

MATHEMATICAL MODELS OF BRANCHING

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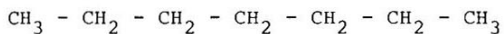
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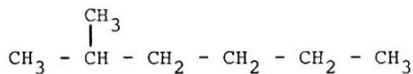
Introduction

Many properties of molecules and molecular assemblies depend largely on the degree of skeletal branching¹. These include molecular properties like viscosity, surface tension, refractive index, boiling point, density, volume, vapour pressure coefficient, heat of combustion, residual entropy of ice problem, chromatographic retention index, etc.

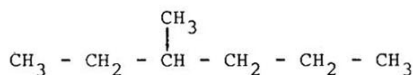
Example:



heptane (b.p. 98.4⁰C)



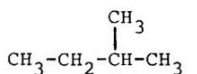
2-methyl-hexane (b.p. 90.1⁰C)



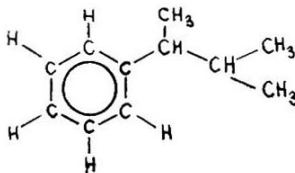
3-methyl-hexane (b.p. 91.9⁰C)

The aim of the present work is to discuss various mathematical models, based on the theory of graphs², proposed for studying molecular branching. Branching is an intuitive concept not uniquely defined³, though there have been attempts to define it rigorously⁴. Branching in a molecular graph⁵ is identified through the appearance of the branched vertices. Branched vertices have valencies (degrees)⁶ with values three and higher. Examples of branched hydrocarbons and their corresponding molecular graphs⁷ are given below (branched vertices are denoted by black circles).

MOLECULAR FORMULAE

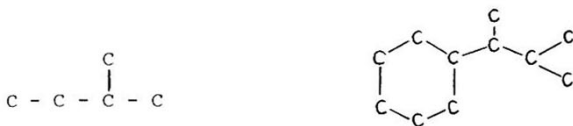


2-methyl-butane

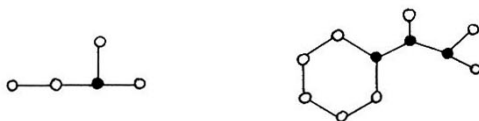


1-phenyl-1,2,2-trimethyl-ethane

HYDROGEN-SUPPRESSED STRUCTURES



MOLECULAR GRAPHS



Most of the proposed mathematical (graph-theoretical) models for characterizing molecular branching are related either to the vertex adjacency relationship (connectivity) in a graph or to the topological distances in a graph. In another words, the information about the molecular branching is contained, respectively, in the adjacency, \underline{A} , and distance, \underline{D} , matrices of a graph⁸.

Models based on connectivity

The molecular connectivity is well reflected in the adjacency matrix of the graph G , $\underline{A}(G)$. The elements of $\underline{A}(G)$ are of the type $A_{ii}=0$, $A_{ij}=1$ (if there is a connection between the ver-

tices i and j), and $A_{ij}=0$ (otherwise). The sum of non-zero entries in the row of the adjacency matrix specifies the degree (valency), D_j , of a particular vertex in the graph G . The sum of all D_j 's is equal twice the number of edges (bonds), v , in G : $\sum_j D_j = 2v$. This result (often called the handshaking lemma) was already known to Euler (1736)⁹. There is a relationship according to the theorem of Fröbenius¹⁰, between the eigenvalues of the adjacency matrix and the maximal degree D_{\max} of a vertex in G . The interval in which the eigenvalues of a graph, x_j ($j=1,2,\dots,N$), lie is limited: $-D_{\max} \leq x_j \leq D_{\max}$.

