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A Collective Property of Trees and Chemical Trees

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The Wiener index (W) and the Hosoya polynomial (H) have been calculated for all trees (and thus for all chemical trees) with 20 and fewer vertices. Corroborating an earlier observation (Razinger, M. et al. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 23−27), we show that the ability of W to distinguish between nonisomorphic n-vertex trees (respectively, chemical trees) depends on n in an alternating manner: it increases for even values of n and decreases for odd values of n. An analogous behavior is also found in the case of H.

1. INTRODUCTION

The ability of a topological index TI to distinguish between isomers is usually expressed in terms of its *mean isomer degeneracy*, MID = MID($\mathcal{G}$,TI) = N/t, where N = N($\mathcal{G}$) is the number of elements of the set $\mathcal{G}$ of molecular graphs of the isomeric compounds under consideration, and $t = t(\mathcal{G}$,TI) is the number of distinct values which TI assumes for these isomers.[1,2] Another, equivalent, way of expressing the same property is by means of the *isomer−discriminating power*, IDP = IDP($\mathcal{G}$,TI) = t/N, which will be used throughout this paper.

The IDP concept is straightforwardly extended to any set $\mathcal{G}$ of graphs, in which case N is the number of nonisomorphic elements of $\mathcal{G}$ and t is the number of distinct values that the given TI (= graph invariant) assumes in $\mathcal{G}$. In a more formal notation:

$$N = |\mathcal{G}| \qquad t = |\{\mathrm{TI}(G)|G\in\mathcal{G}\}| \tag{1}$$

In such a general case, we will speak about the *isomorphism−discriminating power*, for which the same symbol IDP = *IPD*($\mathcal{G}$,TI) may be used.

According to the definition, IDP=1 means that among the elements of the set considered, no two nonisomorphic graphs have the same TI. If IDP = 0, then all graphs (from the set considered) have equal TI values.

The fact that the isomer−discriminating power of the Wiener index is very low has been observed already by the first scholars who systematically investigated it,[3] but was first explicitly pointed out by Razinger, Chretien, and Dubois[1] and then confirmed by several subsequent studies.[2,4−6] In particular, it was demonstrated[4] that for the set of all connected graphs with n vertices and m edges (m having a fixed, but otherwise arbitrary value), IDP tends to zero when $n \to 0$.

The isomer−discriminating power of many other TIs was also studied.[6,7] These studies were much faciliated after the design and implementation of an efficient algorithm for enumerating trees and chemical trees up to 270 vertices (see ref 6 and the references quoted therein).

In this work, we study the Wiener indices of n-vertex trees and of n-vertex chemical trees. The respective two sets will be denoted by $\mathcal{T}_n$ and $\mathcal{T}_n^{ch}$. Clearly, $\mathcal{T}_n^{ch}$ is a subset of $\mathcal{T}_n$. [Recall that a tree is a connected graph without cycles. A chemical tree is a tree in which no vertex has degree greater than four.[6,8] Chemical trees are the graph representations of alkanes, or more precisely, of the carbon atom skeleton of the molecules of alkanes.] For this purpose a computer program for generating trees has been designed with this program, all the 1 346 024 trees (including the 618 050 chemical trees) with up to 20 vertices were obtained and saved in form of adjacency matrixes.[9]

Let G be a connected graph and let v_1, v_2, ..., v_n be its vertices. The distance $d(v_i,v_j|G)$ of the vertices v_i and v_j in the graph G is the length (= number of edges) of the shortest path of G, of which v_i and v_j are the endpoints. The *Wiener index* is defined as the sum of the distances of all pairs of vertices:

$$W = W(G) = \sum_{i<j} d(\nu_i,\nu_j|G) \tag{2}$$

The theory and chemical applications of the Wiener index are well documented; details on this oldest topological index can be found in the literature.[1,2,4,5,8,10,11]

Denote by $d(G,k)$, the number of vertex pairs of the graph G that are at distance k. Then the *Hosoya polynomial* is defined as[12]

$$H = H(G) = H(G,x) = \sum_{k\geq 1} d(G,k)x^k \tag{3}$$

This counting polynomial has not been studied much to date. Its two fundamental properties are[12]

$$H(G,1) = \binom{n}{2} \tag{4}$$

$$H'(G,1) = W(G) \tag{5}$$

where $H'(G,x)$ is the first derivative of $H(G,x)$ with respect to the variable x.

