

A Comparison of the Schultz Molecular Topological Index with the Wiener Index

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The Schultz molecular topological index (MTI) is compared with the Wiener index (W) of a molecular graph. It is shown that $2v_{\min}W < \text{MTI} \leq 4v_{\max}W$ holds for any (connected) graph Γ , with v_{\min} and v_{\max} denoting the smallest and the largest valency, respectively, of the vertices of Γ . For molecular graphs these bounds can be further improved. For instance, for benzenoid systems we have the following: $4W < \text{MTI} < 6.93W$. This implies that W and MTI are linearly correlated not only in the case of acyclic molecules (which is a previously known result) but also in the case of molecules with arbitrarily many cycles.

1. INTRODUCTION

Let Γ be a molecular graph on N vertices. The “molecular topological index” (MTI) of the graph Γ introduced by Schultz¹ in 1989 is defined in the following way:^{1,2}

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

Here \mathbf{A} is the $N \times N$ adjacency matrix^{3,4} of Γ , \mathbf{D} is the $N \times N$ distance matrix^{3,4} of Γ and $\mathbf{v} = (v_1, v_2, \dots, v_N)$ is the $1 \times N$ vector of the valencies (degrees) of the vertices of the molecular graph Γ . Recall that the valency v_i of the vertex i is the number of first neighbors of this vertex.

The (i,j) th entry of the distance matrix \mathbf{D} , denoted by D_{ij} , is just the distance^{3,4} between the vertices i and j , namely the length of a shortest path connecting i and j . Recall that molecular graphs are necessarily connected.^{3,4} Therefore, if Γ is a molecular graph, then for all values of i and j , $1 \leq i, j \leq N$, the quantity D_{ij} is well-defined, finite, and integer-valued.

The Wiener index (or Wiener number) of a connected graph Γ is equal to the sum of distances between all pairs of vertices of Γ :

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

For details on the Wiener index, which is among the most frequently employed molecular-structure-descriptors in chemical graph theory, see the books^{3,4} or the recent reviews.^{5,6}

After the main mathematical properties and chemical applications of the molecular topological index were established,^{2,7–9} one gradually became aware that MTI and W are closely related. The most evident relation of this kind

is found in the case of regular graphs¹⁰ (molecular graphs of annulenes, fullerenes, and similar), for which $v_1 = v_2 = \dots = v_N = v$; recall that $v = 2$ for annulenes and $v = 3$ for fullerenes. Then MTI turns out to be a linear function of W :

$$\text{MTI} = 2vW + v^2N$$

A less obvious connection between MTI and W was discovered by Klein et al.¹¹ They, namely, showed that if Γ is a tree (i.e., if Γ is acyclic, i.e., if Γ is the molecular graph of an alkane) then the following relation holds:

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

Generalizations of this result were also obtained.¹² The fact that in the case of alkanes MTI and W are linearly correlated was verified by extensive numerical testing.¹⁰

In this paper we show that for arbitrary (polycyclic) molecular graphs MTI can be estimated as

$$\alpha W \leq \text{MTI} \leq \beta W$$

where α and β are pertinently chosen constants. These bounds imply that MTI and W must have basically the same dependence on molecular structure and that they must be (at least roughly) linearly correlated within any class of chemical graphs.¹⁰

2. GENERAL MOLECULAR GRAPHS

Recall¹² that MTI can be written as $\text{MTI} = M_2 + S$, where

$$M_2 = \sum_{i=1}^N (v_i)^2$$

and

$$S = -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N [v_i + v_j] D_{ij}$$

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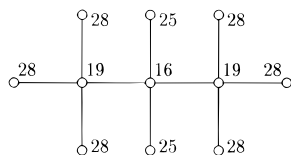


Figure 1. The corresponding D_i values of G_0 .

