

# Some properties of the topological bond order

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## Abstract

The *topological bond order* is a bond-order-like quantity, put forward in the 1970s. It is defined as  $p_{rs}^T = Z(G_{rs})/Z(G)$ , where  $G$  is the molecular graph,  $G_{rs}$  is obtained from  $G$  by deleting from it the adjacent vertices labelled by  $r$  and  $s$ , and  $Z$  stands for the respective topological (Hosoya) index. Because no easy way for the calculation of  $p_{rs}^T$  is known, its properties were studied only to a limited degree. We now introduce a *modified topological bond order*,  $\tilde{p}_{rs}^T$ , that can (easily) be calculated from the eigenvalues of  $G$  and  $G_{rs}$ . For acyclic systems,  $\tilde{p}_{rs}^T = p_{rs}^T$ . In the case of polycyclic systems a reasonably accurate linear correlation exists between  $\tilde{p}_{rs}^T$  and  $p_{rs}^T$ . Thus, by studying  $\tilde{p}_{rs}^T$  the main properties of  $p_{rs}^T$  can be established.

## 1. Introduction

In the topological theory of conjugated molecules [1, 2] several bond-order-like quantities are considered. Of these the best known are the Pauling [3], the Coulson [4], and the Ham-Ruedenberg [5] bond orders. In the 1970s one of the present authors proposed [6] the *topological bond order*, defined by means of the *topological index*.<sup>1</sup> Thus, the topological bond order pertaining to the bond between atoms  $r$  and  $s$  is defined as

$$p_{rs}^T = \frac{Z(G_{rs})}{Z(G)} \quad (1)$$

where  $G$  is the molecular graph,  $G_{rs}$  is the subgraph obtained from  $G$  by deleting from it the vertices corresponding to the atoms  $r$  and  $s$ , and  $Z$  stands for the respective

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<sup>1</sup>The quantity  $Z$ , put forward in [7] and named “topological index”, is nowadays in the chemical literature usually referred to as the “Hosoya index”. We, nevertheless, call it by its original name.

topological index. The topological index is defined as [7]

$$Z(G) = \sum_{k \geq 0} m(G, k) \quad (2)$$

where  $m(G, 0) = 1$  ,  $m(G, 1) =$  number of edges of the graph  $G$  , and  $m(G, k)$  ,  $k \geq 2$  , is the number of selections of  $k$  mutually independent (that is, mutually non-touching) edges in the graph  $G$  .

Some fundamental properties of the topological bond order were established in two papers published in the 1970s [6, 8], where also its relations to the Coulson and Pauling bond orders were analyzed. After that not much research in this area was done, as seen from the reviews [9, 10].

An object, closely related to  $Z$  is the matching polynomial, defined as [11]

$$\alpha(G, \lambda) = \sum_{k \geq 0} (-1)^k m(G, k) \lambda^{n-2k} \quad (3)$$

where  $n$  is the number of vertices of  $G$  . Details of the theory of the topological index and matching polynomial can be found in the books [12] and [13], respectively. Comparative studies of various bond orders (including the topological bond order) were reported in [14, 15].

Combining (2) and (3) one immediately obtains

$$Z(G) = i^{-n} \alpha(G, i) \quad (4)$$

where  $i = \sqrt{-1}$  . Furthermore, if  $\mu_1, \mu_2, \dots, \mu_n$  are the zeros of the matching polynomial, then

$$Z(G) = \sqrt{\prod_{j=1}^n [1 + (\mu_j)^2]} . \quad (5)$$

Formulas (4) and (5) are applicable to any (molecular) graph  $G$  . If  $G$  is acyclic, then the matching polynomial  $\alpha(G, \lambda)$  coincides with the characteristic polynomial  $\phi(G, \lambda)$  [13], implying

$$Z(G) = i^{-n} \phi(G, i) \quad (6)$$

and

$$Z(G) = \sqrt{\prod_{j=1}^n [1 + (\lambda_j)^2]} . \quad (7)$$

where  $\lambda_1, \lambda_2, \dots, \lambda_n$  are the respective graph eigenvalues. In contrast to the zeros of the matching polynomial, graph eigenvalues are easily computed (using the powerful methods of linear algebra). Therefore, in contrast to (5), formula (7) provides a convenient route for the computation of the topological index. Combined with (1), formula (7) makes it possible to easily evaluate the topological bond orders of acyclic  $\pi$ -electron systems. Unfortunately, this graph-eigenvalue-based method for computing  $p_{rs}^T$  is not applicable in the case of cycle-containing conjugated molecules, which, from both experimental and theoretical points of view, are the most interesting and most frequently examined  $\pi$ -electron systems.

