# Bounds for the Schultz Molecular Topological Index of Benzenoid Systems in Terms of the Wiener Index

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Let MTI and $W$ be the Schultz molecular topological index and the Wiener index, respectively, of a benzenoid system. It has been shown previously [Klavžar, S.; Gutman, I. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 1001−1003] that MTI is bounded as $4W < \mathrm{MTI} < 6.93\,W$. We now improve this result by deducing the estimates $4W + \lambda_1 W^{2/3} + \lambda_2 W^{1/3} - 15 < \mathrm{MTI} < 6W + \lambda_3 W^{2/5} - \lambda_4 W^{1/6}$ where $\lambda_1 = 4.400$, $\lambda_2 = 1.049$, $\lambda_3 = 14.760$, and $\lambda_4 = 17.739$.

## 1. INTRODUCTION

The fact that the molecular topological index (MTI) and the Wiener index ($W$) are mutually related has been noticed some time ago.[1−3] One finding along these lines is[4]

$$4W < \mathrm{MTI} < \lambda_0 W \tag{1}$$

where

$$\lambda_0 = 6 + \sqrt{\frac{108}{125}} = 6.9295...$$

The inequalities (1) hold for benzenoid hydrocarbons. In this paper we report improvements of (1), namely further bounds for MTI in terms of $W$:

$$4W + \lambda_1 W^{2/3} + \lambda_2 W^{1/3} - 15 < \mathrm{MTI} < 6W + \lambda_3 W^{2/5} - \lambda_4 W^{1/6} \tag{2}$$

where

$$\lambda_1 = \left(\frac{120}{13}\right)^{2/3} = 4.4003977... \tag{3}$$

$$\lambda_2 = \left(\frac{120}{104}\right)^{1/3} = 1.0488562... \tag{4}$$

$$\lambda_3 = 9\left(\frac{45\sqrt{6}}{32}\right)^{2/5} = 14.7603879... \tag{5}$$

$$\lambda_4 = \sqrt{150}\left(\frac{120}{13}\right)^{1/6} = 17.7385702... \tag{6}$$

Using the same notation as in our previous paper,[4] a molecular graph is denoted by $\Gamma$ and the number of its vertices by $N$. The vertices of $\Gamma$ are labeled by $p_1, p_2, ..., p_N$. The "*molecular topological index*" (MTI) of the graph $\Gamma$ was introduced by Schultz[5] in 1989 and is defined as follows:[5,6]

$$\mathrm{MTI} = \mathrm{MTI}(\Gamma) = \sum_{i=1}^{N} [\mathbf{d}(\mathbf{A} + \mathbf{D})]_i$$

Here $\mathbf{A}$ is the $N \times N$ adjacency matrix[7,8] of $\Gamma$, $\mathbf{D}$ is the $N \times N$ distance matrix[7,8] of $\Gamma$, and $\mathbf{d} = (d_1, d_2, ..., d_N)$ is the $1 \times N$ vector of the degrees of the vertices of $\Gamma$. Recall that the degree $d_i$ of the vertex $p_i$ is the number of first neighbors of this vertex or, what is the same, the sum of the entries of the $i$th column of $\mathbf{A}$. Note that in the mathematical literature instead of "degree" the name "valency" is sometimes used, which, of course, should be distinguished from valency in chemistry. The smallest and the largest degree of a vertex of $\Gamma$ will be denoted by $d_{\min}$ and $d_{\max}$, respectively.

The *Wiener index* of $\Gamma$ is equal to the sum of distances between all pairs of vertices of $\Gamma$:

$$W = W(\Gamma) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} D_{ij}$$

Another way of writing the above definition is

$$W(\Gamma) = \frac{1}{2}\sum_{i=1}^{N} D_i$$

where $D_i$ stands for the sum of distances between the vertex $p_i$ and all other vertices of the graph $\Gamma$. Of course, $D_i$ is equal to the sum of the entries of the $i$th column of the distance matrix $\mathbf{D}$.

