MOLECULAR CONNECTIVITY INDICES REVISITED

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It is shown that the product $v_i v_j$ of degrees v of vertices ij, incident with the edge ij, is the number of paths of length 1, 2, and 3 in which the edge is in the center. The unified connectivity index $\chi_m = \sum_e (v_i v_j)^m$, where the sum is made over all edges, with $m = 1$, is the sum of the number of edges, the Platt number and the polarity number. And it is identical with the half sum of the cube $\mathbf{A}^3$ of the adjacency matrix $\mathbf{A}$. The Randić index $\chi_{-1/2}$ of regular graphs does not depend on their connectivity.

Recent reviews[1,2] of topological indices of chemical graphs show that the development of this field is very intensive. There are many topological indices, new ones are invented[3] and thus their ordering becomes very important.

The topological indices are usually[4] divided into two groups wheather are based on the adjacency matrix $\mathbf{A}$ (a_{ij}) or on the distance matrix $\mathbf{D}$ (d_{ij}).

The number of bonds $A = 1/2 \sum a_{ij} = 1/2 \sum v_i$ where v_i is the degree of the vertex i (usually in the hydrogen supressed graph).

The Zagreb group indices

$$M_1 = \sum_v v_i^2 \,, \quad M_2 = \chi_1 = \sum_e (v_i v_j)$$

The Randić connectivity index $\chi_{-1/2} = \sum_e (v_i v_j)^{-1/2}$. The sums $\sum_v$ are made over all vertices of the graph, the sums $\sum_e$ over all its edges, the sums $\sum$ over all elements.

The Randić index was generalized in the form

$$^{\mathbf{h}}\chi_{-1/2} = \sum_h (v_i v_j v_k)^{-1/2} \,,$$

where h is the path of length h.

The Platt index $F = \sum_e e_k$, where e_k is the degree of the edge k, the sum of edges adjancent to the edge k: $e_k = (v_i - 1) + (v_j - 1)$. The Platt index is twice the number of paths length 2 in a graph. It is known that

$$F = \sum_v v_i(v_i - 1) = M_1 - 2A \,.$$

The other group of topological indices is based on the distance matrix $\mathbf{D}$ (d_{ij}). It is the Wiener index $w = 1/2 \sum d_{ij}$ and the polarity number p, which is the sum of all selfavoiding paths of length 3 in the graph. Obviously A and F measure distances, too.

Altenburg[5] introduced the polynomial $w = \sum g_h d_h$, where g_h is half the frequency number of distances d_h in $\mathbf{D}$.

In another paper[6], he unified the molecular connectivity indices M_2 and $\chi_{-1/2}$ as $\chi_m = \sum_e (v_i v_j)^m$, $m \neq 0$, and studied their relations with w and p. Altenburg did not explain why he excluded the case of $m = 0$. Because $(v_i v_j)^0 = 1$, χ_0 is simply the number of edges in a graph.

RESULTS

The relation between χ_m and w, observed by Altenburg, can be explained by the fact that product $v_i v_j$ counts the selfavoiding paths of length 1, 2, 3 in which the edge ij is incident as the central edge,if it exists.

The proof short:

Path of length 1	1
Paths of length 2: $(v_i - 1) + (v_j - 1)$	$v_i + v_j - 2$
Paths of length 3: $(v_i - 1)(v_j - 1)$	$v_i v_j - v_i - v_j + 1$
Sum:	$v_i v_j$

In χ_1, the sum is made over all edges. Paths of length 1 are counted only once, paths of the length 3 too, since each edge ij is in the centre of the counted paths provided that the path does not form a triangle, then it is counted thrice. The path, of lenght 2 are counted twice with both their edges, Thus, with rare exceptions, $M_2 = \chi_1 = A + F + p$.

This is the beginning of the Altenburg polynom (there is $3p$, of course), which makes the greatest or regular contribution of w. That explains regularities observed by Altenburg at χ_1, for other m changes are rather regular. The relation can be approximated at alkanes by the formula $\chi_m = (n - 1) \exp(am)$. (See Fig. 1).

