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ASYMPTOTIC VALUES OF TOPOLOGICAL INDICES J AND J' (AVERAGE DISTANCE SUM CONNECTIVITIES) FOR INFINITE ACYCLIC AND CYCLIC GRAPHS

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Abstract

The topological index J (average distance sum connectivity) has the asymptotic value π for an infinitely long n-alkane. A general formula is demonstrated for index J of an infinite graph having b branches emerging from a common nucleus, and having a repeating pattern with r edges on the stem of each branch and R-r off-stem edges. There exist however acyclic infinitely branched systems whose J_∞ value is no longer finite but ∞. For graphs with an infinite number of vertices and cycles, a related index $J' = (\mu + 1)J$ is shown to have in many cases a finite asymptotic value. A general formula is proposed for the asymptotic values of J and J' in infinite acyclic and polycyclic systems, respectively, with a finite number of branches, b, and a repeating pattern of R edges on each branch : J_∞ or $J'_\infty = R^2 \cdot f(b)/A$ where f(b) is a given function of the number of branches, and A is the main coefficient in the expression of the smallest distance sum in the infinite graph. A notation list is appended. A series of J_∞ and J'_∞ values for various infinite graphs is presented, which may prove useful in correlation.

1. Introduction

For quantitative correlations between chemical structure and chemical, physical or biological properties, during the last forty years various topological indices (TI's) have been proposed. Several reviews have been published on topological indices and their use in QSAR.[1-7] A hydrocarbon structure (constitutional formula) is converted into a hydrogen-depleted graph by omitting all hydrogen atoms and replacing the other atoms by vertices of the graph.

In previous papers,[8,9] a new highly-discriminating topological index J was defined. This index is based on distance sums s_i for each vertex : s_i is the sum of the distances from vertex i to all other vertices in a graph. The (topological) distance between two vertices in a graph is the length of the shortest path joining these two vertices, i.e. the number of edges along that path. If q is the number of edges in a graph having m vertices, the number of cycles (cyclomatic number) is :

$$\mu = q - m + 1 \tag{1}$$

The topological index J is the mean distance sum connectivity :

$$J = \frac{q}{\mu+1} \sum_{\text{edge } i,j} (s_i s_j)^{-\frac{1}{2}} \tag{2}$$

So far J is the TI with the lowest degeneracy.[10] Unlike most other topological indices, owing to the factor $q/(\mu+1)$, the index J does not increase with the increasing number of vertices and of rings. It is the purpose of this paper to discuss the behaviour of J for various infinite graphs. In many cases, J tends towards a constant finite value for infinite acyclic graphs. For graphs having an infinite number of vertices and of cycles a related topological index J' is relevant :

$$J' = (\mu+1)J = q \sum_{\text{edge } i,j} (s_i s_j)^{-\frac{1}{2}} \tag{3}$$

It will be seen that J' for infinite polycyclic graphs can be

treated similarly to J of infinite trees. In the former graphs one has to use dualist graphs (for definitions and examples in the case of cata-condensed polycyclic benzenoid hydrocarbons, see ref.11; in the case of polymantanes see ref.12). In dualist graphs angles are significant.

2. Definitions and examples

The centre, O, of a graph is constituted by the vertex or vertices with the smallest distance sum, whose value is denoted by s_0. We shall consider only centrosymmetric graphs. Their symmetry can be two-fold or higher, e.g. for b branches emerging from the centre, the symmetry is b-fold.

Graphs which differ by a constant pattern of vertices and edges (pattern called elementary cell) form a cell-homologous series. The first term (n=1) in such series is called nucleus and contains the vertex (vertices) of the centre O ; in addition it may contain other vertices. The nucleus may or may not be equal to the elementary cell. As the graphs are b-fold symmetric, the n-th term in a cell-homologous series has in addition to a unique nucleus, b(n-1) elementary cells, i.e. n-1 cells on each branch.

An infinite graph is constructed by adding an infinite number of cells on each of the b branches ; this corresponds to the n-th term of the cell-homologous series, where $n \rightarrow \infty$.

Figure 1 represents the first three terms of two cell-homologous series which have both a one-vertex centre and the same nucleus but different cells. The first series has two branches, (b=2), two vertices and two edges in the cell ; the second series has three branches (b=3) and an elementary cell with four vertices and four edges. The numbers accompanying each vertex in the graphs of the first series are the

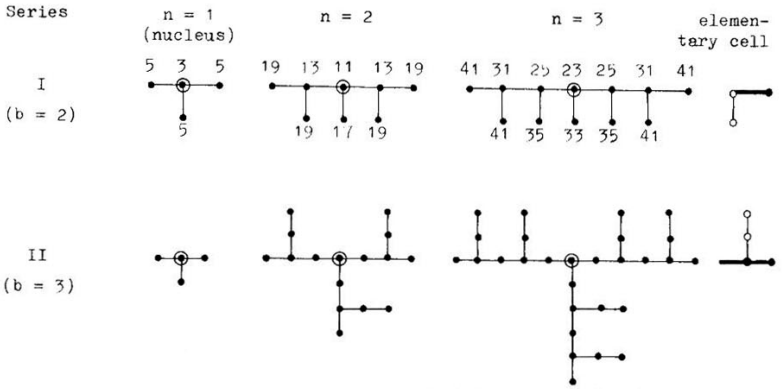


Fig. 1. Two cell-homologous series I and II, their nuclei and elementary cells.

distance sums of those vertices. In both cases of Fig. 1, each branch consists of vertices and edges which may be either on the stem or off--stem. The distinction is illustrated in the elementary cells of Fig. 1 by black points and heavy lines for the stem, and by white off-stem points and thin lines for off-stem edges.

