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Isomer combinatorics for acyclic conjugated polyenes: enumeration and beyond

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Abstract. A combinatorial approach to fully conjugated acyclic polyenes (C_NH_{N+2}) is considered with a view to the extension of standard enumeration techniques to treat a widened range of chemically interesting features. As a first step, enumerations are made respecting: placement of single and double bonds, the occurrence of *cis*/*trans* isomers, and the degree (and type) of "radicality" of such conjugated networks. As a further extension, several structural (graph-theoretic) invariants averaged over various types of isomer classes and sub-classes are made, and then these invariants are utilized to estimate several physicochemical properties averaged over these same classes or sub-classes. The properties currently so considered are heats of formation, indices of refraction, and magnetic susceptibilities. Finally, the asymptotic behaviors of isomer counts and isomer properties in the many-atom limit is elaborated.

Key words: Conjugated polyenes – Structural isomers – Stereoisomers – Isomer enumeration – Isomer-class characterization

1 Introduction

One of the classic areas of chemistry concerns isomerism, the history of which (as in chapter 2 of [1]) dates back to the first part of the 1800s. Around 1860, with the introduction of structural formulas, it was realized [2] that there were different possible structural arrangements for the same formula, with such different structures corresponding to different compounds. The occurrence of such structural isomers provided important evidence for the validity of classical structural chemical ideas. Then, a little later, the occurrence of stereoisomerism was crucial for the more detailed tetrahedral-carbon- atom model of Van't Hoff and Le Bel [3]. Even today, isomerism continues to be of central importance as generally reviewed by Slanina [1], and for example in the characterization of different possible fullerene structures [4], or in consideration of different possibilities [5] for linking or knotting of molecular cycles.

Over the years, much effort has been devoted to the generation of isomer lists or just to the enumeration of a type of isomer. The problem of isomer enumeration [6] in a formal manner was initiated in 1874 for the case of alkanes, and continued as a topic of interest for some time. Then, in 1935, motivated by the chemical isomer problem, Polya [7, 8] developed a powerful combinatorial enumeration theory, which is now standard fare in combinatorics texts. Polya [7] applied his theory to alkane isomer enumeration, and following this there have been further refinements in numerous papers, e.g. as reviewed by Polya and Read [9], who also give a translation of Polya's foundational paper. During the last decade or so, more elaborated permutation group-theoretical techniques have been refined and developed [10–12], e.g. to enumerate isomers of certain selected symmetries [12, 13]. On the other hand, Cyvin and co-workers [14, 15] have noted that many of Polya's general cycle-index-laden formalities may be foregone in several chemical applications, so as to yield more straightforward derivations, especially for systems of "lower" symmetry.

Here we adopt this straightforward point of view, and investigate the possibility of some extensions to new chemically oriented applications for the case of fully conjugated acyclic polyenes. Indeed, such species have recently been subjected to enumeration by Cyvin and co-workers [15] and by Yeh [16], though their approach ignores the placement of double bonds, so that by paying attention just to the σ-electron structure the development parallels closely the classical case of what can be done for alkanes – now with restriction to degree-3 sites and possibly with distinguishment of *cis*/*trans* arrangements. Here we reformulate this work, taking into account the placement of double bonds, so that enu-

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merations of the chemically relevant sub-classes of non-radicals, mono-radicals, di-radicals etc. are obtained. That the placement of double bonds (and also triple bonds) may be explicitly taken into account has been noted by Read [10] in a framework building more directly on Polya's work, but the results for polyenes (and polyenoids) here are much more extensive. For the (non-radical) conjugated polyenes, enumerations are here made both distinguishing and not distinguishing *cis/trans* structures around double bonds (as are commonly isolatable). We view this separately from the problem of *cis/trans* structures around single bonds (where the different conformations are often not separately isolated – the associated barriers to internal rotation being notably less than for rotation about double bonds). Also we count the average number of such conformations per isomer. In the case of di-radicals a further refinement is here made in separate enumerations for what are identified as singlet or triplet di-radicals (as judged by a simple [17] yet seemingly fairly accurate graphical rule). Thus the earlier enumeration work on polyenes is notably extended in different relevant manners.

