

Investigation of Alkane Branching (and Resulting Partial Ordering) by Topological Indices

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A topological index is a structural descriptor (derived from the molecular graph) that represents an efficient way to express in a numerical form the molecular size, shape, cyclicity, and branching. Using a large variety of mathematical equations, the structural information encoded into the molecular graph is transformed into local (atomic) and global (molecular) descriptors. As a result of the considerable interest for structural descriptors, new topological indices were recently defined and used in modeling physical, chemical, or biological properties. The molecular branching of heptanes and octanes is characterized with these new descriptors and the properties of the partial ordering of alkanes induced by each topological index is analyzed. The advantages and limitations of each partial ordering of alkane isomers are highlighted.

Introduction

Numerous attempts have been made in theoretical chemistry to express in a numerical form the chemical structure with structural descriptors from various classes, such as constitutional, graph-theoretical, topological, geometrical, electrostatic and quantum descriptors. Such structural descriptors, usually used in quantitative structure-property relationship (QSPR) and quantitative structure-activity relationship (QSAR) models to compute physical, chemical, or biological properties, can be interpreted as measures of the molecular size, shape, branching, cyclicity, or electron distribution.

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Each structural descriptor emphasizes different structural characteristics of chemical compounds and organizes them on a numerical scale, providing a simple and useful tool for ordering molecules. Obviously, different descriptors induce different orderings, each numerical scale offering a partial view of the chemical structure. The whole process that offers partially ordered chemical structures is the basis of the quantitative interpretation of the paradigm that molecular properties are determined by the chemical structure.

The concept of partially ordered structures has a much larger relevance for chemistry,^{1,2} but in this paper we consider the characterization of molecular branching by topological indices. Topological indices (TIs) represent a class of structural descriptors derived from the molecular graph. In the graph representation of molecules the geometrical features, such as bond lengths or bond angles, are not considered and the chemical bonding of atoms is regarded as being their most important characteristic. In molecular graphs vertices correspond to atoms and edges represent covalent bonds between atoms. Using various mathematical formulas, numerous TIs were proposed to measure the molecular shape and branching.³⁻¹⁶ Graph theory is widely used in deriving branching rules and theoretical models for ordering chemical structures.¹⁷⁻²⁸ The majority of these studies consider alkanes as the model compounds for devising branching rules, because they are devoid of the influence of heteroatoms and multiple bonds.

As a result of the interest for structural descriptors, new topological indices were recently defined and used in QSPR and QSAR models. In the present study we use some of these new TIs to investigate the partial ordering of heptanes and octanes. The way in which the chemical structure is encoded into a TI determines the usefulness of that TI in devising structure-property models. The advantages and limitations of each TI in establishing a partial ordering of alkane isomers are emphasized.

Method

The theory of molecular graphs and the computation of topological indices are presented in numerous review articles,²⁹⁻⁴⁴ in order to make the paper more coherent, we will present here the definitions of some graph operators recently introduced for the computation of families of topological indices, derived with the same mathematical formula from different molecular matrices.

Because alkanes represent a convenient model to study the partial ordering induced by different TIs, we have selected heptanes and octanes to investigate how the molecular branching is reflected by the new TIs. Bertz studied the same two sets of alkanes and established an order in which branching increases in the two series of isomers.²⁶ The approach proposed by Bertz comprises a mathematical process based on some axioms and theorems that define the graph complexity in an objective way. The first axiom is applied whenever the addition of a vertex to a graph can be made in several ways, resulting in a family of isomeric graphs. This axiom is based on the fact that the order of branching at a vertex is determined by the degree of that vertex.

Axiom 1. Of two graphs derived by the addition of a vertex or group of vertices to a given graph, the one in which the new vertex or group has been affixed to the precursor vertex with the higher degree is the more branched.

The first theorem states that whenever two graphs are joined together with an edge the resulting graph is more branched than the two initial graphs:

Theorem 1. If an additional vertex or group of vertices is affixed to a graph, the resulting graph is more branched.

The second theorem has been assumed in all studies concerning branching in molecular graphs:

Theorem 2. The linear graph is the least-branched member of a family of isomeric graphs.

With the aid of Axiom 1, one can demonstrate that the third theorem, which determines the most branched graph from a family of isomers, is true:

Theorem 3. The n -star, $K_{1,n}$, is the most highly branched isomer of the graphs with $n + 1$ vertices.

Bertz proposed also a branching index, which is consistent with Axiom 1, and permits the ranking of graphs according to their branching. The branching index for the fused graph M obtained from a graph R with branching index B_R and a graph S with branching index B_S by joining with an edge two atoms from R and S , respectively, with degrees (before branching) r and s is: $B_M = B_R + B_S + r + s$.

The fourth theorem permits a simple calculation of the branching index B of a graph without having to decompose it into simpler graphs with known values for B :

Theorem 4. The branching index B_M of a graph M is equal to the number of pairs of adjacent edges in M , provided that for a vertex $B_M = 0$:

$$B_M = \frac{1}{2} \sum_{i=1}^N \text{deg}_i (\text{deg}_i - 1)$$

where deg_i is the degree of the vertex v_i .

There are many pairs of isomers which have identical branching indices and cannot be ordered using Axiom 1 or Theorem 4, thus generating only a partial order. To order all trees, Axiom 2 discriminates non-isomorphic graphs by repeatedly computing the branching indices of their line graphs or derivative graphs:

Axiom 2. Pairs of graphs are ordered by comparing the sequences of branching indices obtained by counting the number of edges in the iterated line graphs so that the one which ultimately has the highest branching index is the more branched.

This axiom uses the property that the number of pairs of adjacent edges in a graph is equal to the number of edges in its line graph. The rigorous mathematical derivation of the branching order of graphs with the above axioms and theorems has clear advantages when compared with other widely used to compare and order molecules according to their branching. The largest eigenvalue of the characteristic polynomial, proposed by Lovász and Pelikán,⁸ is of limited usefulness, since there are many non-isomorphic graphs with identical spectral radius. The same drawback applies to all topological indices and other graph invariants proposed as branching measures, which can induce only a partial order whenever for two or more non-isomorphic graphs they present degenerate (identical) values.

Other procedures used to order molecular graphs are based on the use of Muirhead and Kamarata theorems for comparing structures.^{18,19} This approach can be applied to any TI or graph invariant, giving results that depend on the particular graph invariant. Moreover, a number of graphs remain non-comparable, thus inducing only a partial order.

Due to its obvious advantages and straightforward mathematical definition, in our investigation we adopt the order proposed by Bertz and we will investigate how a specific TI varies with increasing branching of alkanes. The nine heptanes are considered in the following order:

1 <i>n</i> -heptane	2 2-methylhexane	3 3-methylhexane
4 2,4-dimethylpentane	5 3-ethylpentane	6 2,3-dimethylpentane
7 2,2-dimethylpentane	8 3,3-dimethylpentane	9 2,2,3-trimethylbutane

The order of increasing branching of the 18 octanes, as proposed by Bertz, is:

10 <i>n</i> -octane	11 2-methylheptane	12 2,5-dimethylhexane
13 3-methylheptane	14 4-methylheptane	15 2,4-dimethylhexane
16 3-ethylhexane	17 2,3-dimethylhexane	18 3,4-dimethylhexane
19 3-ethyl-2-methylpentane	20 2,3,4-trimethylpentane	21 2,2-dimethylhexane
22 2,2,4-trimethylpentane	23 3,3-dimethylhexane	24 3-ethyl-3-methylpentane
25 2,2,3-trimethylpentane	26 2,3,3-trimethylpentane	27 2,2,3,3-tetramethylbutane

In the following sections we investigate the branching properties and the partial ordering of heptanes and octanes induced by several novel TIs; several TIs previously introduced as branching measures will be also presented for comparison purposes.