For such series the topological index J_∞ is defined by :

$$J_\infty = \lim_{n \to \infty} J(n) \qquad (4)$$

where J(n) represents the topological index J of the n-th term in the series. In order to calculate J(n), the distance sums for each vertex of the n-th term in the series must be evaluated. The distance sum of such a vertex is expressed as a function of n and of the position of that vertex in the elementary cell.

The following example illustrates the evaluation of distance sums for the n-th term in the first series (I) shown in Fig. 1. Let us consider its n-th term represented in Fig. 2. Let s_i be the distance sum of the i-th elementary cell vertex on the stem, and s'_i the distance for the off-stem vertex in the i-th elementary cell (where i = 0 to n-1).

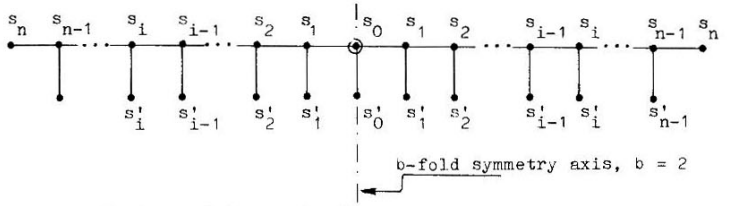


Fig. 2. The n-th term of the series I.

For a given n, The smallest distance sum of the centre vertex, $s_0(n)$, is obtained by induction. From Fig. 1, $s_0(1) = 3$; $s_0(2) = 11$; $s_0(3) = 23$; each term of the series I differs from the preceding one with two vertices on each branch, i.e. the distance sum $s_0(n)$ contains another four distances equal to n in addition to $s_0(n-1)$. Therefore, for every $n \in \mathbb{N}$:

$$s_0(n) = 3 + 4\times2 + 4\times3 + \ldots + 4\times n = 2n^2 + 2n - 1 \qquad (5)$$

One should note that the expression of $s_0(n)$ is a second degree polynomial : $s_0(n) = An^2 + Bn + C$. The distance sums $s_i(n)$ are given by the summation :

$$s_i(n) = 3\times1 + 4\times2 + 4\times3 + \ldots + 4(n-i) + 2(n-i+1) + 2(n-i+2) + \ldots$$
$$\ldots + 2(n+i) = 2n^2 + 2n - 1 + 2i^2 \quad , \qquad i = 1 \text{ to } n-1.$$

Indeed, for vertex i, there are four vertices at distances lower than or equal to n-i, but only two vertices at higher distances. The distance sums $s_i(n)$ may be expressed either using (5), or recursively :

$$s_i(n) = s_0(n) + 2i^2 \qquad (6)$$

$$s_i(n) = s_{i-1}(n) + 4i - 2 \qquad (7)$$

where i varies from 1 to n-1. Similarly, the distance sums $s'_i(n)$ for the off-stem vertices are given by the summation :

$$s'_i(n) = 1\times1 + 2\times2 + 4\times3 + \ldots + 4(n-i+1) + 2(n-i+2) + \ldots + 2(n+i+1) =$$
$$= 2n^2 + 6n - 3 + 2i^2 \quad , \text{ or using (5) :}$$

$$s'_i(n) = s_i(n) + 4n - 2 \quad ; \quad i = 1 \text{ to } n-1 \qquad (8)$$

Obviously, as seen from Fig. 2, $s'_{n-1}(n) = s_n(n)$ as distance sums of equivalent vertices.

The total number of lines in the n-th term, q(n), can be easily evaluated from the number of edges in the elementary cell and in the nucleus :

$$q(n) = 2(n-1)\times 2 + 3 = 4n - 1$$

Applying formula (2) we obtain for J(n) :

$$J(n) = (4n-1)\left[(s_0 s'_0)^{-\frac{1}{2}} + 2\sum_{i=1}^{n-1} (s_{i-1}s_i)^{-\frac{1}{2}} + 2\sum_{i=1}^{n-1} (s_i s'_i)^{-\frac{1}{2}} + 2(s_{n-1}s_n)^{-\frac{1}{2}} \right]$$

The limit of the above series, J_∞, can be obtained either by analytical integration, or by means of a program on a small calculator as an approximation of large n values. As $s_0(n)$ is a second-degree polynomial and all other terms are expressed recursively via relationships derived from $s_0(n)$, the series for J(n) is convergent.

The analytical integration is easily performed with the following simplifications : 1) The terms $(s_0 s'_0)^{-\frac{1}{2}}$ and $(s_{n-1}s_n)^{-\frac{1}{2}}$ are omitted, being insignificant for large n values ; 2) Only the homogeneous part of second order (in n and/or i) of the distance sums s_i or s'_i is retained (the homogeneous part will be denoted by a bar, e.g. $\bar{s}_i = \bar{s}_{i-1} = \bar{s}'_i = 2n^2+2i^2$); 3) The expression for the number of edges, q(n), is truncated to the first order term (i.e. 4n) since it multiplies summations of terms with an order of magnitude of n^{-2}. With these simplifications we can write :

$$J_\infty = \lim_{n\to\infty} 4n\left[2\sum_{i=1}^{n-1} (\bar{s}_{i-1}\bar{s}_i)^{-\frac{1}{2}} + 2\sum_{i=1}^{n-1} (\bar{s}_i \bar{s}'_i)^{-\frac{1}{2}} \right] = \lim_{n\to\infty} 16n \sum_{i=1}^{n-1} (2n^2+2i^2)^{-1}$$

or,
$$J_\infty = \lim_{n\to\infty} 8 \sum_{i=1}^{n-1} \frac{1/n}{(i/n)^2 + 1} \quad ; \text{ with } 1 \leqslant i \leqslant n-1.$$

As $i/n < 1$, the last expression can be converted to the definite integral :

$$J_{\infty} = 8\int_0^1 \frac{dx}{1 + x^2} = 2\pi$$

As an alternative method for the analytical integration, a computer program was devised for calculating with formulas (5) - (8) the distance sums of vertices in the n-th term of the cell-homologous series ; from these distance sums, J(n) is calculated with formula (2). Results of the calculation are presented in Table 1. One notes that J(2000) comes within 0.9992 of 2π, the analytically established value for J_{∞}.

