Formula Periodic Table for the Isomer Classes of Acyclic Hydrocarbons – Enumerative and Asymptotic Characteristics

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The overall set of acyclic hydrocarbons C_nH_{2m} with classical valence structures is considered, the structural isomers are enumerated, and the results displayed in the form of a »periodic table« with the C atom count n and H atom half-count m respectively identifying rows and columns. Asymptotic $n \to \infty$ behaviors of these enumerations are developed, first for fixed degree $u \equiv n+1-m$ of unsaturation and second for fixed number $2m$ of H-atoms. The first-set isomer classes increase in size exponentially fast with n, whereas with the second set, the isomer-class sizes increase sub-exponentially, as a power of n.

Key words: acyclic hydrocarbons, asymptotic behavior, enumeration, isomer classes

1. INTRODUCTION

Chemical isomerism was recognized in a general way in the first part of the nineteenth century when substances with the same overall molecular formula were found though they exhibited different properties, a brief history of such being found in Ref. 1. Starting in the 1860s structural isomerism was recognized (as in Ref. 2) when it provided a crucial piece of evi-

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dence for the validity of classical structural formulas and the existence of structured molecules. Following Cayley's formal enumeration[3] of isomers for the case of alkanes, the area of combinatoric enumeration continued into the twentieth century as a topic of interest,[4] particularly with the group of Henze[5] (in Texas) making several enumerations, for alkanes and homologous sequences of various derivatives. In 1936 Polya's[6] powerful combinatorial techniques introduced a new era, with a systematic enumeration scheme for a variety of types of substitutional isomers on fixed skeletons. And following Polya there has been further (often very formal) refinements for this chemical problem in numerous (*i.e.*, perhaps more than 100) papers, with a nice review of the work up to 1986 being given by R. C. Read[7] where also there is given a translation (by D. Aeppli) of Polya's foundational paper. Much of the work since Polya emphasizes the generality of the method in dealing with additional systems beyond alkanes, but often is directed to the enumeration of substitutional isomers. The book[8] of Harary and Palmer concerns more purely mathematical graph-theoretic applications of Polya's theory. The review of Balasubramanian[9] focuses on chemical enumerative problems, especially involving non-identity irreducible representations of the concerned symmetry groups, typically for counts other than for isomers. The more recent book[10] of S. Fujita considers in detail many recent theoretical extensions, primarily concerning chirality and symmetry questions, for isomers and also for reaction processes. The even more recent book[11] of Trinajstić *et al.* reviews Polya's approach and extends previous enumerations. C.-Y. Yeh[12] and S. J. Cyvin and co-workers[13] have repeatedly noted that much of Polya's general mathematical formalism can be foregone in many specific isomer enumerations. And indeed a similar point seems to be made in a slightly different more purely mathematical context by Polya in Ref. 14. That is, whole chapters often occurring in standard combinatorics texts concerning formalities of permutation groups, general »cycle-index« functions, »pattern inventories«, *etc.* need not be gone through (in a general formal manner) for a number of specific cases.

We seek to make extensions of such theoretical work, here in application to the set of all acyclic hydrocarbons with classical valence structures. We adopt the straight-forward point of view of Refs. 12 and 13 to make enumerations, with details of the generating-function approach described in section 2. Since earlier isomer-enumeration work beyond that on alkanes has tended to focus on substitutional isomers, the present problem (with different arrangements of multiple bonds) seems to have been little considered in previous articles, with the exception by Read,[15] where isomer classes of

acyclic hydrocarbons are partitioned up in accordance with the numbers of double and triple bonds and the enumerations are made to only about 10 carbons. In our present work here exact enumerations are pursued to much higher numbers of carbons. Further we report our results in the form of a »formula periodic table« for isomer classes of acyclic hydrocarbons. That is, the acyclic structural-isomer count for C_nH_{2m} (for all possible collections of bond types) appears in the nth row and m^{th} column of such a »periodic table«, and as such this may be viewed as analogous to Dias'[16] formula periodic table of polycyclic aromatic hydrocarbon isomer classes. Different characteristics and trends appearing in the table as a whole then are of interest, though here we focus primarily on one characteristic, that of (structural) isomer counts, including their asymptotic behavior. In section 3 attention is directed to the large $n \to \infty$ behavior of these enumerations as one proceeds along a diagonal with the *degree of unsaturation* $u \equiv n+1-m$ fixed. Large-n asymptotics for isomer enumerations have been made only occasionally,[6,17–20] and then primarily for alkanes. For our acyclic hydrocarbon problem it is found that just as for the alkanes, the numbers of isomers in these isomer classes increase exponentially with n as one proceeds down the constant-unsaturation diagonals. And indeed the »growth-constants« for these diagonal sequences are argued all to be exactly the same as for the alkanes, the asymptotic behaviors only varying in less dominant terms, which also are here characterized to the extent that the relation between adjacent diagonals is made. Sections 4 and 5 concern the behavior of the isomer counts in proceeding vertically down columns of the periodic table. Such a sequence presents variations in C-atom number while the number of H-atoms is fixed, so that here the degree of unsaturation scales with system size. Then in any such (columnar) sequence a multiple bond ultimately occurs attached to most C-atoms in any (large-n) isomer. Section 4 gives precise analytic results for all n for the first »non-trivial« column, *i.e.*, for the species C_nH_4. Section 5 presents an argument to establish that for a general C_nH_{2m} column the $n \to \infty$ asymptotic form for the isomer-count is sub-exponential, with leading order apparently $\sim n^{4(m-1)}$. Variations in the remnant proportionality depending on the column (as labelled by m) are also elucidated, and further the inter-relation between different columns is characterized. Overall our »periodic table« is advocated as a potentially useful tool for the consideration of the general class of acyclic hydrocarbons – and the present considerations of isomer counts for the table is a first step in its characterization and utilization.

2. ENUMERATION FOR ALL ACYCLIC HYDROCARBONS

The enumeration may be viewed as corresponding to a step-wise con-
structive generation of the acyclic hydrocarbons. The molecular structures
are represented in a »hydrogen-deleted« form where only the carbon atoms
and the C–C, C=C, and C≡C bonds are explicitly represented. Contraction
of the usual symbols C in such formulas leads to what we here call *graphs*,
though often in the literature they are termed »multi-graphs« (as multiple
bonds are allowed). These resulting acyclic graphical structures are termed
trees (though sometimes they might be termed »multi-trees«). Initially the
treatment considers »radicals«, or graph-theoretically speaking, *rooted*
trees, each of which is defined as a tree with a distinguished site called a
root, which represents the radical site with a dangling bond – the (dangling
bond) root may have different *degrees*: single, double, or triple. Now with
the valence of carbon being 4, an n-site rooted tree with a root of degree d
may be obtained from up to 4-d smaller rooted trees, whose site numbers
add up to n-1: the smaller trees are to be adjoined at the new root via the
process indicated in Figures 1, 2, and 3, for trees with roots of respective de-
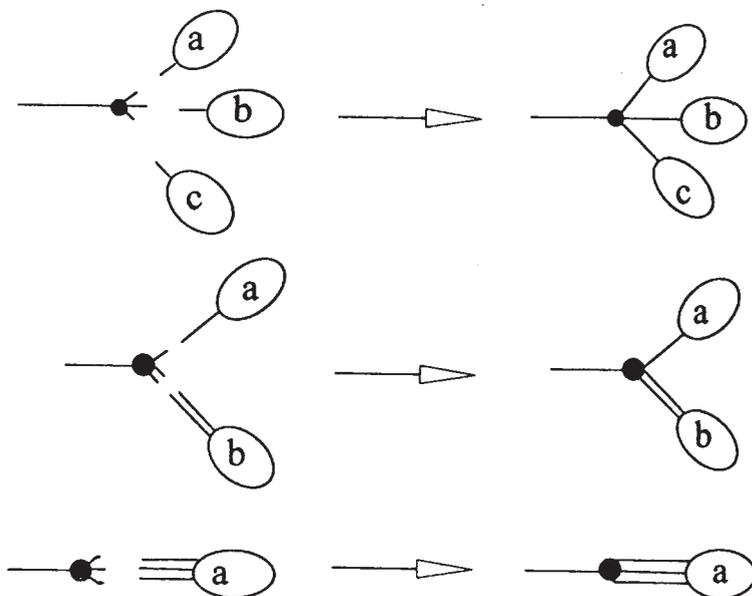grees 1, 2, or 3. Once the various rooted trees are obtained they are then