The Wiener index is one of the most thoroughly studied, best understood, and most frequently used graph-theory-based molecular-shape descriptors; more information on $W$ can be found in the reviews.[9,10]

The main chemical applications and mathematical properties of the molecular topological index were established in a series of researches.[6,11−13] A noteworthy property of MTI is its relation to the Wiener index. Klein et al.[1] showed that if $\Gamma$ is a tree (i.e., if $\Gamma$ is the molecular graph of an alkane),

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then the following relation holds

$$\mathrm{MTI} = 4\,W + \sum_{i=1}^{N}(d_i)^2 - N(N-1)$$

which immediately implies that MTI and $W$ of alkanes are linearly correlated.[2] Eventually, it was demonstrated[4] that because of the inequalities

$$2d_{\min}\,W < \mathrm{MTI} \le 4d_{\max}\,W \qquad (7)$$

$W$ and MTI are linearly correlated for all molecules. In the special case of benzenoid hydrocarbons, instead of (7) one obtains (1).[4]

## 2. MTI AND *W* OF BENZENOID SYSTEMS

The graph representation of a benzenoid hydrocarbon is called a *benzenoid system* or *benzenoid graph*.[14] A formal (and mathematically rigorous) definition of benzenoid systems reads as follows.[15] *Benzenoid systems are finite connected plane graphs with no cut vertices, in which every interior region is bounded by a regular hexagon of side length 1*. More details on this important class of molecular graphs can be found in the book cited in ref 14.

The vertices of a benzenoid system are either of degree two or of degree three. This implies $d_{\min} = 2$ and $d_{\max} = 3$. A vertex that belongs to three hexagons is said to be internal. The number of internal vertices is denoted by $n_i$. Recall that there are numerous benzenoids for which $n_i = 0$, namely the catacondensed systems.[14] If $N$ is the number of vertices and $h$ the number of hexagons, then

$$N = 4h + 2 - n_i \qquad (8)$$

The number of vertices of degree two and three is then $2h + 4 - n_i$ and $2h - 2$, respectively.[14]

In Figure 1, all the 16 benzenoid systems with up to 20 vertices are presented.[14] In addition, a benzenoid system $B_{17}$ on 24 vertices is depicted, namely the coronene graph. In Table 1 the Wiener index, the MTI, as well as the old (1) and the new (2) bounds for MTI are given.

Without loss of generality we may assume that the vertices of a benzenoid system are labeled so that $p_1, p_2, \ldots, p_{2h-2}$ are of degree three, and $p_{2h-1}, p_{2h}, \ldots, p_N$ are of degree two. With such a labeling, the following identity between MTI and $W$ is satisfied:

$$\mathrm{MTI} = 4W + \frac{13N + 5n_i - 30}{2} + \sum_{i=1}^{2h-2} D_i \qquad (9)$$

In order to deduce (9) we start with the relation

$$\mathrm{MTI} = \sum_{i=1}^{N}(d_i)^2 + \sum_{i=1}^{N} d_i D_i \qquad (10)$$

which holds for all molecular graphs.[4] In view of the fact that benzenoid systems have only degree-two and degree-three vertices, the first term on the right-hand side of (10)

