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ON THE GENERATION OF MEAN WIENER NUMBERS OF THORNY GRAPHS#

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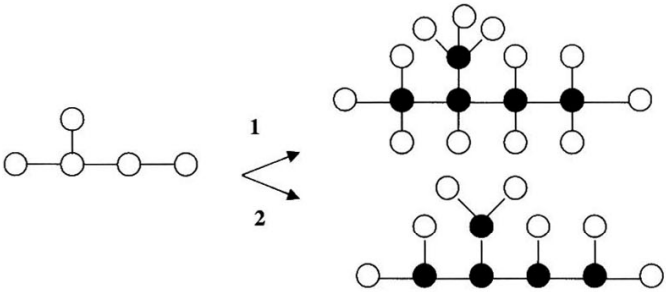
Abstract. Thorny graphs are graphs having only branched and terminal vertices. Their properties have not been previously studied in detail, though it may be noted that they appear in a couple chemically interesting contexts. First, they may be viewed as non-H-deleted graphs of hydrocarbons, with the C and H atoms not distinguished. Second, they may be viewed as the H-deleted graphs exhibiting extremal characteristics for certain graph invariants, and thence also for certain chemical properties corresponding to such graph invariant. This paper considers a special case, namely trees having all non-terminal vertices of a fixed degree d, and termed d-thorn acyclic graphs. An algorithm and a program are developed for the evaluation of the average Wiener number of isomeric d-thorn trees having up to a hundred atoms, for $d = 3$ and $d = 4$.

INTRODUCTION

The Wiener number (and many other graph invariants) have developed as useful "topological indices" for molecular structures, with Professor Alexandru T. Balaban (Sandy) being a leading advocate for such approaches. See, e.g., [1] or [2]. As such, special methods to compute Wiener numbers, or theorems they satisfy, or analogues, or extensions all have become of interest.

Dedicated on the occasion of the 70th birthday to Professor Alexandru T. Balaban, who has long pursued the use of topological indices as QSAR and QSPR descriptors

In 1997-1998, Ivan Gutman [3,4] discussed the graph theoretical representation of some special classes of organic compounds. He introduced the term "thorn graph" for the graph G^* obtained from a parent connected graph G by attaching p_i new vertices of degree one ($p_i \geq 0$) to all of its vertices i. Special attention has been paid to some classes of thorny graphs having a chemical relevance. These classes are determined by the condition $p_i = d_{max} - d_i$, where d_{max} is a constant, and d_i is the degree of the ith vertex in G, G being a tree. For organic acyclic molecules, $d_{max} = 4$ or 3 for the respective classes of alkanes **1** and "polyeneoids" **2**.



The classes of alkanes and polyeneoid compounds have only two types of vertices: nonterminal vertices of degree d and terminal vertices of degree 1. Such graphs have been known in graph theory as *proper graphs* [5]. Therefore, proper graphs are a special case of thorny graphs with a uniform degree d of all nonterminal vertices. We will call such graphs *d-thorn* graphs.

The d-thorn graphs are of importance for polymer theory [6,7], especially for dendrimers [8,9], where they are termed Cayley trees [10]. The Wiener number of such classes of polymer graphs could be of use in the quantitative characterization of polymer topology, as well as for specific structure-property relationships. Formulae for the Wiener number of individual dendrimer species (such as with "uniform radius") have been reported by Gutman [11] and Diudea [12]. However, the number of isomeric structures without restrictions increases rapidly with the number of atoms. One is thus confronted with the problem of isomer enumeration such as has been a topic of permanent interest since 19th century when it stimulated the genesis of

graph theory. Some of this history and much of the related mathematical work, especially following Polya's fundamental enumeration theory of the 1930s, is described by Kerber [13].

As a consequence of the extreme variety of molecular architectures, ensembles of molecules are better characterized by averages or distributions. Bytautas and Klein [14] calculated recently the mean values of several properties of alkane isomers having up to 40 carbon atoms. They also extended from 20 to 100 carbon atoms [15] the work of Gutman et al. [16,17] on average Wiener numbers of isomeric alkanes C_NH_{2N+2}. In this study, we calculate the average Wiener numbers for 3-thorn and 4-thorn trees (isomeric alkanes and polyeneoids).