The Graph Spectrum Indices $\text{MinSp}(\mathbf{M})$ and $\text{MaxSp}(\mathbf{M})$

The matrix spectrum operator $\text{Sp}(\mathbf{M}, G) = \{x_i, i = 1, 2, \dots, N\}$ represents the eigenvalues of the matrix \mathbf{M} or the roots of the polynomial $\text{Ch}(\mathbf{M}, G, x)$, i.e. $\text{Ch}(\mathbf{M}, G, x) = 0$. The spectral operators $\text{MinSp}(\mathbf{M}, G)$ and $\text{MaxSp}(\mathbf{M}, G)$ are equal to the minimum and maximum values of $\text{Sp}(\mathbf{M}, G)$, respectively:⁴⁵

$$\text{MinSp}(\mathbf{M}, G) = \min\{\text{Sp}(\mathbf{M}, G)\} \quad (1)$$

$$\text{MaxSp}(\mathbf{M}, G) = \max\{\text{Sp}(\mathbf{M}, G)\} \quad (2)$$

Molecular graph descriptors computed with these two spectral operators were used with success in QSPR studies to compute the boiling points, heat of vaporization, molar refraction, molar volume, critical pressure, critical temperature, and surface tension of alkanes,^{46,47} to estimate the boiling points of acyclic compounds containing oxygen or sulfur atoms,⁴⁸ and to model the amine boiling points.⁴⁹ It is interesting to note that the BCUT descriptors,⁵⁰⁻⁵³ used in combinatorial chemistry, virtual screening, and diversity measure, are computed with the same formula as the MinSp and MaxSp operators, using different molecular matrices; the BCUT topological indices are based on Burden's (B) modified adjacency matrix⁴ validated by the Chemical Abstracts Service (C) as a similarity searching method and extended by Pearlman at the University of Texas (UT). Lovász and Pelikán demonstrated that the largest eigenvalue (spectral radius) $\text{MaxSp}(\mathbf{A}, G)$ of the adjacency matrix of the graph G reflects the graph branching.⁸

The values of the spectral indices MinSp and MaxSp computed from the adjacency \mathbf{A} , distance \mathbf{D} , and reciprocal distance⁵⁵⁻⁵⁸ \mathbf{RD} matrices for the nine alkanes with seven carbon atoms are presented in Table 1 (since for alkanes $\text{MinSp}(\mathbf{A}, G) = -\text{MaxSp}(\mathbf{A}, G)$, only the MaxSp index is given for the adjacency matrix). For the nine heptane isomers, the values of the $\text{MaxSp}(\mathbf{A}, G)$ index increases with branching; the least branched is *n*-heptane, $\text{MaxSp}(\mathbf{A}, 1) = 1.84776$, and the most branched is 2,2,3-trimethylbutane, $\text{MaxSp}(\mathbf{A}, 9) = 2.17533$. A degenerate value for this index is found in this small collection of heptane isomers, where $\text{MaxSp}(\mathbf{A}, 4) = \text{MaxSp}(\mathbf{A}, 5) = 2$, showing that $\text{MaxSp}(\mathbf{A}, G)$ is not a very selective branching index. In the case of $\text{MinSp}(\mathbf{D})$, one observes an increase with branching

for heptanes 1-4, followed by an ordering that differs from that proposed by Bertz; a degenerate pair of heptanes is found in Table 1 for this index, namely $\text{MinSp}(\mathbf{D},5) = \text{MinSp}(\mathbf{D},8) = -5.23607$. The index $\text{MaxSp}(\mathbf{D})$ decreases with the increase of heptane branching, with two inversions for the pairs (4, 5) and (6, 7). The values of the index $\text{MinSp}(\mathbf{RD})$ decrease exactly with the increasing branching order, without degenerate values or inversions; the least branched is *n*-heptane, $\text{MinSp}(\mathbf{RD},1) = -1.34311$, and the most branched is 2,2,3-trimethylbutane, $\text{MinSp}(\mathbf{RD},9) = -1.45807$. The values of $\text{MaxSp}(\mathbf{RD})$ increase with the increasing branching order with an inversion for the pair (4, 5).

Table 1. The graph spectrum indices $\text{MaxSp}(\mathbf{A})$, $\text{MinSp}(\mathbf{D})$, $\text{MaxSp}(\mathbf{D})$, $\text{MinSp}(\mathbf{RD})$, and $\text{MaxSp}(\mathbf{RD})$ for the alkanes with seven carbon atoms 1-9.

<i>G</i>	$\text{MaxSp}(\mathbf{A})$	$\text{MinSp}(\mathbf{D})$	$\text{MaxSp}(\mathbf{D})$	$\text{MinSp}(\mathbf{RD})$	$\text{MaxSp}(\mathbf{RD})$
1	1.84776	-10.09783	16.62538	-1.34311	3.25530
2	1.93185	-8.89317	15.40477	-1.37268	3.36485
3	1.96962	-7.69291	14.86358	-1.38805	3.41768
4	2.00000	-7.46410	14.17597	-1.39003	3.47637
5	2.00000	-5.23607	14.29695	-1.40120	3.46724
6	2.05288	-6.22265	13.63462	-1.41948	3.54053
7	2.10100	-6.82455	13.63526	-1.42336	3.56628
8	2.13578	-5.23607	13.06981	-1.44250	3.62569
9	2.17533	-5.02789	12.39448	-1.45807	3.69539

Table 2. The graph spectrum indices $\text{MaxSp}(\mathbf{A})$, $\text{MinSp}(\mathbf{D})$, $\text{MaxSp}(\mathbf{D})$, $\text{MinSp}(\mathbf{RD})$, and $\text{MaxSp}(\mathbf{RD})$ for the alkanes with eight carbon atoms 10-27.

<i>G</i>	$\text{MaxSp}(\mathbf{A})$	$\text{MinSp}(\mathbf{D})$	$\text{MaxSp}(\mathbf{D})$	$\text{MinSp}(\mathbf{RD})$	$\text{MaxSp}(\mathbf{RD})$
10	1.87939	-13.13707	21.83635	-1.35275	3.51238
11	1.94986	-12.01667	20.47922	-1.37659	3.61219
12	2.00000	-10.72999	19.11148	-1.39514	3.71089
13	1.98904	-10.75351	19.76280	-1.39344	3.67019
14	2.00000	-10.09783	19.54202	-1.39521	3.68911
15	2.04208	-9.35977	18.39644	-1.40652	3.77365
16	2.02852	-8.23539	18.77877	-1.40806	3.74205
17	2.07431	-8.95139	18.18148	-1.42457	3.80437
18	2.09529	-7.97186	17.67587	-1.43195	3.84559
19	2.10100	-6.53114	17.41874	-1.43301	3.86113
20	2.13578	-7.46410	16.80790	-1.44362	3.92034
21	2.11199	-9.96804	18.41326	-1.42756	3.80913
22	2.14896	-8.40425	17.03382	-1.43258	3.91287
23	2.15664	-7.91899	17.44265	-1.44596	3.89524
24	2.18890	-5.23607	16.67049	-1.46144	3.96009
25	2.20595	-6.95518	16.31517	-1.46521	3.99367
26	2.22158	-6.27701	16.06828	-1.47329	4.01941
27	2.30278	-5.64575	14.93725	-1.50000	4.14575

The partial orderings of the octane isomers **10-27** according to the values of graph spectrum indices **MaxSp(A)**, **MinSp(D)**, **MaxSp(D)**, **MinSp(RD)**, and **MaxSp(RD)** are presented in Table 2. The values of the **MaxSp(A)** index for the 18 octanes varies between that of *n*-octane, **MaxSp(A,10)** = 1.87939, and that of 2,2,3,3-tetramethylbutane, **MaxSp(A,27)** = 2.30278, exhibiting an increase with the increase of molecular branching; however, three inversions from the Bertz order are observed for the pairs (12, 13), (15, 16) and (20, 21). A degenerate value appears for 2,5-dimethylhexane and 4-methylheptane, **MaxSp(A,12)** = **MaxSp(A,14)** = 2. In general, **MinSp(RD)** decreases and **MaxSp(RD)** increases with the increasing branching order, but both present several inversions. A less apparent order is offered by **MinSp(D)** and **MaxSp(D)** indices.

The Hosoya Operator **Ho(M)**

The characteristic polynomial operator **Ch(M,G,x)** represents the characteristic polynomial of the matrix **M** = **M(G)** for a molecular graph *G* with *N* vertices:⁴⁵

$$\mathbf{Ch}(\mathbf{M}, G, x) = \det(x\mathbf{I} - \mathbf{M}(G)) = \sum_{n=0}^N c_n x^{N-n} \quad (3)$$

where **I** is the unit matrix of order *N*, and *c_n* is the *n*th coefficient of the characteristic polynomial. The Hosoya operator **Ho(M)** = **Ho(M,G)** is defined as the sum of the absolute values for the coefficients *c_n* of the characteristic polynomial of the matrix **M**:⁴⁵

$$\mathbf{Ho}(\mathbf{M}, G) = \sum_{n=0}^N |c_n| \quad (4)$$

When *G* is an acyclic graph and **M** is the adjacency matrix **A**, the **Ho(M)** index is identical to the Hosoya index *Z*.⁷ The values of the Hosoya indices **Ho** computed from the adjacency **A**, Chi χ ,⁵⁹ distance **D**, and reciprocal distance **RD** matrices for the nine heptane isomers are presented in Table 3. While **Ho(A)** and **Ho(D)** are indices with integer values, **Ho(χ)** and **Ho(RD)** have real values. The partial orderings of heptanes induced by the Hosoya indices **Ho(A)**, **Ho(χ)**, and **Ho(RD)** is not in line with the branching of alkanes. The values of **Ho(D)** decrease with the increasing branching with an inversion for the pair (4, 5). An inspection of the Hosoya indices from Table 3 shows that there is no degenerate value for heptanes.