Models for characterization of molecular branching based on the atom-atom connectivity are founded either on the total sum of some combination of degrees of the adjacent vertices or on the properties of the graph spectrum of a molecule. Several of these will be reviewed below roughly in the order of their historical development:

(1) In the early work on π -electron energy by the Zagreb Group¹¹ two terms appeared in the topological formula for the energy which may be used to represent the branching of the graph¹²:

$$M_1(G) = \sum_{j=1}^N D_j^2 \quad (1)$$

$$M_2(G) = \sum_{\text{edges}} D_i D_j \quad (2)$$

The first sum is over all vertices of G and the second one over all edges in G .

(2) Randić's connectivity index¹³, $\chi_R(G)$, has a form similar to the above indices, though it was obtained after the search for the specific index to characterize branching of acyclic saturated hydrocarbons unlike indices $M_1(G)$ and $M_2(G)$ which resulted from studies on the π -energy of conjugated systems:

$$\chi_R(G) = \sum_{\text{edges}} (D_i D_j)^{-\frac{1}{2}} \quad (3)$$

The summation is over all edges in the graph G.

Randić has used his index for correlations with boiling points and enthalpies of formation of alkane isomers from C₅ to C₈ atoms, with Kováts empirical branching index¹⁴, derived from chromatographic retention data of isomeric alkanes¹⁵ from C₅ to C₈ atoms, with theoretically calculated total surface area of selected saturated acyclic hydrocarbons based on the model of Hermann¹⁶, etc.

The connectivity index χ_R is later used by Randić, Kier and co-workers^{1,17} in their studies on anaesthetics. These research workers¹⁸ have also generalized the connectivity index by considering a path of a length L instead of an edge in the graph,

$$\chi_R^L(G) = \sum_{\text{paths}} (D_i D_j \dots D_{L+1})^{-\frac{1}{2}} \quad (4)$$

where D_i, D_j, \dots, D_{L+1} are the degrees of vertices in the considered path L. An edge is a path of length one. In addition, in the same work it was shown that χ_R^L can be obtained from the L-th po-

wer of the adjacency matrix, i.e., $\underline{\underline{A}}^L$. This index was used for density correlations.

(3) Several authors^{12,19,20} have observed that there is a relationship between the maximal eigenvalue of a tree and branching. However, Cvetković and Gutman²¹ were the first to show that the largest element of the graph spectrum, x_1 , is closely related to the total number of walks²² $W(L)$ in the graph,

$$W(L) = N(x_1)^L \quad (5)$$

where N is the number of vertices in a tree.

Eq. (5) is derived in the following way²¹. The relation:

$$W_{pq}(L) = (\underline{\underline{A}}^L)_{pq} \quad (6)$$

represents a relationship between the number of walks and the adjacency matrix². The total number of walks of length L , $W(L)$, in the graph is given by,

$$W(L) = \sum_{p=1}^N \sum_{q=1}^N W_{pq}(L) \quad (7)$$

Using the relations²³,

$$\underline{\underline{C}}_j \underline{\underline{A}} = x_j \underline{\underline{C}}_j; \quad j = 1, 2, \dots, N \quad (8)$$

and

$$\underline{\underline{C}} \underline{\underline{A}}^L \underline{\underline{C}}^T = \text{diag} \quad (x_1)^L, (x_2)^L, \dots, (x_N)^L \quad (9)$$

eq. (6) reads as,

$$v_{pq}^{(L)} = \sum_{j=1}^N (x_j)^L C_{jp} C_{jq} \quad (10)$$

By introducing eq. (10) into (7) the following relation for the total number of walks is obtained,

$$W(L) = \sum_{j=1}^N \sum_{p=1}^N (x_j)^L C_{jp}^2 \quad (11)$$

The eigenvectors of a regular graph²⁵ have the interesting property,

$$\sum_{p=1}^N C_{jp} = \begin{cases} \sqrt{N} & \text{if } j=1 \\ 0 & \text{if } j>1 \end{cases} \quad (12)$$

This result and the use of the Fröbenius theorem ($D_{\text{Max}}=x_1$) leads to the simple expression for the total number of walks in the graph G,

$$W(L) = N D_{\text{Max}}^L = N(x_1)^L \quad (13)$$

For non-regular graphs formula (5) is valid.