METHOD

Each thorny graph T^* has a *parent* graph T obtained by deleting all degree-1 sites from T^*. Conversely, given a parent, the corresponding d-thorn graph T^* is obtained by adding new degree-1 vertices to T, so as to bring all the vertices of T up to degree d. Gutman [3] derived a formula that relates the Wiener number of thorny trees T^* with the Wiener number of the parent tree-graph T:

$$W(T^*) = (d-1)^2 W(T) + [(d-1)N+1]^2 \tag{1}$$

where N is the number of vertices in T, and d is uniform degree of the nonterminal vertices in T^*. The formula includes also the case of $N = 1$, for which the parent graph is a single vertex, $W(T) = 0$, and $W(T^*) = W(Star) = d^2$. The d-thorn graph has a number of vertices:

$$N^* = N(d-1) + 2 \tag{2}$$

We apply formula (1) to the computation of mean Wiener numbers of d-thorn trees with $d = 3$ and $d = 4$. The parent tree-graphs are those of isomeric alkanes. Their enumeration may be done via a generating function technique which is intimately related to the approach taken to make enumerations of isomers, *e.g.*, as pioneered by G. Polya [18,19]. In fact to understand the

approach it is best to first understand the Polya-theoretic enumeration of isomers. To obtain the counts $\#'_N$ of N-carbon alkane structural isomers the Polya-theoretic approach develops a generating function

$$P(t) = \sum_{N \geq 0} \#'_N \, t^N \tag{3}$$

with t a dummy parameter. The development of $P(t)$ is by way of a sequence of recursions for various auxiliary generating functions, and computer generation of the coefficients up through a desired number N of atoms is feasible, often with the limitation being the size of the integers $\#'_N$ which can be handled exactly (with $\#'_{40}$ having 14 digits). This overall procedure may be (and indeed has been) implemented in a few different ways, one of which is detailed in ref. [14]. With this enumerative procedure in hand then a similar (but slightly more complicated) development may be made of a generating function

$$W(t) = \sum_{N \geq 0} W'_N \, t^N \tag{4}$$

where W'_N is the sum of Wiener numbers for all N-carbon alkane structural isomers. The details of the development of $W(t)$ for alkanes are incompletely explained in [14], where also two relevant equations are in error, but the completed explanation and corrected equations are given in [15] (along with some results for other measures of mean "extension" of alkanes). The recursions for the polyenoids may be obtained from those of [15] simply by deletion of all terms corresponding to the building in of degree-4 sites. Granted results for $\#'_N$ and W'_N one readily obtains the average Wiener number for N-carbon alkanes as

$$\langle W(G) \rangle_N = W'_N / \#'_N \tag{5}$$

Numerical results (for alkane structural isomers) up to N = 40 and N = 90 are given in [14] and [15], respectively. Here using this approach we report results for d-thorn graphs for d =

3 and $d = 4$, up through N = 101, using the relation of Gutman [3,4] to obtain these results from the mean Wiener numbers for alkanes (when $d = 4$), and for "polyeneoids" (when $d = 3$).

RESULTS AND DISCUSSION

It is to be emphasized that the 4-thorn graphs need not be interpreted as H-included alkane graphs, without a distinction between C and H atoms. All the atoms of a d-thorn graph may be identified as C atoms, whence they form a special subclass of alkanes, containing only primary and quaternary carbons for 4-thorn graphs and only primary and tertiary carbons for 3-thorn graphs. Notably, such graphs realize [20] extreme values for certain graph invariants, and thence also often realize extreme values for various molecular properties of interest. A general approach to identifying these and other classes of extreme graphs is indicated in [20]. Because of this, we believe that such d-thorn graphs should be of much interest.

We performed calculations of the mean Wiener index of 3- and 4-thorn trees having up to 100 parent-graph vertices, i.e., up to 200 carbon-atom polyeneoids, and up to 300 quaternary carbon-atom alkanes. The results obtained are shown in Tables 1 and 2, respectively. The total number of parent polyeneoids is also shown in Table 1. Both Table 1 and Table 2 contain the mean graph distance $<d>$, a quantity closely related to the mean Euclidean distance, which has long been a subject of inquiry related to the size and rheological properties of macromolecules [21,22].