Beyond such enumerations which might be considered "classical", we here treat average values for different properties of the various polyene classes. It is shown how the same type of generating-function techniques involved in enumeration can be extended to the computation of average values of certain graph-theoretic invariants as averaged over the members of a given isomer class or subclass. Average graph-theoretic diameters and average numbers of conformations per isomer are computed; also (for the non-radical) case, average counts of primary, secondary, and teritary carbons are made, as well as average values for different "types" of single and double bonds. These average graph-theoretic invariants are used in conjunction with so-called "group-function" [18] or "cluster-expansion" [19, 20] ideas to obtain values for heats of formation, indices of refraction, and magnetic susceptibilities averaged over these same isomer classes or sub classes. Finally, the techniques are further extended to obtain standard deviations over such classes for these properties. A variety of tabulated results for classes with up to a few hundred billion members are reported. Such tabulations of average values for properties then provide a more thorough overview of the overall polyene class of compounds and how different properties vary. Comparison of the standard deviations within isomer classes to the differences of averages between classes provides a measure of a degree of distinction arising from the isomer classification. Finally, we investigate the asymptotic behavior of isomer counts and isomer average properties to get some insight on what happens at the many-atom (high- polymer) limit.

The mathematical technique utilized for enumeration and averages is that of "generating functions". Generally it is imagined that there is a given classification of isomers into classes $C(\alpha)$ where α is a class label. Then the associated generating function is

$$P(t) \equiv \sum_{\alpha} \#(\alpha) t^{\alpha} \tag{1}$$

where t is an "indeterminate" (or variable) and $\#(\alpha)$ is the number of members in the class $C(\alpha)$. Here α is often the number N of atoms and the class $C(N)$ is a set of all N-atom isomers, with different possibilities for the definition of an isomer – says as a structural isomer, or a geometric isomer (paying attention to *cis/trans* arrangements), or the "polyenoid" isomer classes of Cyvin et al. [14, 15] and of Yeh [16]. However, in order to develop useful formulas for the desired generating functions, it turns out that auxiliary generating functions corresponding to other subdivisions of such isomer-like classes are appropriate to introduce. In some circumstances, derivatives of the generating functions and their associated recursions are useful, particular in obtaining average values for different structural invariants and properties. Some such general ideas may be found in several combinatorics texts [21, 22], but the focus here is within the context of some explicit chemical-isomer examples, as we proceed with in the next section.

2 Non-radical acyclic conjugated polyene enumeration

The approach for enumerating isomer structures that is based on the "rooted tree" concept is well known [6, 7, 9, 10, 14, 15], and provides an especially nice tool for generating these structures via a recursion. A rooted tree corresponds to a (non-cyclic) mono-radical species with the radical site identified as the root and considered as having a dangling bond. The hydrogen atoms are "deleted", with the graphical structure corresponding just to C atoms, C—C bonds, and C=C bonds. Now as an example, in alkanes an N-site rooted tree may be obtained from three smaller rooted a-, b-, c-site rooted trees (Where $a+b+c=N-1$ and $a,b,c \geq 0$) by the process indicated in Fig. 1. Once the rooted trees are obtained, they are then joined together to form alkanes as shown in Fig. 2.

2.1 Structural isomers

In this section we are concerned with the enumeration of non-radical fully conjugated polyene (C_NH_{N+2}) isomers.