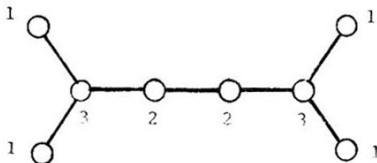
Since x_1 can be interpreted as a certain kind of mean vertex degree²⁷ it correlates nicely with any properly defined measure of branching.

(4) In this area an interesting criterion has been proposed by Gutman and Randić⁴. These authors have used the algebraic con-

cept of comparability of functions, introduced many years ago by Muirhead²⁸, in order to discuss the concept of branching. Two functions $F_1 = F_1(v_1, v_2, \dots, v_L)$ and $F_2 = F_2(v_1, v_2, \dots, v_L)$ are said to be comparable if there is an inequality between them, $F_1 \geq F_2$ or $F_1 \leq F_2$, valid for all values of the variables v_i from a given interval²⁹. A special class of such functions of many variables of particular interest are $v_1^{a_1}, v_2^{a_2}, \dots, v_L^{a_L}$, where a_i are non-negative integers. These functions may be considered as configurations defined on the set v_i , where the parameters a_i define a particular population. For such functions Muirhead defined a relative order considering conditions,

$$a'_1 + a'_2 + \dots + a'_i \geq a_1 + a_2 + \dots + a_i \quad \text{and}$$

$a'_1 + a'_2 + \dots + a'_L = a_1 + a_2 + \dots + a_L$, where L is the number of variables and $1 < i < L$. These conditions mean that only configurations with the same overall population can be compared. The a_i 's are ordered in a non-increasing series, $a_i > a_{i+1}$ for all i . This approach can be directly applied to the concept of branching and ordering structures. The variables v_i may be thought of as degrees of the vertices and a_i the frequency of their occurrence. For example, the structure



the symbolic representation as $3^2 2^2 1^4$. However, this is not a unique representation, because four more structures have the same

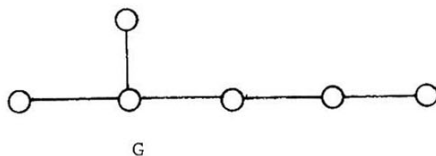
symbols. This approach may be of some use in coding structures³⁰.

(5) Hosoya's Z index³¹ has at first sight no relationship with the other models based on the adjacency matrix. Z index is defined as follows,

$$Z(G) = \sum_{k=0}^m p(G;k) \quad (14)$$

where $p(G;k)$ is the number of ways in which k edges may be selected in such a manner that two of them are never connected, whereas m is the maximum number of k for G .

Example



$$p(G;0) = 1 \text{ (per definitionem)}$$

$$p(G;1) = 5$$

$$p(G;2) = 5$$

$$Z(G) = 11$$

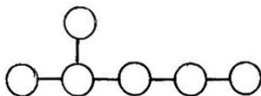
However, for chain molecules (tree graphs, T) the Z index is closely related to the characteristic polynomial, $P(T;x)$, derived from the adjacency matrix,

$$P(T;x) = \sum_{k=0}^m p(T;k) x^{N-2k} = \det \left| \underline{x} \underline{1} - \underline{A} \right| \quad (16)$$

where $\underline{1}$ is unit matrix. This relation makes it possible to obtain

the Z index as the sum of the absolute values of the coefficients in the characteristic polynomial $(P(T;x) = \sum_{n=0}^N a_n x^{N-n})$.

Example



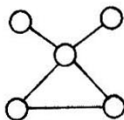
T

$$P(T;x) = x^6 - 5x^4 + 5x^2$$

$$Z(G) = 11$$

Hosoya has applied his index to cyclic structures, the extension being straightforward.