TABLE 1. J(n) values for graphs of cell-homologous series I.

n	1	2	3	10	100	1000	2000
J(n)	2.3238	3.4642	4.0849	5.4078	6.1822	6.2729	6.2780

The procedures for obtaining J_{∞} for the cell-homologous series I of Fig. 1 can be applied to any other case. We have studied cell-homologous series for various acyclic and polycyclic graphs. In the latter case J_{∞} is 0 because μ increases linearly with n while J(n) has a finite asymptotic value. A non-vanishing, meaningful index is obtained in the case of polycyclic systems if J(n) is replaced by J'(n) defined by formula (3).

3. Asymptotic J and J' values

A general expression can be inferred for J_{∞} (or J'_{∞}). Let R be the number of edges in the elementary cell of a cell-homologous series, A - the coefficient which multiplies n^2 in the expression of $s_0(n)$, and f(b) a function whose numerical values depend only on the number b of branches. Then J_{∞} or J'_{∞} are given by formula (9) :

$$J_{\infty} \text{ or } J'_{\infty} = R^2 \cdot f(b)/A \qquad (9)$$

3.1. J_∞ for various acyclic series (infinite trees)

Let us consider an arbitrary acyclic cell-homologous series. As before, b branches emerge from the centre of the graph. An arbitrary elementary cell with R edges is constructed so that r edges are on the stem while R-r edges are off-stem (Fig. 3).

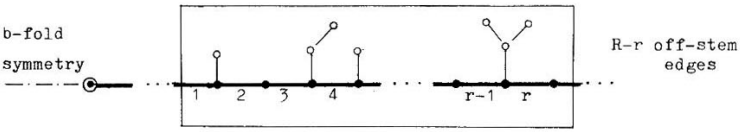


Fig. 3. Arbitrary elementary cell of an infinite tree.

It can be shown that J_∞ is independent of the way in which the off--stem vertices are disposed. For convience, we can modify all off-stem edges to become incident with the first vertex of the elementary cell (Fig. 4).

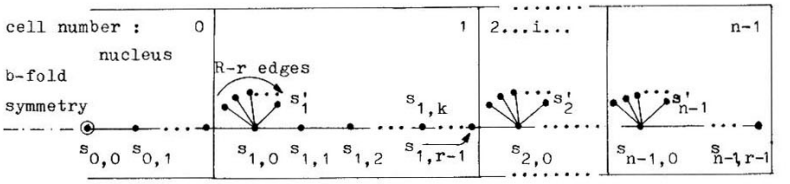


Fig. 4. The n-th term of a modified cell-homologous series.

With the notation from Fig. 4, the n-th term of the corresponding cell-homologous series has the following minimal distance sum :

$$s_{0,0} = b\times 1 + b\times 2 + \ldots + b\times r + b(R-r+1)(r+1) + b(r+2) + \ldots + b\times 2r +$$
$$+ \ldots + b(R-r+1)(nr-r+1) + b(nr-r+2) + \ldots + bnr$$

$$s_{0,0} = \frac{b}{2}\cdot Rr\cdot n^2 - \frac{b}{2}\cdot(Rr-r^2-2R+r)\cdot n - b(R-r) = An^2 + Bn + C \qquad (10)$$

The distance sums $s_{i,k}$ ($k = 0, 1, \ldots r-1$) and s'_i, where $i = 1$ to $n-1$, are expressed by means of recursive formulas similar to (7) and (8), and have as first term $s_{0,0}$. From formula (2) we obtain :

$$J(n) = \frac{q}{l}\Big[\, b \cdot \sum_{k=1}^{r} (s_{0,k-1}s_{0,k})^{-\frac{1}{2}} + b \cdot \sum_{i=1}^{n-1} \sum_{k=1}^{r} (s_{i,k-1}s_{i,k})^{-\frac{1}{2}} +$$

$$+ b(R-r) \cdot \sum_{i=1}^{n-1} (s_{i,0}s'_i)^{-\frac{1}{2}}\Big] \qquad (11)$$

One notes that as there are **r** edges on the stem, the distance sums $s_{i,r}$ and $s_{i+1,0}$ refer to the same vertex and must therefore be equal.

When evaluating J_∞ with the above formula, the same simplifications as in the case of series I can be operated : 1) The isolated terms (distance sums in the nucleus) are omitted because they are insignificant for large n values ; 2) The distance sums $s_{i,k}$ and s'_i, when expressed as recursive formulas have the same homogeneous part (denoted by $\bar{s}_i$ as it is independent of k) ; this leads to a simple evaluation of the subsidiary summings :

$$\lim_{n\to\infty} \sum_{k=1}^{r} (s_{i,k-1}s_{i,k})^{-\frac{1}{2}} = \lim_{n\to\infty} \sum_{k=1}^{r} (\bar{s}_{i,k-1}\bar{s}_{i,k})^{-\frac{1}{2}} =$$

$$= \lim_{n\to\infty} \sum_{k=1}^{r} (\bar{s}_i)^{-1} = \lim_{n\to\infty} \frac{r}{\bar{s}_i} \quad ;$$

$$\lim_{n\to\infty} \sum_{i=1}^{n-1} (s_{i,0}s'_i)^{-\frac{1}{2}} = \lim_{n\to\infty} \sum_{i=1}^{n-1} (\bar{s}_{i,0}\bar{s}'_i)^{-\frac{1}{2}} = \lim_{n\to\infty} \sum_{i=1}^{n-1} (\bar{s}_i)^{-1}$$