Figure 1. A diagrammatic representation for the recursive manner of building up
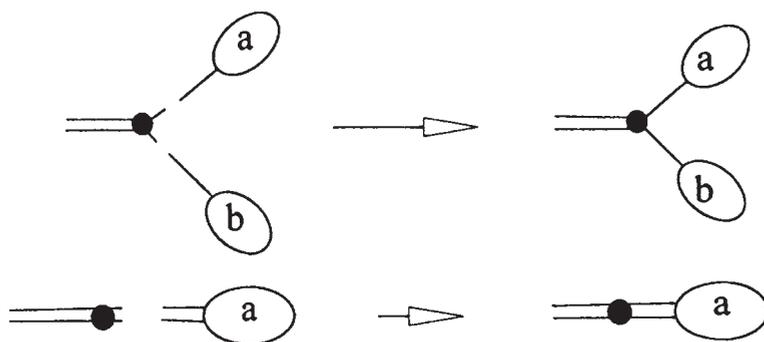single-bond rooted hydrocarbon trees (which can be termed radicals).

Figure 2. Diagrammatic representation for the recursion for double-bond rooted hydrocarbon trees (such being viewable as a special type of diradical).
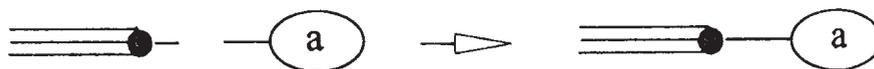

Figure 3. Diagrammatic representation for the recursion for triple-bond rooted hydrocarbon trees (such being viewable as a special type of triradical).

joined together to form non-radical acyclic hydrocarbons as indicated in Figures 4 or 5. In these constructions it is of use to attend to the length of chains, as can be done for the rooted trees in terms of *generation number g* identifiable as the number of carbon sites in a longest path from the root. Exactly what is done with these general ideas depends on just what type of isomer one wishes to consider.
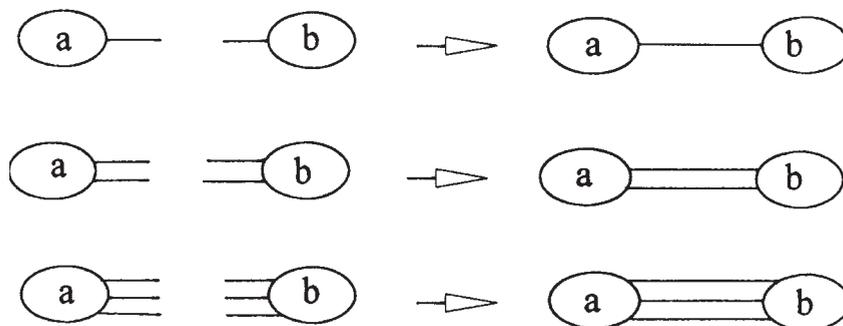

Figure 4. Diagrammatic representation for the generation of odd-diameter hydrocarbon trees.
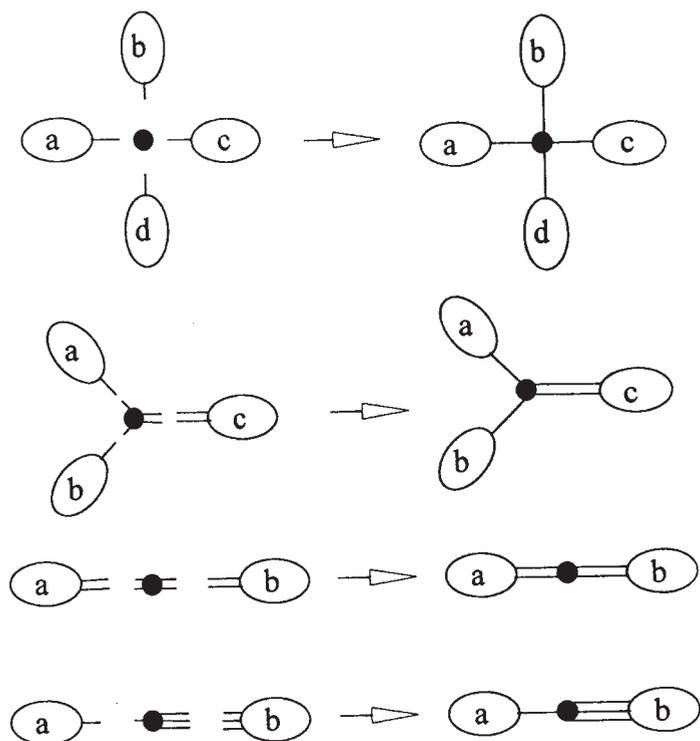
Figure 5. Diagrammatic representation for the generation of even-diameter hydrocarbon trees.

The earliest classical considerations were in terms of structural isomers, as we now also consider, initially for »radicaloid« rooted trees. Let $\#'_{g,n,m}$, $\#''_{g,n,m}$ and $\#'''_{g,n,m}$ denote the numbers of g-generation rooted trees with n C-atoms, $2m$ (implicit) H-atoms, and roots of degrees 1, 2, and 3, respectively. The corresponding generating functions are

$$\phi_g^*(t,u) \equiv \sum_{n \geq 0} \#^*_{g,n,m} \, t^n u^{2m}, \quad *=',\,'',\,''' \tag{2.1}$$

where t and u are »dummy« variables. The constructions of Figures 1, 2, and 3 lead to (coupled) recursions for the corresponding generating functions

$$\phi'_{g+1}(t,u) = t\{\phi'_g \cdot Z_2[\phi'_{<g}] + Z_2[\phi'_g] \cdot \phi'_{<g} + Z_3[\phi'_g]\} + t\{\phi''_g \cdot \phi'_{<g} + \phi'_g \cdot \phi''_{<g}\} + t\,\phi'''_g$$

$$\phi''_{g+1}(t,u) = t\{\phi'_g \cdot \phi'_{<g} + Z_2[\phi'_g]\} + t\phi''_g \tag{2.2}$$

$$\phi'''_{g+1}(t,u) = t\phi'_g$$

where the auxiliary functions are

$$\phi_{<g+1}^{*}(t,u) \equiv \phi_{<g}^{*}(t,u) + \phi_{g}^{*}(t,u)$$
$$Z_2[f] \equiv \{[f(t)]^2 + f(t^2)\}/2 \qquad (2.3)$$
$$Z_3[f] \equiv \{[f(t)]^3 + 3f(t)f(t^2) + 2f(t^3)\}/6$$
$$Z_4[f] \equiv \{[f(t)]^4 + 6[f(t)]^2 f(t^2) + 8f(t)f(t^3) + 3[f(t^2)]^2 + 6f(t^4)\}/24 \ .$$

If p different sub-structures each with associated generating function $f(t)$ were combined together such that no two were to be symmetry equivalent, then a factor $[f(t)]^p/p!$ would be involved in our ϕ generating functions. But if several of these p sub-structures are mutually equivalent, then this equivalence symmetry would imply that the corresponding combination structure would be constructed fewer than $p!$ times in the product $\{f(t)\}^p$, and this symmetry-mediated manner of redundancy (which is generally different for different combinations) is taken into account by the $Z_p[f;t]$. (Here a term involving $f(t^p)$ is accounting for circumstances with p equivalent sub-structures.) Indeed these $Z_p[f;t]$ are Polya's[6,7,8,11] »cycle-index« functionals (for the special case of symmetric groups $\mathscr{S}_p$), but their form and effect (most easily for smaller p) can be understood in detail in a less general context, as in Refs. 12 and 13.