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Table 1. The Isomer-Discriminating Powers (IDP) of the *n*-Vertex Chemical Trees Pertaining to the Wiener Index (*W*) and the Hosoya Polynomial (*H*)[a]

n	$N(T_n^{ch})$	$t(T_n^{ch}, W)$	IDP(T_n^{ch}, W)	$t(T_n^{ch}, H)$	IDP(T_n^{ch}, H)
4	2	2	1.0000	2	1.0000
5	3	3	1.0000	2	1.0000
6	5	5	1.0000	5	1.0000
7	9	7	0.7778	9	1.0000
8	18	16	0.8889	18	1.0000
9	35	16	0.4571	34	0.9714
10	75	40	0.5333	74	0.9867
11	159	37	0.2327	145	0.9119
12	355	87	0.2451	338	0.9521
13	802	69	0.0860	736	0.9177
14	1858	163	0.0877	1714	0.9225
15	4347	116	0.0267	3861	0.8882
16	10359	276	0.0266	9300	0.8978
17	24894	185	0.0074	21519	0.8644
18	60523	431	0.0071	52958	0.8750
19	148284	277	0.0019	125544	0.8466
20	366319	632	0.0017	312072	0.8519

[a] The quantities *N* and *t* are defined with eq 1.

Table 2. The Isomorphism-Discriminating Powers (IDP) of the *n*-Vertex Trees[a]

n	$N(\mathcal{T}_n)$	$t(\mathcal{T}_n, W)$	IDP$(\mathcal{T}_n, W)$	$t(\mathcal{T}_n, H)$	IDP$(\mathcal{T}_n, H)$
4	2	2	1.0000	2	1.0000
5	3	3	1.0000	2	1.0000
6	6	6	1.0000	6	1.0000
7	11	9	0.8182	11	1.0000
8	23	20	0.8696	23	1.0000
9	47	21	0.4468	45	0.9574
10	106	53	0.5000	104	0.9811
11	235	51	0.2170	215	0.9149
12	551	113	0.2051	522	0.9474
13	1301	92	0.0707	1184	0.9101
14	3159	217	0.0687	2894	0.9161
15	7741	151	0.0195	6832	0.8826
16	19320	355	0.0184	17180	0.8892
17	48629	230	0.0047	41563	0.8547
18	123867	538	0.0043	106831	0.8625
19	317955	331	0.0010	265102	0.8338
20	823065	760	0.0009	687395	0.8352

[a] Other details same as in Table 1.

Evidently, if the Hosoya polynomials of two nonisomorphic graphs coincide, then these graphs also have equal Wiener indices. The reverse statement is, however, not true: there exist numerous pairs of graphs with equal *W* but with different *H*. As a consequence, the IDP values pertaining to *W* cannot exceed the IDP values pertaining to *W*. As reported in the subsequent section, in the case of trees, and chemical trees the isomorphism- and isomer-discriminating power of *H* is significantly greater than that of *W*.

2. AN ODD−EVEN REGULARITY FOR THE ISOMER- AND ISOMORPHISM-DISCRIMINATING POWER

Razinger, Chretien, and Dubois[1] noticed a peculiar property of the IDP of the Wiener indices of alkanes: With increasing *n*, IDP$(\mathcal{T}_n^{ch}, W)$ alternately increases (if *n* is even) and decreases (if *n* is odd). In other words, for *n* being an even integer,

$$\mathrm{IDP}(\mathcal{T}_{n-1}^{ch}, W) \leq \mathrm{IDP}(\mathcal{T}_n^{ch}, W) \geq \mathrm{IDP}(\mathcal{T}_{n+1}^{ch}, W) \quad (6)$$

whereas for *n* being odd,

$$\mathrm{IDP}(\mathcal{T}_{n-1}^{ch}, W) \geq \mathrm{IDP}(\mathcal{T}_n^{ch}, W) \leq \mathrm{IDP}(\mathcal{T}_{n+1}^{ch}, W) \quad (7)$$