3) The number of lines, $q = bRn - b(R-r)$ can be truncated to $q = brn$. With these simplifications, when $n\to\infty$, formula (11) yields :

$$J_\infty = \lim_{n\to\infty} \Big\{ bRn \Big[br \cdot \sum_{i=1}^{n-1} \frac{1}{\bar{s}_i} + b(R-r) \cdot \sum_{i=1}^{n-1} \frac{1}{\bar{s}'_i} \Big] \Big\} = b^2R^2 \cdot \lim_{n\to\infty} \Big[n \cdot \sum_{i=1}^{n-1} \frac{1}{\bar{s}_i} \Big]$$

The evaluation of the distance sums after solving the recursive equations leads to the following homogenous part $\bar{s}_i$:

$$\bar{s}_i = Rr \cdot \frac{b}{2} \cdot n^2 + (b-2) \cdot ni + i^2 \qquad (12)$$

which after substitution and rearrangement yields for J_{∞} :

$$J_{\infty} = b^2 \cdot \frac{R}{r} \cdot \lim_{n \to \infty} \sum_{i=1}^{n-1} \frac{\frac{1}{n}}{\left(\frac{i}{n}\right)^2 + (b-2)\cdot\frac{i}{n} + \frac{b}{2}}$$

As $1 \leqslant i \leqslant n-1$; $\frac{i}{n} < 1$, we can write :

$$J_{\infty} = b^2 \cdot \frac{R}{r} \int_0^1 \frac{dx}{x^2 + (b-2)x + b/2} \tag{13}$$

We shall denote by f(b) the following function :

$$f(b) = \frac{b^3}{2} \int_0^1 \frac{dx}{x^2 + (b-2)x + b/2} \tag{14}$$

The function f(b) can be explicited, (15), and has numerical values (for a few integer b values) indicated in Table 2.

$$f(b) = \begin{cases} \dfrac{b^3}{2\sqrt{\frac{3b}{2} - 1 - \frac{b^2}{4}}} \operatorname{arctg} \dfrac{\sqrt{\frac{3b}{2} - 1 - \frac{b^2}{4}}}{b-1} & , \text{ for } b \in \left\{2,3,4,5\right\} \\ \dfrac{b^3}{2\sqrt{1 + \frac{b^2}{4} - \frac{3b}{2}}} \ln \left| \dfrac{b - 1 + \sqrt{1 + \frac{b^2}{4} - \frac{3b}{2}}}{b - 1 - \sqrt{1 + \frac{b^2}{4} - \frac{3b}{2}}} \right| & , \text{ for } b > 5,\ b \in \mathbb{N}. \end{cases} \tag{15}$$

TABLE 2. Values of f(b).

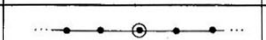
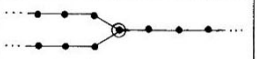
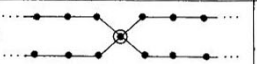
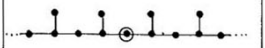
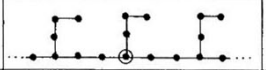
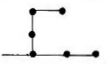
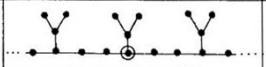
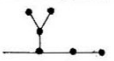
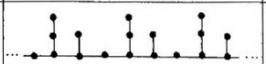
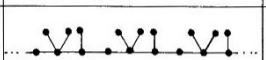
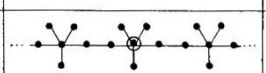
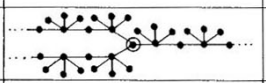
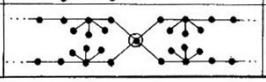
b	2	3	4	5	6	7	10	10^m
f(b)	π	6.1550	10.2960	15.5444	21.8951	29.3464	58.2976	$5.49\times10^{2m-1}$

From (10), $A = \frac{b}{2} \cdot Rr$, thus formula (13) can be obtained from the general expression (9) for J_{∞}, if f(b) is the function given by (14). It can be seen that A (and hence J_{∞}) is independent of the pattern in which the R-r off-stem edges are distributed in the elementary cell, justifying

the modification from Fig. 3 to Fig. 4.

Table 3 presents J_{∞} values for various trees.

TABLE 3. J_{∞} values for infinite trees.#

No.	Structure	Elementary cell	b	R	r	A	J_{∞}
1			2	1	1	1	π
2			3	1	1	$\frac{3}{2}$	4.1033
3			4	1	1	2	5.1480
4			2	3	2	6	$\frac{3}{2}\pi$
5			2	4	2	8	2π
6			2	6	3	18	2π
7			2	6	3	18	2π
8			2	6	3	18	2π
9			2	6	3	18	2π
10			2	6	3	18	2π
11			3	5	2	15	10.2583
12			4	6	3	36	10.2960

#It will be noted that J_{∞} is a rational multiple of π iff b = 2.

3.2. J'_{∞} expressions for polycyclic series

For graphs with an infinite number of cycles, we replace J_{∞} by J'_{∞} defined by formula (3) ; it can be shown that in this case we can still apply formula (9), where f(b) is the same as for the acyclic series, formula (14) ; b represents the number of branches emerging from the centre of the dualist graph.

For linear infinite polycyclic graphs (b=2), J'_{∞} values correspond to rational multiples of π, since $f(2) = 4\text{arctg}(1) = \pi$. Table 4 presents J'_{∞} values for various polycyclic series. Formula (9) is applicable to almost any structure. Once the elementary cell is identified and the expression for $s_0(n)$ is calculated, one can obtain directly J'_{∞}. For instance, an infinite linear polymantane (Fig. 5) with a zig-zag dualist graph,[12] has a 12-line elementary cell. In such a two-branch system (b=2), one obtains by induction that $s_0(n) = 16n^2 - 4n - 1$. According to formula (9) : $J'_{\infty} = \frac{144}{16}\pi = 9\pi$. A computer program which calculates J'(n), for n = 1500 yielded J'(1500) = 28.25501, a value within 0.9993 of 9π .