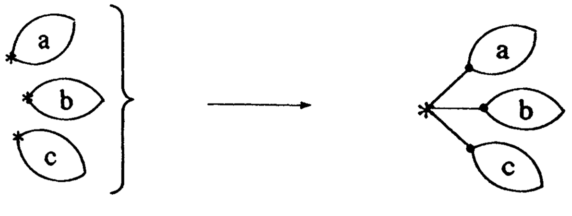

Fig. 1. The process of generation of an n-site rooted tree from three smaller rooted a-, b-, and c-site rooted trees (where $a+b+c=n-1$) for alkanes

Fig. 2. The formation of an alkane structure using rooted trees

A similar rooting procedure can be conveniently used for such a purpose, where now the root might more naturally be identified to the dangling bond (rather than a site) because there can be either a dangling single bond or a dangling double bond. We begin here with the case of structural isomers. The generating functions for such rooted trees may be [23] built up, paying attention to the rooted tree's generation number g, defined as the number of (carbon) atoms in a longest path starting from the root. The generating functions for rooted trees of a given generation number g then are

$$S_g(t) \equiv \sum_N S_{g,N}\, t^N \tag{2}$$

$$D_g(t) \equiv \sum_N D_{g,N}\, t^N \tag{3}$$

where the coefficient $S_{g,N}$ represents the number of single-bond-rooted $\leq$3-valent Kekulean trees of g generations and N carbon atoms, and $D_{g,N}$ is a number of double-bond-rooted $\leq$3-valent Kekulean trees of g generations and N atoms. In addition to the functions above, use is also made of auxiliary generating functions $S_{<g}(t)$ and $D_{<g}(t)$ that contain the contribution of all the generating functions of a given type of generation less than g:

$$S_{<g}(t) \equiv \sum_{g'<g} S_{g'}(t) \tag{4}$$

$$D_{<g}(t) \equiv \sum_{g'<g} D_{g'}(t) \tag{5}$$

Recursion relations for the generating functions are easily constructed from considerations indicated in Fig. 3:

$$S_{g+1}(t) = t\Big\{S_g(t)D_{<g}(t) + S_{<g}(t)D_g(t) + S_g(t)D_g(t)\Big\} \tag{6}$$

$$D_{g+1}(t) = t\Big\{S_g(t)S_{<g}(t) + Z[S_g;t]\Big\} \tag{7}$$

where

$$Z[f;x] \equiv (1/2)[(f(x))^2 + f(x^2)] \tag{8}$$

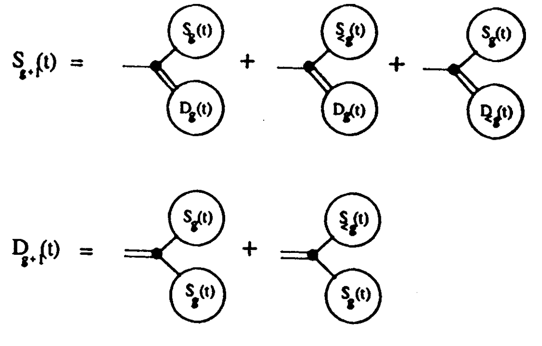

Fig. 3. Pictorial representation of the recursion relations for the generating functions S_{g+1} (with a dangling single bond) and D_{g+1} (with a dangling double bond)

$$S_{<g+1}(t) = S_{<g}(t) + S_g(t)$$

and

$$D_{<g+1}(t) = D_{<g}(t) + D_g(t) \tag{9}$$

Note that for the second term in Eq. (7) the form (1/2) $[(S_g(t))^2 + S_g(t^2)]$ is used instead of $S_g(t)^2$ in order to avoid the counting of the same isomers twice. The terms of the form A-A enter the sum once while terms of the form A-B enter the sum twice, so that by adding the "symmetric" term $S_g(t^2)$ representing A-A contributions to $S_g(t)^2$ and dividing the whole thing by two it is ensured that every isomer is properly counted. The initial conditions for the recursion relations are

$$S_{<1}(t) = S_0(t) = 1$$

and

$$S_{<0}(t) = D_{<1}(t) = D_0(t) = 0 \tag{10}$$

where the unity value in the first equality represents the dangling single bond from a hydrogen atom ($g = 0$). The procedure for generating functions $S_{g+1}(t)$ and $D_{g+1}(t)$ is illustrated in Fig. 4. Then the polyene structural isomers are easily obtained by joining together the rooted trees specified above in a proper manner as indicated in Fig. 5. Each of these structures (now unrooted trees) can be either of diameter $D = 2g - 1$ or $D = 2g$, where *diameter D* is defined as the longest distance in the walk

