_{1}^{r_m} xs_r(ts_r) \qquad (6)$$

When ts_r is a molecular property, the $xs_r(ts_r)$ has the meaning of that property on the considered orbit.

The external endsubgraphs are counted according to:

$$ys_r = xs_r * ps_r \qquad (7)$$

Vertex enumeration is related to the subgraph parameters by:

$$x_r(t_r) = (1 + z) * \left(\prod_{j \in s_0} \rho_j + 1 - z \right) * t_r * \prod_{1}^{r-1} \left(\prod_{j \in s} \rho_j \right)_r \qquad (8)$$

Wedgeal enumeration

In convergent syntheses of dendrimers,[4,9] a number of wedges are bonded at the core to give the desired hyperbranced structure. A dendritic wedge is a substructure (a dendron[1]) of a dendrimer which starts in a focal point and ends by a number of terminal (surface) groups. Here, the focal point is just the point of attachement of the wedge at the core.

It is useful to enumerate the orbital subgraph population in such substructures. Thus, the orbital wedgeal subgraph population, xws_r, can be computed by:

$$xws_r(ts_r) = ts_r * \prod_{1}^{r-1} \rho s_r \qquad (9)$$

with the same specification for $r-1$ as above, and the next orbital population, according to:

$$xws_{r+1}(ts_{r+1}) = xws_r * \rho s_r * ts_{r+1} \qquad (10)$$

The total number of branching subgraphs, except the core, will be:

$$xws = \sum_{1}^{r_m} xws_r(ts_r) \qquad (11)$$

The external endsubgraphs are counted according to:

$$yws_r = xws_r * ps_r \tag{12}$$

Vertex enumeration is related to the subgraph parameters by:

$$xw_r(t_r) = t_r * \prod_{1}^{r-1} (\prod_{j \in s} \rho_j)_r \tag{13}$$

It is obvious that the global orbital parameters are easily obtainable from the wedgeal parameters by multiplication with $(1+z) * (ps_0 + 1 - z)$

A point of attachement of a wedge on a hypercore can be also viewed as a local promoting core (encountered in rodlike dendrimers[1] in divergent syntheses).

The core population, $x_0(ts_0)$, can be counted by:

$$x_0(ts_0) = (1+z) * ts_0 \tag{14}$$

if the core subgraph is monoatomic, or according to eqs. (6) or (11) and adding the central population given by eq. (14), in the case of a hypercore[9].

Volume congesting criterion

In a homogeneous irregular dendrimer, one can permute the subgraphs/fragments within the limits of a given diameter (or length of radial sequence) in generating isodiametric families of dendrimers.

The fragment density (congestion) at the level of a given generation can be expressed either as a surface congestion (*i.e.* the surface area per fragment) or as a volume congestion (*i.e.* the volume per radius). *Tomalia et al.*[1] stated that the self-limiting dendrimer dimensions are a function of the radial length: "larger radial length will delay the congestion" at the level of a generation. This idea led us to formulate a ***congesting criterion***, cc_{rm}, as follows:

$$cc_{rm} = a_{rm} * vs_{rm} / rm \qquad (15)$$

where: as_{rm} counts the fragments on the r^{th} orbit/generation.

vs_{rm} stands for the van der Waals volume of a subgraph in the r^{th} orbit

rm represents the the maximal topological radius of subgraph location in wedge (starting from the attachement point)

vs - values were taken form *Motoc et al.*[19] and they allow the estimation of the wedge van der Waals volume V_w :

$$V_w = \Sigma_{rm}\, as_{rm} * vs_{rm} \qquad (16)$$

where the summation runs over all orbits in the wedge.

The product $a_{rm} * vs_{rm}$ accounts for the orbital volume and the ratio $a_{rm} * vs_{rm} / V_w$ means the volume distribution in a wedge.

Fig. 2. shows a wedge in an irregular dendrimer along with the vs_{rm}, ms_{rm} (see below) and rm values. Table 1 lists the above parameters for the wedge in Fig. 2, as well as for the whole family of its isodiametric congeners.

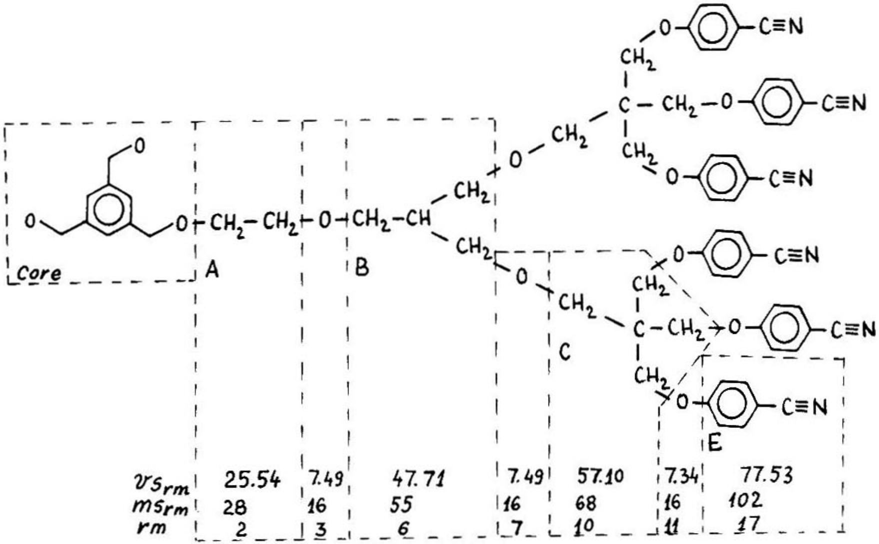

Fig. 2. A wedge in an irregular dendrimer:
vs_{rm} ($Å^3$), ms_{rm} (mass units) and rm (edges), see text