In order to evade the computational difficulties encountered in the study of the topological bond orders of cyclic molecules we consider an approximation whose essence is that the right-hand sides of Eqs. (6) and (7) are extended to all (molecular) graphs. The *modified topological index*  $\tilde{Z}$  thus obtained, namely

$$\tilde{Z}(G) = i^{-n} \phi(G, i) \quad (8)$$

was also investigated already in the 1970s [16], when also the expression

$$\tilde{Z}(G) = \sqrt{\prod_{j=1}^n [1 + (\lambda_j)^2]} . \quad (9)$$

was established [17]. However, the analogous *modified topological bond order*, viz.,

$$\tilde{p}_{rs}^T = \frac{\tilde{Z}(G_{rs})}{\tilde{Z}(G)} \quad (10)$$

was, so far, not investigated in due detail.

Recall that  $\Delta Z = \tilde{Z} - Z$  is considered as an “aromaticity index” [10, 16].

In the case of non-alternant conjugated systems, the right-hand side of (8) is complex-valued, in which case one has to take only its real part. In what follows we restrict our considerations to alternant hydrocarbons, in which case this difficulty does not occur.

## 2. Relations between $\tilde{p}_{rs}^T$ and $p_{rs}^T$

For acyclic systems, the topological bond order (1) and its modified version (10) coincide. In the case of polycyclic (molecular) graphs the relation between the two bond orders is much more complicated.

Let  $G$  be a graph and  $C, C', C'', \dots$  be its cycles. Let  $|C|$  denote the size of the cycle  $C$  and let  $G - C$  be the subgraph obtained from  $G$  by deleting from it all vertices of  $C$ . Two cycles  $C$  and  $C'$  are said to be disjoint if they have no common vertex. For an example see Fig. 1.

Fig. 1 comes about here

Let, as before,  $\phi(G) = \phi(G, \lambda)$  and  $\alpha(G) = \alpha(G, \lambda)$  denote the characteristic and matching polynomials of  $G$ . Then [13, 18, 19],

$$\begin{aligned}\phi(G) &= \alpha(G) - 2 \sum_C \alpha(G - C) + 4 \sum_{C, C'} \alpha(G - C - C') \\ &\quad - 8 \sum_{C, C', C''} \alpha(G - C - C' - C'') + \dots \\ \alpha(G) &= \phi(G) + 2 \sum_C \phi(G - C) + 4 \sum_{C, C'} \phi(G - C - C') \\ &\quad + 8 \sum_{C, C', C''} \phi(G - C - C' - C'') + \dots\end{aligned}$$

where the summations go over all cycles, over all pairs of disjoint cycles, over all triples of mutually disjoint cycles, etc, of the graph  $G$ .

In the case of alternant hydrocarbons, when all  $|C|$ -values are even, by means of (4) and (8) we get

$$\begin{aligned}\tilde{Z}(G) &= Z(G) - 2 \sum_C (-1)^{|C|/2} Z(G - C) + 4 \sum_{C, C'} (-1)^{(|C|+|C'|)/2} Z(G - C - C') \\ &\quad - 8 \sum_{C, C', C''} (-1)^{(|C|+|C'|+|C''|)/2} Z(G - C - C' - C'') + \dots \\ Z(G) &= \tilde{Z}(G) + 2 \sum_C (-1)^{|C|/2} \tilde{Z}(G - C) + 4 \sum_{C, C'} (-1)^{(|C|+|C'|)/2} \tilde{Z}(G - C - C') \\ &\quad + 8 \sum_{C, C', C''} (-1)^{(|C|+|C'|+|C''|)/2} \tilde{Z}(G - C - C' - C'') + \dots\end{aligned}$$

