Topological Properties of Benzenoid Systems XXIX. On Hosoya's Topological Index

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Some properties of Hosoya's topological index Z and the modified topological index $\tilde{Z}$ of benzenoid hydrocarbons are examined. A simple relation between $\tilde{Z}$ and Z has been established, namely $\tilde{Z} = Z^{1+a}$, where $a = 0.02$.

Hosoya introduced [1] a topological index Z and demonstrated [2] its applicability for predicting physico-chemical properties of saturated hydrocarbons. Attempts [3] to use Z in the topological theory of unsaturated conjugated molecules resulted in the modified topological index $\tilde{Z}$ [4, 5]. In the present paper we report some relations between Z and $\tilde{Z}$, which hold for benzenoid hydrocarbons [6].

Let G be a (molecular) graph with n vertices and m edges. Then the corresponding topological index of Hosoya is defined as

$$Z = Z_G = \sum_{k=0}^{n/2} p\,(G, k)\,,$$

where $p\,(G, k)$ is the number of k-matchings of G. Note that $p\,(G, 0) = 1$ and $p\,(G, 1) = m$. In addition, since the matching polynomial of G is [7]

$$\alpha\,(G, x) = \sum_{k=0}^{n/2} (-1)^k\, p\,(G, k)\, x^{n-2k}\,,$$

one immediately gets

$$Z_G = i^{-n}\, \alpha\,(G, i)\,, \tag{1}$$

where $i = \sqrt{-1}$. The modified topological index is defined in full analogy with (1), viz.,

$$\tilde{Z} = \tilde{Z}_G = i^{-n}\, \Phi\,(G, i)\,,$$

where $\Phi\,(G, x)$ is the characteristic polynomial of the graph G.

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If G is a benzenoid graph [6], then its characteristic polynomial can be written in the form [8]

$$\Phi\,(G, x) = \sum_{k=0}^{n/2} (-1)^k\, q\,(G, k)\, x^{n-2k}\,,$$

where $q\,(G, k) \geqq 0$ for all k, $q\,(G, 0) = 1$ and $q\,(G, 1) = m$. Hence

$$\tilde{Z}_G = \sum_{k=0}^{n/2} q\,(G, k)\,.$$

For alternant hydrocarbons (and therefore also for benzenoids), the relation between Z and $\tilde{Z}$ reads as follows: Let $C_1, C_2, \ldots, C_r$ be the cycles contained in the molecular graph G. Let $G - C_i$ be the subgraph obtained by deleting the vertices of C_i from G. Let the subgraphs $G - C_i - C_j$, $G - C_i - C_j - C_k$ etc. be defined analogously. Then [4]

$$\tilde{Z}_G = Z_G + 2\sum_i S_i Z_{G-C_i} + 4\sum_{i,j} S_i S_j Z_{G-C_i-C_j} + 8\sum_{i,j,k} S_i S_j S_k Z_{G-C_i-C_j-C_k} + \ldots\,, \tag{2}$$

where $S_i = -1$ if the size of the cycle C_i is divisible by four, and $S_i = +1$ if the size of C_i is not divisible by four. The second, third etc. summations on the right-hand side of (2) go over all pairs, triplets etc. of mutually independent cycles in G (i.e. cycles which do not possess common vertices).

If G is acyclic (i.e. $r = 0$), then $\tilde{Z}_G$ is equal to Z_G. If G possesses $(4k)$-membered cycles, then $\tilde{Z}_G$ may be smaller than Z_G. According to [8], for benzenoid

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systems $p(G,k) \leqq q(G,k)$ and consequently, $\tilde{Z}_G$ is always greater than Z_G.

In the present paper we wish to point at the relation

$$\tilde{Z} = (Z)^{1+a}, \tag{3}$$

where $a \approx 0.02$. The above equation holds (as a good approximation) for all benzenoid systems.

Formula (3) is supported by the following numerical results: For 127 benzenoid hydrocarbons with not more than 42 carbon atoms [9], a least-squares fitting procedure gave

$$\ln \tilde{Z} = 1.02266 \ln Z + 0.032 \tag{4}$$

with a correlation coefficient 0.9997. Note that the constant term in (4) is negligibly small.

The Z and $\tilde{Z}$ values have been correlated for linear polyacenes A_h with h hexagons (see [10]) according to the recursion relations [11]

$$Z(A_h) = 9Z(A_{h-1}) - 7Z(A_{h-2}) + Z(A_{h-3}),$$
$$\tilde{Z}(A_h) = 10\tilde{Z}(A_{h-1}) - 14\tilde{Z}(A_{h-2}) + 10\tilde{Z}(A_{h-3}) - \tilde{Z}(A_{h-4}).$$

For the first one hundred members of this homologous series

$$\ln \tilde{Z} = 1.01894 \ln Z + 0.041$$

with a correlation coefficient $1 - 10^{-10}$.