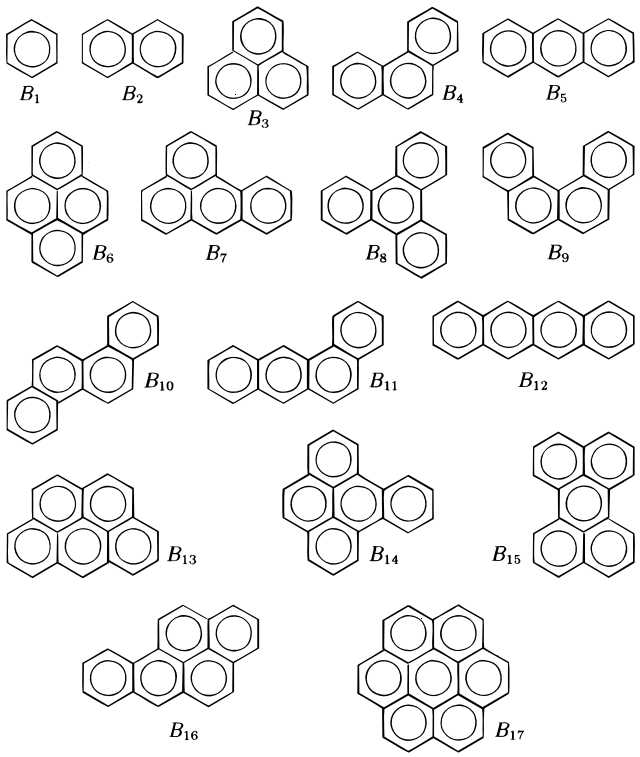


**Figure 1.** Some benzenoid systems.

**Table 1.** Wiener and Molecular Topological Indices of the Benzenoid Systems from Figure 1

| benzenoid system | $N$ | $W$ | lower bound (1) | lower bound (2) | MTI | upper bound (2) | upper bound (1) |
|---|---|---|---|---|---|---|---|
| $B_1$ | 6 | 27 | 108.0 | 135.8 | 132 | 186.4 | 187.1 |
| $B_2$ | 10 | 109 | 436.0 | 526.4 | 520 | 711.3 | 755.3 |
| $B_3$ | 13 | 210 | 840.0 | 986.7 | 1017 | 1342.1 | 1455.2 |
| $B_4$ | 14 | 271 | 1084.0 | 1260.1 | 1284 | 1719.6 | 1877.9 |
| $B_5$ | 14 | 279 | 1116.0 | 1295.7 | 1324 | 1769.0 | 1933.3 |
| $B_6$ | 16 | 362 | 1448.0 | 1664.0 | 1770 | 2280.4 | 2508.5 |
| $B_7$ | 17 | 440 | 1760.0 | 2007.5 | 2114 | 2759.5 | 3049.0 |
| $B_8$ | 18 | 513 | 2052.0 | 2327.4 | 2424 | 3206.9 | 3554.8 |
| $B_9$ | 18 | 529 | 2116.0 | 2397.3 | 2504 | 3304.9 | 3665.7 |
| $B_{10}$ | 18 | 545 | 2180.0 | 2467.2 | 2584 | 3402.8 | 3776.6 |
| $B_{11}$ | 18 | 553 | 2212.0 | 2502.1 | 2624 | 3451.8 | 3832.0 |
| $B_{12}$ | 18 | 567 | 2268.0 | 2563.1 | 2704 | 3537.4 | 3929.0 |
| $B_{13}$ | 19 | 566 | 2264.0 | 2558.8 | 2787 | 3531.3 | 3922.1 |
| $B_{14}$ | 20 | 652 | 2608.0 | 2933.0 | 3160 | 4056.9 | 4518.0 |
| $B_{15}$ | 20 | 654 | 2616.0 | 2941.7 | 3172 | 4069.1 | 4531.9 |
| $B_{16}$ | 20 | 680 | 2720.0 | 3054.5 | 3302 | 4227.9 | 4712.1 |
| $B_{17}$ | 24 | 1002 | 4008.0 | 4444.1 | 5040 | 6190.0 | 6943.4 |

can be written as

$$\sum_{i=1}^{N}(d_i)^2 = 4(2h + 4 - n_i) + 9(2h - 2) = \frac{13N + 5n_i - 30}{2} \qquad (11)$$

where we have taken into account (8).

For the second term on the right-hand side of (10) we get

$$\sum_{i=1}^{N} d_i D_i = 3\sum_{i=1}^{2h-2} D_i + 2\sum_{i=2h-1}^{N} D_i = \sum_{i=1}^{2h-2} D_i + 2\sum_{i=1}^{N} D_i = \sum_{i=1}^{2h-2} D_i + 4W \qquad (12)$$

Substituting (11) and (12) back into (10) yields (9).

## 3. THE LOWER BOUND

If $p_i$ is a vertex of degree three of a benzenoid system with at least four hexagons, then $p_i$ has three first neighbors (at distance 1), at least four second neighbors (at distance 2), and at least six vertices whose distance from $p_i$ is 3 or more. Consequently, if $p_i$ is a degree-three vertex of a benzenoid system with $N \geq 18$, then $D_i$ is not smaller than $2N$.

Therefore,

$$\sum_{i=1}^{2h-2} D_i \geq (2h-2)(2N) = (N + n_i - 6)N$$

which combined with (9) yields

$$\mathrm{MTI} \geq 4W + \frac{13N + 5n_i - 30}{2} + (N + n_i - 6)N$$

and because of $n_i \geq 0$,

$$\mathrm{MTI} \geq 4W + \frac{2N^2 + N - 30}{2} \qquad (13)$$

The Wiener index of the linear polyacene with $h$ hexagons is given by[16]

$$W(L_h) = \frac{1}{3}(16h^3 + 36h^2 + 26h + 3) = \frac{1}{12}(N^3 + 3N^2 + 2N - 12)$$

and this is the maximum $W$-value among benzenoid systems with $N$ vertices.[17] In other words, if $\Gamma$ is an $N$-vertex benzenoid system, then