Example



G

m=2

$$p(G;0) = 1$$

$$p(G;1) = 5$$

$$p(G;2) = 2$$

$$Z(G) = 8$$

Hosoya and co-workers correlated the Z-index with boiling points and entropies.³¹⁻³³ This index was also used for coding chemical structures in the computer-oriented chemical documentation³⁴. In addition, Z-indices of acyclic and cyclic structures are available in the form of tables^{35,36}.

Models based on distances

The distance matrix of the graph G , $\underline{D}(G)$, contains information on distances in G . $\underline{D}(G)$ consists of elements $D_{ij}(G)$ which represent the length of the shortest paths between i -th and j -th vertices of G . All elements of the type $D_{ii}(G)$ are, by definition, zero. The distance matrix is related to adjacency matrix by the relation³⁷:

$$\underline{D}(G) = \underline{A}(G) + \sum \underline{B}(G) \quad (17)$$

where $\underline{B}(G)$ are topological matrices containing only those non-zero entries which represent the shortest paths between the second, third, etc., neighbours.

Very early models which appeared for characterizing molecular branching were based on distance matrix albeit these early authors were not aware of this fact.

Here we summarize some of the models based on distances in a graph:

(1) Wiener³⁸ in his studies on additive physical parameters of hydrocarbons introduced a path number W which is defined as the sum of the distances between any two carbon atoms in the molecule in terms of carbon-carbon bonds. We call this path number the Wiener number of the graph, $W(G)$. It can be shown that the Wiener number is equal to half the sum of the off-diagonal elements of the distance matrix,

$$W(G) = \frac{1}{2} \sum_{(i,j)} D_{ij}(G) \quad (18)$$

Wiener has also introduced a polarity number, $P(G)$, which is equal to the number of pairs of vertices separated by three bonds. The Wiener number was used for correlations with boiling points, heats of formation, heats of vaporization, molecular volume, and molecular refraction for alkanes^{38,39}.

Recently we have applied the Wiener number to acyclic⁴⁰ and cyclic structures^{41,42}, and made an extensive study about its validity for characterization of molecular branching and cyclicity^{41,43}.

(2) Platt³⁹ was also interested in additive bond properties of paraffins. He introduced an index $F(G)$ resulting from considering the first neighbours; for each edge the number of adjacent edges is calculated and then these numbers are summed for all edges to give $F(G)$. Therefore, $F(G)$ represents the first neighbours sum.

The Platt index $F(G)$ is related to the Gordon and Scantlebury index⁴⁴ of graph, $S(G)$. The index $S(G)$ is equal to the number of distinct ways in which the C_3 acyclic fragment may be embedded on the skeleton of a given molecule. It can be shown that that the $S(G)$ index is equal to half the value of $F(G)$,

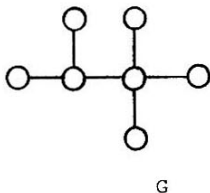
$$S(G) = \frac{1}{2} F(G) \quad (19)$$

(3) Altenburg⁴⁵ proposed a polynomial,

$$Al(G;a) = \sum_{j=1}^N n_j a_j \quad (20)$$

for characterization of a given carbon skeleton. In the above equation n_j stands for the number of pairs of atoms whose distance is j .

Example

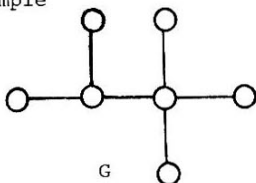


$$Al(G;a) = 6a_1 + 9a_2 + 6a_3$$

The Altenburg polynomial $Al(G;a)$ can be related to the Wiener number $W(G)$ if a_j 's are substituted by j -values ($j=1,2,\dots,N$). Then the Wiener number is simply obtained by multiplying n_j with j ,

$$W(G) = \sum_{j=1}^N j n_j \quad (21)$$

Example



$$Al(G;a) = 6a_1 + 9a_2 + 6a_3$$

$$a_1; \quad j=1$$

$$a_2; \quad j=2$$

$$a_3; \quad j=3$$

$$W(G) = 6 \times 1 + 9 \times 2 + 6 \times 3 = 42$$

(4) Hosoya and co-workers⁴⁶ introduced the distances polynomial of a graph, $D(G;x)$, for characterization of various structures. The distance polynomial is defined as follows,

$$D(G;x) = \det \left| x \underset{\sim}{I} - \underset{\sim}{D} \right| = \sum_{n=0}^N a_n x^{N-n} \quad (22)$$