The Z and $\tilde{Z}$ values have been correlated for zigzag polyacenes B_h with h hexagons (see [10]) according to the recursion relations [11]

$$Z(B_h) = 9Z(B_{h-1}) - 5Z(B_{h-2}) - 5Z(B_{h-3}) + Z(B_{h-4}),$$
$$\tilde{Z}(B_h) = 10\tilde{Z}(B_{h-1}) - 10\tilde{Z}(B_{h-2}) - 10\tilde{Z}(B_{h-3}) + 10\tilde{Z}(B_{h-4}) - \tilde{Z}(B_{h-5}).$$

For the first one hundred members of this homologous series

$$\ln \tilde{Z} = 1.02268 \ln Z + 0.027$$

with a correlation coefficient $1 - 2 \cdot 10^{-10}$.

The (empirical) fact that in formula (3) the constant a is much smaller than unity has a few interesting consequences. For all benzenoid systems of chemical interest, $a \cdot \ln Z$ does not exceed unity. Therefore, as a good approximation,

$$Z^a = 1 + a \cdot \ln Z. \tag{5}$$

Substituting (5) back into (3) and using (2), we get

$$a Z_G \ln Z_G = 2 \sum_i S_i Z_{G-C_i} + 4 \sum_{i,j} S_i S_j Z_{G-C_i-C_j} + \ldots. \tag{6}$$

Since Z_G is an exponentially increasing function of n and m (see below), we may conclude that the dominant terms which determine the value of the right-hand side of (6) are the topological indices of the subgraphs $G - C_i$, where C_i is a hexagon. For hexagons, of course, $S_i = +1$, and we arrive at the seemingly very rough approximation

$$a Z_G \ln Z_G = 2 \sum_{\text{hexagons}} Z_{G-C_i} = 2h \langle Z_{G-H} \rangle, \tag{7}$$

where h is the number of hexagons in G and $\langle Z_{G-H} \rangle$ denotes the mean value of the topological index of hexagon-deleted subgraphs of G.

It is known [4] that the modified topological index and the total π-electron energy are related as $E = C \ln \tilde{Z}$, where C is a constant. For benzenoid systems we found the regression

$$E = 2.695 \ln Z + 0.302$$

(correlation coefficient 0.997). Since, in addition, E can be approximated by [12]

$$E = 0.714n + 0.566m + 0.395,$$

we conclude that (at least) for benzenoid hydrocarbons, Z increases exponentially with the size of the molecular graph:

$$\ln Z = 0.265n + 0.210m + 0.035. \tag{8}$$

Therefore, if m_H is the number of edges which are incident to the hexagon H,

$$\ln Z_{G-H} = 0.265(n-6) + 0.210(m - 6 - m_H) + 0.035$$

i.e.

$$\ln \langle Z_{G-H} \rangle = \ln Z_G - (2.850 + 0.210 \langle m_H \rangle)$$

i.e.

$$2h \langle Z_{G-H} \rangle = 2h Z_G \exp(-2.850 - 0.210 \langle m_H \rangle), \tag{9}$$

where $\langle m_H \rangle$ is the mean value of m_H.

For benzenoid graphs with h hexagons, $n = 4h + 2 - n_i$ and $m = 5h + 1 - n_i$, where n_i is the number of internal vertices [6]. Having this in mind, (8) becomes

$$\ln Z = 2.110h + (0.775 - 0.255 n_i). \tag{10}$$

The expression in brackets on the right-hand side of (10) is small relative to $\ln Z$ and can be neglected. Then by combining (9) and (10), we get

$$2h\langle Z_{G-H}\rangle = [0.948 \exp(-2.850 - 0.210\langle m_H\rangle)] Z_G \ln Z_G ,$$

which, when combined with (7), implies that

$$a = 0.948 \exp(-2.850 - 0.210\langle m_H\rangle) . \quad (11)$$

The value of $\langle m_H\rangle$ depends on the actual structure of the benzenoid system considered, however it must range between 2 and 6. Setting $\langle m_H\rangle$ equal to 3, 4 and 5, we obtain the values 0.029, 0.024 and 0.019, respectively, for the right-hand side of (11). These results are in fairly good agreement with the empirically determined value for a (c.f. (4)).

Thus, by means of the above graph-theoretical analysis the approximate relation (3) between the two topological indices Z and $\tilde{Z}$ has been explained. The coincidence between the calculated (using (11)) and the empirically determined values of the parameter a also shows that the numerous approximations used in our considerations were justified.

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