TABLE 1. Number of isomers #, mean Wiener number $<W(3)>$, and mean distance $<d(3)>$ of 3-thorn trees

N^a	isomer #	$<W(3)>$	$<d(3)>$	N	isomer #	$<W(3)>$	$<d(3)>$
2	0.1000E+01	29.00	1.93	53	0.5133E+17	60988.04	10.56
3	0.1000E+01	65.00	2.32	54	0.1217E+18	63914.05	10.66
4	0.2000E+01	119.00	2.64	55	0.2889E+18	66923.22	10.77
5	0.2000E+01	197.00	2.98	56	0.6860E+18	70016.33	10.87
6	0.4000E+01	296.00	3.25	57	0.1631E+19	73194.16	10.97
7	0.6000E+01	425.00	3.54	58	0.3879E+19	76457.51	11.08
8	0.1100E+02	580.27	3.79	59	0.9234E+19	79807.13	11.18

Table 1. (continued)

9	0.1800E+02	769.44	4.05	60	0.2200E+20	83243.79	11.28
10	0.3700E+02	986.73	4.27	61	0.5243E+20	86768.25	11.38
11	0.6600E+02	1244.03	4.51	62	0.1251E+21	90381.26	11.48
12	0.1350E+03	1533.95	4.72	63	0.2985E+21	94083.56	11.58
13	0.2650E+03	1864.43	4.93	64	0.7130E+21	97875.90	11.67
14	0.5520E+03	2232.67	5.13	65	0.1704E+22	101759.01	11.77
15	0.1132E+04	2644.17	5.33	66	0.4074E+22	105733.61	11.87
16	0.2410E+04	3096.93	5.52	67	0.9747E+22	109800.43	11.96
17	0.5098E+04	3595.30	5.71	68	0.2333E+23	113960.19	12.06
18	0.1102E+05	4138.42	5.89	69	0.5588E+23	118213.60	12.15
19	0.2384E+05	4729.32	6.06	70	0.1339E+24	122561.36	12.24
20	0.5223E+05	5368.19	6.23	71	0.3211E+24	127004.18	12.34
21	0.1148E+06	6057.13	6.40	72	0.7701E+24	131542.75	12.43
22	0.2544E+06	6796.80	6.57	73	0.1848E+25	136177.77	12.52
23	0.5657E+06	7588.92	6.73	74	0.4437E+25	140909.92	12.61
24	0.1266E+07	8434.37	6.89	75	0.1066E+26	145739.89	12.70
25	0.2842E+07	9334.55	7.04	76	0.2561E+26	150668.35	12.79
26	0.6409E+07	10290.49	7.19	77	0.6157E+26	155695.98	12.88
27	0.1450E+08	11303.44	7.34	78	0.1480E+27	160823.45	12.97
28	0.3294E+08	12374.44	7.49	79	0.3563E+27	166051.42	13.05
29	0.7502E+08	13504.66	7.63	80	0.8576E+27	171380.55	13.14
30	0.1714E+09	14695.14	7.77	81	0.2065E+28	176811.50	13.23
31	0.3927E+09	15946.98	7.91	82	0.4975E+28	182344.92	13.31
32	0.9018E+09	17261.20	8.05	83	0.1199E+29	187981.46	13.40
33	0.2076E+10	18638.88	8.18	84	0.2890E+29	193721.77	13.49
34	0.4791E+10	20080.99	8.32	85	0.6968E+29	199566.48	13.57
35	0.1108E+11	21588.56	8.45	86	0.1681E+30	205516.23	13.65
36	0.2566E+11	23162.59	8.58	87	0.4056E+30	211571.67	13.74
37	0.5957E+11	24804.03	8.70	88	0.9790E+30	217733.41	13.82
38	0.1385E+12	26513.87	8.83	89	0.2364E+31	224002.08	13.90
39	0.3227E+12	28293.04	8.95	90	0.5710E+31	230378.30	13.99
40	0.7529E+12	30142.49	9.08	91	0.1379E+32	236862.70	14.07
41	0.1759E+13	32063.15	9.20	92	0.3334E+32	243455.89	14.15
42	0.4116E+13	34055.92	9.32	93	0.8060E+32	250158.48	14.23
43	0.9646E+13	36121.72	9.44	94	0.1949E+33	256971.09	14.31
44	0.2263E+14	38261.43	9.55	95	0.4715E+33	263894.31	14.39
45	0.5317E+14	40475.96	9.67	96	0.1141E+34	270928.74	14.47
46	0.1251E+15	42766.15	9.78	97	0.2761E+34	278075.00	14.55
47	0.2945E+15	45132.89	9.90	98	0.6683E+34	285333.68	14.63
48	0.6943E+15	47577.04	10.01	99	0.1618E+35	292705.36	14.71
49	0.1639E+16	50099.42	10.12	100	0.3920E+35	300190.65	14.79
50	0.3871E+16	52700.88	10.23	101	0.9496E+35	307790.12	14.86
51	0.9154E+16	55382.26	10.34				
52	0.2167E+17	58144.38	10.45				

[a] The number of vertices N refers to the parent graph. The corresponding number for the 3-thorn trees is $N^* = 2N + 2$.