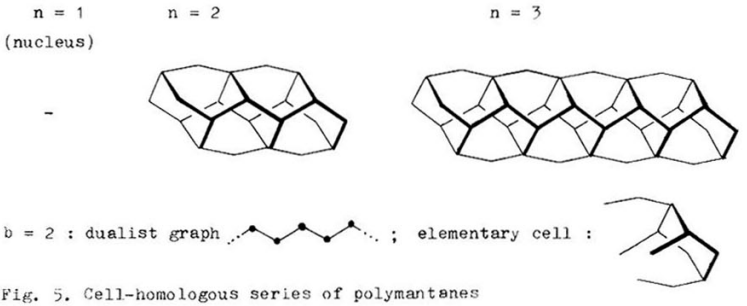


Fig. 5. Cell-homologous series of polymantanes

Unlike the acyclic series, for the polycyclic series, the coefficient A of n^2 in the expression of $s_0(n)$, is dependent on the pattern, i.e. the mode in which the vertices in the elementary cell are disposed.

TABLE 4. J_{∞} values of various polycyclic series.

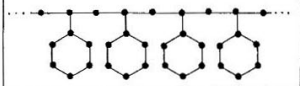
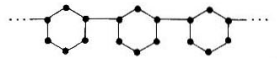
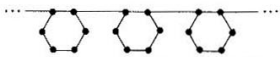
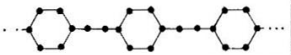
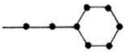
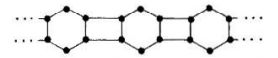
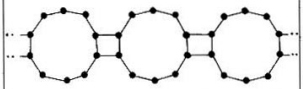
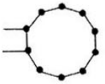
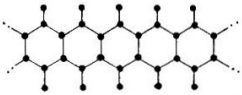
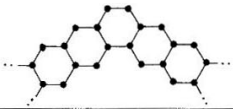
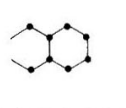
No.	Structure	Elementary cell	b	R	A	J_{∞}
1			2	9	16	$\frac{81}{16}\pi$
2			2	7	24	$\frac{49}{24}\pi$
3			2	7	18	$\frac{49}{18}\pi$
4			2	7	12	$\frac{49}{12}\pi$
5			2	9	48	$\frac{81}{48}\pi$
6			2	8	18	$\frac{64}{18}\pi$
7			2	10	32	$\frac{100}{32}\pi$
8			2	12	50	$\frac{144}{50}\pi$
9			2	7	12	$\frac{49}{12}\pi$
10			2	5	8	$\frac{25}{8}\pi$
11			2	10	28	$\frac{100}{28}\pi$

Table 4 (continued).

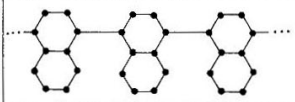
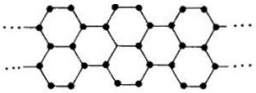
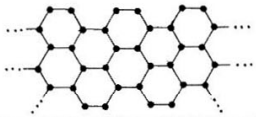
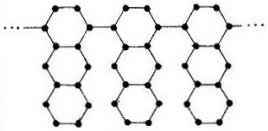
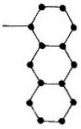
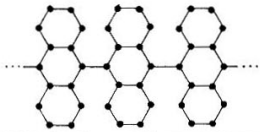
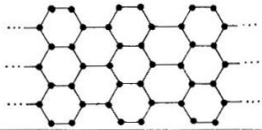
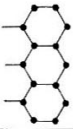
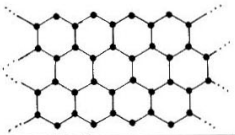
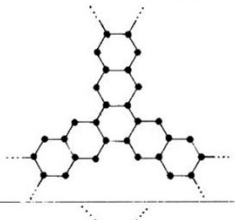
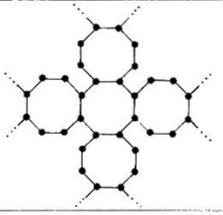
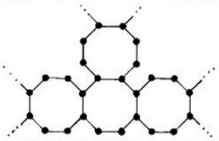
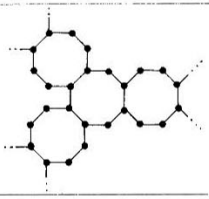
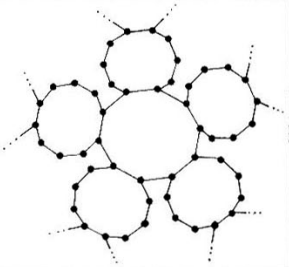
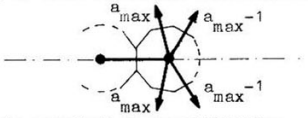
No.	Structure	Elementary cell	b	R	A	Ψ_∞
12			2	12	40	$\frac{144}{40}\pi$
13			2	13	40	$\frac{169}{40}\pi$
14			2	8	12	$\frac{64}{12}\pi$
15			2	8	12	$\frac{64}{12}\pi$
16			2	17	56	$\frac{289}{56}\pi$
17			2	17	56	$\frac{289}{56}\pi$
18			2	19	56	$\frac{361}{56}\pi$
19			2	11	16	$\frac{121}{16}\pi$

Table 4 (continued).