$$W(\Gamma) \leq \frac{1}{12}(N^3 + 3N^2 + 2N - 12) \qquad (14)$$

If $N$ exceeds 10, then

$$N^3 > \frac{10}{3}(3N^2 + 2N - 12),$$

and from (14) we obtain a weaker, but simpler upper bound

$$W(\Gamma) < \frac{1}{12}\left(N^3 + \frac{3}{10}N^3\right)$$

from which it immediately follows

$$N > \left(\frac{120}{13}\right)^{1/3} W^{1/3} \qquad (15)$$

Substituting (15) back into (13) we arrive at

$$\mathrm{MTI}(\Gamma) > 4W(\Gamma) + \lambda_1 [W(\Gamma)]^{2/3} + \lambda_2 [W(\Gamma)]^{1/3} - 15$$

where $\lambda_1$ and $\lambda_2$ are given by (3) and (4). Note that in the above calculations it was assumed that $N \geq 18$. Direct checking (see Table 1) shows that the last inequality is true also for $N < 18$, except for the benzenoid systems $B_1$ and $B_2$. Thus we can state the following theorem.

**Theorem 1.** *If $\Gamma$ is a benzenoid system, $\Gamma \neq B_1, B_2$, then*

$$\mathrm{MTI}(\Gamma) > 4W(\Gamma) + \lambda_1 [W(\Gamma)]^{2/3} + \lambda_2 [W(\Gamma)]^{1/3} - 15$$

*where $\lambda_1$ and $\lambda_2$ are given by (3) and (4).*

## 4. THE UPPER BOUND

Among benzenoid systems, the benzene−coronene−circumcoronene series ($H_k$, $k = 1, 2, 3, \ldots$) has a minimum Wiener index,[4]

$$W(H_k) = \frac{1}{5}(164k^5 - 30k^3 + k)$$

i.e., for every $N$-vertex benzenoid graph,

$$W(\Gamma) \geq \frac{1}{5}\left[164\left(\sqrt{\frac{N}{6}}\right)^5 - 30\left(\sqrt{\frac{N}{6}}\right)^3 + \sqrt{\frac{N}{6}}\right] = \frac{1}{5}\sqrt{\frac{N}{6}}\left(\frac{41}{9}N^2 - 5N + 1\right) \qquad (16)$$

Recall that $H_k$ has $6k^2$ vertices. A detailed explanation concerning the relation (16) is found elsewhere.[4]

For all benzenoids $N \geq 6$ and thus $N^2 - 5N + 1 > 0$. Therefore

$$\frac{41}{9}N^2 - 5N + 1 = \frac{32}{9}N^2 + (N^2 - 5N + 1) > \frac{32}{9}N^2$$

i.e.,

$$W > \frac{1}{5}\sqrt{\frac{N}{6}}\frac{32}{9}N^2$$

i.e.,

$$N < \left(\frac{45\sqrt{6}}{32}\right)^{2/5} W^{2/5} \qquad (17)$$

In order to deduce an upper bound for MTI in terms of $W$ we again start from the identity (9).

The graph $H_k$ possesses $N = 6k^2$ vertices, of which $6(k-1)^2 = N - \sqrt{24N} + 6$ are internal. This is the maximum number of internal vertices an $N$-vertex benzenoid system may possess.[14,18] Therefore,

$$n_i \leq N - \sqrt{24N} + 6 \qquad (18)$$

Combining (9) with (18) and taking into account the obvious inequality

$$\sum_{i=1}^{2h-2} D_i < \sum_{i=1}^{N} D_i = 2W$$

we obtain

$$\mathrm{MTI} < 6W + 9N - \sqrt{150N} \qquad (19)$$

Replacing $N$ in the second term on the right-hand side of (19) by the upper bound (17) and replacing $N$ in the third term by the lower bound (15) we have the following theorem.

**Theorem 2.** *If* $\Gamma$ *is a benzenoid system, then*

$$\mathrm{MTI}(\Gamma) < 6W + \lambda_3[W(\Gamma)]^{2/5} - \lambda_4[W(\Gamma)]^{1/6}$$

*where* $\lambda_3$ *and* $\lambda_4$ *are given by* (5) *and* (6).

In the calculations yielding theorem 2 we have used (15) which is only true for $N > 10$. But from Table 1 we see that the bound of theorem 2 also holds for $B_1$ and $B_2$. Therefore, theorem 2 indeed holds for any benzenoid system.

Theorems 1 and 2 are, of course, equivalent to the bounds (2) which—as we just have seen—hold for all benzenoid systems (except benzene and naphthalene). The data given in Table 1 show that the new bounds (2) are much tighter than the previously reported ones (1). The bounds (2) reveal that the relation between MTI and $W$ is more complicated than originally anticipated. Whereas globally speaking MTI and $W$ are linearly correlated, the fine details of their relation are nonlinear.

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