The quantity S can be further expressed as

$$\begin{aligned} S &= -\sum_{i=1}^N \sum_{j=1}^N v_i D_{ij} + \sum_{i=1}^N \sum_{j=1}^N v_j D_{ij} \\ &= -\sum_{i=1}^N v_i \sum_{j=1}^N D_{ij} + \sum_{j=1}^N v_j \sum_{i=1}^N D_{ij} \\ &= \sum_{i=1}^N v_i \sum_{j=1}^N D_{ij} \end{aligned}$$

where we have used the fact that \mathbf{D} is a symmetric matrix. Setting $D_i = \sum_{j=1}^N D_{ij}$ we can express MTI also in the following manner:

$$\text{MTI} = \sum_{i=1}^N (v_i)^2 + \sum_{i=1}^N v_i D_i \quad (1)$$

As $W = \frac{1}{2} \sum_{i=1}^N D_i$, eq 1 implies that it is no more difficult to compute MTI than W , provided the quantities D_i are known. In fact, the classical Dijkstra's algorithm for finding the shortest distances¹³ basically computes the D_i 's.

Consider, for instance, the molecular graph G_0 from Figure 1, representing the carbon-atom skeleton of hexamethylpentane, the most branched undecane isomer, $C_{11}H_{24}$. Next to each vertex of G_0 the corresponding D_i value is given. Then by (1) we have $\text{MTI}(G_0) = (8 + 3 \times 4^2) + 6 \times 28 + 2 \times 25 + 2 \times 4 \times 19 + 4 \times 16 = 490$. On the other hand, $S = 4W - N(N - 1)$ for acyclic graphs.^{11,12} Thus knowing that $W(G_0) = 136$, we can compute $\text{MTI}(G_0)$ also as $M_2 + S = (8 + 3 \times 4^2) + 4 \times 136 - 11 \times 10 = 490$.

In the following theorem we estimate the Schultz molecular topological index in terms of the Wiener index for arbitrary connected graphs.

Theorem 1. Let Γ be a connected graph. Then

$$2v_{\min} W(\Gamma) < \text{MTI}(\Gamma) \leq 4v_{\max} W(\Gamma)$$

where v_{\min} and v_{\max} denote the smallest and largest valency, respectively, of a vertex of Γ . In addition, the equality on the right-hand side holds if and only if Γ is a complete graph.

Proof. By definition we have $v_{\min} \leq v_i \leq v_{\max}$ for all $i = 1, 2, \dots, N$. Therefore from (1) we straightforwardly conclude that

$$v_{\min}^2 N + 2v_{\min} W \leq \text{MTI} \leq v_{\max}^2 N + 2v_{\max} W$$

with equality (on both sides) if and only if Γ is a regular graph (when, of course, $v_{\min} = v_{\max}$). Rewriting the above inequalities as

$$\left[2 + \frac{v_{\min} N}{W} \right] v_{\min} W \leq \text{MTI} \leq \left[2 + \frac{v_{\max} N}{W} \right] v_{\max} W \quad (2)$$

and using the well-known fact^{3,5} that for all connected graphs

with N vertices

$$N(N - 1)/2 \leq W \leq N(N^2 - 1)/6$$

we obtain

$$\left[2 + \frac{v_{\min} N}{N(N^2 - 1)/6} \right] v_{\min} W \leq \text{MTI} \leq \left[2 + \frac{v_{\max} N}{N(N - 1)/2} \right] v_{\max} W$$

i.e.,

$$2v_{\min} \left[1 + \frac{3v_{\min}}{N^2 - 1} \right] W \leq \text{MTI} \leq 2v_{\max} \left[1 + \frac{v_{\max}}{N - 1} \right] W \quad (3)$$

Neglecting the term $3v_{\min}/(N^2 - 1)$ in the left-hand side expression of (3) we arrive at the lower bound for MTI stated in Theorem 1; it necessarily is strictly smaller than MTI.

The maximum possible value for v_{\max} is $N - 1$ and therefore $v_{\max}/(N - 1) \leq 1$. This yields the upper bound for MTI, stated in Theorem 1. Because $N(N - 1)/2$ is just the Wiener index of the complete graph (which is a regular graph of degree $v_{\max} = N - 1$), equality between the upper bound and MTI occurs if (and only if) Γ is the complete graph.

For molecular graphs v_{\min} is usually equal to 1 or 2, whereas v_{\max} is 3 or, exceptionally, 4. Bearing this in mind and using (3) we easily obtain bounds for MTI, better than those given in Theorem 1. If v_{\min} , v_{\max} , and N are known (which is practically always the case), then we just have to substitute them into formula (3). For instance, for the graph G_0 , $v_{\min} = 1$, $v_{\max} = 4$, and $N = 11$, resulting in

$$2.05 W < \text{MTI} < 11.2 W$$

Needless to say that these bounds hold for all molecular graphs with 11 vertices. Furthermore, $11.2W$ is an upper bound for MTI also for molecular graphs possessing more than 11 vertices.