No.	Structure	Elem. cell	b	R	A	I_∞
20			3	5	12	12.8229
21			4	7	36	14.0140
22			3	7	27	11.1702
23			3	7	27	11.1702
24			5	9	80	15.7387

This dependency of A on the disposition of vertices in the elementary cell can be exemplified for linearly cata-condensed polycyclic graphs with cycles of the same size.

For such linearly cata-condensed systems (b=2), if g is the ring size, there exist g-3 annelation possibilities because the end-ring in a string of cata-condensed g-membered rings has g-3 free edges on which it can be cata-annelated. Coefficient A is dependent upon this annelation pattern. In order to describe this dependency we introduce two parameters : (i) The annelation angle parameter, a, defined by means of the dualist graph of two adjacent cycles in the system. Parameter a takes integer values between 0 and $\lceil \frac{g-3}{2} \rceil$ and increases as the angle in the dualist graph[11] decreases from 180^{o} towards 0^{o}, e.g. for 6-membered rings (g=6), a can be 0 or $\lceil 1.5 \rceil = 1$.‡ Linear annelation, which corresponds to a=0, is possible only with even-membered rings, as shown in Fig. 6. For infinite systems a regular annelation pattern must exist : the simplest is the one in which the angle of the dualist graph is constant, i.e. parameter a is constant. This, in turn, corresponds to two possibilities : compounded and alternate annelation. The former case leads to helix-like structures, while the latter case leads to zig-zag structures. This annelation regularity is described by a second parameter, (ii) helicity, h, which is 1 for helix-like annelation and 0 for zig-zag annelation. Figure 7 represents the first three terms of helix and zig-zag series defined by a nonlinear annelation with a=1, for graphs consisting of cata-condensed six-membered rings.



$$a_{max} = \lceil \frac{g-3}{2} \rceil$$

Fig. 6. Cata-annelation possibilities.

‡ $\lceil x \rceil$ denotes the integer part of x.

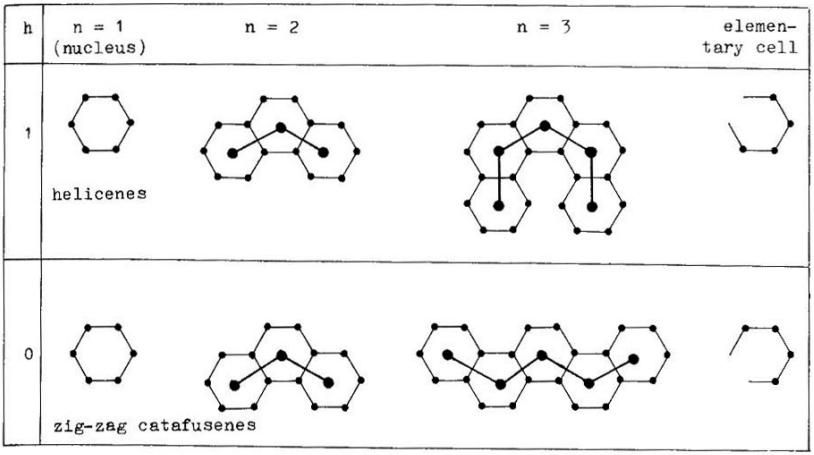


Fig. 7. Two cell-homologous series for b=2 ; g=6 ; a=1.

For convenience, linear annelation is considered helix like (a=0, implies h=1), not zig-zag like. As seen from fig. 6, the g-3 annelation directions are divided into two symmetrical sets because a_{max} appears twice ; there exist a total of g-3 regular annelation possibilities because of helix or zig-zag annelations.

Induction leads to the following expressions for the coefficient of n^2 in $s_0(n)$:

$$A = \left(\left\lceil \frac{g+1}{2} \right\rceil - a - h \right) \cdot (g-2) \qquad (16)$$

The above formula is not valid for odd g = 2k+1 values, of the first zig-zag annelation possibility (h=0, a=1). In this case :

$$A = \frac{(g-2)^2}{2} \quad , \text{ for } a = 1 \; ; \; h = 0 \; ; \; g = 2k+1. \qquad (17)$$

ψ_∞' values for polycyclic systems with two branches are presented in Table 5. These values can be obtained directly by substituting A from (16) or (17) into the general formula (9).

TABLE 5. $\mathcal{J}_{\infty}$ values for polycyclic linearly cata-condensed series (b = 2).