Table 1. Orbital volume ($a_{rm} * vs_{rm}$), orbital volume distribution ($a_{rm} * vs_{rm} / V_w$) and the congesting criterion (cc_{rm}) in a wedge of isodiametric family of irregular dendrimers cf. Fig. 2. (see text)[a]

Sequence (population)	V_w (Å^3)	$a_{rm} * vs_{rm}$ / $a_{rm} * vs_{rm} / V_w$ / cc_{rm}						
A,B,C,E	719.14	25.54	7.49	47.71	14.98	114.20	44.04	465.18
(A,B,2C,6E)		0.036	0.010	0.066	0.021	0.159	0.061	0.647
		12.770	2.497	7.952	2.140	11.420	4.004	27.364
A,C,B,E	764.95	25.54	7.49	57.10	22.47	143.13	44.04	465.18
(A,C,3B,6E)		0.033	0.010	0.075	0.029	0.187	0.058	0.608
		12.770	2.497	9.517	3.210	14.313	4.004	27.364
B,A,C,E	752.17	47.71	14.98	51.08	14.98	114.20	44.04	465.18
(B,2A,2C,6E)		0.063	0.020	0.068	0.020	0.152	0.059	0.618
		15.903	3.745	8.513	2.140	11.420	4.004	27.364
B,C,A,E	884.29	47.71	14.98	114.20	44.94	153.24	44.04	465.18
(B,2C,6A,6E)		0.054	0.017	0.129	0.051	0.173	0.050	0.526
		15.903	3.745	16.314	5.618	15.324	4.004	27.364
C,A,B,E	813.01	57.10	22.47	76.62	22.47	143.13	44.04	465.18
(C,3A,3B,6E)		0.069	0.027	0.092	0.027	0.172	0.053	0.560
		19.033	5.618	12.770	3.210	14.313	4.004	27.364
C,B,A,E	930.10	57.10	22.47	143.13	44.94	153.24	44.04	465.18
(C,3B,6A,6E)		0.061	0.024	0.154	0.048	0.165	0.047	0.500
		19.033	5.618	20.447	5.618	15.324	4.004	27.364

a) oxygen multiplicity equals the subsequent subgraph multiplicity (e.g. for sequence A,B,C,E, the population is: A,O,B,2O,2C,6O,6E, with E being the endsubgraph)

Analogous mass parameters: orbital mass $as_{rm} * ms_{rm}$ and ratio $as_{rm} * ms_{rm} / M_w$ meaning the distribution of wedge mass M_w on orbits are easily conceivable. The values M_w can be computet by:

$$M_w = \Sigma_{rm}\, as_{rm} * ms_{rm} \qquad (17)$$

The mass parameters for the wedge in Fig. 2 and its isodiametric family of irregular dendrimers are shown in Table 2.

Table 2. Orbital mass ($as_{rm} * ms_{rm}$) and orbital mass distribution ($as_{rm} * ms_{rm} / M_w$) in a wedge of isodiametric family of irregular dendrimers, cf. Fig. 2. (see text)[a].

Sequence (population)	M_w			$as_{rm} * ms_{rm}$				
						$as * ms / M_w$		
A,B,C,E	975	28	16	55	32	136	96	612
(A,B,2C,6E)		0.029	0.016	0.056	0.033	0.139	0.098	0.628
A,C,B,E	1033	28	16	68	48	165	96	612
(A,C,3B,6E)		0.027	0.015	0.066	0.046	0.160	0.093	0.592
B,A,C,E	1019	55	32	56	32	136	96	612
(B,2A,2C,6E)		0.054	0.031	0.055	0.031	0.133	0.094	0.601
B,C,A,E	1195	55	32	136	96	168	96	612
(B,2C,6A,6E)		0.046	0.027	0.114	0.080	0.141	0.080	0.512
C,A,B,E	1121	68	48	84	48	165	96	612
(C,3A,3B,6E)		0.061	0.043	0.075	0.043	0.147	0.086	0.546
C,B,A,E	1253	68	48	165	96	168	96	612
(C,3B,6A,6E)		0.054	0.038	0.132	0.077	0.134	0.077	0.488

a) the same specification as in Table 1.

From Table 1. one can see that the increasing lexicographic ordering of isodiametric dendrimers in Fig. 2. is in agreement with the statement of *Tomalia et al*.[1] about the congestion state in dendrimers, and also parallels the lexicographic ordering of the progressive degrees, ps_r , of its subgraphs: the larger progressive degree of subgraphs/monomers in the proximity of the core, the more congesting structure of a dendrimer.

Conclusions

The orbital and wedgeal subgraph population of a dendrimer can be easily counted by the means of two parameters: subgraph progressive degree, ps, and the radius (generation/orbit number), r. The weighted enumeration relations allow one to calculate molecular properties of interest for synthesists.

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