The partial orderings of the octane isomers **10-27** according to the values of Hosoya indices **Ho(A)**, **Ho(χ)**, **Ho(D)**, and **Ho(RD)** are presented in Table 4. An inspection of the values of **Ho(A)** shows that the index is fairly degenerate in the set of octane isomers, with **Ho(A,21)** = **Ho(A,26)** = 23, **Ho(A,12)** = **Ho(A,23)** = 25, **Ho(A,19)** = **Ho(A,24)** = 28, and **Ho(A,11)** = **Ho(A,18)** = 29. Again, the variation of **Ho(A)**, **Ho(χ)**, and **Ho(RD)** with branching is not evident, while **Ho(D)** decreases with the increasing branching, but several differences from the Bertz order can be observed.

Noteworthy is the fact that unlike other indices where the minimal and maximal values coincide with the Bertz ordering, **Ho(RD)** values and to a smaller measure also **Ho(χ)** values are scattered among the alkane isomers, and do not follow a logical trend with only a few reversions of this ordering. Thus, compounds **4** and **7** among heptane isomers, and compound **22** among octane isomers have extremal values; these compounds have a particular structural feature, namely tertiary-butyl groups at the end(s) of linear chains.

Table 3. The Hosoya indices **Ho(A)**, **Ho(χ)**, **Ho(D)**, and **Ho(RD)** for the alkanes with seven carbon atoms 1-9.

<i>G</i>	Ho(A)	Ho(χ)	Ho(D)	Ho(RD)
1	21	4.37500	7669	32.01818
2	18	3.83333	6917	31.49106
3	19	4.16667	6789	29.54228
4	15	3.33333	6203	33.89429
5	20	4.50000	6657	28.28271
6	17	3.77778	6041	31.52951
7	14	3.25000	5807	34.39337
8	16	3.75000	5645	32.02860
9	13	3.00000	5105	35.16667

Table 4. The Hosoya indices **Ho(A)**, **Ho(χ)**, **Ho(D)**, and **Ho(RD)** for the alkanes with eight carbon atoms 10-27.

<i>G</i>	Ho(A)	Ho(χ)	Ho(D)	Ho(RD)
10	34	5.28125	34049	53.68894
11	29	4.62500	31028	55.87946
12	25	4.05556	28181	57.59097
13	31	5.04167	30513	48.78107
14	30	4.95833	30424	44.93234
15	26	4.38889	27656	51.51395
16	32	5.37500	29889	42.93301
17	27	4.50000	27413	48.93445
18	29	4.94444	26969	46.44002
19	28	4.83333	26864	44.50488
20	24	4.07407	24572	51.15278
21	23	3.93750	26516	57.27768
22	19	3.41667	23897	59.76157
23	25	4.43750	25748	48.74943
24	28	5.06250	25049	44.24243
25	22	3.91667	23168	51.56988
26	23	4.08333	22925	48.83931
27	17	3.12500	19685	55.53516

The Wiener Operator **Wi(M)**

The Wiener operator **Wi(M)** = **Wi(M,G)** of a molecular graph *G* with *N* vertices is computed from the symmetric $N \times N$ molecular matrix **M** = **M(G)**:

$$\mathbf{Wi}(\mathbf{M}, G) = \sum_{i=1}^N \sum_{j=i}^N [\mathbf{M}(G)]_{ij} \tag{5}$$

When the molecular graph matrix \mathbf{M} is the distance matrix \mathbf{D} the operator is identical with the Wiener index W ,³⁻⁶ whereas when \mathbf{M} is the reciprocal distance matrix \mathbf{RD} , this operator becomes the *RDSUM* index.⁵⁸

Table 5. The Wiener indices $\mathbf{Wi(D)}$ and $\mathbf{Wi(RD)}$, and connectivity indices ${}^0\chi$, ${}^1\chi$, and ${}^2\chi$ for the alkanes with seven carbon atoms 1-9.

G	$\mathbf{Wi(D)}$	$\mathbf{Wi(RD)}$	${}^0\chi$	${}^1\chi$	${}^2\chi$
1	56	11.15000	5.53553	3.41421	2.06066
2	52	11.48333	5.69867	3.27006	2.53608
3	50	11.61667	5.69867	3.30806	2.30210
4	48	11.83333	5.86181	3.12590	3.02340
5	48	11.75000	5.69867	3.34607	2.09077
6	46	12.00000	5.86181	3.18074	2.62955
7	46	12.08333	5.91421	3.06066	3.31066
8	44	12.25000	5.91421	3.12132	2.87132
9	42	12.50000	6.07735	2.94338	3.52073

Table 6. The Wiener indices $\mathbf{Wi(D)}$ and $\mathbf{Wi(RD)}$, and connectivity indices ${}^0\chi$, ${}^1\chi$, and ${}^2\chi$ for the alkanes with eight carbon atoms 10-27.

G	$\mathbf{Wi(D)}$	$\mathbf{Wi(RD)}$	${}^0\chi$	${}^1\chi$	${}^2\chi$
10	84	13.74286	6.24264	3.91421	2.41421
11	79	14.10000	6.40578	3.77006	2.88963
12	74	14.46667	6.56891	3.62590	3.36504
13	76	14.26667	6.40578	3.80806	2.65565
14	75	14.31667	6.40578	3.80806	2.68252
15	71	14.65000	6.56891	3.66390	3.14297
16	72	14.48333	6.40578	3.84607	2.47120
17	70	14.73333	6.56891	3.68074	3.00998
18	68	14.86667	6.56891	3.71874	2.77106
19	67	14.91667	6.56891	3.71874	2.82059
20	65	15.16667	6.73205	3.55342	3.34715
21	71	14.76667	6.62132	3.56066	3.66421
22	66	15.16667	6.78446	3.41650	4.15863
23	67	15.03333	6.62132	3.62132	3.26777
24	64	15.25000	6.62132	3.68198	2.87132
25	63	15.41667	6.78446	3.48138	3.67532
26	62	15.50000	6.78446	3.50404	3.49684
27	58	16.00000	7.00000	3.25000	4.50000

Table 5 gives the partial orderings of the nine heptane isomers 1-9 obtained with the values of the Wiener indices $\mathbf{Wi(D)}$ and $\mathbf{Wi(RD)}$, and connectivity indices ${}^0\chi$, ${}^1\chi$, and ${}^2\chi$. The

values of the **Wi(D)** index decrease from that of *n*-heptane **1**, **Wi(D,1)** = 56 to that of 2,2,3-trimethylbutane **9**, **Wi(D,9)** = 42, with two pairs of degenerate values, namely **Wi(D,4)** = **Wi(D,5)** = 48, and **Wi(D,6)** = **Wi(D,7)** = 46. The values of the index **Wi(RD)** increase with the increasing branching order with an inversion for the pair (4, 5). Also, **Wi(RD)** is not degenerate in the series of heptanes, showing that the reciprocal distance matrix can generate more discriminant topological indices than the distance matrix. The partial orderings of the connectivity indices does not parallel that proposed by Bertz.

Table 6 gives the partial orderings of the octane isomers **10-27** induced by the indices **Wi(D)**, **Wi(RD)**, ${}^0\chi$, ${}^1\chi$, and ${}^2\chi$. Both **Wi(D)** and **Wi(RD)** indices are degenerate for some pairs of alkanes with eight carbon atoms: **Wi(D,15)** = **Wi(D,21)** = 71, **Wi(D,19)** = **Wi(D,23)** = 67, **Wi(RD,20)** = **Wi(RD,22)** = 15.16667. The connectivity indices ${}^0\chi$ and ${}^1\chi$ are degenerate also in the series of octanes, showing that the most used topological indices in structure-property models are not very discriminant. The **Wi(D)** index decreases and the **Wi(RD)** index increases with the increasing branching, but several differences from the Bertz order can be observed.