For instance, for the phenanthrene graph  $G$  and its subgraph  $G_{12}$  (see Fig. 1) we have:

$$\begin{aligned}\tilde{Z}(G) &= Z(G) + 2 [Z(G - C_1) + Z(G - C_2) + Z(G - C_3) + Z(G - C_4) \\ &+ Z(G - C_5) + Z(G - C_6)] + 4 Z(G - C_1 - C_3)\end{aligned}$$

$$\tilde{Z}(G_{12}) = Z(G_{12}) + 2 [Z(G_{12} - C_2) + Z(G_{12} - C_3) + Z(G_{12} - C_5)]$$

$$\begin{aligned}Z(G) &= \tilde{Z}(G) - 2 [\tilde{Z}(G - C_1) + \tilde{Z}(G - C_2) + \tilde{Z}(G - C_3) + \tilde{Z}(G - C_4) \\ &+ \tilde{Z}(G - C_5) + \tilde{Z}(G - C_6)] + 4 \tilde{Z}(G - C_1 - C_3)\end{aligned}$$

$$Z(G_{12}) = \tilde{Z}(G_{12}) - 2 [\tilde{Z}(G_{12} - C_2) + \tilde{Z}(G_{12} - C_3) + \tilde{Z}(G_{12} - C_5)]$$

Bearing in mind that  $Z(G - C_1) = Z(G - C_3) = 44$ ,  $Z(G - C_2) = 25$ ,  $Z(G - C_4) = Z(G - C_5) = 5$ ,  $Z(G - C_6) = 1$ ,  $Z(G - C_1 - C_3) = 2$ , and  $Z(G_{12} - C_2) = 10$ ,  $Z(G_{12} - C_3) = 12$ ,  $Z(G - C_5) = 2$ , we get

$$\tilde{p}_{12}^T = \frac{Z(G_{12}) + 2(10 + 12 + 2)}{Z(G) + 2(44 + 25 + 44 + 5 + 5 + 1) + 4(2)} = \frac{Z(G_{12}) + 48}{Z(G) + 256}$$

i. e.,

$$\tilde{p}_{12}^T = \frac{p_{12}^T + 48/Z(G)}{1 + 256/Z(G)}.$$

Bearing in mind that  $\tilde{Z}(G - C_1) = \tilde{Z}(G - C_3) = 48$ ,  $\tilde{Z}(G - C_2) = 25$ ,  $\tilde{Z}(G - C_4) = Z(G - C_5) = 5$ ,  $\tilde{Z}(G - C_6) = 1$ ,  $\tilde{Z}(G - C_1 - C_3) = 2$ , and  $\tilde{Z}(G_{12} - C_2) = 10$ ,  $\tilde{Z}(G_{12} - C_3) = 12$ ,  $\tilde{Z}(G - C_5) = 2$ , we get

$$p_{12}^T = \frac{\tilde{Z}(G_{12}) - 2(10 + 12 + 2)}{\tilde{Z}(G) - 2(48 + 25 + 48 + 5 + 5 + 1) + 4(2)} = \frac{\tilde{Z}(G_{12}) - 48}{\tilde{Z}(G) - 256}$$

i. e.,

$$p_{12}^T = \frac{\tilde{p}_{12}^T - 48/\tilde{Z}(G)}{1 - 256/\tilde{Z}(G)}.$$

In the general case

$$\tilde{p}_{rs}^T = \frac{p_{rs}^T + \Delta Z(G_{rs})/Z(G)}{1 + \Delta Z(G)/Z(G)} \quad \text{and} \quad p_{rs}^T = \frac{\tilde{p}_{rs}^T - \Delta Z(G_{rs})/\tilde{Z}(G)}{1 - \Delta Z(G)/\tilde{Z}(G)}.$$

From these expressions and examples one would be inclined to conclude that the connection between the topological bond order and its modified version is relatively complicated. However, our numerical testings show the opposite. These are outlined in the subsequent section.

### 3. Numerical work

In Fig. 2 are plotted the topological bond orders of all bonds of the benzenoid hydrocarbons with 5 and fewer six-membered rings (a total of 25 molecules, 332 symmetry–nonequivalent bonds) versus the respective modified topological bond orders.

