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Testing the quality of molecular structure descriptors. Vertex–degree-based topological indices

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Abstract: The correlation abilities of 20 vertex–degree-based topological indices occurring in the chemical literature were tested for the case of standard heats of formation and normal boiling points of octane isomers. It is found that the correlation ability of many of these indices is either rather weak or nil. The augmented Zagreb index and the atom-bond connectivity index yield the best results.

Keywords: topological index; molecular structure descriptor; vertex–degree-based topological index; molecular graph; chemical graph theory.

INTRODUCTION

According to the IUPAC definition,[1] a *topological index* (or molecular structure descriptor) is a numerical value associated with chemical constitution for the correlation of chemical structure with various physical properties, chemical reactivity or biological activity. In the current literature, countless "structure descriptors" have been and are being proposed,[2,3] in many cases without any examination of whether these correlate with any of the "various physical properties, chemical reactivity or biological activity". Especially numerous are the molecular-graph-based structure descriptors. To use a mild expression, today there are far too many such descriptors and a firm criterion to stop or slow down their proliferation seems to be lacking.

In order to contribute towards a reduction in the number of molecular-graph-based structure descriptors and, at the same time, to single out those that deserve to be used in chemical applications, a comparative testing thereof was undertaken. In this paper, the considerations are restricted to a family of descriptors that all have the general form:[4]

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$$D = D(G) = \sum_{u \approx v} F(d_u, d_v) \quad (1)$$

where the summation goes over all pairs of adjacent vertices u,v of the molecular graph G and d_u denotes the degree (= number of first neighbors) of the vertex u. Hitherto, in the chemical literature, the following special cases of the function $F = F(x, y)$ in Eq. (1) have been considered:

[a] $F(x,y) = \frac{1}{\sqrt{xy}}$, for the Randić (or connectivity) index;[5,6]

[b] $F(x,y) = (x,y)^{\lambda}$, for the general Randić index,[6] where λ is an adjustable parameter;

[c] $F(x,y) = x + y$, for the first Zagreb index;[7–9]

[d] $F(x,y) = xy$, for the second Zagreb index;[7–9]

[e] $F(x,y) = \sqrt{\frac{x+y-2}{xy}}$, for the atom-bond connectivity (ABC) index;[10,11]

[f] $F(x,y) = \frac{1}{\sqrt{x+y}}$, for the sum-connectivity index;[12]

[g] $F(x,y) = (x+y)^{\lambda}$, for the general sum-connectivity index,[13] where λ is an adjustable parameter;

[h] $F(x,y) = \frac{2\sqrt{xy}}{(x+y)}$, for the geometric-arithmetic index;[14–16]

[i] $F(x,y) = \left(\frac{xy}{x+y-2}\right)^3$, for the augmented Zagreb index;[17–19]

[j] $F(x,y) = \frac{2}{x+y}$, for the harmonic index.[20]

Three more vertex-degree-based topological indices were recently proposed, in which Eq. (1) was modified, so that the summation was replaced by multiplication:

$$D^{\otimes} = D^{\otimes}(G) = \prod_{u \approx v} F(f(u), d(v))$$

These indices are the first multiplicative Zagreb index,[21–23] (Π_1), the modified first multiplicative Zagreb index[24] (Π_1^*) and the second multiplicative Zagreb index[23] (Π_2), defined as:

$$\Pi_1 = \prod_v (d_v)^2, \quad \Pi_1^* = \prod_{u \approx v} (d_u + d_v), \quad \Pi_2 = \prod_{u \approx v} d_u d_v$$

The logarithms of the above expressions are then of the form (1), and pertain to the following choices of the function $F(x, y)$:

[k] $F(x, y) = \frac{\ln x}{x} + \frac{\ln y}{y}$, for the logarithm of first multiplicative Zagreb index;[25]

[l] $F(x, y) = \ln(x + y)$, for the logarithm of the modified first multiplicative Zagreb index;

[m] $F(x, y) = \ln x + \ln y$, for the logarithm of second multiplicative Zagreb index.

NUMERICAL WORK

How well the above-specified topological indices are correlated with two simple physico-chemical parameters were tested. The parameters chosen were the standard heats of formation (representative for thermochemical properties) and the normal boiling points (representative for intermolecular, van der Waals-type, interactions). In order to avoid size-dependency problems, a class of isomers was considered. In order to minimize problems caused by steric effects, polar functional groups, hydrogen bonding, and similar, the tests were made on a class of alkanes. The octanes were chosen as they are particularly convenient for such studies, because the number of their structural isomers (18) is large enough to make statistical inferences reliable, and because experimental data are available for all isomers.

From the formulas displayed in the preceding section, it is evident that for $\lambda = -1/2$, the general Randić index and the general sum-connectivity index are equal to the ordinary Randić index and the ordinary sum-connectivity index, respectively. For $\lambda = 1$, the general Randić index and the general sum-connectivity index coincide with the second and first Zagreb indices, respectively. In addition, for $\lambda = -1$, the general sum-connectivity index reduces to the harmonic index. In view of this, the variable Randić index for $\lambda = -3, -2, -1, 2, 3$ and the variable sum-connectivity index for $\lambda = -3, -2, 2, 3$ were tested. Thus, a total of 20 different vertex-degree-based topological indices of the form (1) were tested.