The Ivanciuc-Balaban Operator **IB(M)**

The Balaban index J ,^{12,13} used with success in structure-property and structure-activity studies,⁶⁰⁻⁶³ initially defined from the distance matrix was extended for any molecular matrix. For any graph matrix **M** we introduced the vertex sum operator, representing a generalization of the distance sum. The vertex sum operator for vertex v_i in a graph G , **VS(M, G)_{*i*}**, is defined as the sum of the elements in the column i , or row i , of the molecular matrix **M**.⁴⁵

$$\mathbf{VS}(\mathbf{M}, G)_i = \sum_{j=1}^N [\mathbf{M}]_{ij} = \sum_{j=1}^N [\mathbf{M}]_{ji} \quad (6)$$

If **M** is the adjacency matrix, the operator **VS** is identical with the degree vector **Deg**, if **M** is the distance matrix, the operator is identical with the distance sum **DS**, while if **M** is the reciprocal distance matrix **RD**, this operator gives the reciprocal distance sum **RDS**.⁵⁸

Using the vertex sum local invariant, the Ivanciuc-Balaban operator of a graph G , **IB(M)** = **IB(M, G)** was defined by analogy with the J index.⁴⁸

$$\mathbf{IB}(\mathbf{M}, G) = \frac{M}{\mu + 1} \sum_{e_{ij} \in E(G)} (\mathbf{VS}(\mathbf{M})_i, \mathbf{VS}(\mathbf{M})_j)^{-1/2} \quad (7)$$

where the summation extends over all edges from the edge set $E(G)$. The **IB** operator becomes the J index when **M** is the distance matrix and G is the molecular graph of a hydrocarbon. We investigate here the partial orderings obtained with the Ivanciuc-Balaban operator **IB** computed from the distance **D**, reciprocal distance **RD**,⁵⁵⁻⁵⁸ distance-path **D_p**,^{64,65} reciprocal distance-path **RD_p**,^{64,65} path Szeged **Sz_p**,⁶⁶⁻⁶⁸ and reciprocal path Szeged **RSz_p**.⁶⁶⁻⁶⁸ matrices.

Table 7 gives the partial orderings of the nine heptane isomers **1-9** induced by the Ivanciuc-Balaban indices **IB(D)**, **IB(RD)**, **IB(D_p)**, **IB(RD_p)**, **IB(Sz_p)**, and **IB(RSz_p)**. The **IB(D)** index increases with the increase of heptane branching, according exactly to the order established by Bertz. For the remaining indices, they follow the increase of heptane branching but several inversions appear: **IB(RD)** decreases with one inversion for the pair (4, 5); **IB(D_p)** increases with one inversion for the pair (6, 7); **IB(RD_p)** decreases with one inversion for the

pair (4, 5); $\mathbf{IB}(S_{z_p})$ increases with two inversions for the pairs (3, 4) and (5, 6); $\mathbf{IB}(RS_{z_p})$ decreases with two inversions for the pairs (4, 5) and (6, 7).

Table 7. The Ivanciuc-Balaban indices $\mathbf{IB}(D)$, $\mathbf{IB}(RD)$, $\mathbf{IB}(D_p)$, $\mathbf{IB}(RD_p)$, $\mathbf{IB}(S_{z_p})$, and $\mathbf{IB}(RS_{z_p})$ for the alkanes with seven carbon atoms 1-9.

G	$\mathbf{IB}(D)$	$\mathbf{IB}(RD)$	$\mathbf{IB}(D_p)$	$\mathbf{IB}(RD_p)$	$\mathbf{IB}(S_{z_p})$	$\mathbf{IB}(RS_{z_p})$
1	2.44747	11.04003	1.22323	13.94827	0.64420	52.26515
2	2.67826	10.47812	1.44404	13.07753	0.69216	43.05439
3	2.83182	10.33926	1.62310	12.95444	0.74800	40.40862
4	2.95322	9.92441	1.74066	12.22211	0.74777	35.27743
5	2.99230	10.18771	1.83272	12.80254	0.83904	37.02439
6	3.14421	9.76304	1.97988	12.06732	0.83570	31.61949
7	3.15449	9.62625	1.95600	11.79443	0.85554	32.37232
8	3.36044	9.45270	2.24389	11.60798	0.95690	27.70063
9	3.54120	9.05452	2.45410	10.91975	0.96770	23.24301

The partial orderings of the octane isomers 10-27 according to the Ivanciuc-Balaban indices $\mathbf{IB}(D)$, $\mathbf{IB}(RD)$, $\mathbf{IB}(D_p)$, $\mathbf{IB}(RD_p)$, $\mathbf{IB}(S_{z_p})$, and $\mathbf{IB}(RS_{z_p})$ are presented in Table 8. All six descriptors present several inversions but overall, $\mathbf{IB}(RD)$, $\mathbf{IB}(RD_p)$, and $\mathbf{IB}(RS_{z_p})$ decrease, while $\mathbf{IB}(D)$, $\mathbf{IB}(D_p)$, and $\mathbf{IB}(S_{z_p})$ increase when branching increases.

Table 8. The Ivanciuc-Balaban indices $\mathbf{IB}(D)$, $\mathbf{IB}(RD)$, $\mathbf{IB}(D_p)$, $\mathbf{IB}(RD_p)$, $\mathbf{IB}(S_{z_p})$, and $\mathbf{IB}(RS_{z_p})$ for the alkanes with eight carbon atoms 10-27.

G	$\mathbf{IB}(D)$	$\mathbf{IB}(RD)$	$\mathbf{IB}(D_p)$	$\mathbf{IB}(RD_p)$	$\mathbf{IB}(S_{z_p})$	$\mathbf{IB}(RS_{z_p})$
10	2.53006	13.98013	1.14189	18.17862	0.57088	80.11318
11	2.71584	13.36617	1.30055	17.18781	0.59862	68.44253
12	2.92782	12.76222	1.50029	16.21209	0.62173	56.26337
13	2.86207	13.19414	1.44692	17.03695	0.63281	64.50685
14	2.91961	13.15127	1.51419	17.00932	0.65258	64.47846
15	3.09883	12.58787	1.68624	16.06167	0.66425	54.20246
16	3.07437	12.95769	1.69294	16.81028	0.71512	59.10240
17	3.17082	12.51947	1.76354	15.99880	0.69799	52.84661
18	3.29248	12.37645	1.90704	15.84960	0.73502	49.86759
19	3.35488	12.32028	1.99734	15.79007	0.78627	49.01368
20	3.46423	11.89664	2.09183	15.00289	0.75405	42.77430
21	3.11177	12.41949	1.66720	15.72596	0.68584	53.74073
22	3.38892	11.82604	1.97480	14.77399	0.72014	44.37901
23	3.37338	12.15581	1.98010	15.46061	0.77570	47.53725
24	3.58321	11.92190	2.25702	15.19015	0.87944	41.50225
25	3.62328	11.60430	2.26141	14.54904	0.81669	39.41199
26	3.70832	11.52306	2.37922	14.45238	0.85517	36.81041
27	4.02039	10.84542	2.73986	13.27939	0.91108	29.11017

The Information-Theory Operators $U(\mathbf{M})$, $V(\mathbf{M})$, $X(\mathbf{M})$, and $Y(\mathbf{M})$