The regularity expressed by eqs 6 and 7 is, of course, based on the *W* values of individual alkanes, but it must be considered as a *collective* (or statistical) property of the *sets of all alkane isomers*. The calculations reported by Razinger et al.[1] imply the validity of eqs 6 and 7 only for the first few values of *n*. Our calculations show that the Razinger−Chretien−Dubois rule is obeyed until $n = 15$, but is slightly violated for chemical trees with >15 vertices.

3. RESULTS AND DISCUSSION

In Table 1 we give the IDP values of *n* -vertex chemical trees ($4 \leq n \leq 20$), together with the respective values of *N* and *t* (see eq 1; $G = \mathcal{T}_n^{ch}$, TI = *W*). It is evident that the IDP$(\mathcal{T}_n^{ch})$ values alternate until $n = 15$, and monotonically decrease for $n \geq 16$. However, a closer inspection of the actual numerical values of IDP$(\mathcal{T}_n^{ch})$ shows that the violation of the Razinger−Chretien−Dubois rule (occurring for $n \geq 16$) is very small and its cause is easily recognized (vide infra).

A not too surprising finding is that the Razinger−Chretien−Dubois-type collective regularity is not restricted to chemical trees, but applies to general trees as well; that is, in eqs 6 and 7, $\mathcal{T}^{ch}$ may be replaced by $\mathcal{T}$. However, also in this case, the alternation is slightly violated for larger values of *n*, (i.e., for $n \geq 12$). The respective data are presented in Table 2.

In an expected manner,[4] both IDP$(\mathcal{T}^{ch}, W)$ and IDP$(\mathcal{T}_n^{ch}, W)$ rapidly tend to zero as $n \rightarrow 0$.

An inspection of Tables 1 and 2 easily reveals the origin of the Razinger−Chretien−Dubois rule. Except for the first few values of *n*, both $t(\mathcal{T}_n^{ch})$ and $t(\mathcal{T}_n)$ have an odd−even alternating dependence on *n*. Thus, $t(\mathcal{T}_n^{ch})$ monotonically increases until $n = 8$ and begins to alternate at $n = 9$. Similarly, $t(\mathcal{T}_n)$ monotonically increases until n=10 and alternates for $n \geq 10$. This odd−even alternation of *t* seems to be a generally valid property of trees and chemical trees, and seems to hold for all values of *n*, $n \geq 10$.

Because all the earlier reported calculations of the isomer-discriminating ability of the Wiener index of alkanes[1,2,4,5] were restricted to smaller number of vertices (*n* up to ∼10), the regularity just mentioned could hardly be envisaged. Our calculations (*n* up to 20) make the regularity quite transparent.

In the subsequent section we offer a rationalization (yet not an exact proof) of the odd−even alternating property of $t(\mathcal{T}_n^{ch})$ and $t(\mathcal{T}_n)$.

We have also determined the IDP values pertaining to the Hosoya polynomial. The results of these calculations are also found in Tables 1 and 2. As already explained, the discriminating power of the Hosoya polynomial must be greater than that of the Wiener index. From the data given in Tables 1 and 2 we see that this indeed is the case. Furthermore, except for the first few values of *n*, IDP(*H*) significantly exceeds IDP(*W*). It looks as if the limit values of IDP$(\mathcal{T}_n, H)$ and IDP$(\mathcal{T}_n^{ch}, H)$ are different from zero, and are both ≈0.8.

Both IDP($\mathcal{T}_n$, H) and IDP($\mathcal{T}_n^{ch}$, H) exhibit a Razinger–Chretien–Dubois-type odd–even alternation. In other words, eqs 6 and 9 remain valid if W is exchanged by H and also if $\mathcal{T}^{ch}$ are is exchanged by $\mathcal{T}$. No violation of these alternations are found until $n = 20$, which, however, is no guarantee that violations will not occur at some greater values of n.