The first two coefficients of $D(G;x)$ are, respectively, $a_0=1$ and $a_1=0$. This result allows the presentation of distance polynomial in somewhat different form,

$$D(G;x) = x^N - \sum_{n=2}^N a_n x^{N-n} \quad (23)$$

These authors have proposed several rules for direct construction of the distance polynomial instead of going through the expansion of the distance matrix in the form of a secular determinant.

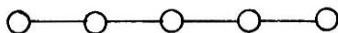
For example, the coefficients a_n ($n=2,3,\dots,N$) for linear acyclic structures may be evaluated using the following expression,

$$a_n = 2^{n-2} (n-1) \frac{N^2(N^2-1^2)(N^2-2^2)\dots [N^2-(n-1)^2]}{n^2(n^2-1^2)(n^2-2^2)\dots [n^2-(n-1)^2]} \dots \quad (24)$$

In addition, the a_N coefficient is given by,

$$a_N = - 2^{N-2} (N-1) \quad (25)$$

Example



G

$$a_2 = \frac{5^2(5^2-1^2)}{2^2(2^2-1^2)} = 50$$

$$a_3 = 2 \times 2 \frac{5^2(5^2-1^2)(5^2-2^2)}{3^2(3^2-1^2)(3^2-2^2)} = 140$$

$$a_4 = 4 \times 3 \frac{5^2(5^2-1^2)(5^2-2^2)(5^2-3^2)}{4^2(4^2-1^2)(4^2-2^2)(4^2-3^2)} = 120$$

$$a_5 = 2^3 \times 4 = 32$$

$$D(G; x) = x^5 - 50x^3 - 140x^2 - 120x - 32$$

(5) Rouvray⁴⁷ has proposed an index, which is the sum of all off-diagonal elements of the distance matrix,

$$R(G) = \sum_{(i,j)} D_{ij}(G) \quad (26)$$

He has applied this index to the thermodynamic properties of alkanes. However, the Rouvray's index is equal to a double Wiener number of a graph,

$$R(G) = 2W(G) \quad (27)$$

(6) We introduced⁴⁰ a topological index called the information on distances in the graph G , $I_D(G)$, obtained by considering all the elements of the distance matrix as the elements of a finite probability scheme associated with the graph G . A certain distance denoted by j ($1 \leq j \leq N-1$) appears $2k_j$ times in the distance matrix. All N^2 elements of $\underline{D}(G)$ can be partitioned into $n+1$ groups (n is the highest value of j). The $n+1$ group contains only diagonal elements of $\underline{D}(G)$ ($2k_j=N$), which are, of course, all equal to zero. Thus the statistical analysis of the distance matrix on the basis of information theory⁴⁸ and taking into account that the distance matrix of a graph is symmetric matrix with the consequence that the upper triangle of it preserves all the information about the corresponding system, leads to the relation,

$$I_D(G) = \frac{N(N-1)}{2} \log_2 \frac{N(N-1)}{2} - \sum_{j=1}^n k_j \log_2 k_j \quad (28)$$

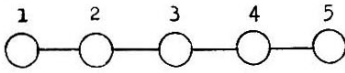
where n is the number of different sets of matrix elements and $\frac{N(N-1)}{2}$ is the total number of upper off-diagonal elements in $\underline{D}(G)$. The logarithm is taken at basis 2 for measuring the information content in bits. This index is an easily calculable quantity and can be used as a structural index for characterizing branching of molecular skeleton⁴⁰⁻⁴². It is applied for correlation with the chromatograph retention indices of monoalkyl- and dialkyl-benzenes⁴².

