Techniques for counting the structural isomers of alkanes and monosubstituted alkanes

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Problem description

The problem our group was tasked with solving was the problem of counting the number of isomers of a class of chemical compounds known as the alkanes, that are given by the chemical formula

$$C_n H_{2n+2}$$

This is an interesting problem with an obvious application in chemistry.

Counting the monosubstituted alkanes

In order to figure out the more advanced problem we first considered rooted trees with each vertex having degree at most 3. For further simplification we considered planar trees, i.e. symmetric trees were counted as distinct. Let a_n denote the number of such trees with exactly n vertices. We define the generating polynomial (power series) as:

$$f(x) = a_0 + a_1 x + a_2 x^2 + \ldots$$

Then notice that $a_n = \sum_{i+j=n-1} a_i a_j$. Which yields the constraint

$$f(x) = xf(x)^2 + 1$$

Solving this yields:

$$f(x) = \frac{1 - \sqrt{1-4x}}{2x}$$

Rearranging and expanding using Newton's generalized binomial theorem gives:

$$f(x) = \sum_{k \geq 0} \frac{1}{k+1} \binom{2k}{k} x^k$$

It is worth pointing out that $\frac{1}{n+1}\binom{2n}{n}$ the coefficients of $f(x)$ are the celebrated Catalan numbers.

Now we consider the rooted planar trees with each vertex having degree at most 4. Again, let a_n denote the number of such trees with exactly n vertices. We define the generating polynomial (power series) as:

$$f(x) = a_0 + a_1 x + a_2 x^2 + ...$$

Then notice that $a_n = \sum_{i+j+k=n-1} a_i a_j a_k$. Which yields the constraint

$$f(x) = x f(x)^3 + 1$$

We can use the recurrence relation to generate the coefficients.

Up to now we have considered only the planar trees. Now we must eliminate the symmetric trees. It was Pólya who popularized counting ordered colourings on a set using group theory to account for symmetry. Applying Pólya's theory of enumeration yields:

$$f(x) = 1 + xZ_{S_2}(f(x))$$

where

$$Z_{S_2}(f(x)) = \frac{1}{2}(f(x)^2 + f(x^2))$$

Which gives the recurrence relation:

$$a_n = \frac{1}{2}(\sum_{i+j=n-1} a_i a_j + \sum_{2i=n-1} a_i)$$

Now we count the distinct rooted ternary trees (accounting for symmetry). Similarly to before we can derive:

$$f(x) = 1 + xZ_{S_3}(f(x))$$

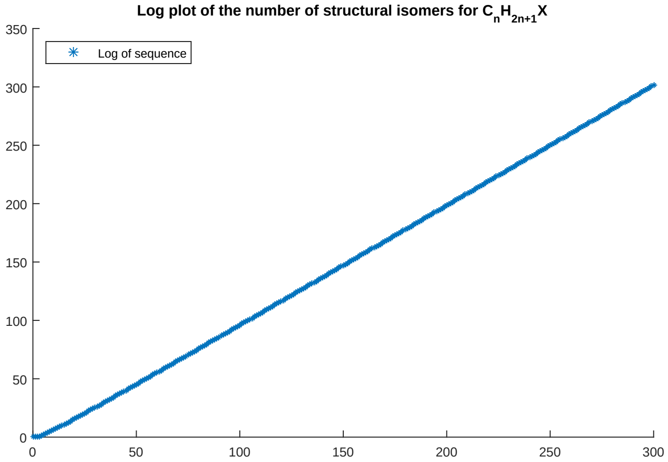
where:

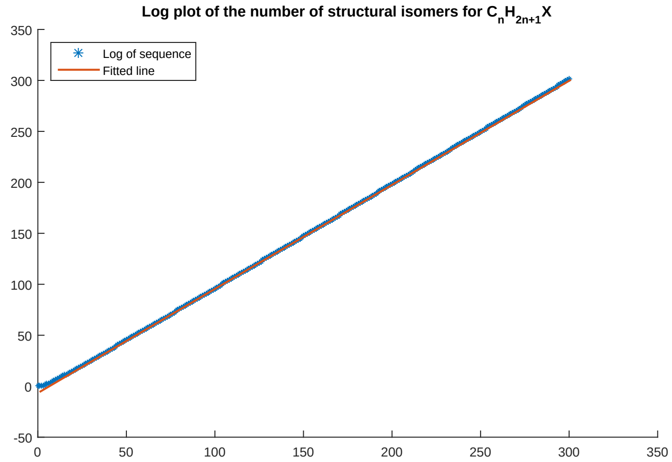
$$Z_{S_3}(f(x)) = \frac{1}{6}(f(x)^3 + 3f(x)f(x^2) + 2f(x^3))$$

Then we have the recurrence relation:

$$a_{n+1} = \frac{1}{6}(\sum_{i+j+k=n} a_i a_j a_k + 3\sum_{i+2j=n} a_i a_j + 2\sum_{3i=n} a_i)$$

Plotting $n = 0, 1, 2, ..., 300$ against the log of our results we get the following:


Log plot of the number of structural isomers for $C_nH_{2n+1}X$
Log of sequence
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300


Log plot of the number of structural isomers for $C_nH_{2n+1}X$
Log of sequence
Fitted line
350
300
250
200
150
100
50
0
-50
0
50
100
150
200
250
300
350

And finally we tackled the main problem: counting the number of ternary unrooted trees (accounting for symmetry). Using the center method define:

$$f_0 = 1, f_k = 1 + Z_{S_3}(f) \textit{ for } k \geq 1$$

$$F_k = x(Z_{S_4}(f_k - f_{k-1}) + Z_{S_3}(f_k - f_{k-1})(f_{k-1}) + Z_{S_2}(f_k - f_{k-1})Z_{S_2}(f_{k-1}))$$

$$G_k = Z_{S_2}(f_{k+1} - f_k)$$

And then the actual generating polynomial is:

$$T(x) = 1 + x + \sum_{k \geq 1}(G_k(x) + F_k(x))$$

Or equivalently using the centroid method, we let F_n denote the number of isomers of $C_nH_{2n+1}X$ and

$$B(x) = 1 + \sum_{0 \le k \le \frac{n-1}{2}} F_k x^k$$

Then we have the generating polynomial:

$$T(x) = \frac{1}{24}(B(x^4) + 6B(x^2)B(x)^2 + 8B(x)B(x^3) + 3B(x^2)^2 + B(x^4))$$

And for bicentroid trees:

$$G(x) = \frac{1}{2}(B(x^2) + B(x)^2) - B(x)$$

Results

Here are the results for the number of isomers of C_nH_{2n+2} for n = 0, 1, ..., 12.

n	0	1	2	3	4	5	6	7	8	9	10	11	12
x	1	1	1	2	3	5	9	18	35	75	159	355	802

Bibliography

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