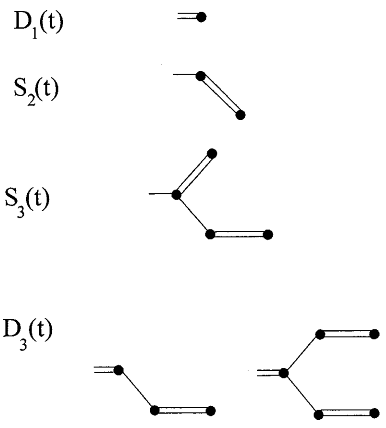

Fig. 4. The structures enumerated for rooted polyenes up to generation $g = 3$. The absence of displayed structures for $S_1(t)$ and $D_2(t)$ is because there are no such structures, and as consequence $S_1(t) = D_2(t) = 0$

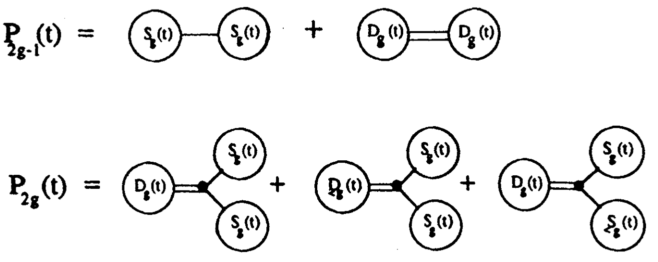

Fig. 5. Representation of recursions for generating functions P_{2g} and P_{2g+1} for conjugated polyenes of a given diameter

along the bonds in the conjugated polyene structure (unrooted tree). The center of a polyenoid structure is either the central site of a diameter (if D is even) or the cental bond of a diameter (if D is odd). The general form that represents all polyenes of diameter D is

$$P_D(t) \equiv \sum_N P_{D,N}\, t^N \tag{11}$$

where the coefficient $P_{D,N}$ represents the count of N-atom D-diameter Kekulean polyenes. Evidently the manner of joining in Fig. 5 is different depending on whether the center of a polyene is a site or a bond, whence two constructions for the generating functions $P_D(t)$ result:

$$P_{2g-1}(t) = Z[S_g; t] + Z[D_g; t] \tag{12}$$

$$P_{2g}(t) = t\Big\{(D_{<g}(t) + D_g(t)) \cdot Z[S_g; t] + D_g(t)S_g(t)S_{<g}(t)\Big\} \tag{13}$$

Finally, one obtains the structural isomer count for polyenes by summing over all diameters:

$$P(t) \equiv \sum_D P_D(t) \tag{14}$$

In applications, only D up to a given value are dealt with and the corresponding $P_D(t)$ summed over. Nevertheless, exact coefficients $\#_N$ for t^N in $P(t)$ are obtained for smaller values of N, since for each N there is a maximum value of $D(=N-1)$ which contributes to $\#_N$.

To make explicit enumerations one uses recursions (6)–(9) to build up the auxiliary rooted-tree counting polynomials, then consolidates these into polyene-counting polynomials as in Eqs. (12)–(14). The result of the structural isomer count for non-radical polyenes up to $N=44$ is given in Table 1 (along with some results developed in the next section). Although these counts are not new (the book by Knop et al. [24] lists structural isomer counts up to $N=80$), the case of structural isomers (as the simplest one) is worked out in this section both to demonstrate the technique of generating functions in the enumeration of isomers, and to make the overall analysis of polyenes presented in this manuscript more complete. Furthermore, some results of this section will be later used in the analysis of the asymptotic behavior of these counts.