Fig. 2 comes about here

From Fig. 2 is seen that a reasonably good, but far from perfect, linear correlation exists between the two bond orders. The respective regression formula is

$$p_{rs}^T = (0.929 \pm 0.006) \tilde{p}_{rs}^T + (0.036 \pm 0.001)$$

which is not very far from  $p_{rs}^T \approx \tilde{p}_{rs}^T$ .

For non-benzenoid molecules (both alternant and non-alternant) the results are similar, yet somewhat more irregular. Details may be obtained from the authors (S.R.), upon request.

As already mentioned, the relation between the Coulson and topological bond orders was much studied in the past [6, 8]. In Fig. 3 we show such correlations for the carbon–carbon bonds of catacondensed benzenoid hydrocarbons. In these conjugated systems the carbon–carbon bonds can be classified into three groups, referred to as 3-3, 3-2, and 2-2. The vertices of the molecular graph, corresponding to an  $i$ - $j$  bond have degrees equal to  $i$  and  $j$ . (Recall that the degree of a vertex is the number of its first neighbors. In benzenoid graphs only vertices of degree 2 and 3 occur.)

Fig. 3 comes about here

From Fig. 3 three characteristic features are immediately recognized. First, there is a great deal of similarity between the diagrams (a) and (b), something that could be anticipated from the above discussed linear correlation between  $p^T$  and  $\tilde{p}^T$ . Second, the correlation between  $p^T$  and  $p^C$  is of very poor quality; the same is true for the correlation between  $\tilde{p}^T$  and  $p^C$ . Third, there is an obvious clustering of the data points with regards to above described classification of the carbon–carbon bonds.

This clustering is indicated by using different symbols (triangles, circles, squares) for 3-3, 3-2, and 2-2 bonds.

Within each of these three clusters there is a further grouping of the data points, determined by the finer details of molecular topology. For instance, the data points pertaining to 2-2 bonds (squares) are separated into three groups, depending on the degrees of the first neighbors of the vertices participating in the respective bond; those belonging to the upper right group have first neighbors of degree 3; those in the lower left group have first neighbors of degree 2. The data points pertaining to 3-3 bonds (triangles) are separated into two groups, with the upper left group of points corresponding to bonds lying on the perimeter.

#### 4. Concluding remarks

The main conclusion resulting from of the present study is that instead of the topological bond order  $p^T$  one may use its modified version  $\tilde{p}^T$ . Between these two bond-order-like quantities there is a relatively good linear correlation, and, if not a very high accuracy is required, one may accept that  $p_{rs}^T \approx \tilde{p}_{rs}^T$ . The numerical calculation of the modified topological bond order goes via the graph eigenvalues and is thus much easier than the calculation of  $p^T$ . Therefore, in future applications of the topological-bond-order concept, one could safely employ its modified version.

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## Figure Captions

**Fig. 1.** The molecular graph  $G$  of phenanthrene and of its vertex-deleted subgraph  $G_{12}$ . The cycles contained in  $G$  are  $C_1, C_2, \dots, C_6$  and are indicated by heavy lines. The only two disjoint cycles in  $G$  are  $C_1$  and  $C_3$ . The graph  $G$  does not possess triples, quadruples, etc. of mutually disjoint cycles. The subgraph  $G_{12}$  contains only the cycles  $C_2, C_3, C_5$ . Some typical subgraphs of the form  $G - C$  and  $G_{rs} - C$  are also shown.

**Fig. 2.** Correlation between the topological and modified topological bond orders, pertaining to benzenoid hydrocarbons with 5 and fewer six-membered rings. Empty and full circles correspond to catacondensed and pericondensed molecules, respectively. Correlation coefficient: 0.993.

**Fig. 3.** (a) Correlation between topological ( $p^T$ ) and Coulson bond orders ( $p^C$ ), pertaining to catacondensed benzenoid hydrocarbons with 5 and fewer six-membered rings. (b) The analogous correlation between modified topological ( $\tilde{p}^T$ ) and Coulson bond orders ( $p^C$ ). Triangles, circles and squares correspond to carbon-carbon bonds of type 3-3, 3-2, and 2-2, respectively; for details see text.