4. AN ODD–EVEN PROPERTY OF THE WIENER INDEX

In the set $\mathcal{T}_n$, the trees with minimal and maximal Wiener index are the star and the path graph, having $W = (n - 1)^2$ and $W = n(n^2 - 1)/6$, respectively.[13,14] Therefore, if T is an n-vertex tree, then $W(T)$ belongs to the interval

$$\left[(n-1)^2, \frac{n(n^2-1)}{6}\right] \tag{8}$$

implying

$$t(\mathcal{T}_n) \le \frac{n(n^2-1)}{6} - (n-1)^2 + 1 = \frac{n^3 - 6n^2 + 11n}{6} \tag{9}$$

Thus, the number of distinct values that the Wiener index can assume in $\mathcal{T}_n$ increases with n relatively slowly, at most as a cubic polynomial in n.[15]

A graph is said to be *bipartite* if its vertices can be partitioned into two groups, such that no two vertices within one group are adjacent.[16] We say that the vertices from the first group are colored "red" and the vertices from the second group are colored "blue". Then adjacent vertices necessarily have different colors.

Let G a connected bipartite graph with a red and b blue vertices, $a + b = n$.

Let $x \equiv v_0$ and $y \equiv v_k$ be two red vertices of G. Then the length of *any* path starting at x and ending at y is even.

To see this, suppose that $[v_0, v_1, v_2, ..., v_{k-1}, v_k]$ is a path of G. This means that $v_0, v_1, v_2, ..., v_{k-1}, v_k$ are distinct vertices of G, such that v_{i-1} is adjacent to v_i , $i = 1, 2, ..., k$. The length of this path is k. Because v_0 is a red vertex, then v_1 must be a blue vertex, v_2 must be a red vertex, etc. Then, v_k can be a red vertex only if k is an even number.

Now, the distance between x and y is the length of the shortest path, and, consequently, must be an even number.

In full analogy to the aforementioned, we conclude that if both x and y are blue vertices of G, then the distance between them is even, and if x is red and y blue (or vice versa), then the distance between them is odd.

The Wiener index of G can be decomposed as

$$W(G) = W_{rr} + W_{bb} + W_{rb} \tag{10}$$

with W_{rr} being the sum of the distances of all pairs of two red vertices, W_{bb} the sum of distances of all pairs of two blue vertices, and W_{rb} the sum of distances of all pairs of differently colored vertices. Recall that the number of pairs of differently colored vertices is ab.

All summands in W_{rr} and W_{bb} are even-valued, and therefore W_{rr} and W_{bb} are even-valued. All summands in W_{rb} are odd–valued. Consequently, W_{rb} will be odd-valued if, and only if, it contains an odd number of summands (i.e., if, and only if, ab is odd, i.e., if, and only if, both a and b are odd).

If $n = a + b$ is an odd number, then a and b cannot simultaneously be odd numbers. Then the product ab cannot be odd, so W_{rb} cannot be odd, and $W(G)$ cannot be odd-valued.

Thus, if the number of vertices n of a bipartite graph G is odd, then the Wiener index of this graph must be an even number.[17]

The aforementioned conclusion applies to trees because these are typical bipartite graphs.[16] This means that if n is an odd number, then all elements of the sets $\{W(T)|T \in \mathcal{T}_n\}$ and $\{W(T)|T \in \mathcal{T}_n^{ch}\}$ are even–valued integers. In other words, odd-valued integers are "forbidden".

Consequently, in the case of odd n, only every second number from the interval in eq 8 may occur, which implies that the estimate of eq 9 is tightened as

$$t(\mathcal{T}_n) \le \frac{1}{2}\,\frac{n^3 - 6n^2 + 11n}{6} \tag{11}$$

For trees with an even number of vertices, no selection rule of the aforementioned kind applies, and their t-values can be estimated only by eq 9. As a consequence, for even n, the t -values pertaining to $\mathcal{T}_n$ and $\mathcal{T}_n^{ch}$ are roughly two times greater than the t-values pertaining to, respectively, $\mathcal{T}_{n-1}$ and $\mathcal{T}_{n-1}^{ch}$. The quality of this estimation can bee seen from the data given in Tables 1 and 2.