For special classes of chemical graphs the bounds for MTI can be made significantly narrower. We demonstrate this in the subsequent section on the case of benzenoid systems.

3. BENZENOID SYSTEMS

Benzenoid systems (or *benzenoid graphs*) are graphs pertaining to the network constructed by arranging congruent regular hexagons in a plane, so that two hexagons are either disjoint or have one edge in common. For more details on this important and frequently encountered class of molecular graphs see the book.¹⁴

Theorem 2. If Γ is a benzenoid system then

$$4W(\Gamma) < \text{MTI}(\Gamma) < \lambda W(\Gamma)$$

where $\lambda = 6 + \frac{6}{25}\sqrt{15} = 6.9295\dots$

Proof. The valency of any vertex of a benzenoid system is either 2 or 3. Hence $v_{\min} = 2$ and the lower bound follows immediately from Theorem 1.

In order to obtain the upper bound we first observe that the most compact benzenoid systems are those belonging to the coronene/circumcoronene series (H_k), see Figure 2. For

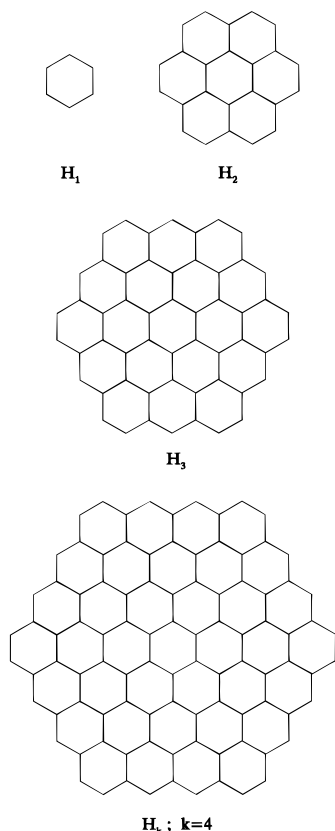


Figure 2. The benzenoid systems H_k with minimum Wiener indices; the first members of the series H_k are benzene ($k = 1$), coronene ($k = 2$), circumcoronene ($k = 3$), ...; $N(H_k) = 6k^2$, $W(H_k) = \frac{1}{5}(164k^5 - 30k^3 + k)$.

these molecular graphs it was recently demonstrated that^{15,16}

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

If a benzenoid system Γ has $N = 6k^2$ vertices, then clearly

$$W(\Gamma) \geq W(H_k)$$

i.e.,

$$W(\Gamma) \geq \frac{1}{5}(164k^5 - 30k^3 + k) \quad (4)$$

with equality only if $\Gamma = H_k$. If the number N of vertices of Γ cannot be expressed in the form $6k^2$, the inequality (4) nevertheless holds, but then k is to be interpreted as a noninteger parameter defined via

$$k = \sqrt{N/6}$$

In this latter case equality in (4) is never achieved.

Now, the polynomial $P(k) = 29k^5 - 30k^3 + k$ is positive-valued for all $k > 1$ and is zero for $k = 1$. Therefore,

$$\begin{aligned} \frac{1}{5}(164k^5 - 30k^3 + k) &= \frac{1}{5}(135k^5 + P(k)) \geq \frac{1}{5}135k^5 \\ &= 27k^5 = 27(N/6)^{5/2} = \frac{\sqrt{6}}{8}N^{5/2} \end{aligned}$$

that is, for a benzenoid system Γ with N vertices

$$W(\Gamma) \geq \frac{\sqrt{6}}{8}N^{5/2}$$

Combining the above relation with the upper bound (2) for MTI we get

$$\left[2 + \frac{v_{\max}N}{W}\right]v_{\max}W \leq \left[2 + \frac{v_{\max}N}{\frac{\sqrt{6}}{8}N^{5/2}}\right]v_{\max}W \quad (5)$$

For all benzenoid systems (except for benzene) $v_{\max} = 3$ and $N \geq 10$. Therefore $v_{\max} = 3$ and $N = 10$ may be substituted into the expression on the right-hand side of (5), resulting in the upper bound given in Theorem 2. By direct checking we verify that the statement of Theorem 2 holds also for benzene.

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