Eq. (28) can be normalized by dividing $I_D(G)$ with $\frac{N(N-1)}{2}$.

The index thus obtained represents the mean value of the information on distances in the graph G , $\bar{I}_D(G)$,

$$\bar{I}_D = - \sum_{j=1}^n \frac{2k_j}{N(N-1)} \log_2 \frac{2k_j}{N(N-1)} \quad (29)$$

Example



G

$$D(G) = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 \\ 1 & 0 & 1 & 2 & 3 \\ 2 & 1 & 0 & 1 & 2 \\ 3 & 2 & 1 & 0 & 1 \\ 4 & 3 & 2 & 1 & 0 \end{bmatrix}$$

$$j = 1, 2, 3, 4$$

$$k_j = 4, 3, 2, 1$$

$$\frac{2k_j}{N(N-1)} = 0.4, 0.3, 0.2, 0.1$$

$$I_D(G) = 18.4644$$

$$\bar{I}_D(G) = 1.8464$$

Comparison between the branching indices

As an illustrative example the Table contains comparisons between the various branching indices evaluated for the isomeric tree graphs with seven vertices shown in Fig.1. The compared indices are $M_1(G)$, $M_2(G)$, the Randić connectivity index $\chi_R(G)$, the greatest eigenvalue of the characteristic polynomial $x_1(G)$, the Hosoya $Z(G)$ index, the Wiener number $W(G)$, the Platt index $F(G)$, the Gordon-Scantlebury index $S(G)$, and the information index $I_D(G)$. An inspection of the Table indicates that for the eleven isomeric trees with $N=7$ the greatest sensitivity to branching is shown by the Hosoya index, the Randić index and the information index. Other investigated topological indices often have the same value for the different graphs. Thus, $M_1(G)$ index is the same for two pairs (nos. 4,7 and 6,8) and one triplet (Nos. 2,3,5) of trees, $M_2(G)$ gives two identical pairs (Nos.4,5 and 6,7), $x_1(G)$ one pair (Nos. 4,5), the Wiener number two pairs of trees (Nos. 4,5 and 6,7), $F(G)$ and $S(G)$ two pairs (Nos. 4,7 and 6,8) and one triplet (Nos. 2,3,5) and finally the Rouvray index gives two identical pairs (Nos. 4,5 and 6,7). Similar results are achieved as expected by the Wiener number and the Rouvray index and by the Platt and Gordon-Scantlebury indices.

An interesting observation is that $M_1(G)$, $F(G)$ and $S(G)$ indices have shown the same behaviour. It appears that $M_1(G)$ is re-

Table

Branching indices of all tree graphs having seven vertices

Graph*	$M_1(G)$	$M_2(G)$	$\chi_R(G)$	$x_1(G)$	$z(G)$	$w(G)$	$F(G)$	$S(G)$	$R(G)$	$I_D(G)$
1	22	20	3.4142	1.848	21	56	10	5	112	50.3644
2	24	22	3.2700	1.932	18	52	12	6	104	46.4642
3	24	23	3.3081	1.970	19	50	12	6	100	44.8546
4	26	24	3.1251	2.000	15	48	14	7	96	41.0774
5	24	24	3.3461	2.000	20	48	12	6	96	40.9544
6	28	26	3.0607	2.101	14	46	16	8	92	39.9740
7	26	26	3.1807	2.053	17	46	14	7	92	39.5676
8	28	28	3.1213	2.136	16	44	16	8	88	37.2191
9	30	30	2.9432	2.175	13	42	18	9	84	32.6898
10	34	32	2.8121	2.288	11	40	22	11	80	30.6752
11	42	36	2.4495	2.449	7	36	30	15	72	18.1255

* Numbers correspond to the isomeric trees with seven vertices given in Fig. 1.