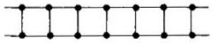
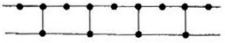
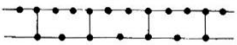
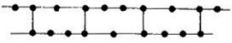
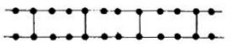
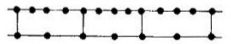
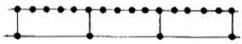
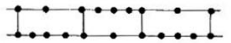
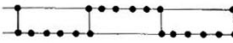
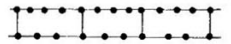
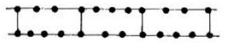
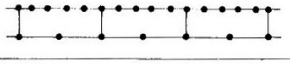
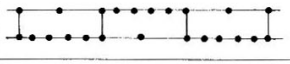
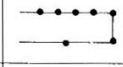
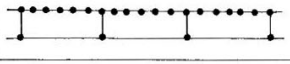
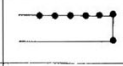
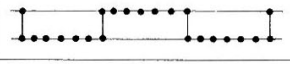
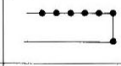
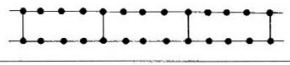
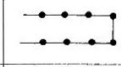
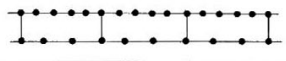
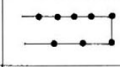
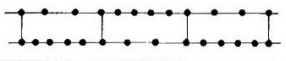
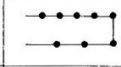
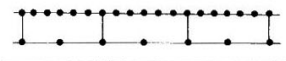
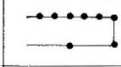
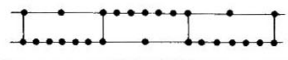
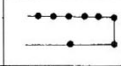
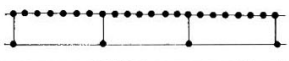
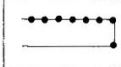
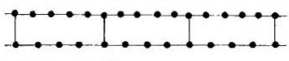
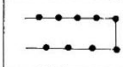
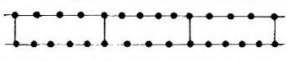
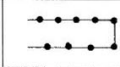
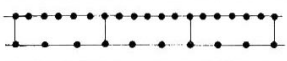
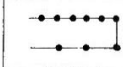
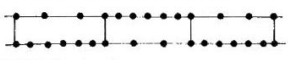
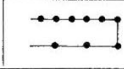
No.	Structure	Elementary cell	R	A	g	a	h	$\mathcal{J}_{\infty}$
1			3	2	4	0	1	$\frac{9}{2}\pi$
2			4	3	5	1	1	$\frac{16}{3}\pi$
3			4	$\frac{9}{2}$	5	1	0	$\frac{32}{9}\pi$
4			5	8	6	0	1	$\frac{25}{8}\pi$
5			5	4	6	1	1	$\frac{25}{4}\pi$
6			5	8	6	1	0	$\frac{25}{8}\pi$
7			6	5	7	2	1	$\frac{36}{5}\pi$
8			6	10	7	1	1	$\frac{36}{10}\pi$
9			6	$\frac{25}{2}$	7	1	0	$\frac{72}{25}\pi$
10			6	10	7	2	0	$\frac{36}{10}\pi$
11			7	18	8	0	1	$\frac{49}{18}\pi$
12			7	12	8	1	1	$\frac{49}{12}\pi$
13			7	6	8	2	1	$\frac{49}{6}\pi$
14			7	18	8	1	0	$\frac{49}{18}\pi$
15			7	12	8	2	0	$\frac{49}{12}\pi$
16			8	21	9	1	1	$\frac{64}{21}\pi$
17			8	$\frac{49}{2}$	9	1	0	$\frac{128}{49}\pi$

Table 5 (continued).

No.	Structure	Elem. cell	R	A	g	a	h	ψ_∞
18			8	14	9	2	1	$\frac{64}{14}\pi$
19			8	21	9	2	0	$\frac{64}{21}\pi$
20			8	7	9	3	1	$\frac{64}{7}\pi$
21			8	14	9	3	0	$\frac{64}{14}\pi$
22			9	32	10	0	1	$\frac{81}{32}\pi$
23			9	24	10	1	1	$\frac{81}{24}\pi$
24			9	32	10	1	0	$\frac{81}{32}\pi$
25			9	16	10	2	1	$\frac{81}{16}\pi$
26			9	24	10	2	0	$\frac{81}{24}\pi$
27			9	8	10	3	1	$\frac{81}{8}\pi$
28			9	16	10	3	0	$\frac{81}{16}\pi$
29			10	36	11	1	1	$\frac{100}{36}\pi$
30			10	$\frac{81}{2}$	11	1	0	$\frac{200}{81}\pi$
31			10	27	11	2	1	$\frac{100}{27}\pi$
32			10	36	11	2	0	$\frac{100}{36}\pi$

3.3. Topological index J for infinite acyclic and monocyclic multigraphs

There exist two alternative definitions of J for multigraphs, which will be denoted by A and B, and discussed separately.

Definition A. Distance sums are obtained normally, disregarding the presence of multiple bonds. In chains having double or triple bonds, each edge is treated independently in formula (2). The final summation therefore includes for each double bond twice, and for each triple bond thrice the product $(s_i s_j)^{-\frac{1}{2}}$; accordingly, in counting the total number q of edges, each double bond is counted as two edges, and each triple bond is counted as three edges. In short one can consider in this definition a double bond as a 2-membered ring, and a triple bond as a [0,0,0] bicyclic system. The drawback of this definition is that in aromatic systems a single conventional Kekule structure must be considered, e.g. naphthalene gives two different J indices according to its Kekule structures.

Definition B.[9] An older definition of J for multigraphs ascribes to single bonds, delocalized aromatic bonds, double bonds and triple bonds, bond orders BO = 1, 1.5, 2, and 3, respectively. Then the distance sums are calculated ascribing to the topological distance between two adjacent vertices the value d = 1/BO. Finally, formula (2) is applied ; in calculating q, a multiple bond is counted as a single bond irrespective of its multiplicity. Thus, whereas in definition A topological distances are integers, in definition B these distances are rational multiples of 1/BO.

By means of a simple computer program[9] one may obtain easily the asymptotic value for an infinitely long conjugated polyene ($J_\infty = \frac{4}{3}\pi$) and for an infinitely long conjugated polyyne ($J_\infty = \frac{3}{2}\pi$) or infinite cumulene ($J_\infty = 2\pi$) ; in the latter two cases, it may be seen that also this definition leads to different J values for two limiting electronic structures (this is, however, an isolated case).

Cycloalkanes with even number m of carbon atoms have for each carbon

atom the distance sum $m^2/4$, hence J(m) = 2.0000 irrespective of m ; when the cycloalkane is odd-membered, 2.0000 is the asymptotic value for infinite size.

Delocalized m[annulenes] (monocyclic multigraphs) with bond order 2/3 between adjacent carbons have for each carbon atom the distance sum $m^2/6$, hence J(m) = 3.0000 irrespective of the ring size (definition B). In definition A, the distance sum is the same as for the cycloalkane but the number of lines is 3m/2, therefore J(m) = 4.5000 irrespective of m.