TABLE 2. Mean Wiener number <$W(4)$> and mean distance <$d(4)$> for isomeric 4-thorn trees

N^a	<$W(4)$>	<$d(4)$>	N	<$W(4)$>	<$d(4)$>
2	58.00	2.07	52	118847.99	9.58
3	136.00	2.48	53	124573.17	9.67
4	254.50	2.80	54	130460.26	9.76
5	418.00	3.07	55	136510.74	9.85
6	640.00	3.37	56	142726.09	9.94
7	916.00	3.62	57	149107.74	10.02
8	1251.00	3.85	58	155657.15	10.11
9	1654.17	4.07	59	162375.74	10.19
10	2126.68	4.29	60	169264.93	10.28
11	2670.26	4.49	61	176326.13	10.36
12	3291.60	4.68	62	183560.72	10.44
13	3990.93	4.87	63	190970.08	10.52
14	4773.71	5.05	64	198555.59	10.61
15	5641.61	5.22	65	206318.61	10.69
16	6598.00	5.39	66	214260.48	10.77
17	7645.03	5.55	67	222382.54	10.85
18	8786.10	5.71	68	230686.12	10.93
19	10023.13	5.86	69	239172.54	11.00
20	11359.03	6.01	70	247843.11	11.08
21	12796.00	6.15	71	256699.13	11.16
22	14336.58	6.29	72	265741.88	11.24
23	15982.97	6.43	73	274972.65	11.31
24	17737.54	6.57	74	284392.70	11.39
25	19602.44	6.70	75	294003.32	11.46
26	21579.91	6.83	76	303805.74	11.54
27	23672.05	6.96	77	313801.21	11.61
28	25880.99	7.08	78	323990.98	11.68
29	28208.77	7.20	79	334376.27	11.76
30	30657.43	7.32	80	344958.30	11.83
31	33228.96	7.44	81	355738.30	11.90
32	35925.32	7.56	82	366717.46	11.97
33	38748.44	7.67	83	377896.99	12.04
34	41700.21	7.79	84	389278.08	12.12
35	44782.51	7.90	85	400861.92	12.19
36	47997.17	8.01	86	412649.68	12.26
37	51346.03	8.11	87	424642.53	12.33
38	54830.86	8.22	88	436841.64	12.39
39	58453.44	8.33	89	449248.17	12.46
40	62215.52	8.43	90	461863.27	12.53

TABLE 2. (continued)

41	66118.81	8.53	91	474688.09	12.60
42	70165.01	8.63	92	487723.75	12.67
43	74355.81	8.73	93	500971.40	12.73
44	78692.88	8.83	94	514432.17	12.80
45	83177.84	8.93	95	528107.16	12.87
46	87812.33	9.02	96	541997.50	12.93
47	92597.95	9.12	97	556104.29	13.00
48	97536.28	9.21	98	570428.64	13.07
49	102628.91	9.31	99	584971.64	13.13
50	107877.38	9.40	100	599734.38	13.20
51	113283.23	9.49	101	614717.96	13.26

[a] N is number of vertices in the parent alkane tree. The number of vertices in the 4-thorn tree is $N^* = 3N + 2$.

Because of the relation of eq. (1), the asymptotic behavior for alkanes

$$< W(T) >_N \approx AN^{5/2} \tag{6}$$

carries over to the 4-thorn trees as

$$< W(T^*) >_{N^*} \approx A^*(N^*)^{5/2} \tag{6a}$$

with $A^* = A(d\text{-}1)^{-1/2}$. A similar relation applies between polyeneoids and 3-thorn graphs.

Further studies on the properties of d-thorn graphs are in progress [23]. Hopefully these various results can find application in polymer theory, related to polymer statistics and polymer properties.

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