Table 1. Enumeration of conjugated polyene isomers

N	Structural isomers	Geometric isomers (C=C)	$\langle \#\ \text{conformations} \rangle_N$
2	1	1	1.00
4	1	1	2.00
6	2	3	4.50
8	4	7	12.50
10	11	28	35.00
12	30	108	110.40
14	96	507	324.87
16	319	2431	965.79
18	1135	12441	2783.40
20	4150	65169	8024.34
22	15690	351156	22883.50
24	60506	1926372	65180.20
26	237853	10746856	185019.32
28	948455	60762760	524787.44
30	3831226	347664603	1486698.24
32	15642947	2009690895	4209746.92
34	64484774	11723160835	11914179.69
36	268055006	68937782355	33708741.50
38	1122646262	408323575275	95345651.97
40	4733357618	2434289046255	269632735.19
42	20078203381	14598013278960	762375144.51
44	85637471487	88011196469040	2155281381.83

2.2 Geometric isomers

In the problem of enumerating the geometrical isomers of polyenes there are two possibilities of interest: one can distinguish *cis*/*trans* arrangements about the double bond only, or one can distinguish *cis*/*trans* possibilities about both single and double bonds in the conjugated network. *Cis*/*trans* conformational transformations ordinarily being much more facile about single bonds (even in conjugated networks) than double, we begin by distinguishing just *cis*/*trans* about a double bond.

Much the same technique as used for the enumeration of structural isomers can be applied for the enumeration of geometric isomers as well, only with some simple modifications. These modifications must reflect that *cis* and *trans* arrangements across a C=C bond may be different (unless symmetry causes indistinguishability between them). One can proceed by assigning two orientations for each $D_g(t)$ generating function, and correct for the symmetry whenever it is required. This symmetry is associated with the reflection plane that is perpendicular to the plane of the polyene network and that contains the dangling double bond, whence the structures (rooted trees) from $D_g(t)$ that are symmetric with regard to this plane we call *symmetric*, $D_g^{(s)}(t)$, and those that are not we call *asymmetric*, $D_g^{(a)}(t)$. Then we can write the generating function $D_g(t)$ as consisting of two parts:

$$D_g(t) = \Big\{D_g^{(s)}(t) + D_g^{(a)}(t)\Big\} \tag{15}$$

with recursion relations (yielding the term for $g+1$ generation):

$$D_{g+1}^{(a)}(t) = t\Big\{2S_g(t)S_{<g}(t) + \Big[(S_g(t))^2 - S_g(t^2)\Big]\Big\} \tag{16}$$

$$D_{g+1}^{(s)}(t) = t\Big\{S_g(t^2)\Big\} \tag{17}$$

Note that $D_g^{(a)}(t)$ contains a factor of 2 corresponding to the two possible orientation for "$=$ C" of Fig. 3 (up and down) in 2-D space. At the same time the recursion relations for the $S_g(t)$ term remain exactly the same as we have had for structural isomers. Now, having the generating functions $D_g(t)$ and $S_g(t)$, it is easy to build the polyene isomer structures. For the even-diameter generating function $P_{2g}(t)$ representing polyene isomers with a center site, we have

$$P_{2g}(t) = \{(\text{term-1}) + (\text{term-2}) + (\text{term-3})\} \tag{18}$$

where

$$(\text{term-1}) = t\Big\{D_g(t)S_g(t)S_{<g}(t)\Big\} \tag{19}$$

$$(\text{term-2}) = t(1/2)\Big\{D_g(t)(S_g(t))^2 + D_g^{(\mathrm{s})}(t)S_g(t^2)\Big\} \tag{20}$$

$$(\text{term-3}) = t(1/2)\Big\{D_{<g}(t)(S_g(t))^2 + D_{<g}^{(\mathrm{s})}(t)S_g(t^2)\Big\} \tag{21}$$