The IDP values are obtained by dividing t by the number of n-vertex trees or chemical trees. Because these latter numbers increase exponentially[17], with n, whereas t increases as n^3, the IDP s vanish for $n \rightarrow 0$. In addition, their odd–even alternation vanishes too.

In connection with the aforementioned considerations one may ask which positive integers are "forbidden" as Wiener indices of trees. In a previous study[18] it has been established that the first few such "forbidden" numbers are 2, 3, 5, 6, 7, 8, 11, 12, 13, 14, 15, 17, 19, 21, 22, 23, 24, 26, 27, 30, and 33, but their list could not be completed. Our calculations reveal that there are 49 integers that are not Wiener indices of any tree, viz., 2, 3, 5, 6, 7, 8, 11, 12, 13, 14, 15, 17, 19, 21, 22, 23, 24, 26, 27, 30, 33, 34, 37, 38, 39, 41, 43, 45, 47, 51, 53, 55, 60, 61, 69, 73, 77, 78, 83, 85, 87, 89, 91, 99, 101, 106, 113, 147, and 159. Furthermore, we find that if there is any other "forbidden" integer, its value must be >1206. We conjecture that our list is complete and that the Wiener index of trees may assume any positive integer value, except the 49 "forbidden" values, just specified.

5. CHEMICAL TREES WITH MINIMAL WIENER INDEX

The present computer search made it possible to identify and characterize the chemical trees with minimal Wiener indices. Such trees with up to 21 vertices are depicted in Figure 1. (Recall that the n-vertex tree with maximum Wiener index is the path graph;[13,14] this, of course, is also the n-vertex chemical tree with maximal W. The n-vertex tree with minimal W is the star, but this is a chemical tree only until $n = 5$.)

Denote the n-vertex chemical tree with minimal Wiener index by M_n. This tree is unique. It can be constructed

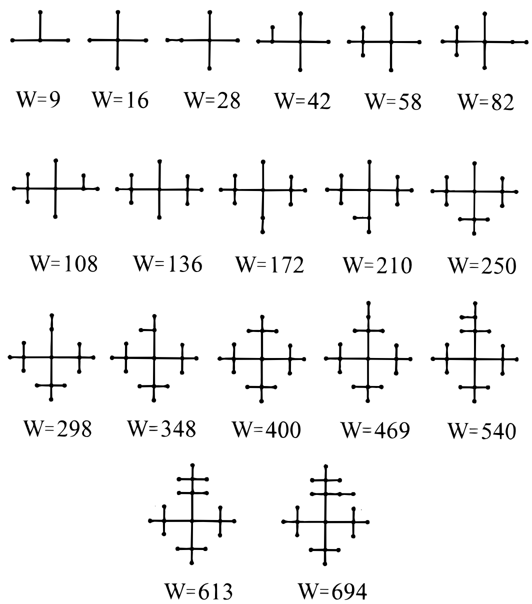

Figure 1. The *n*-vertex chemical trees, $4 \leq n \leq 21$, with minimal Wiener index (W).

recursively as follows. We say that a vertex of a graph is a k-vertex if its degree (= number of first neighbors) is equal to k. For $n = 1, 2, 3, 4$, and 5, M_n is the n-vertex star. For $n \geq 4$, M_n is obtained by attaching a new 1-vertex to a vertex x of M_{n-1}. The vertex x is chosen according to the following recipe:

(a) If M_{n-1} possesses a 2- or a 3-vertex, then x is chosen to be this vertex.

(b) If M_{n-1} possesses no 2- or 3-vertex, then x is chosen among the 1-vertices, such that

(b_1) the 4-vertex adjacent to x has maximum number of 4-vertex first neighbors.

If there are several symmetry—nonequivalent vertices satisfying condition (b_1) then we additionally require that

(b_2) the 4-vertex adjacent to x has maximum number of 4-vertex second neighbors.