An infinite cyclic cumulene has, in definition B, the bond order between adjacent carbons equal to 0.5, leading to a distance sum $m^2/8$ for all carbon atoms, therefore to J(m) = 4 irrespective of m. However, for the polyacetylenic limiting structure of the same molecule, the distance sum is $m^2/6$, therefore J(m) = 3. In definition A, the distance sum is the same as for the cycloalkane but the number of lines is 2m, therefore J(m) = 8 irrespective of m and of the limiting structure. Such a cyclic polyacetylene or cumulene would actually be an allotropic form of elemental carbon ("cyclocarbyne").

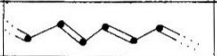
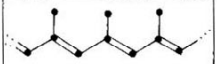
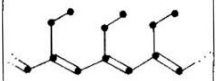
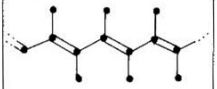
Table 6 presents the values of the topological index J_∞ for several infinite acyclic multigraphs, using both definitions A and B for J.

It may be seen that in all cases definition A leads to larger J_∞ values than definition B. The general formula (9) is valid for all infinite graphs and can be applied for obtaining J_∞ using either definition. Although the elementary cell is the same for a given multigraph, in definition A all edges are counted independently ; in definition B the number of lines in the elementary cell, R, is smaller because multiple bonds are counted as single bonds. In Table 6, the coefficient A of n^2 in the expression of s_0 was calculated according to the two definitions resulting in different values for A for one and the same graph. In both definitions exemplified by Table 6 the graph has a linear stem : the number of branches in formula (9) is b = 2, hence f(b) = π so that J_∞

is a rational multiple of π .

We illustrate by the last two infinite graphs in Table 6 the fact that the distribution pattern of off-stem vertices in the elementary cell of acyclic series does not affect the value of J_∞.

TABLE 6. J_∞ values for infinite acyclic multigraphs.

No.	Structure	Elem. cell	Definition A			Definition B		
			R	A	J_∞	R	A	J_∞
1			3	4	$\frac{9}{4}\pi$	2	3	$\frac{4}{3}\pi$
2			4	4	$\frac{16}{4}\pi$	2	2	$\frac{4}{2}\pi$
3			4	4	$\frac{16}{4}\pi$	2	$\frac{8}{3}$	$\frac{12}{8}\pi$
4			4	6	$\frac{16}{6}\pi$	3	$\frac{9}{2}$	$\frac{18}{9}\pi$
5			5	8	$\frac{25}{8}\pi$	4	6	$\frac{16}{6}\pi$
6			5	8	$\frac{25}{8}\pi$	4	6	$\frac{16}{6}\pi$

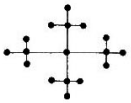
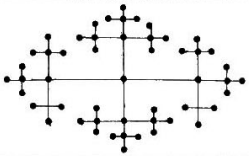
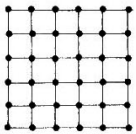
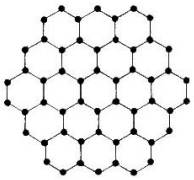
3.4. Checking the numerical asymptotic values of J (or J')

All J_∞ (or J'_∞) values listed in Tables 3-6 were checked by computing J(n) or J'(n) with $n \geqslant 1000$ by means of a program on a HP-97 calculator. These calculated values came at least within 0.9990 of J_∞ (or J'_∞) for all structures. The calculations showed in all cases a relatively rapid convergence towards the asymtotic value.

4. Infinite graphs with infinite J and J' indices

When $s_0(n)$ is a polynomial of degree higher than two, divergent J(n) series are obtained. This is the case of infinitely branched trees and of infinite lattices. Table 7 presents a few examples of infinite graphs with infinite J or J' values. One notes that formula (9) can no longer be applied since either b or R depends on n, therefore there exists no constant elementary cell. For trees with an infinite number of branches emerging from a nucleus ($b \longrightarrow \infty$), as shown by Table 2, f(b) diverges leading also to an infinite J_∞ value.

TABLE 7. Cell-homologous series with infinite J_∞ or J'_∞ values.

$s_0(n)$	n = 1	n = 2	n = 3
$3[2^n(n-1) + 1]$			
$3^n(2n-1) + 1$			
$4n^3$			
$8n^3 + n$			

5. Conclusions

The topological index J (or alternatively, index J' for graphs containing cycles) of infinite graphs with regular patterns may tend asymptotically towards finite values. Thus J of infinite trees having a nucleus from which b branches emerge (each branch possessing elementary cells repeated ad infinitum) was shown to have the expression (9) which via (10) and (14) leads to the equivalent expression (13). For graphs with an infinite number of cycles, J' is also given by formula (9). There exist, however, both cyclic and acyclic infinite graphs for which J' and J, respectively, are infinite.

The present data were obtained by analytical integration and checked by computer programs. The asymptotic results presented here may be used for correlations with properties of polymers. Recently, several such correlations using Wiener topological index extrapolations within the Hückel approximation,[13] or using PPP calculations[14] were published by Bonchev, Mekenyan and Polansky.

Notation

A = coefficient of n^2 in the expression of s_0

a = annelation angle parameter

b = number of branches which emerge from the nucleus of the graph

BO = bond order

d = topological distance

f(b) = a function of the number of branches

h = indicator variable for helicity

m = total number of vertices (points) in a graph

N = set of natural numbers

n = the serial number of a term in a cell-homologous series

O = centre of a graph

q = total number of edges (lines) in a graph

R = number of edges in the elementary cell

r = number of edges on the stem of a branch

$s_0(n)$ = the smallest distance sum of the n-th term in a cell-homologous series

s_i = distance sum of vertex i

s'_i = distance sum of off-stem vertex i

$\bar{s}_i$ = homogeneous part relative to n and to the running index i of s_i

TI = topological index

μ = cyclomatic number

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