The indices U , V , X , and Y for information on distances are computed from the elements of the distance matrix of the molecular graph,^{69,70} and these TIs provided good results both for structure discrimination and in structure-property models.⁷¹ Because new graph matrices were defined in recent years,⁴³ it is possible to extend the definition of these four indices for all dense molecular matrices \mathbf{M} (a dense matrix is a matrix without zero non-diagonal elements). We present below four information-theory operators that can be applied to a matrix with integer value elements such as the distance matrix \mathbf{D} , or to a matrix with real value elements such as the reciprocal distance matrix \mathbf{RD} . The graph vertex operators $\mathbf{VUinf}(\mathbf{M}, G)$, $\mathbf{VVinf}(\mathbf{M}, G)$, $\mathbf{VXinf}(\mathbf{M}, G)$, and $\mathbf{VYinf}(\mathbf{M}, G)$ apply the information theory equations to the non-zero elements of the matrix \mathbf{M} that correspond to a vertex v_i .⁷²

$$\mathbf{VUinf}(\mathbf{M})_i = - \sum_{j=1}^N \frac{[\mathbf{M}]_{ij}}{\mathbf{VS}(\mathbf{M})_i} \log_2 \frac{[\mathbf{M}]_{ij}}{\mathbf{VS}(\mathbf{M})_i} \quad (8)$$

$$\mathbf{VVinf}(\mathbf{M})_i = \mathbf{VS}(\mathbf{M})_i \log_2 \mathbf{VS}(\mathbf{M})_i - \mathbf{VUinf}(\mathbf{M})_i \quad (9)$$

$$\mathbf{VXinf}(\mathbf{M})_i = \mathbf{VS}(\mathbf{M})_i \log_2 \mathbf{VS}(\mathbf{M})_i - \mathbf{VYinf}(\mathbf{M})_i \quad (10)$$

$$\mathbf{VYinf}(\mathbf{M})_i = \sum_{j=1}^N [\mathbf{M}]_{ij} \log_2 [\mathbf{M}]_{ij} \quad (11)$$

where \mathbf{M} is a molecular graph matrix, $\mathbf{VS}(\mathbf{M})_i$ represents the vertex sum of the vertex v_i , and the summations in equations (8) and (11) are done for the non-zero elements of the molecular matrix \mathbf{M} , $[\mathbf{M}]_{ij} \neq 0$.

For a general dense molecular graph matrix \mathbf{M} , the matrix elements $[\mathbf{M}]_{ij}$ may have values lower than 1, giving negative terms for certain vertex structural descriptors computed with the graph vertex operators $\mathbf{VUinf}(\mathbf{M}, G)$, $\mathbf{VVinf}(\mathbf{M}, G)$, $\mathbf{VXinf}(\mathbf{M}, G)$, and $\mathbf{VYinf}(\mathbf{M}, G)$. The Randić-like formula used in the case of the indices U , V , X , and Y is therefore replaced by the following equation:

$$f(x, y) = \begin{cases} (xy)^{-1/2} & \text{if } xy > 0 \\ -(|xy|)^{-1/2} & \text{if } xy < 0 \end{cases} \quad (12)$$

The operators $U(\mathbf{M})$, $V(\mathbf{M})$, $X(\mathbf{M})$, and $Y(\mathbf{M})$, representing information on matrix elements, are computed with the equations:

$$U(\mathbf{M}, G) = \frac{M}{\mu + 1} \sum_{g \in (G)} f(\mathbf{VUinf}(\mathbf{M})_i, \mathbf{VUinf}(\mathbf{M})_j) \quad (13)$$

$$V(\mathbf{M}, G) = \frac{M}{\mu + 1} \sum_{g \in (G)} f(\mathbf{VVinf}(\mathbf{M})_i, \mathbf{VVinf}(\mathbf{M})_j) \quad (14)$$

$$X(\mathbf{M}, G) = \frac{M}{\mu + 1} \sum_{g \in (G)} f(\mathbf{VXinf}(\mathbf{M})_i, \mathbf{VXinf}(\mathbf{M})_j) \quad (15)$$

$$Y(\mathbf{M}, G) = \frac{M}{\mu + 1} \sum_{g \in (G)} f(\mathbf{VYinf}(\mathbf{M})_i, \mathbf{VYinf}(\mathbf{M})_j) \quad (16)$$

In this section we explore the partial orderings of heptane and octane isomers according to the information-theory operators $U(\mathbf{M})$, $V(\mathbf{M})$, $X(\mathbf{M})$, and $Y(\mathbf{M})$ computed with the distance \mathbf{D} , reciprocal distance \mathbf{RD} , distance-path \mathbf{D}_p , reciprocal distance-path \mathbf{RD}_p , path Szeged \mathbf{Sz}_p , and reciprocal path Szeged \mathbf{RSz}_p matrices.

Table 9 presents the partial orderings of the heptane isomers 1-9 according to the information-theory indices $U(\mathbf{D})$, $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$. The $U(\mathbf{D})$ index decreases with the increase of heptane branching, with one inaccuracy for 7. Both $V(\mathbf{D})$ and $X(\mathbf{D})$ indices increase exactly with the increase of heptane branching, while $Y(\mathbf{D})$ presents an inversion for the pair (6, 7). The partial orderings of the octane isomers 10-27 according to the indices $U(\mathbf{D})$, $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$ are presented in Table 10. All four information-theory descriptors present several inversions but overall, $U(\mathbf{D})$ decreases, while $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$ increase when branching increases. $U(\mathbf{D})$, $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$

Table 9. The information-theory indices $U(\mathbf{D})$, $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$ for the alkanes with seven carbon atoms 1-9.

G	$U(\mathbf{D})$	$V(\mathbf{D})$	$X(\mathbf{D})$	$Y(\mathbf{D})$
1	15.01829	0.66608	1.01950	1.72971
2	14.90594	0.75846	1.10780	2.10696
3	14.74170	0.82597	1.15881	2.45966
4	14.72927	0.87522	1.20739	2.67238
5	14.55947	0.89925	1.20952	2.93297
6	14.55360	0.96551	1.27065	3.25311
7	14.65354	0.97049	1.28380	3.20968
8	14.44425	1.07370	1.34790	4.09592
9	14.38209	1.15855	1.41474	4.65633

Table 10. The information-theory indices $U(\mathbf{D})$, $V(\mathbf{D})$, $X(\mathbf{D})$, and $Y(\mathbf{D})$ for the alkanes with eight carbon atoms 10-27.

G	$U(\mathbf{D})$	$V(\mathbf{D})$	$X(\mathbf{D})$	$Y(\mathbf{D})$
10	18.82699	0.61700	0.97065	1.57427
11	18.75167	0.68026	1.03795	1.81211
12	18.62847	0.75510	1.11164	2.12495
13	18.59865	0.73364	1.08551	2.04896
14	18.52039	0.75574	1.10261	2.16497
15	18.45031	0.82024	1.16594	2.45120
16	18.34148	0.81441	1.15017	2.48080
17	18.39748	0.84921	1.18983	2.60998
18	18.27498	0.89719	1.22755	2.88695
19	18.18297	0.92273	1.24448	3.08241
20	18.20926	0.96384	1.28678	3.26482
21	18.57233	0.82546	1.17910	2.43561
22	18.36328	0.93187	1.26942	3.00460
23	18.29374	0.93100	1.25914	3.07064
24	18.07934	1.01912	1.32174	3.75049
25	18.16020	1.03055	1.34275	3.66997
26	18.07682	1.06838	1.36777	4.01260
27	17.96937	1.20117	1.47446	4.97561

Table 11 presents the partial orderings of the heptane isomers **1-9** according to the information-theory indices **U**, **V**, **X**, and **Y** computed with the reciprocal distance matrix **RD**. All four indices follow the increase of heptane branching but several inversions appear: **U(RD)** decreases with one inversion for the pair (6, 7); **V(RD)** and **X(RD)** decreases with one inversion for the pair (4, 5); **Y(RD)** increases but compounds **2-5** are not in line with the Bertz order.

Table 12 gives the partial orderings of the octane isomers **10-27** obtained with the values of the information-theory indices **U(RD)**, **V(RD)**, **X(RD)**, and **Y(RD)**. All four information-theory descriptors present several inversions but overall, **Y(RD)** increases, while **U(RD)**, **V(RD)**, and **X(RD)** decrease when branching increases.

Table 11. The information-theory indices **U(RD)**, **V(RD)**, **X(RD)**, and **Y(RD)** for the alkanes with seven carbon atoms **1-9**.

<i>G</i>	U(RD)	V(RD)	X(RD)	Y(RD)
1	15.24441	13.01558	4.68496	17.30474
2	15.02846	10.98026	4.38158	18.11887
3	14.90141	10.79283	4.28807	18.09194
4	14.80983	9.15790	4.08599	18.89863
5	14.77651	10.39335	4.18885	18.09799
6	14.67298	9.00241	3.98364	19.11318
7	14.68284	8.80252	3.93320	20.89862
8	14.54945	8.40708	3.82586	21.17142
9	14.44847	7.24075	3.63550	22.25045

Table 12. The information-theory indices **U(RD)**, **V(RD)**, **X(RD)**, and **Y(RD)** for the alkanes with eight carbon atoms **10-27**.