Next the rooted trees are to be joined together to form the non-radicaloid hydrocarbons, involving particular longest chain lengths. The chain lengths are attended to in terms of the *diameter* of a carbon network of one of these acyclic hydrocarbons, such diameter of an acyclic network being definable as the length of the longest path between two sites of the network. Let $P_D(t,u)$ be the generating function for acyclic hydrocarbons of diameter D – *i.e.*, the coefficient of $t^n u^{2m}$ in $P_D(t)$ is the number of such diameter-D hydrocarbons having n C-atoms and $2m$ H-atoms. Then the constructions of Figure 4 lead to the odd-diameter $P_D(t,u)$, while those of Figure 5 lead to the even-diameter $P_D(t,u)$,

$$P_{2g-1}(t,u) = Z_2[\phi_g'] + Z_2[\phi_g''] + Z_2[\phi_g'''] \qquad (2.4)$$
$$P_{2g}(t,u) = t\{Z_4[\phi_g'] + \phi_{<g}' Z_3[\phi_g'] + Z_2[\phi_{<g}'] Z_2[\phi_g']\}$$
$$+ t\{\phi_g'' Z_2[\phi_g'] + \phi_{<g}''' Z_2[\phi_g'] + \phi_g'' \phi_g' \phi_{<g}'\} + tZ_2[\phi_g''] + t\phi_g' \phi_g''' \ .$$

And finally the overall generating function is

$$P(t,u) = \sum_{D \geq 0} P_D(t,u) \ . \qquad (2.5)$$

That is, the coefficient of $t^n u^{2m}$ in $P(t,u)$ is the desired number $\#_{n,m}$ of acyclic structural isomers with n C-atoms and $2m$ H-atoms.

The recursions of equations (2.2), (2.3), (2.4), (2.5) may be used to build up numerically these power series, and yield exact structural-isomer counts $\#_{n,m}$ for n and m not overly large. To so use the recursions one begins with low-order initiating generating functions

$$\phi_0'(t,u)=u, \quad \phi_0''(t,u)=0 \quad and \quad \phi_0'''(t,u)=0 \ . \tag{2.6}$$

The numerical results we have so generated are given in Table I. This table represents our »*Formula Periodic Table for the Isomer Classes of Acyclic Hydrocarbons*«. The empty upper right portion of this table (where $m > n+1$) is all filled with 0s, since here the maximum saturation achievable in a connected classical structure is exceeded. The right-most (0 unsaturation) diagonal is for the alkanes, and the next one just to the left (with degree of unsaturation 1) is for the alkenes. The third diagonal (of unsaturation degree 2) consists of a combination of alka-dienes and alkynes. From a casual inspection of the table the isomer counts seem to increase geometrically in proceeding down (constant unsaturation) diagonals, whereas the isomer counts down (constant H-count) columns seem possibly to show (at least for lower m) a somewhat slower rate of increase. The asymptotic behaviors for these progressions are considered more quantitatively in the next three sections.

3. ISOMER-COUNTS AT CONSTANT UNSATURATION

The alkanes all lie in the first diagonal at the right, the alkenes in the second diagonal from the right, and the third diagonal involves the alkadienes and alkynes. Thence it is natural to consider behaviors along these diagonals, each of which may be labelled by the *degree of unsaturation* $u \equiv n-m+1$, which counts the number of π-bonds in a $C_n H_{2m}$ structure. Of course the alkanes have long been studied (back to Cayley[2] in 1874), and the asymptotic behavior has been empirically observed[18] to be exponentially increasing. Indeed asymptotically for alkanes the counts have been[19] fit to a form

$$\#_{n,n+1} \approx n^{-5/2}\kappa^n\{A+Bn^{-1}+Cn^{-2}\} \tag{3.1}$$

with

TABLE I

Structural isomer counts of acyclic hydrocarbons C_nH_{2m}

n\m	1	2	3	4	5	6	7	8	9	10
1	0	1								
2	1	1	1							
3	0	2	1	1						
4	1	2	4	3	2					
5	0	4	6	9	5	3				
6	1	5	15	22	23	13	5			
7	0	8	24	55	66	58	27	9		
8	1	9	48	122	200	210	152	66	18	
9	0	14	76	261	511	698	629	400	153	35
10	1	17	134	524	1283	2083	2388	1914	1072	377
11	0	23	206	1021	2941	5793	7963	7982	5701	2876
12	1	27	334	1903	6547	15049	24687	29597	26282	17001
13	0	36	497	3445	13772	37074	70838	100372	106558	85237
14	1	43	760	6037	28125	86954	192134	315370	393506	375649
15	0	54	1096	10328	55187	195668	493676	929991	1339640	1496908
16	1	63	1602	17221	105477	423947	1213654	2594570	4266883	5486345
17	0	78	2247	28125	195519	888519	2863259	6897945	12817557	18742790
18	1	92	3170	44983	354234	1806250	6518711	17568561	36603805	60257746
19	0	110	4338	70693	626237	3572571	14359619	43064289	99913191	183720649
20	1	127	5946	109169	1085324	6889666	30714261	101964749	261968498	534421522
21	0	150	7961	166045	1843101	12983135	63927081	233948149	662293724	1490054454
22	1	174	10652	248810	3076236	23946712	129788950	521527337	1619937293	4002420657
23	0	201	13991	367950	5046480	43301964	257481061	1132226598	3844072323	10382647535
24	1	230	18341	537154	8153791	76866509	500017739	2398586601	8871502365	26096114170
25	0	264	23684	775149	12979245	134117551	951829224	4967196606	19953566877	63712325018
26	1	302	30505	1106016	20384794	230258415	1778534077	10071036370	43819960474	151426767846
27	0	341	38801	1562064	31600016	389373160	3265756058	20019153003	94112224532	351033204227

TABLE I (continued)

Structural isomer counts of acyclic hydrocarbons C_nH_{2m}

$n \backslash m$	11	12	13	14	15	16	17	18
10	75							
11	914	159						
12	7783	2281	355					
13	50251	21099	5690	802				
14	273319	148219	57447	14397	1858			
15	1298369	867342	435098	156686	36564	4347		
16	5555262	4418904	2729028	1274177	428438	93650	10359	
17	21785333	20187787	14833489	8521365	3719977	1173253	240916	24894
18	79420721	84310702	72061721	49219405	26434288	10837349	3218346	623338
19	271834324	326471098	319148945	253266571	161643490	81524207	31503100	8839226
20	880597714	1184496890	1307619054	1185277179	878141785	526112733	250132215	91413657
21	2716794618	4059885050	5010226799	5120925629	4328966329	3008519254	1698689033	763913265
22	8023980469	13231529292	18105027877	20654157540	19663780677	15579232935	10198151506	5445565067
23	22783064221	41221891395	62117420073	78443707223	83247286501	74205163355	55336011269	34241510896
24	62413901927	123302692095	203457689339	282481517745	331394029127	328917077506	275727133179	194251904648
25	165468166274	355423763247	639058665195	969918648515	1249251040818	1369090071332	1276737476818	1010414372884
26	425647169313	990403506239	1932244750424	3190109891436	4485119737163	5390084776040	5547700687606	4877655916921
27	1064811333711	2675113431019	5642081827363	10089996187155	15409041823851	20189111658789	22750595150339	22058299159859

$n \backslash m$	19	20	21	22	23	24	25	26
18	60523							
19	1619346	148284						
20	24307593	4224993	366319					
21	264810737	66914812	11062046	910726				
22	2323374632	765993398	184389454	29062341	2278658			
23	17344882955	7039881552	2212720387	508547450	76581151	5731580		
24	113987895832	54924902911	21258589275	6381137895	1403735809	202365823	14490245	
25	674715859793	376521714326	173007473343	63996402252	18398996329	3877614477	536113477	36797588
26	3656669340477	2321168404984	1234953214651	542324088080	192107009353	52971930602	10718843363	1423665699
27	18369184606677	13084120995914	7915795152594	4024424838751	1692487754600	575171070363	152367280905	29649112326

$$\kappa \cong 2.81546003329 \tag{3.2}$$
$$A \cong 0.6570 \quad B \cong -0.068 \quad C \cong 6.2 \ .$$

The form excepting the B- and C-terms has been established rigorously,[5,17] and the method[19] for determining κ is such that all excepting perhaps the last of the 10 digits given in (3.2) should be exact. The constants A, B, C have been obtained by least-squares fitting against exact counts for values of n up to around 50.