If we try to analyze the generalized Randić index similarly, the product $v_x v_y v_z$ can be the sum of terms $v_x v_y$, $v_y v_z$ counting paths of length 1, 2, 3 $(v_x - 1)(v_y - 1)$ counting paths of length 4, $(v_x - 1)(v_y - 2)(v_z - 1)$ counting monosubstituted pentane chains, but is it not possible to obtain a balance. It seems that the succes of the use of ${}^h\chi_m$ was spurious, due to specific properties of carbon atoms, where $v_i \leqq 4$.

Following Altenburg, it is posible to generalize the Platt index as $\chi_m : F_m = \sum_e . [(v_i - 1) + (v_j - 1)]^m$. It is shown of Fig. 1, that both indices behave similarly.

Some important conclusions can be made from orderings of normal and branched alkanes at different m.

Randić[7] correlated the enthalpies of formation of the gaseous alkanes ΔH_f^0 by the three parameter function

$$\Delta H_f^0 = 50\chi_{-1/2} - 46A - 38 \text{ kJ/mol}.$$

The reversed order of branched alkanes against normal ones shows that m in χ_m should be positive in this case, or it should be used the Smolenskii additivity function[4] or kappa indices[8].

Recently Gao and Hosoya[9] proposed a new index A^3 as the half sum of the off diagonal elements of the cube of the adjancency matrix $\boldsymbol{A}$. These elements count the number of all paths of length 3 in a graph. The number of selfavoiding paths is $2p$. On each edge there are two selfreturning path ($i \to j$ and $j \to i$), on a chain of two edges are 4 selfreturning paths of length 3 (e.g. on $i - j - k$ there are $i \to j \to k \to j$, $j \to i \to j \to k$, $j \to k \to j \to i$; $k \to j \to i \to j$). On the diagonal of $\boldsymbol{D}^3$ are counted triangles, each 3 times on all its vertices, everytime with both orientations. This gives another interpretation of χ_1, it is half of the number of all paths of length 3 in a graph and $\chi_1 = 1/2A^3$. The diagonal elements should be counted, too.

But the specific case of alkanes does not mean that Randić index $\chi_{-1/2}$ is superfluous. At regular graphs $v_i = v_j$ and we have

$$\chi_m = \sum_e v_i^{2m}.$$

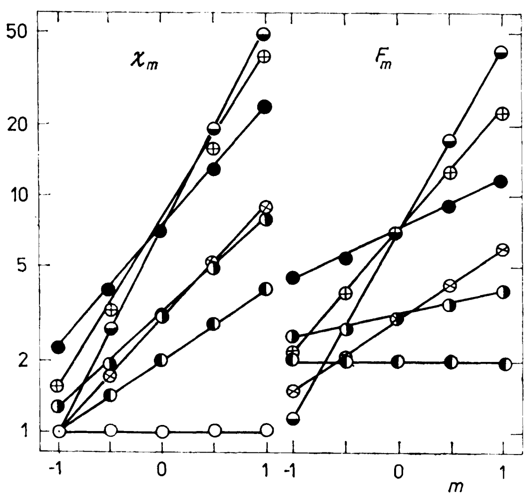

FIG. 1

Dependence of χ_m and F_m on m. The relation of the generalized connectivity index χ_m and of the generalized Platt number F_m with m is on the logarithmic scale approximately linear. The parameter m changes the ranking of linear alkanes against branched ones. ○ Et, ◐ Pr, ◑ n Bu, ⊗ tert. Bu, ● n Oct, ⊕ 2,2,3,3 tetra Me Bu, ◒ S_8, ⊙ all stars

If we replace the sum over all edges by the sum over all vertices as at the Platt number, we get $\chi_m = nv_i^{2m+1}/2$ and $\chi_{-1/2} = n/2$.

The Randić index of regular graphs does not depend on their connectivity, which is contrary to its name. E.g. hydrogen depleted cubane, cyclooctane and a set of 4 ethanes have the Randić index 4 despite that their connectivities are 3, 2 and 0, respectively.

This can be compared with χ_m of stars $(n - 1)^{m+1}$.

The Randić index does not measure connectivity but it is a very elegant measure of the regularity of a graph.

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