<i>G</i>	U(RD)	V(RD)	X(RD)	Y(RD)
10	19.23259	14.57890	5.49990	19.33055
11	19.02510	12.66878	5.19909	19.84690
12	18.81754	10.89639	4.90579	20.31876
13	18.87493	12.48442	5.09332	19.71523
14	18.82744	12.47119	5.06528	19.63351
15	18.66234	10.76734	4.80035	20.19209
16	18.68036	12.01040	4.95031	19.54312
17	18.60427	10.78131	4.76177	20.26289
18	18.49890	10.51175	4.67960	20.23325
19	18.45347	10.35590	4.64618	20.17303
20	18.37964	9.23056	4.46555	20.87571
21	18.66700	10.61402	4.74141	21.43219
22	18.45207	9.05139	4.45716	21.85820
23	18.45855	10.16670	4.58884	21.37532
24	18.30059	9.65185	4.45964	21.45518
25	18.28147	8.84365	4.33413	22.09405
26	18.22676	8.68524	4.29061	22.18506
27	18.05806	7.35154	3.99770	24.19111

The partial orderings of the heptane isomers **1-9** according to the information-theory indices U , V , X , and Y computed with the distance-path matrix D_p are presented in Table 13. The $X(D_p)$ index increases exactly with the increase of heptane branching, while for the remaining indices several inversions appear: $U(D_p)$ decreases with one inversion for the pair (5, 7); both $V(D_p)$ and $Y(D_p)$ increase with one inversion for the pair (6, 7). Table 14 presents the partial orderings of the octane isomers **10-27** obtained with the same four information-theory indices. Similarly with the situation for the distance matrix D , all indices present some deviations from the Bertz order, but in general, $U(D_p)$ decreases, while $V(D_p)$, $X(D_p)$, and $Y(D_p)$ increase when branching increases.

Table 13. The information-theory indices $U(D_p)$, $V(D_p)$, $X(D_p)$, and $Y(D_p)$ for the alkanes with seven carbon atoms **1-9**.

G	$U(D_p)$	$V(D_p)$	$X(D_p)$	$Y(D_p)$
1	16.78272	0.26032	0.56670	0.47481
2	16.49488	0.32398	0.65850	0.62541
3	16.05033	0.38086	0.72210	0.77860
4	15.96644	0.41652	0.76912	0.87962
5	15.45699	0.45262	0.78543	1.02828
6	15.51450	0.50033	0.85200	1.15193
7	15.90045	0.49094	0.86427	1.07804
8	15.23995	0.60114	0.94931	1.53063
9	15.06292	0.67734	1.02718	1.80697

Table 14. The information-theory indices $U(D_p)$, $V(D_p)$, $X(D_p)$, and $Y(D_p)$ for the alkanes with eight carbon atoms **10-27**.

G	$U(D_p)$	$V(D_p)$	$X(D_p)$	$Y(D_p)$
10	21.02374	0.21714	0.48692	0.38954
11	20.81782	0.25631	0.54913	0.47749
12	20.42618	0.30811	0.62139	0.60503
13	20.45785	0.29486	0.60246	0.56913
14	20.22872	0.31372	0.62346	0.61996
15	19.98793	0.36003	0.68549	0.74306
16	19.66395	0.36433	0.67849	0.76933
17	19.91318	0.38295	0.71511	0.80536
18	19.55620	0.42539	0.76040	0.93399
19	19.20741	0.45408	0.78178	1.05428
20	19.33137	0.48078	0.82331	1.11926
21	20.46754	0.35431	0.69553	0.71003
22	19.77390	0.44326	0.79513	0.97352
23	19.67182	0.44839	0.79516	0.99068
24	18.98038	0.53867	0.87370	1.35158
25	19.27344	0.53460	0.88940	1.27926
26	19.01193	0.57552	0.92245	1.45793
27	18.72204	0.69583	1.04721	1.91695

Table 15 presents the partial orderings of the heptane isomers 1-9 according to the information-theory indices U , V , X , and Y computed with the reciprocal distance-path matrix RD_p . Both indices $U(RD_p)$ and $X(RD_p)$ decrease when branching increases, with one inversion for the pair (4, 5). The relationship between the Bertz order of heptanes and the partial orderings offered by $V(RD_p)$ and $Y(RD_p)$ is less apparent. The same general trends appear for octanes, as one can see in Table 16, but the indices $U(RD_p)$ and $X(RD_p)$ have several differences compared with the Bertz ordering of alkanes.

The value of the index $V(RD_p)$ for 2,4-dimethylpentane 4, $V(RD_p,4) = -627.06995$, is unusual when compared with the values of the other indices for the same alkane. We present here some details on the computation of $V(RD_p,4)$ that explain its unusual value. The atomic descriptor $VVinf(RD_p,4)$ is computed from the vertex sum and $VUinf$ vectors of the same molecular graph. Starting from the molecular matrix $RD_p(4)$ the vertex sum $VS(RD_p,4)$ is computed with Eq. (6):

$$VS(RD_p,4) = \{2.03333, 3.66667, 3.33333, 3.66667, 2.03333, 2.03333, 2.03333\}$$

The atomic invariant $VUinf(RD_p,4)$ is computed with Eq. (8):

$$VUinf(RD_p,4) = \{2.08214, 2.25355, 2.37095, 2.25355, 2.08214, 2.08214, 2.08214\}$$

Using Eq. (9) the atomic invariant $VVinf(RD_p,4)$ is computed from the above two vectors:

$$VVinf(RD_p,4) = \{-0.00031, 4.61950, 3.41893, 4.61950, -0.00031, -0.00031, -0.00031\}$$

Finally, the vector of atomic invariants $VVinf(RD_p,4)$ is used in Eq. (14) to compute the information-theory index $V(RD_p,4)$. The use of near-zero negative values in Eq. (12) gives this unusually large negative value for $V(RD_p,4)$.

Table 15. The information-theory indices $U(RD_p)$, $V(RD_p)$, $X(RD_p)$, and $Y(RD_p)$ for the alkanes with seven carbon atoms 1-9.

G	$U(RD_p)$	$V(RD_p)$	$X(RD_p)$	$Y(RD_p)$
1	17.53993	-2.38474	6.85606	20.82321
2	16.89482	-28.31286	6.18233	20.98962
3	16.61757	0.89777	6.03337	20.10149
4	16.27099	-627.06995	5.54267	20.87881
5	16.32835	-15.21834	5.85601	19.39025
6	15.97258	17.81921	5.38321	20.03929
7	15.96209	6.73790	5.27399	22.44712
8	15.65273	-6.59062	5.08331	21.44588
9	15.33662	20.16578	4.66187	22.05038

Table 16. The information-theory indices $U(\mathbf{RD}_p)$, $V(\mathbf{RD}_p)$, $X(\mathbf{RD}_p)$, and $Y(\mathbf{RD}_p)$ for the alkanes with eight carbon atoms **10-27**.

G	$U(\mathbf{RD}_p)$	$V(\mathbf{RD}_p)$	$X(\mathbf{RD}_p)$	$Y(\mathbf{RD}_p)$
10	22.42993	-0.09367	8.40086	24.48483
11	21.75676	-32.38242	7.69075	24.43830
12	21.10622	-98.83581	7.00910	24.24925
13	21.42547	2.37753	7.52243	23.43838
14	21.33659	1.17658	7.48787	23.10264
15	20.77410	41.97530	6.85024	23.15792
16	20.98194	-14.87706	7.27238	22.31628
17	20.65651	19.35382	6.80096	22.82486
18	20.40095	-0.48575	6.65044	22.20133
19	20.30017	2.10520	6.58860	21.96260
20	19.99873	33.71596	6.14441	22.42087
21	20.74342	9.74364	6.72460	24.91008
22	20.11495	35.58398	6.08776	24.30790
23	20.26755	-5.18762	6.46152	23.36625
24	19.87808	-22.03158	6.21345	22.45840
25	19.73627	7.40053	5.89386	23.26346
26	19.60624	8.07234	5.81324	22.88725
27	19.09376	16.15465	5.18078	24.08343

The partial orderings of the heptane isomers **1-9** according to the information-theory indices U , V , X , and Y computed with the path Szeged matrix Sz_p are presented in Table 17. The $X(Sz_p)$ index increases exactly with the increase of heptane branching, while for the remaining indices several inversions appear: $U(Sz_p)$ increases with one inversion for the pair (**4**, **5**); $V(Sz_p)$ has a degenerate value for the pair (**3**, **4**), and increases with one inversion for the pair (**5**, **6**); $Y(Sz_p)$ does not follow the Bertz order of heptanes. Table 18 presents the partial orderings of the octane isomers **10-27** obtained with the same four information-theory indices. The general trend is an increase of the indices with the increase of branching, but several deviations from the Bertz order are present in each case.