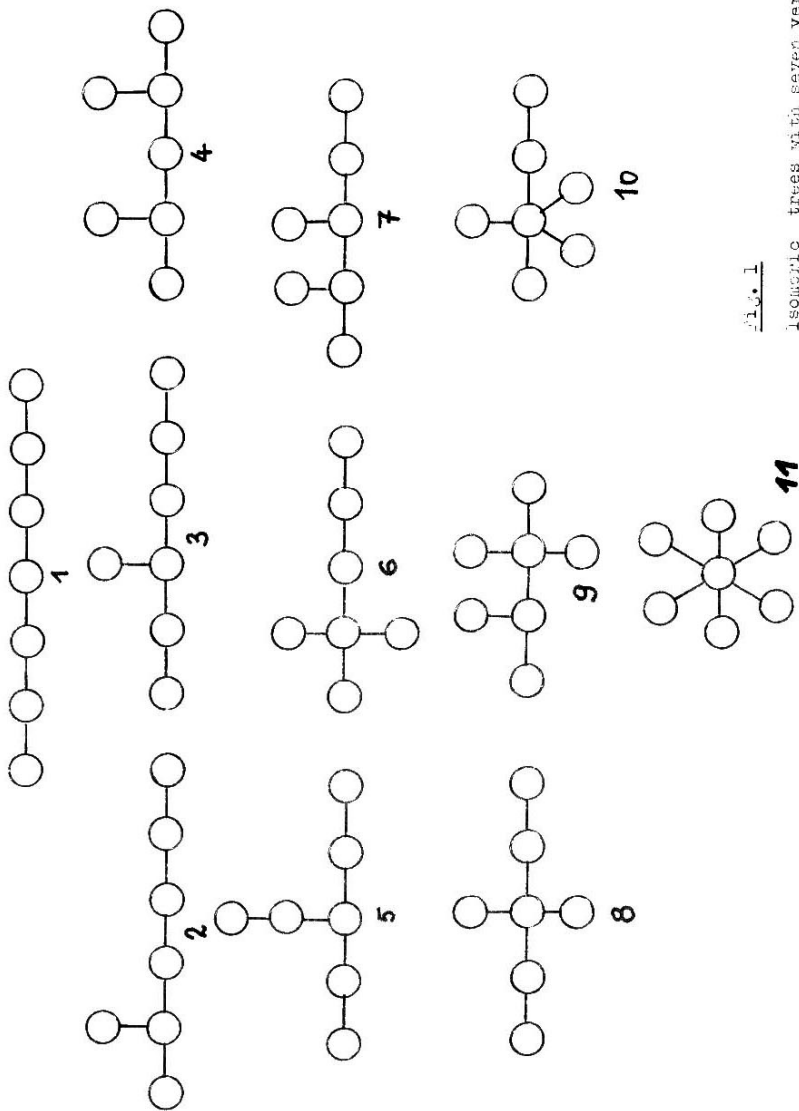


Fig. 1

ISOMORPHIC TREES WITH SEVEN VERTICES

lated to $F(G)$ (and consequently to $S(G)$) by a simple equation,

$$M_1(G) = F(G) + \sum_{j=1}^N D_j \quad (30)$$

or

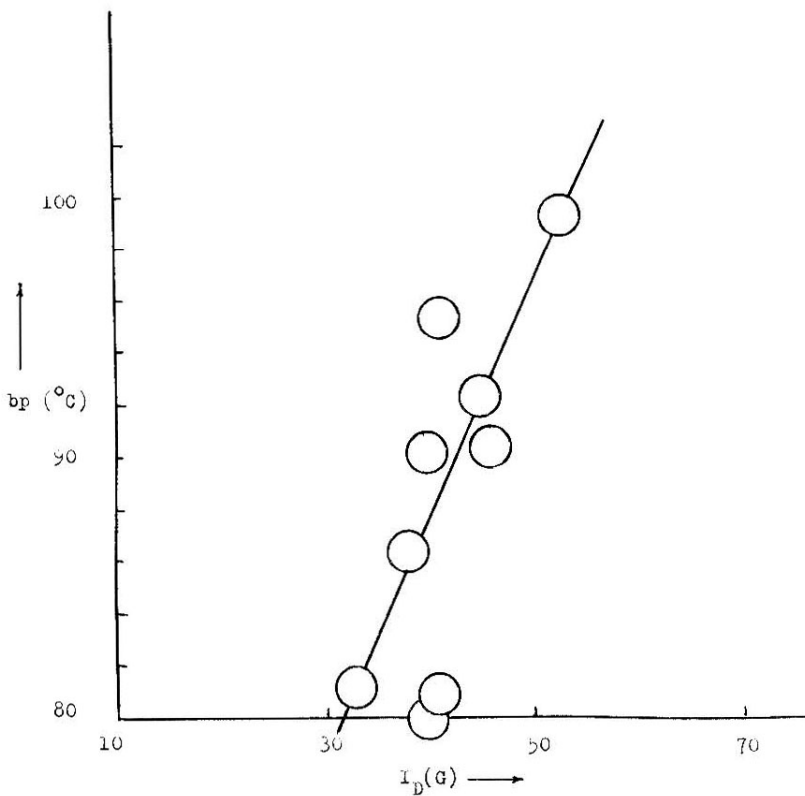
$$M_1(G) = F(G) + 2v \quad (31).$$

Extensive application of all topological indices reviewed in this work has been carried out for acyclic^{40,49} and cyclic structures^{41,42,50}. The information index $I_D(G)$ proved to have in all cases investigated a considerable greater capability of discriminating isomeric structures than any other index.

In fig.2. we gave a plot of $bp(^{\circ}C)$ vs. $I_D(G)$ for 9 isomeric alkanes with seven carbon atoms. There is a fair correlation between the boiling points (observables) and the branching indices $I_D(G)$ (nonobservable mathematical quantities) of these structures. Work in this area is in progress⁵⁰.

Fig. 2

A plot of boiling points, bp ($^{\circ}\text{C}$), vs. the information index, $I_D(\text{G})$, for nine isomeric alkanes with seven carbon atoms



Conclusion

Various mathematical models of branching in the framework of graph theory are presented and compared on a limited sample of isomeric trees. However, even for this rather small number of investigated structures most of the studied indices failed to distinguish uniquely all the isomers. Most promising of all