Now one can make a heuristic argument relating the count in one diagonal to that in an adjacent diagonal (so that from the knowledge of the alkane diagonal the asymptotic forms of all other diagonals follow). We imagine comparing the count for C_nH_{2m} with that for $C_nH_{2(m+1)}$. Evidently to obtain a C_nH_{2m} structure from a $C_nH_{2(m+1)}$ structure one should delete two H-atoms and add one π-bond someplace, there being n-1 σ-bonds at which one might conceive of adding this π-bond. But whenever there is no H-atom attached to the C-atoms at each end of a particular σ-bond in a particular $C_nH_{2(m+1)}$ structure such an addition is not permissible. And further sometimes additions at two different (permissible) σ-bonds may yield the same C_nH_{2m} structure, as when the two σ-bonds are equivalent (under the automorphism group for the graph of the particular $C_nH_{2(m+1)}$ structure under consideration). Thence rather than n-1 new C_nH_{2m} structures from each $C_nH_{2(m+1)}$ structure we should to leading order expect something proportional only to n, with the proportionality factor a (strictly) between 0 and 1. But yet another factor which influences the number of σ-bonds at which a π-bond may be added is any occurrence of π-bonds in the initial $C_nH_{2(m+1)}$ structure. That is, we expect the number of ways of adding a π-bond to give distinct $C_nH_{2(m+1)}$ structures to be $\approx (an\text{-}bu)$ with $0 < a < 1$ and $0 < b < 1$. Finally of these different structures obtained from one $C_nH_{2(m+1)}$ structure each may in general be obtained from other $C_nH_{2(m+1)}$ structures – indeed there are u others, corresponding to just which π-bond is last added, to obtain the target C_nH_{2m} structure. Thus we anticipate that

$$\#_{n,m} \approx (an\text{-}bu)u^{-1}\, \#_{n,m+1} \tag{3.3}$$

with less-dominant-order terms (say involving n^{-1}, un^{-1}, and u^2n^{-1}) also possibly occurring in the proportionality. For the alkene (u=1) case Polya[8] notes a rigorous deduction which gives agreement with our leading n-dependence, regarding the identification of the power of n and the value of κ being the same as for the alkanes.

An empirical test of the surmised general asymptotic relation of (3.3) may be made. To this end we plot

$$u\#_{n,m}/ \#_{n,m+1} \quad vs. \quad n \tag{3.4}$$

for several different values of u in Figure 6. Evidently this is anticipated to give for each u a straight line $y = an - bu$, and the plots tend to confirm this: straight lines are approached with the slopes for each value of u seemingly approaching the same value (a), and to somewhat less accuracy the different lines seem to be approach equal displacements (b) from one another. This second feature involving b is more fully tested by making plots for different u of

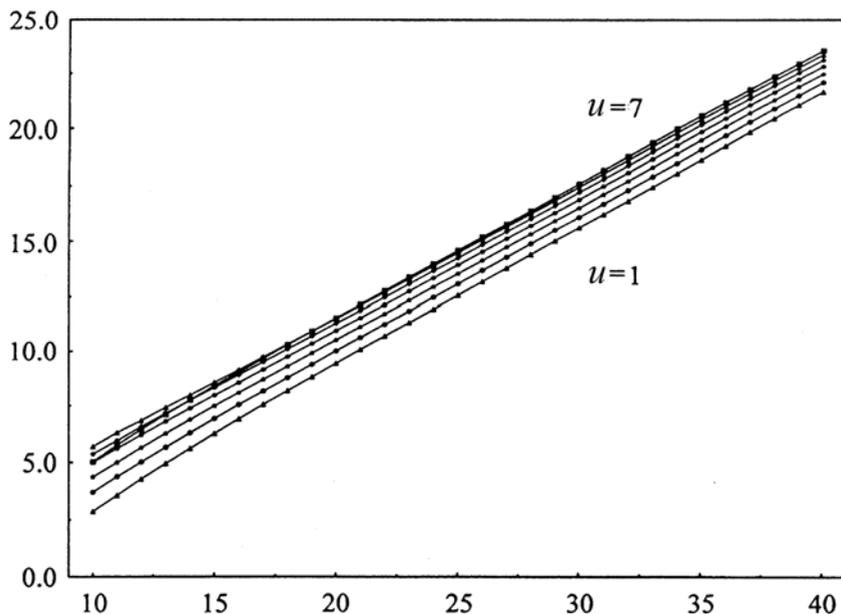$$(u+1)\#_{n,m-1}/ \#_{n,m}-u\#_{n,m}/ \#_{n,m+1} \quad vs. \quad 1/n \tag{3.5}$$

Figure 6. Plot of $(n+1-m)\#_{n,m}/ \#_{n,m+1}$ *versus* n to test the surmised asymptotic form for the isomer counts down diagonals.

as in Figure 7. Evidently the anticipation is that the $n^{-1} \to 0$ limit should for each u approach the same value (b), and the plots are seen to confirm this, at least in the large-n limit. Notably »higher-order« corrections are apparent before this limit is reached.
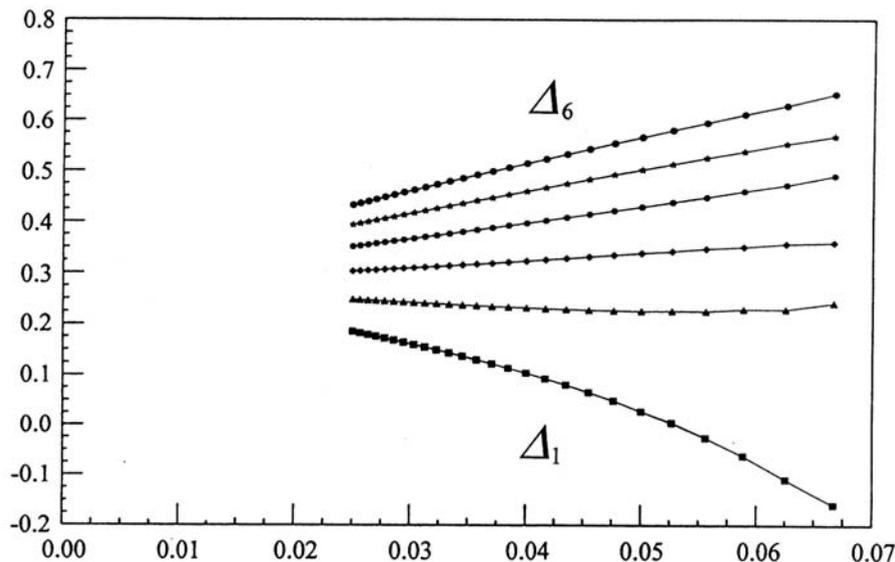
Figure 7. Plot of $\Delta_{n+1-m} \equiv \{(n+2-m)\#_{n,m-1}/\#_{n,m} - (n+1-m)\#_{n,m}/\#_{n,m+1}\}$ *versus* $1/n$.

