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 $\bar{Z}$ of benzenoid hydrocarbons are examined. A simple relation between $Z$ and $\bar{Z}$ has been established, namely $\bar{Z} = Z^{1+\alpha}$, where $\alpha = 0.02$.

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 $\bar{Z}$ [4, 5]. In the present paper we report some relations between $Z$ and $\bar{Z}$, 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]

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

one immediately gets

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

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

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

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

For alternant hydrocarbons (and therefore also for benzenoids), the relation between $Z$ and $\bar{Z}$ 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]

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

(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 $\bar{Z}_G$ is equal to $Z_G$. If $G$ possesses $(4k)$-membered cycles, then $\bar{Z}_G$ may be smaller than $Z_G$. According to [8], for benzenoid...
In the present paper we wish to point at the relation
\[ Z = (Z)^{1+a}, \tag{3} \]
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
\[ \ln Z = 1.02266 \ln Z + 0.032 \tag{4} \]
with a correlation coefficient 0.9997. Note that the constant term in (4) is negligibly small.

The \( Z \) and \( \bar{Z} \) values have been correlated for linear polyacenes \( A_h \) with \( h \) hexagons (see [10]) according to the recursion relations [11]
\[
\begin{align*}
Z(A_h) &= 9 Z(A_{h-1}) - 7 Z(A_{h-2}) + Z(A_{h-3}), \\
\bar{Z}(A_h) &= 10 \bar{Z}(A_{h-1}) - 14 \bar{Z}(A_{h-2}) + 10 \bar{Z}(A_{h-3}) - \bar{Z}(A_{h-4}).
\end{align*}
\]
For the first one hundred members of this homologous series
\[ \ln \bar{Z} = 1.01894 \ln Z + 0.041 \]
with a correlation coefficient \( 1 - 10^{-10} \).

The \( Z \) and \( \bar{Z} \) values have been correlated for zigzag polyacenes \( B_h \) with \( h \) hexagons (see [10]) according to the recursion relations [11]
\[
\begin{align*}
Z(B_h) &= 9 Z(B_{h-1}) - 5 Z(B_{h-2}) - 5 Z(B_{h-3}) + Z(B_{h-4}), \\
\bar{Z}(B_h) &= 10 \bar{Z}(B_{h-1}) - 10 \bar{Z}(B_{h-2}) - 10 \bar{Z}(B_{h-3}) + 10 \bar{Z}(B_{h-4}) - \bar{Z}(B_{h-5}).
\end{align*}
\]
For the first one hundred members of this homologous series
\[ \ln \bar{Z} = 1.02268 \ln Z + 0.027 \]
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
\[ a Z_G \ln Z_G = 2 \sum_{\text{hexagons}} Z_{G-C_i} = 2 h \langle Z_{G-H} \rangle, \tag{7} \]
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 \( \pi \)-electron energy are related as
\[ E = C \ln Z, \]
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]
\[ E = 0.714 n + 0.566 m + 0.395, \]
we conclude that (at least) for benzenoid hydrocarbons, \( Z \) increases exponentially with the size of the molecular graph:
\[ \ln Z = 0.265 n + 0.210 m + 0.035. \tag{8} \]
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.
\[ 2 h \langle Z_{G-H} \rangle = 2 h Z_G \exp (- 2.850 - 0.210 \langle m_H \rangle), \tag{9} \]
where \( \langle m_H \rangle \) is the mean value of \( m_H \).

For benzenoid graphs with \( h \) hexagons, \( n = 4 h + 2 - n_i \) and \( m = 5 h + 1 - n_i \), where \( n_i \) is the number of internal vertices [6]. Having this in mind, (8) becomes
\[ \ln Z = 2.110 h + (0.775 - 0.255 n_i). \tag{10} \]
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.