Bounds for the Schultz Molecular Topological Index of Benzenoid Systems in Terms of 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.[**?**, **?**, **?**] One finding along these lines is[**?**]

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

where

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

The inequalities (**??**) hold for benzenoid hydrocarbons. In this paper we report improvements of (**??**), 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

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

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

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

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

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

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

Here $\mathbf{A}$ is the $N \times N$ adjacency matrix[**?**, **?**] of Γ, $\mathbf{D}$ is the $N \times N$ distance matrix[**?**, **?**] of Γ and $\mathbf{v} = (v_1, v_2, \ldots, v_N)$ is the $1 \times N$ vector of the valencies (degrees) of the vertices of Γ. Recall that the valency v_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 $\mathbf{A}$. The smallest and the largest valency of a vertex of Γ will be denoted by v_{min} and v_{max}, respectively.

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

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

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 Γ. 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.[**?**, **?**]

The main chemical applications and mathematical properties of the molecular topological index were established in a series of researches.[**?**, **?**, **?**, **?**] A noteworthy

property of MTI is its relation to the Wiener index. Klein et al.[**?**] showed that if Γ is a tree (i.e., if Γ is the molecular graph of an alkane) then the following relation holds:

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

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

$$2v_{min}\ W \ < \ \mathrm{MTI} \ \leq \ 4v_{max}\ W \tag{7}$$

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

2. MTI AND W OF BENZENOID SYSTEMS

The graph representation of a benzenoid hydrocarbon is called a *benzenoid system* or *benzenoid graph*.[**?**] A formal (and mathematically rigorous) definition of benzenoid systems reads as follows.[**?**] *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.[**?**]

The vertices of a benzenoid system are either of degree two or of degree three. This implies $v_{min} = 2\ ;\ v_{max} = 3$. 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.[**?**] If N is the number of vertices and h the number of hexagons, then

$$N = 4h + 2 - n_i\ . \tag{8}$$

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

In Fig. 1. all the 16 benzenoid systems with up to 20 vertices are presented.[**?**] 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 (**??**) and the new (**??**) bounds for MTI are given.