topological indices presented in this work appears to be the information index obtained from the distance matrix of a graph. However, more research is needed before it can be established that the information index always differentiates between isomeric structures.

Acknowledgement

One of us (N.T.) was supported in part by National Science Foundation grant No. F6F006Y.

References and Notes

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22. A walk² of the length L in a graph is sequence of L+1 vertices and L edges, $v_1, e_1, v_2, e_2, \dots, v_L, e_L, v_{L+1}$, such that the edge e_j is incident to the vertices v_j and v_{j+1} ($j=1, 2, \dots, L$).
23. The eigenvalues x_j and the eigenvectors $\underline{C}_j = (C_{j1}, C_{j2}, \dots, C_{jN})$ of the graph G fulfil the relation²⁴ $\underline{C}_j \underline{A} = x_j \underline{C}_j$ ($j=1, 2, \dots, N$). Since \underline{A} is a symmetric matrix, its eigenvalues and eigenvectors are real. These eigenvalues form the elements of the graph spectrum and are usually ordered in non-increasing order: $x_1 \gg x_2 \gg \dots \gg x_N$. The orthogonal matrix $\underline{C} = (\underline{C}_1, \underline{C}_2, \dots, \underline{C}_N)^T$ has, hence, the property, $\underline{C} \underline{A} \underline{C}^T = \text{diag}(x_1, x_2, \dots, x_N)$, from which follows eq. (9).
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