Table 17. The information-theory indices $U(Sz_p)$, $V(Sz_p)$, $X(Sz_p)$, and $Y(Sz_p)$ for the alkanes with seven carbon atoms **1-9**.

G	$U(Sz_p)$	$V(Sz_p)$	$X(Sz_p)$	$Y(Sz_p)$
1	14.16374	0.11190	0.25347	0.19756
2	14.49061	0.12256	0.27892	0.21539
3	14.50206	0.13516	0.30143	0.24094
4	14.77417	0.13516	0.30687	0.23762
5	14.49269	0.15644	0.33781	0.28568
6	14.88455	0.15559	0.34562	0.27789
7	15.03132	0.16097	0.35847	0.28656
8	15.05942	0.18528	0.40045	0.33717
9	15.53035	0.18790	0.41747	0.33547

Table 18. The information-theory indices $U(Sz_p)$, $V(Sz_p)$, $X(Sz_p)$, and $Y(Sz_p)$ for the alkanes with eight carbon atoms 10-27.

G	$U(Sz_p)$	$V(Sz_p)$	$X(Sz_p)$	$Y(Sz_p)$
10	17.72558	0.08935	0.20655	0.15609
11	18.01797	0.09477	0.22034	0.16479
12	18.34140	0.09925	0.23282	0.17142
13	18.07504	0.10147	0.23357	0.17766
14	18.00534	0.10539	0.23982	0.18608
15	18.37432	0.10771	0.24908	0.18786
16	18.08248	0.11808	0.26397	0.21116
17	18.39657	0.11457	0.26229	0.20126
18	18.46645	0.12213	0.27704	0.21593
19	18.38847	0.13292	0.29514	0.23883
20	18.75383	0.12610	0.28858	0.22138
21	18.61185	0.11232	0.26150	0.19495
22	18.87063	0.11927	0.27763	0.20683
23	18.58553	0.13083	0.29466	0.23238
24	18.60712	0.15290	0.33400	0.27783
25	19.03440	0.13946	0.31768	0.24580
26	19.03596	0.14760	0.33224	0.26231
27	19.68966	0.15989	0.36581	0.28140

Table 19 presents the partial orderings of the heptane isomers 1-9 according to the information-theory indices U , V , X , and Y computed with the reciprocal path Szeged matrix RSz_p . The $X(RSz_p)$ index decreases exactly with the increase of heptane branching, while each of the three remaining indices present several inversions. The same trend can be observed for octanes from the values presented in Table 20, but in this case even $X(RSz_p)$ has several deviations from the Bertz order.

Table 19. The information-theory indices $U(RSz_p)$, $V(RSz_p)$, $X(RSz_p)$, and $Y(RSz_p)$ for the alkanes with seven carbon atoms 1-9.

G	$U(RSz_p)$	$V(RSz_p)$	$X(RSz_p)$	$Y(RSz_p)$
1	14.22713	12.43444	20.65417	17.04354
2	15.13857	17.90186	17.88405	16.98653
3	14.79599	14.44274	16.57567	15.68324
4	15.80152	23.74460	15.39996	17.00606
5	14.51596	14.33782	14.92835	14.69484
6	15.62380	21.40288	13.65412	15.36995
7	15.13725	-0.46682	13.44259	17.02107
8	15.16930	5.46962	11.65578	14.86206
9	16.13941	5.93771	10.38072	16.57000

Table 20. The information-theory indices $U(\text{RSz}_p)$, $V(\text{RSz}_p)$, $X(\text{RSz}_p)$, and $Y(\text{RSz}_p)$ for the alkanes with eight carbon atoms **10-27**.

G	$U(\text{RSz}_p)$	$V(\text{RSz}_p)$	$X(\text{RSz}_p)$	$Y(\text{RSz}_p)$
10	17.83617	15.42690	29.15342	23.17929
11	18.98087	20.36148	26.07891	23.06047
12	20.27241	25.19031	22.94956	22.94662
13	18.68414	17.25920	24.48193	21.49505
14	18.32909	16.78995	24.09485	21.14264
15	19.68876	22.22675	21.64906	21.43120
16	18.19413	16.88443	21.93411	19.95177
17	19.57902	22.58694	20.80625	20.72740
18	19.24928	19.47001	19.57610	19.53471
19	18.93040	23.69546	18.81430	19.43803
20	20.51859	28.86585	17.78199	20.34156
21	19.31109	-0.12302	20.73569	22.78873
22	20.20722	5.06863	18.18836	22.82803
23	19.07306	1.37849	18.36976	19.88313
24	18.95053	23.96572	16.04420	18.00484
25	19.93232	1.83171	15.92192	20.47954
26	20.12245	6.72900	15.03413	19.20566
27	20.67142	-19.39335	12.19369	21.39103

The Information-Theory Indices I_D^E , \bar{I}_D^E , I_D^W , and \bar{I}_D^W

The information-theory indices I_D^E , \bar{I}_D^E , I_D^W , and \bar{I}_D^W based on the distance matrix **D** were introduced by Bonchev and Trinajstić as numerical descriptors of molecular branching.¹⁰ The partial orderings of the heptane isomers **1-9** according to these four indices are presented in Table 21. The values of the first three indices decrease from *n*-heptane to 2,2,3-trimethylbutane with increasing branching: for I_D^E , between 50.36436 and 32.68979 with one inversion for the pair (**6**, **7**); for \bar{I}_D^E , between 2.39830 and 1.55666 with one inversion for the pair (**6**, **7**); for I_D^W , between 233.46327 and 179.94801 with one inversion for the pair (**4**, **5**). The index \bar{I}_D^W increases with increasing branching, between 4.16899 and 4.28448, with an exception for compound **7** that fits between **4** and **5**. Table 22 presents the partial orderings of the octane isomers **10-27** obtained with the same four information-theory indices. Overall, when branching increases, I_D^E , \bar{I}_D^E , and I_D^W decrease while \bar{I}_D^W increases, but several deviations from the Bertz order are present in each case.

Table 21. The information-theory indices I_D^E , \bar{I}_D^E , I_D^W , and \bar{I}_D^W for the alkanes with seven carbon atoms 1-9.

G	I_D^E	\bar{I}_D^E	I_D^W	\bar{I}_D^W
1	50.36436	2.39830	233.46327	4.16899
2	46.46423	2.21258	218.18403	4.19585
3	44.85459	2.13593	210.80873	4.21617
4	41.07741	1.95607	203.05865	4.23039
5	40.95445	1.95021	203.54888	4.24060
6	39.56763	1.88417	195.55452	4.25119
7	39.97400	1.90352	195.06430	4.24053
8	37.21912	1.77234	187.68567	4.26558
9	32.68979	1.55666	179.94801	4.28448

Table 22. The information-theory indices I_D^E , \bar{I}_D^E , I_D^W , and \bar{I}_D^W for the alkanes with eight carbon atoms 10-27.

G	I_D^E	\bar{I}_D^E	I_D^W	\bar{I}_D^W
10	73.08015	2.61001	383.68027	4.56762
11	68.93844	2.46209	362.37577	4.58704
12	63.34481	2.26231	341.28655	4.61198
13	67.03831	2.39423	349.97447	4.60493
14	66.18355	2.36370	345.90302	4.61204
15	61.83504	2.20839	328.88344	4.63216
16	62.04184	2.21578	333.73111	4.63515
17	61.30297	2.18939	324.54632	4.63638
18	58.95445	2.10552	316.29873	4.65145
19	55.34481	1.97660	312.38888	4.66252
20	54.42513	1.94375	303.41481	4.66792
21	62.06060	2.21645	328.02869	4.62012
22	54.61576	1.95056	307.15557	4.65387
23	58.77364	2.09906	311.53412	4.64976
24	53.14092	1.89789	299.20601	4.67509
25	52.98028	1.89215	294.52954	4.67507
26	51.20585	1.82878	290.36618	4.68333
27	43.40558	1.55020	272.96891	4.70636