Finally, being convinced of the form of the leading u-dependence, one may make high-accuracy fits including even some less dominant than those displayed in (3.3). We fit to a form

$$\#_{n,n-u} \approx \{an - bu + c + (d + eu + fu^2)n^{-1}\}u^{-1}\#_{n,n-u+1} \qquad (3.6)$$

via a standard least-squares minimization. Using the data for n and u in the ranges $20 \leq n \leq 40$ and $1 \leq u \leq 7$, we find

$$a \cong 0.59283 \qquad b \cong 0.2823 \qquad c \cong 0.235 \qquad (3.7)$$
$$d \cong -10.1 \qquad e \cong 6.42 \qquad f \cong -0.99 \ .$$

As a (partial) test of the resulting overall formula (from (3.1), (3.2), (3.6), and (3.7)) one might compare their predictions to our exact enumeration results at some n where these exact results are available. The per-cent errors $\%\mathrm{err}_{n,u}$ for actual counts $\#_{n,n+1-u}$ as compared to the result following from our asymptotic formulas turn out at $n = 40$ to be

$$\%\mathrm{err}_{40,0} \cong 0.005 \qquad \%\mathrm{err}_{40,1} \cong 0.021 \qquad \%\mathrm{err}_{40,2} \cong 0.029$$
$$\%\mathrm{err}_{40,3} \cong 0.021 \qquad \%\mathrm{err}_{40,4} \cong 0.008 \qquad \%\mathrm{err}_{40,5} \cong 0.029 \qquad (3.8)$$
$$\%\mathrm{err}_{40,6} \cong 0.021 \qquad \%\mathrm{err}_{40,7} \cong 0.037$$

Evidently this seems to give a fairly accurate relation for the asymptotics down diagonals in our periodic table, as desired.

4. ISOMER-COUNT FOR C_nH_4

Exact analytic counts are possible for the columns furthest to the left in our acyclic hydrocarbon periodic table. The counts for the first column with $m = 1$ are trivial, involving poly-yne chains of even length with one H-atom on each end. The second column with $m = 2$ is less trivial, and is the focus of this section, the ideas involved in treating this being conceivably analytically extendable to a few further columns, though in the next section these ideas are utilized only in a heuristic manner to deal only approximately with further columns.

Our initial key step in treating the acyclic C_nH_4 structures entails noting that there can be no more than 4 terminal (*i.e.*, primary) C-atoms, since at each such end there must occur (at least) one H-atom. That is, a sort of generic underlying C_nH_4 structure is as indicated in Figure 8, where the curves there represent not simply σ-bonds but rather *strings* of σ-bonds. Indeed this figure encompasses all possible C_nH_4 structures if we understand that H-atoms are to occur solely at the end of each string and we allow strings of 0-length. Then the four strings with a terminal C-atom must all be of even length (being poly-ynic, consisting of alternating triple and single bonds, still allowing 0 such alternating pairs). The central string (with no terminal C-atom) is either of length 0 or else-wise of any positive length with every bond along this string being double. That is, decoration of these strings with these allowed lengths leads to a unique label for each possible
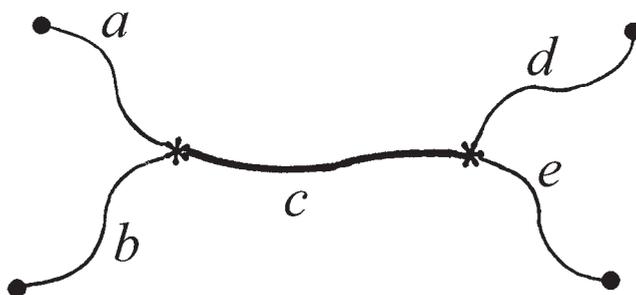

Figure 8. Generic string structure for C_nH_4 acyclic hydrocarbons. Here the labels *a*, *b*, *c*, *d*, *e* may be viewed to identify the numbers of carbon-carbon σ-bonds along each of the »strings« so labelled. The poly-ynic *a,b,c,d* strings are to be of even length, whereas the cumulenic *e* string can be of either even or odd length.

C_nH_4 structure, so long as equivalent labellings (involving permutation of equivalent string positions) are taken into account. Thus we can represent each possible C_nH_4 structure by a *code* $(a,b : e : c,d)$ corresponding to this string structure. Here since the string structures are to be equivalent under a (order-8) permutation group $\mathscr{P}$, which in correspondence with the labellings of Figure 8 we might indicate thusly

$$\mathscr{P} = \{\mathscr{I}, (a,b)\} \{\mathscr{I}, (c,d)\} \{\mathscr{I}, (a,c)(b,d)\} \tag{4.1}$$

(with $\mathscr{I}$ the identity). And in the special case when $e = 0$, the four terminal strings are all mutually equivalent (for any permutation of the four), so that the invariance group is the full symmetric group

$$\mathscr{S}_4 = \mathscr{P}\cup(a,c)\mathscr{P}\cup(a,d)\mathscr{P} \;. \tag{4.2}$$

Thence for the code $(a,b : e : c,d)$ one may choose

$$\begin{aligned} & a \leq b \text{ and } a \leq c \leq d \\ & \text{if } a = c, \text{ then } b \leq d \\ & \text{if } e = 0, \text{ then } b \leq c \;. \end{aligned} \tag{4.3}$$

Examples of this code and the associated acyclic structures are indicated in Figure 9.

With these geometro-topological ideas for construction of C_nH_4 structures in mind one may build up an explicit generating function for the enumeration of the structural isomers (or also the geometric isomers if so wished). The overall generating function $F(t)$ is to be built up from auxiliary generating functions $f(t)$ for the adjoined pairs of terminal strings – this overall construction being indicated in Figure 10. These generating functions are viewed to be power series in a variable t, with the coefficient of t^L counting the number of structures with a total length L of σ-bonds between C-atoms. The generating function $f(t)$ in turn is given in terms of that for a single terminal string, this evidently being given as

$$1+t^2+t^4+t^6+t^8+... = (1-t^2)^{-1} \;. \tag{4.4}$$

Then for the radicaloid terminal-string-pair

$$f(t) = \{(1-t^2)^{-2}+(1-t^4)^{-1}\}/2 \;. \tag{4.5}$$

$(0,0:0:0,0)$

$(0,0:1:0,0)$

$(0,0:2:0,0)$

$(0,0:0:0,2)$

$(0,0:3:0,0)$

$(0,0:1:0,2)$

$(0,0:4:0,0)$
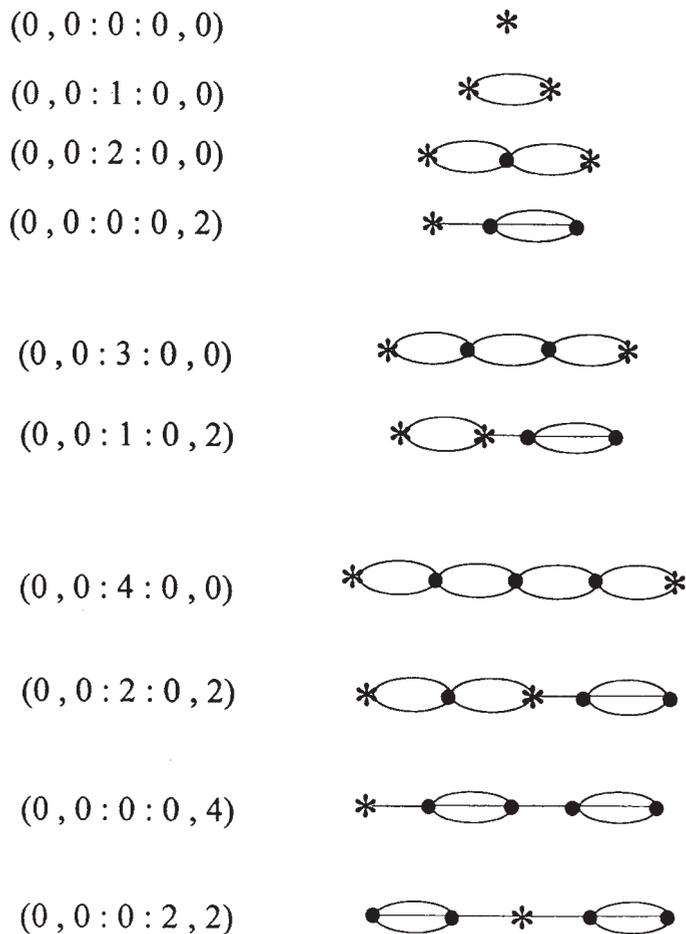
$(0,0:2:0,2)$

$(0,0:0:0,4)$

$(0,0:0:2,2)$

Figure 9. Acyclic C_nH_4 hydrocarbon structures and corresponding codes for species of up to $n = 7$ carbons. The asterisked sites identify those at the ends of the internal cumulenic string. Note that when the cumulenic string is of length 0 the two asterisks coincide, so that only one is seen.