If this is not sufficient, it is also required that

(b_3) the 4-vertex adjacent to x has maximum number of 4-vertex third neighbors, etc.

One should observe that the trees M_n represent alkanes belonging to the class of so-called dendrimers, molecules with highly branched carbon atom skeletons, whose Wiener indices have been examined in due detail.[19,20]

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REFERENCES AND NOTES

(1) Razinger, M.; Chretien, J. R.; Dubois, J. Structural Selectivity of Topological Indexes in Alkane Series. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 23−27.
(2) Rouvray, D. H. The Modeling of Chemical Phenomena Using Topological Indices. *J. Comput. Chem.* **1987**, *8*, 470−480.
(3) Bonchev, D.; Trinajstić, N. Information Theory, Distance Matrix, and Molecular Branching. *J. Chem. Phys.* **1977**, *67*, 4517−4533.
(4) Gutman, I.; Soltés, L. The Range of the Wiener Index and Its Mean Isomer Degeneracy. *Z. Naturforsch.* **1991**, *46a*, 865−868.
(5) Gutman, I.; Luo, Y. L.; Lee, S. L. The Mean Isomer Degeneracy of the Wiener Index. *J. Chin. Chem. Soc.* **1993**, *40*, 195−198.
(6) Trinajstić, N.; Nikolić, S.; Knop, J. V.; Müller, W. R.; Szymanski, K. *Computational Chemical Graph Theory: Characterization, Enumeration and Generation of Chemical Structures by Computer Methods*; Horwood: New York, 1991.
(7) Müller, W. R.; Szymanski, K.; Knop, J. V.; Ttinajstić, N. Molecular Topological Index. *J. Chem. Inf. Comput. Sci.* **1990**, *30*, 161−163.
(8) Trinajstić, N. *Chemical Graph Theory*; CRC: Boca Raton, FL, 1993.
(9) Details on our software are available from M. L. upon request.
(10) Nikolić, S.; Trinajstić, N.; Mihalić, Z. The Wiener Index: Developments and Applications. *Croat. Chem. Acta* **1995**, *68*, 105−129.
(11) Gutman, I.; Potgieter, J. H. Wiener Index and Intermolecular Forces. *J. Serb. Chem. Soc.* **1997**, *62*, 185−192.
(12) Hosoya, H. On Some Counting Polynomials in Chemistry. *Discrete Appl. Math.* **1988**, *19*, 239−257.
(13) Entringer, R. C.; Jackson, D. E.; Snyder, D. A. Distance in Graphs. *Czech. Math. J.* **1976**, *26*, 283−296.
(14) Gutman, I. A Property of the Wiener Number and Its Modifications. *Indian J. Chem.* **1997**, *36A*, 128−132.
(15) Recall that the number of n-vertex trees and n-vertex chemical trees increases asymptotically as $A\, B^n\, n^{-5/2}$ with A and B being pertinent (known) constants different for $\mathcal{T}_n$ and $\mathcal{T}_n^{ch}$; for further details see: Harary, F.; Palmer, E. M. *Graphical Enumeration*; Academic: New York, 1973; Chapter 9.
(16) Harary, F. *Graph Theory*; Addison-Wesley: Reading, MA, 1969.
(17) This result was first communicated in: Bonchev, D.; Gutman, I.; Polansky, O. E. Parity of the Distance Numbers and Wiener Numbers of Bipartite Graphs. *Commun. Math. Chem. (MATCH)* **1987**, *22*, 209−214.
(18) Gutman, I.; Yeh, Y. N. The Sum of All Distances in Bipartite Graphs. *Math. Slovaca* **1995**, *45*, 327−334.
(19) Gutman, I.; Yeh, Y. N.; Lee, S. L.; Chen, J. C. Wiener Numbers of Dendrimers. *Commun. Math. Chem. (MATCH)* **1994**, *30*, 103−115.
(20) Diudea, M. V. Molecular Topology. 21. Wiener Index of Dendrimers. *Commun. Math. Chem. (MATCH)* **1995**, *32*, 71−83.

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