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

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Received January 1997

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.

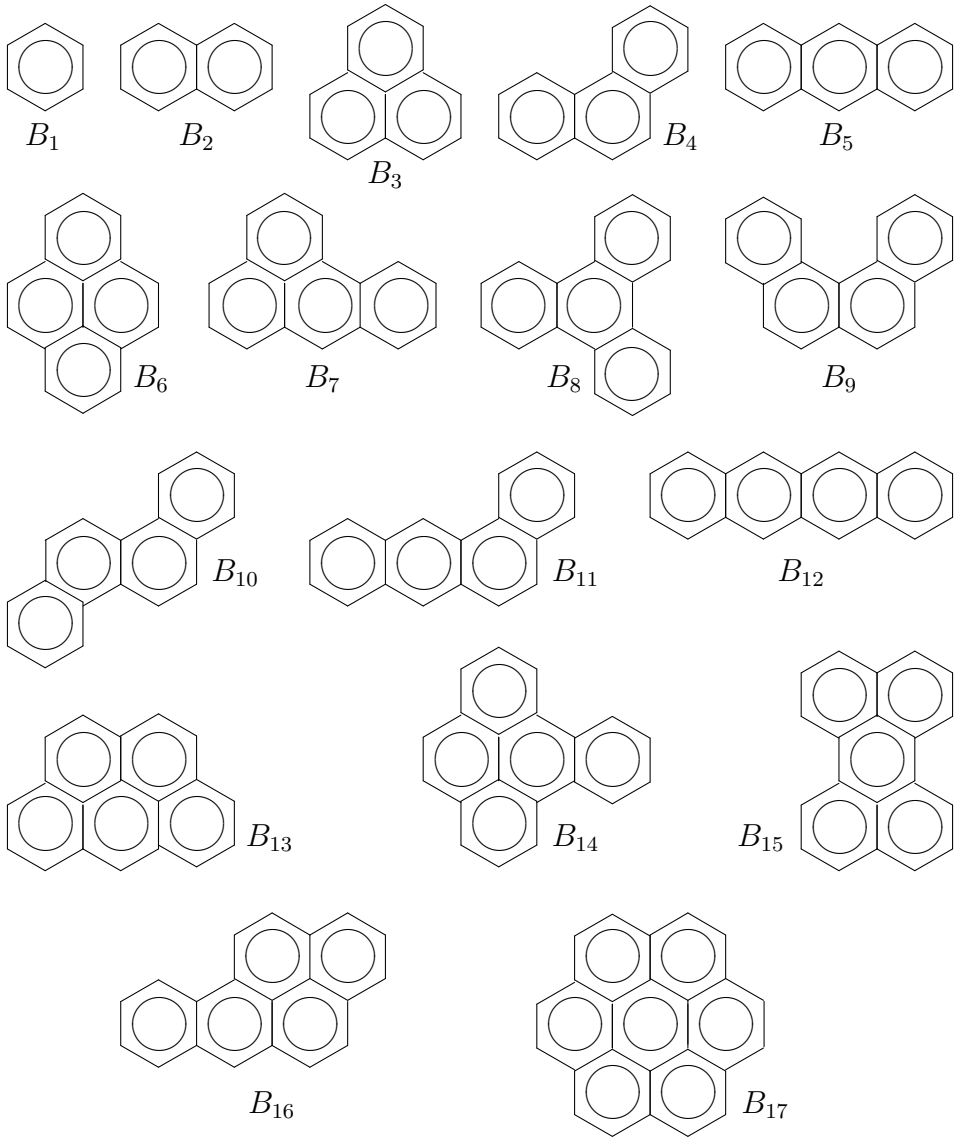

Figure 1: Some benzenoid systems

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.

ACKNOWLEDGEMENT

The work of one author (S.K.) was supported in part by the Ministry of Science and Technology of Slovenia under the grant J1-7036.

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