The auxiliary generating function for the central (non-terminal) string if of non-zero length is

$$t+t^2+t^3+t^4+\ldots = t(1-t)^{-1} \ . \tag{4.6}$$

Then $Z_2[f(t);t]t(1-t)^{-1}$ is sufficient to count all the C_nH_4 species where the central internal string is of non-zero length. For the case that the central internal string is of length 0, then all the terminal strings are more
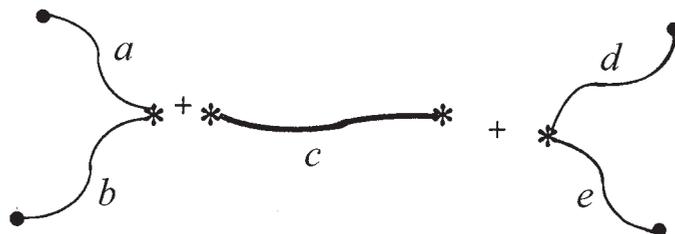
Figure 10. Construction scheme for joining two terminal string-pairs and one internal string (in boldface) together to form acyclic C_nH_4 structures.

fully equivalent, such that $Z_4[(1-t)^{-1};t]$ generates this subclass of species. Thus for all C_nH_4 species the total generating function is

$$F(t) = Z_4[(1-t)^{-1};t] + t(1-t)^{-1} \{[f(t)]^2 + f(t^2)\}/2 \tag{4.7}$$

as desired. It is again emphasized that in this section the power of t counts the total length of σ-bonds. If instead one wishes a generating function with the power of t counting C-atoms, this is simply given as $tF(t)$.

Now granted this comparatively simple generating function one may make the indicated expansions and collect together the different terms to obtain the isomer-counts as the coefficients of the different powers of t. The coefficient of t^{ℓ} result is the number $\#_{n,4}$ of C_nH_4 isomers with a total C–C σ-bond length of ℓ, so that $n = \ell+1$, and the substitutions when made (rather tediously albeit straightforwardly) lead to

$$\#_{4k,4} = \frac{1}{2}g(k) + \frac{1}{36}k^{\uparrow 3} + \frac{1}{36}(k-1)^{\uparrow 3} + \frac{1}{6}\lfloor k/2 \rfloor + \frac{1}{2} + \frac{1}{6}(k+1)^2 + \frac{1}{3}\lfloor 2k/3 \rfloor + \frac{1}{6}\delta_{k.\text{even}}$$

$$\#_{4k-1,4} = \frac{1}{2}g(k) \tag{4.8}$$

$$\#_{4k-2,4} = \frac{1}{2}g(k) - \frac{1}{9}(k-1)^{\uparrow 3} + \frac{1}{6}(k-1)^{\uparrow 2} + \frac{1}{3}\lfloor (2k-1)/3 \rfloor + \frac{1}{3}$$

$$\#_{4k-3,4} = \frac{1}{2}g(k) - \frac{1}{6}(k-1)^{\uparrow 3}$$

where $\lfloor x \rfloor$ denotes the greatest integer less than x, where $\delta_{k.\text{even}}$ is 1 or 0 as k is even or odd, and where

$$x^{\uparrow m} \equiv (x+1) \cdot (x+2) \cdot ... \cdot (x+m) \tag{4.9}$$

$$g(m) \equiv \frac{1}{6}(m-1)^{\uparrow 4} - \frac{1}{6}(m-1)^{\uparrow 3} + \frac{1}{4}(m-1)^{\uparrow 2} - \frac{1}{2}\lfloor m/2 \rfloor + \frac{m}{2} .$$

Notably this resultant formula of (4.8) agrees with our earlier independently generated results in the $m = 2$ column of our periodic table. And next we turn to the asymptotics of this and especially larger-m columns of our periodic table.

5. ASYMPTOTICS FOR ISOMER COUNTS DOWN COLUMNS

A heuristic argument can be given for the asymptotic forms for isomer counts in proceeding down columns of our acyclic-hydrocarbon periodic table. From the derivation in the preceding section the isomer count in the C_nH_4 column evidently is (to leading order) $\sim n^4$. The reason for this is basically that this is the scaling behavior for partitioning $n-1$ into 5 non-negative parts ($a, b, c, d,$ and e, with $a, b, c,$ and d even) – that is, there are $\sim n^4$ choices for a, b, c, d with the last string length e being specified as $e = n - 1 - (a+b+c+d)$. And evidently one can imagine much this same argument extended to the case for the C_nH_6 species, there now being a new generic string structure, as in Figure 11. Here the two strings shown in bold are to consist of (cumulenic) double bonds, so that these strings may be of either even or odd length; whereas the remaining (non-bold) strings are comprised of alternating single- and triple-bonds, so that these strings are of even length (including the possibility of 0 length). Since there are a net of 9 strings, the isomer counts should asymptotically scale as $\sim n^8$. For C_nH_8 there are however 2 generic string structures, also shown in Figure 11, again with bold strings being all double bonds, and the net number of strings (for either generic string structure) being 13, so that the C_nH_8 isomer counts should scale as $\sim n^{12}$. In proceeding to C_nH_{2m} columns with a higher value of m there may be several generic string structures (incidently being in correspondence with acyclic polyene structures). But all such string structures for a given m exhibit the same number $4m-3$ of strings. [This invariance of string number at fixed m is seen because: first, each string structure has $2m$ terminal positions, whereat the H-atoms occur; second, any such string structure, having the form of a tree with only degree-1 and degree-3 sites, must have $2m-2$ nodes where three strings come together; and third, again because of the tree-like nature of the string structure, the number of strings being one more than twice the number of nodes is given as $2 \cdot (2m-2) + 1 = 4m - 3$]. Thus the number of C_nH_{2m} isomers should scale as $\sim n^{4(m-1)}$ in proceeding down the mth column of our periodic table. Notably the form of this dependence is qualitatively different than the exponential dependence along the diagonals.
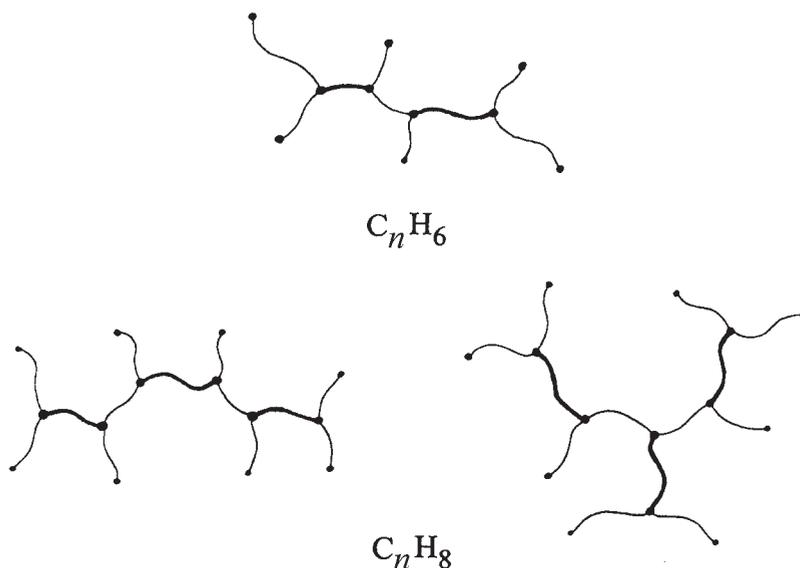
C_nH_6

C_nH_8

Figure 11. The generic string structure for acyclic C_nH_6 species, and the two generic string structures of acyclic C_nH_8 species. The terminal (non- boldface) poly-ynic strings are of even length, the (internal) cumulenic boldface strings are of arbitrary length, and the poly-ynic internal non-boldface strings are of odd length.