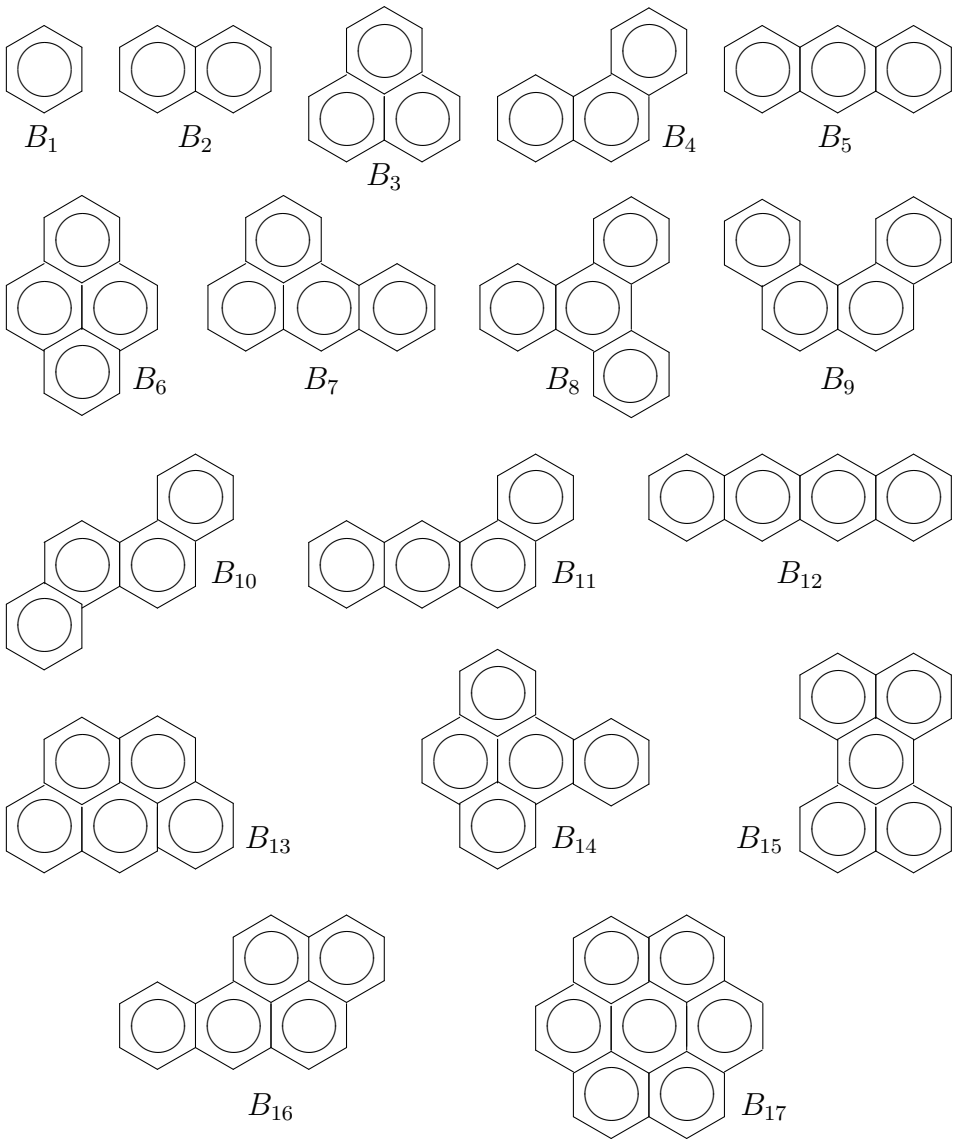

Figure 1: Some benzenoid systems

benze-noid 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

Table 1. Wiener and molecular topological indices of the benzenoid systems from Fig. 1

Without loss of generality we may assume that the vertices of a benzenoid system are labelled 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:

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

In order to deduce (**??**) we start with the relation

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

which holds for all molecular graphs.[**?**] 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 (**??**) can be written as

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

where we have taken into account (**??**).

For the second term on the right–hand side of (**??**) we get

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

Substituting (**??**) and (**??**) back into (**??**) yields (**??**).

3. THE LOWER BOUND

If p_i is a vertex of degree three of a benzenoid system with at least 4 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 (**??**) 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[**?**]

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

and this is the maximum W-value among benzenoid systems with N vertices.[**?**] In other words, if Γ 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 (**??**) 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

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

Substituting (**??**) back into (**??**) we arrive at:

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

where λ_1 and λ_2 are given by (**??**) and (**??**). 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:

Theorem 1. *If Γ 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 λ_1 and λ_2 are given by (**??**) and (**??**).*

4. THE UPPER BOUND

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

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

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

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

$$\frac{1}{5} \sqrt{\frac{N}{6}} \; \left(\frac{41}{9} \; N^2 - 5N + 1\right) \; . \tag{16}$$

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

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.,

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

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

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.[**?**, **?**] Therefore,

$$n_i \; \leq \; N - \sqrt{24N} + 6 \; . \tag{18}$$

Combining (**??**) with (**??**) and taking into account the obvious inequality

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

we obtain

$$\mathrm{MTI} \; < \; 6W + 9N - \sqrt{150N} \; . \tag{19}$$

Replacing N in the second term on the right-hand side of (**??**) by the upper bound (**??**) and replacing N in the third term by the lower bound (**??**) we have:

Theorem 2. *If* Γ *is a benzenoid system, then*

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

where λ_3 *and* λ_4 *are given by (**??**) and (**??**).*

In the calculations yielding Theorem 2 we have used (**??**) 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 (**??**) 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 (**??**) are much tighter than the previously reported ones (**??**). The bounds (**??**) reveal that the relation between MTI and W is more perplexed than originally anticipated. Whereas globally speaking MTI and W are linearly correlated, the fine details of their relation are nonlinear.

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