The Triplet Indices T.P.R

A new class of vertex structural descriptors, related with graph potentials, was defined as the solution of the system of equations:⁷³

$$\mathbf{Q} \cdot \mathbf{P} = \mathbf{R} \tag{17}$$

where \mathbf{Q} is a matrix derived from a molecular graph matrix, \mathbf{R} is a column vector, and \mathbf{P} is another (or the same) column vector of Local Vertex Invariants (LOVIs). Matrix \mathbf{Q} is obtained from a graph topological matrix \mathbf{T} , by replacing its diagonal elements $[\mathbf{T}]_{ii}$ with the components P_i of a nonzero column vector \mathbf{P} representing a vertex property. The vertex property encoded in the column vectors \mathbf{P} and \mathbf{R} can be either topological (vertex degree, distance sum, or reciprocal distance sum), chemical (the atomic number Z , the atomic mass A , electronegativity, ionization potential) or simply numerical (e.g. 1). The system of equations and the type of LOVIs obtained is denoted by a three-element notation $\mathbf{T.P.R}$, where \mathbf{T} represents the type of graph topological matrix, \mathbf{P} is the vertex property that replaces the main diagonal of the matrix \mathbf{T} , and \mathbf{R} is the descriptor used as free term. For example, the LOVIs obtained using the adjacency matrix \mathbf{A} , the atomic number Z as the property \mathbf{P} , and the vector of vertex degrees \mathbf{Deg} as property \mathbf{R} , is denoted by $\mathbf{A.Z.Deg}$, and that obtained when \mathbf{T} is the reciprocal distance matrix \mathbf{RD} , the property \mathbf{P} is the distance sum \mathbf{DS} , and the descriptor \mathbf{P} is the degree \mathbf{Deg} is denoted with $\mathbf{RD.DS.Deg}$. Analytical formulas for the $\mathbf{T.P.R}$ invariants for certain classes of graphs were obtained.⁷⁴ From the $\mathbf{T.P.R}$ vertex descriptors one can generate molecular indices with an aggregation formula; the most simple is the sum of the vertex invariants, denoted $\mathbf{Sum(T.P.R)}$.

The partial orderings of the heptane isomers **1-9** according to the triplet indices $\mathbf{Sum(A.Z.Deg)}$, $\mathbf{Sum(A.DS.Deg)}$, and $\mathbf{Sum(A.Z.RDS)}$ are presented in Table 23. While for the first index the relationship with the alkane branching is not apparent, $\mathbf{Sum(A.Z.RDS)}$ follows exactly the Bertz order, and $\mathbf{Sum(A.DS.Deg)}$ has one inversion for the pair (6, 7). Table 24 presents the partial orderings of the octane isomers **10-27** obtained with the same three triplet indices. The trend of the octanes is the same as the one observed for the heptane isomers, but this time $\mathbf{Sum(A.DS.Deg)}$ and $\mathbf{Sum(A.Z.RDS)}$ have several inversions.

Table 23. The triplet indices $\mathbf{Sum(A.Z.Deg)}$, $\mathbf{Sum(A.DS.Deg)}$, $\mathbf{Sum(A.Z.RDS)}$, and the Schultz index MII for the alkanes with seven carbon atoms **1-9**.

G	$\mathbf{Sum(A.Z.Deg)}$	$\mathbf{Sum(A.DS.Deg)}$	$\mathbf{Sum(A.Z.RDS)}$	MII
1	1.53033	0.72465	2.87227	204
2	1.48487	0.77752	2.95117	190
3	1.49241	0.81507	2.98107	182
4	1.43750	0.83841	3.03472	176
5	1.50000	0.85473	3.01042	174
6	1.45621	0.88410	3.07049	168
7	1.38914	0.87143	3.10012	170
8	1.40787	0.91844	3.13596	162
9	1.36464	0.95284	3.19613	156

Table 24. The triplet indices **Sum(A.Z.Deg)**, **Sum(A.DS.Deg)**, **Sum(A.Z.RDS)**, and the Schultz index *MTI* for the alkanes with eight carbon atoms 10-27.

<i>G</i>	Sum(A.Z.Deg)	Sum(A.DS.Deg)	Sum(A.Z.RDS)	<i>MTI</i>
10	1.78033	0.65899	3.52559	306
11	1.73483	0.69893	3.61137	288
12	1.68966	0.74369	3.69971	270
13	1.74263	0.73182	3.64903	276
14	1.74107	0.74449	3.66104	272
15	1.69553	0.78113	3.74183	258
16	1.74892	0.77963	3.69789	260
17	1.70515	0.79674	3.75936	254
18	1.71265	0.82347	3.78885	246
19	1.71113	0.83727	3.80037	242
20	1.66726	0.85647	3.86225	236
21	1.63965	0.77617	3.77914	260
22	1.59052	0.83154	3.87717	242
23	1.65515	0.83132	3.83888	244
24	1.67234	0.87620	3.88541	232
25	1.61940	0.88084	3.92977	230
26	1.62903	0.89796	3.94736	226
27	1.53846	0.94798	4.07692	214

The Molecular Topological Index *MTI*

The last structural descriptor from our investigation is the molecular topological index *MTI*, introduced by Schultz.⁷⁵ The partial orderings of the heptane and octane isomers induced by the *MTI* index are presented in Tables 23 and 24, respectively. The general trend indicates a decrease of *MTI* with increasing branching; in the case of heptanes there is one inversion for the pair (6, 7), while several inversions are exhibited by octanes. As is apparent from Table 24 there are two pairs of alkanes with eight carbons that have identical *MTI* values: $MTI(16) = MTI(21) = 260$, and $MTI(19) = MTI(22) = 242$.

Conclusions

As a result of the considerable interest in developing QSPR and QSAR equations for molecular modeling and drug design, a large number of structural descriptors are used to express in a numerical form the chemical structure, i.e. the molecular size, shape, branching, cyclicity, or electron distribution. Although for a chemist the notion of branching is an essentially intuitive one, the mathematical approach proposed by Bertz is able to offer a numerical index of branching that is a powerful tool for ordering molecular graphs. Because branching greatly influences the physical properties of organic compounds, a large number of topological indices were proposed as numerical measures of branching and destined to be

used as descriptors in QSPR and QSAR models.^{3,7-17,76} Several examples of physical properties modeled with topological indices may be found both in the original papers where various TIs were defined, and in comparative studies involving a large number of TIs⁷⁷⁻⁸⁰ in QSPR modeling, namely boiling temperature, entropy, heat of atomization, heat of formation, heat of vaporization, critical temperature, critical pressure, critical volume, surface tension, octane number, molecular volume, molar refraction, density, carbon-13 chemical shift sum, heat capacity, retention index. Although the graph invariants are (more or less) degenerate and, as a consequence, can induce only a partial ordering of the molecular graph, they encode in an efficient way the branching effect onto various physical properties of alkanes.

Recently, new molecular graph operators were defined for the computation of families of topological indices, derived with the same mathematical formula from different molecular matrices. In the present study we have used some of these new TIs to investigate the partial ordering of heptanes and octanes. Structural descriptors (computed with the spectral operators **MinSp** and **MaxSp**, Hosoya operator **Ho**, Wiener operator **Wi**, Ivanciuc-Balaban operator **IB**, information-theory operators **U**, **V**, **X**, and **Y**, triplet indices **T.P.R**) were compared with several topological indices that gained a wider use in the characterization of molecular branching (such as the connectivity indices ${}^0\chi$, ${}^1\chi$, and ${}^2\chi$, the information-theory indices I_D^E , \bar{I}_D^E , I_D^W , and \bar{I}_D^W , as well as the molecular topological index *MTI*). The ordering of heptanes and octanes according to each TI was compared with the increasing branching order proposed by Bertz. For heptanes several TIs give exactly the same order as that proposed by Bertz, namely **MinSp(RD)**, **IB(D)**, **V(D)**, **X(D)**, **X(D_p)**, **X(Sz_p)** and **X(RSz_p)**; in addition, **MaxSp(A)** and **Wi(D)** indices preserve this ordering with one and two degenerate pairs, respectively. One should recall that **IB(D)** is the Balaban *J* index, and **Wi(D)** is the Wiener number. It is remarkable that in addition to the *J* index (as it was discussed by Bertz in his paper²⁶) so many of the **X(D)**, **X(D_p)**, **X(Sz_p)** and **X(RSz_p)** descriptors conserve the Bertz ordering of heptane isomers. In the case of octanes not a single index from the large set investigated here agrees fully with the Bertz order. One can state in general that our results with most of the descriptors tested in the present paper indicate good agreement in the ordering of the first and last few isomers in Bertz's list of heptanes and octanes; the intermediate isomers, however, lead to a partial ordering of heptanes and octanes.

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