Experimental data for the heats of formations and boiling points of all octane isomers were taken from standard reference databases[26] (for details see Ref. 11). The topological indices were evaluated by an in-house computer program. Correlations between experimental data and topological indices were analyzed by a standard statistical software package.

In each particular case, the possibility of a curvilinear correlation was tested. In not a single case, could the existence of such a correlation be established. Therefore, the quality of the examined correlations could be assessed and compared by their correlation coefficients. These are collected in Table I.

TABLE I. Correlation coefficients $R(\Delta H_f^0)$ and $R(b.p.)$ for the correlations between the vertex-degree-based topological indices and the standard heats of formation (ΔH_f^0) and normal boiling points ($b.p.$) of isomeric octanes. The considered topological indices are defined *via* Eq. (1), in which the function $F(x,y)$ is given by the formulas [a]–[m]

Index	$R(\Delta H_f^0)$	$R(b.p.)$
[a]	–0.846	0.816
[b], $\lambda = -3$	–0.827	0.791
[b], $\lambda = -2$	–0.869	0.832
[b], $\lambda = -1$	–0.886	0.853

TABLE I. Continued

Index	$R(\Delta H_f^0)$	$R(b.p.)$
[b], $\lambda = 2$	0.447	–0.372
[b], $\lambda = 3$	0.437	–0.335
[c]	0.757	–0.713
[d]	0.536	–0.491
[e]	0.890	–0.860
[f]	–0.827	0.797
[g], $\lambda = -3$	–0.870	0.851
[g], $\lambda = -2$	–0.865	0.844
[g], $\lambda = 2$	0.705	–0.649
[g], $\lambda = 3$	0.655	–0.587
[h]	–0.854	0.818
[i]	–0.921	0.922
[j]	–0.844	0.817
[k]	–0.745	0.728
[l]	0.806	–0.772
[m]	0.752	–0.723

From Table I, it can be see that for each topological index, the two correlation coefficients were nearly equal, thus implying almost identical conclusions concerning the quality of the index. This detail confirms that the choice of the two test parameters (the physicochemical nature of which were quite different) was a reasonable one, and that the results of the comparison were indeed representative for the general quality of the topological indices considered.

DISCUSSION AND CONCLUDING REMARKS

By inspection of the data given in Table I, it is possible to draw a number of conclusions, some quite unfavorable for several well-established topological indices.

First, the famous and much studied Zagreb indices ([c] and [d]) were found to be completely inadequate for any structure–property correlation. This important detail seems to have been ignored in recent comprehensive surveys[27,28] on Zagreb indices.

In addition, the results for [k], [l] and [m] revealed that the recently advocated idea of using the multiplicative Zagreb indices[22–24] did not pass the test. Consequently, it may be justified to halt any further elaboration of the theory of these multiplicative indices.

The Randić index ([a]) is one of the most often applied molecular-graph-based structure descriptors. It is therefore remarkable to realize that its modification [b] with exponent $\lambda = -1$ (and to a lesser extent with exponent $\lambda = -2$) performs significantly better than the ordinary variant (with exponent $\lambda = -0.5$). This fact was mentioned neither in a recent review[29] by Randić himself, nor in some books.[2,6]

From a practical point of view, topological indices for which the absolute value of the correlation coefficients is less than 0.8 can be characterized as useless. This especially applies to the variable Randić index [b] and the variable sum-connectivity index [g] with exponents $\lambda > 1$.

The newly proposed sum-connectivity index [f][12] and harmonic index [j],[20] although having reasonably good correlation abilities, are outperformed by several older indices. Therefore, the justification of their use in structure–property correlations is questionable.

The only vertex-degree-based topological index that has correlation coefficients over 0.9 is the augmented Zagreb index [i], recently invented by Furtula *et al*.[17] It may be stated that only this index successfully passed the tests applied in the present study. Consequently, this index should be preferred in designing quantitative structure–property relations.

The second-best vertex-degree-based molecular structure-descriptor appears to be the Estrada atom-bond connectivity (ABC) index [e].

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И З В О Д

ТЕСТИРАЊЕ КВАЛИТЕТА МОЛЕКУЛСКИХ СТРУКТУРНИХ ДЕСКРИПТОРА. ТОПОЛОШКИ ИНДЕКСИ ЗАСНОВАНИ НА СТЕПЕНИМА ЧВОРОВА

ИВАН ГУТМАН и ЈЕЛЕНА ТОШОВИЋ

Природно–математички факултет Универзитета у Крагујевцу

За 20 тополошких индекса заснованих на степенима чворова, а који су разматрани у хемијској литератури, тестирана је корелација са стандардним топлотама образовања и нормалним тачкама кључана изомерних октана. Показано је да су за већину ових индекса ове корелације или веома слабе или непостојеће. Најбоље резултате дају "појачани индекс Загреб" (*augmented Zagreb index*) и ABC индекс.

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