The heuristic arguments of the preceding paragraph may be further re-fined to suggest the m-dependence of the proportionality constants to the scaling factors $n^{4(m-1)}$. If we define #(N,p) to be the number of ways into which N can be broken up into p non-negative (distinguishable) contribu-tions, then evidently there is a recursion

$$\#(N,p) = \sum_{q=0}^{N} \#(N-q, p-1) \quad , p \geq 2 \tag{5.1}$$

with #$(N,1) = 1$. The solution to this is

$$\#(N,p) = \prod_{i=1}^{p-1} (N+i) / i \equiv N^{\uparrow(p-1)} / (p-1)! \tag{5.2}$$

where we have introduced the *ascending power* notation, and the veracity of the solution may be checked by substitution in (5.1). But generally there is some degree of equivalence between different strings (as for $m = 2$ between the a and b strings and between the c and d strings of section 4), so that the number of inequivalent ways to break up N is reduced, on the average by division by an average number $\bar{\sigma}$ of equivalent ways to break up N. For our

string-structure problem the $2m$ terminal strings frequently come in equivalent pairs, so that (for large n) there arise break-up equivalence classes with many (~2 to a power often proportional to m) members – and there may be additional equivalences beyond that of such pairs. That is, $\bar{\sigma}$ should be some average order of the automorphism group of the string structures with $2m$ terminal strings ($2m–2$ tertiary nodes, and $2m–3$ internal strings), and we might reasonably guess that for large m it is

$$\bar{\sigma} \sim m^{\beta} \mu^{m} \ . \tag{5.3}$$

Further in dealing with our string problem with a breaking of $n–1$ into $4m–3$ parts, most of these parts are required to be of even length, so that it seems a little more appropriate to think of the number of unconstrained ways to partition the integer part $\lfloor n/2 \rfloor$ of $n/2$ into $4m–3$ parts. But not quite all of the strings need be even (as when they are composed of all double bonds), so that in place of $n/2$ something like n/c might be better with c just a bit less than 2. In fact, $m–1$ of the total of $4m–3$ strings are not so restricted (and can be either odd or even), so that we might take an average value

$$c \approx \{(m–1) \cdot 1 + [(4m–3) – (m–1)] \cdot 2\}/(4m–3) \approx 7/4 \ . \tag{5.4}$$

That is, in accounting for the parity restrictions on the string structures, our proposed asymptotic refinement to count $C_{n}H_{2m}$ isomers is

$$\#_{n,m} \sim \{(N/c)^{\uparrow(p-1)}/\bar{\sigma}\} \ \{\text{average \# string structures}\} \ . \tag{5.5}$$

Now this average number of conceivable generic string structures (already noted to be 1 for $m = 2$, as in Figure 6, and 1 and 2 for $m = 3$ and 4, as in Figure 11) is just a Polya-count for ordinary (alkane) trees with only primary and tertiary sites. But if one imagines clipping off the terminal strings, one notes that each generic string structure devolves to what is evidently in correspondence with a unique conjugated polyene (with the ordinary and bold-face strings respectively corresponding to single and double C-C bonds in the conjugated polyene). Thus the generic string structures for $C_{n}H_{2m}$ are in one-to-one correspondence with the $2m–2$-site conjugated polyene structural isomers. Then noting that the count for these polyenes parallels the form for alkane enumeration, we conclude that the number of string structures should be proportional to a form

$$\sim m^{-\alpha} \eta^{2m-2} \ . \tag{5.6}$$

Thus collecting together different constants involved in similar functional dependences (*e.g.*, the growth constants μ and η are imagined collected together in a single growth constant $\lambda \equiv \mu \eta^4$), we suggest an overall form

$$\#_{n,m} \approx C \ m^\gamma \lambda^m \cdot (n/c)^{\uparrow 4(m-1)}/(4m-4)! \tag{5.7}$$

as appropriate for going down columns of our acyclic-hydrocarbon table.

This surmised functional form of (5.7) may be tested. In particular at a fixed value of m one may make a plot of

$$\log \left\{ \frac{\#_{n,m+1} \ (n \ / \ c)^{\uparrow 4(m-1)}}{\#_{n,m} \ (n \ / \ c)^{\uparrow 4m}} \right\} \quad vs. \quad 1 \ / \ n \tag{5.8}$$

which from (5.7) should approach a fixed intercept at $1/n = 0$. In Figure 12 this plot is made for m values from 2 to 9, and indeed our expectation of a fixed intercept is bourne out. A quantitative value for this intercept ρ_m is obtained by making least-squares fits for the curves of this plot to a short power series in $1/n$. This is done using the data for n from $30 \rightarrow 120$ with terms in the power series being retained up through a power p – it being found that as one varies p from 3 to 9 intercepts ρ_m varying slowly with m
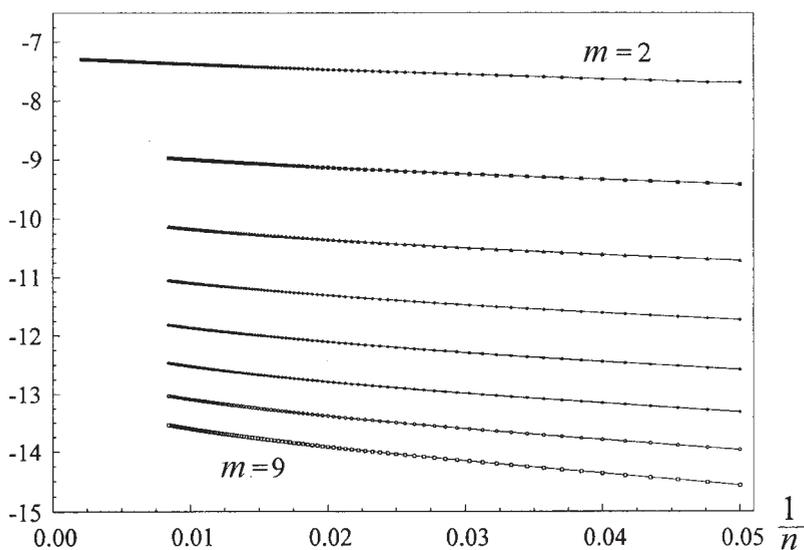

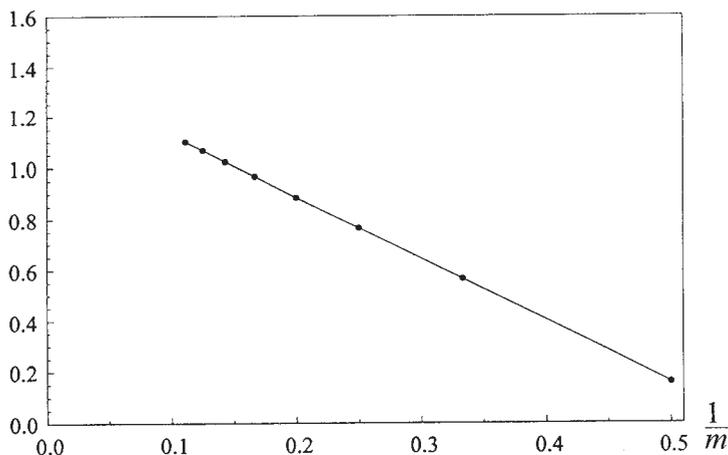Figure 12. A plot as explained in Eq. (5.8) for different $m = 2 \rightarrow 9$.

Figure 13. A plot of $\rho_m + \log\{4m(4m\text{-}1)(4m\text{-}2)(4m\text{-}3)\}$ vs. $1/m$.

result. Next the remaining m-dependences manifested in the various ρ_m may be addressed, by making a plot

$$\rho_m + \log\{4m(4m\text{-}1)(4m\text{-}2)(4m\text{-}3)\} \qquad vs. \quad 1/m \qquad (5.9)$$

which from (5.7) should approach a straight line with slope γ and intercept $\log(\lambda)$. In Figure 13 this plot is made, whence it is seen that our expectations are bourne out to a high degree of accuracy. A least squares fit yields $\gamma \cong -2.423$ and $\lambda \cong 3.935$ (with only the last digits varying with a weighting of the square errors by 1, m, or m^2). We make a rational choice for the exponent of γ, then fit the factor λ, to obtain

$$\gamma = -63/26 \text{ and } \lambda \cong 3.9351 . \qquad (5.10)$$

The considered m values seem somewhat distant from the $m \to \infty$ limit (and for larger-m columns the large-n region of $n \gg 4m$ is farther down the columns), so that additional non-leading-order terms in the coefficient C of (5.7) are desirable, say as an inverse power series in m. Thence with the extrapolated intercepts of Figure 12 along with the accurate results of section 5 for $m=2$ we obtain estimates to

$$C = \lim_{n \to \infty} \frac{\#_{n,m} (4m-4)!}{m^\gamma \lambda^m \cdot (n/c)^{\uparrow 4(m-1)}} \qquad (5.11)$$

which then are shown in Figure 14 plotted versus $1/m$. Also shown there is a curve which results from a least-squares fit
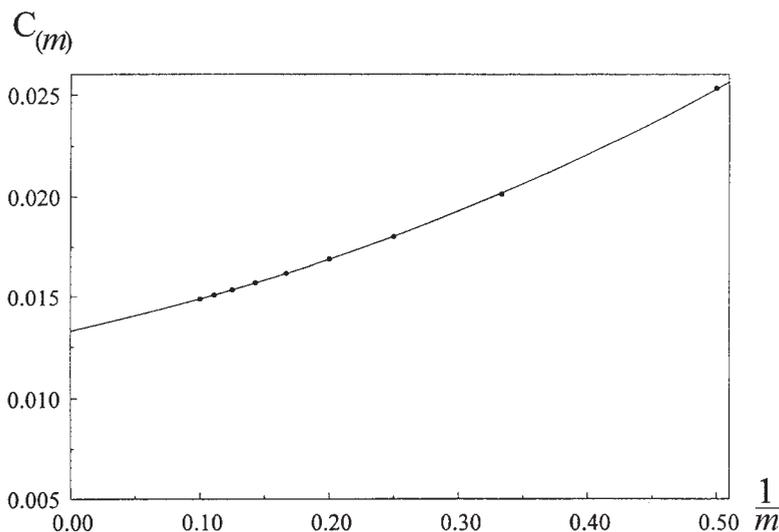
Figure 14. Estimated $C \equiv C_{(m)}$ values of (5.11) plotted *versus* $1/m$.

$$C = 0.01327 + 0.01421\, m^{-1} + 0.01961\, m^{-2} \qquad (5.12)$$

of the data points. Overall it seems we have in hand correct leading asymptotics.

Now a final attempt at a numerical fit can be made, including yet higher order terms. We use the values of (5.10) and (5.12) and amend the form of (5.7) with some terms higher order in n, thusly

$$\#_{n,m} \approx \frac{m^{\gamma}\,\lambda^{m}\,(n/c)^{\uparrow 4(m-1)}}{(4m-4)!}\left\{C + a_1\,\frac{m}{n} + b_1\,\frac{1}{n} + c_1\,\frac{1}{mn} + a_2\,\frac{m^2}{n^2} + b_2\,\frac{m}{n^2} + c_2\,\frac{1}{n^2}\right\}. \qquad (5.13)$$

Fitting with the data for n = 30→120 for m = 2→10, we obtain

$$
\begin{array}{lll}
a_1 = -0.19684 & b_1 = 0.08029 & c_1 = 0.70598 \qquad (5.14)\\
a_2 = 0.45082 & b_2 = 0.37568 & c_2 = -0.62989 \ .
\end{array}
$$

Then as a check the per cent errors %err$_{n,m}$ at $n = 120$ carbons may be noted

$$
\begin{array}{lll}
\%\mathrm{err}_{120,2} \cong 10 & \%\mathrm{err}_{120,3} \cong 37 & \%\mathrm{err}_{120,4} \cong 6 \\
\%\mathrm{err}_{120,5} \cong 9 & \%\mathrm{err}_{120,6} \cong 16 & \%\mathrm{err}_{120,7} \cong 18 \qquad (5.15)\\
\%\mathrm{err}_{120,8} \cong 18 & \%\mathrm{err}_{120,9} \cong 16 & \%\mathrm{err}_{120,10} \cong 12 \ .
\end{array}
$$

Evidently the errors are disappointingly large, despite our efforts. This presumably is due to some difficulty with the form of the higher corrections (involving the a_j, b_j, and c_j) as assumed in (5.13) – the difficulty might be rationalized as being due to the data considered in going down columns not meeting so well the presumed asymptotic criteria $1<<4m<<n$ as does the data considered in going along diagonals (where the presumed asymptotic criterion is $u<<n$). Still our theoretical arguments for the leading form of (5.7) seem well-founded, and the arguments are nicely supported from the tests of the preceding paragraph and the associated Figures (12, 13, and 14). That is, we still seem to have correctly identified at least the leading form of the asymptotic behavior.

6. CONCLUSION AND PROSPECTS

A formula »periodic table« for the isomer classes of all acyclic hydrocarbons has been proposed, with rows and columns respectively specifying numbers of C- and H-atoms. The numbers of structural isomers in each isomer class has been calculated, with isomer counts for species C_nH_{2m} up to a few dozen C- and H-atoms being given exactly. An analytic formula has been obtained for all species C_nH_4, and presumably with some additional tedious work such formula could be extended to $m = 6$ and perhaps a little farther. More generally asymptotic $n \rightarrow \infty$ isomer-counts are developed, first focusing on fixed degree $u \equiv n+1-m$ of unsaturation, and second focusing on a fixed number of H-atoms. These first sequences of isomer counts at fixed u are found to increase exponentially fast with n. Indeed the geometric growth factor is found to be independent of the diagonal u, with the counts for the diagonals differing in a systematic sub-exponential manner described in section 3. In contrast the isomer counts for the second type of sequence with fixed number $2m$ of H-atoms are found to increase as a power $(4m-4)$ of n. Though the numbers of such near maximally unsaturated hydrocarbons then are typically substantially less than that of the alkanes with the same number of C-atoms, it seems that usually smaller fractions of these interesting unsaturated species have actually been synthesized (especially when the species are more highly branched).

It may be noted in passing that some of the qualitative aspects concerning asymptotics should remain the same if instead of enumerating structural isomers one enumerates geometric isomers, where *cis*- and *trans*-isomerization across double bonds is taken into account. In particular with these

modifications being confined to double bonds, the asymptotic forms of equation (3.1), (3.3), and (5.7) should remain unchanged. Indeed all that should change are the values of the parameters a and b in (3.3) and of γ, λ, and C in (5.7).

Beyond enumeration various properties of the different isomer classes may be surmised to vary in a systematic manner with position in the periodic table. Such systematic property variation is already generally qualitatively understood for our table's alkane diagonal sequence, which is studied in some quantitative detail in three other works.[19] A similar study[20] has been made for property variations of fully conjugated acyclic polyenes. The isomer counts reported here constitute a first step in such a more extensive study of the whole of the current periodic table for acyclic hydrocarbons, with the second step[21] concerning distributions of graph invariants within an isomer class. A third step[22] concerns similar distributions for »cluster-expansion« approximants for selected molecular properties.

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SAŽETAK

Periodička tablica za izomerne klase acikličkih ugljikovodika – Prebrojavanje i asimptotske karakteristike

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Razmatrani su aciklički ugljikovodici C_nH_{2m} i njihove klasične valentne strukture. Prebrojavani su njihovi strukturni izomeri, a rezultati su prikazani u obliku »periodičke tablice« u kojoj su redovi i stupci određeni brojem ugljikovih (n) i vodikovih atoma (m). Proučavano je asimptotsko ponašanje ($n{\to}\infty$) tih prebrojavanja, najprije za stalan stupanj nezasićenosti ($u \equiv n{+}1{-}m$), a zatim za stalan broj vodikovih atoma (m). Prvi skup izomernih klasa raste eksponencijalno brzo s brojem ugljikovih atoma (n), a drugi skup raste podeksponencijalno s potencijom broja ugljikovih atoma (n).