Here, (term-1) represents those even-diameter structure where the diameter must go through the double bond attached to the central site and can only go through one of the single bonds attached to this central site; (term-2) represents the circumstance where the three branches from the central site are all of the same length (*g*), so that there are three possible choices for how a diameter passes through the center; (term-3) represents the case that a diameter must pass through the two single bonds at that site. Similarly, for the odd-diameter polyene generating function $P_{2g-1}(t)$, where the center is a bond, we have

$$\begin{aligned} P_{2g-1}(t) = {} & (\text{term-I}) + (\text{term-II}) \\ & + (\text{term-III}) + (\text{term-IV}) \end{aligned} \tag{22}$$

where

$$(\text{term-I}) = Z[D_g^{(\mathrm{s})}; t] \tag{23}$$

$$(\text{term-II}) = (1/2)\ Z[D_g^{(\mathrm{a})}; t] \tag{24}$$

$$(\text{term-III}) = \Big\{(1/2)D_g^{(\mathrm{s})}(t)D_g^{(\mathrm{a})}(t)\Big\} \tag{25}$$

$$(\text{term-IV}) = Z[S_g; t] \tag{26}$$

Above, (term-I) represents the structures that are symmetric about C=C bond (above and below) and the second term is added (followed by multiplication by 1/2) to count terms of the form A/A=A/A and A/A=B/B ("=" is a double bond here) just once. For (term-II), representing the contribution of structures that are asymmetric about "C=C" bond (above and below), the first sub-term counts isomers of the type A/B=C/D as two different structures and those of the type A/B=A/B as only one structure, so that we must add the second sub-term to obtain correct *cis*/*trans* isomer count. Next, (term- III) counts the isomers of the type A/A=B/C only once. Finally, (term-IV) for "C—C" bond centres has the same form as that for the structural isomers.

Next, the enumeration of geometric isomers that represent *cis*/*trans* arrangements about both single (C—C) and double (C=C) bonds is a straightforward extension of the technique just used for enumerating geometric isomers for *cis*/*trans* arrangements about a C=C bond only. Thus, we do not provide the details but just list the final expression. The recursion relation for $S_{g+1}(t)$ term is

$$\begin{aligned} S_{g+1}(t) = {} & (2t)\Big\{S_g(t)D_{<g}(t) + S_{<g}(t)D_g(t) \\ & + S_g(t)D_g(t)\Big\} \end{aligned} \tag{27}$$

where $D_g(t) \equiv \{D_g^{(\mathrm{s})}(t) + D_g^{(\mathrm{a})}(t)\}$ and the recursion relations for that are given by Eqs. (16) and (17). The generation of the geometric isomers in this case is quite straightforward. In particular, for the generating function $P_{2g}(t)$ with a center site we have

$$P_{2g}(t) = \{(\text{term-1}) + (\text{term-2}) + (\text{term-3})\} \tag{28}$$

where

$$(\text{term-1}) = t\Big\{D_g(t)S_g(t)S_{<g}(t)\Big\} \tag{29}$$

$$(\text{term-2}) = t(1/2)\ \Big\{D_g(t)(S_g(t))^2 + D_g^{(s)}(t)S_g(t^2)\Big\} \tag{30}$$

$$(\text{term-3}) = t(1/2)\ \Big\{D_{<g}(t)(S_g(t))^2 + D_{<g}^{(s)}(t)S_g(t^2)\Big\} \tag{31}$$

Similarly, for the generating function $P_{2g-1}(t)$ with a center bond we have

$$\begin{aligned} P_{2g-1}(t) = {} & (\text{term-I}) + (\text{term-II}) \\ & + (\text{term-III}) + (\text{term-IV}) \end{aligned} \tag{32}$$

where

$$(\text{term-I}) = Z[D_g^{(s)}; t] \tag{33}$$

$$(\text{term-II}) = (1/2)\ Z[D_g^{(a)}; t] \tag{34}$$

$$(\text{term-III}) = (1/2)D_g^{(s)}(t)D_g^{(a)}(t) \tag{35}$$

$$(\text{term-IV}) = (1/2)\ Z[S_g; t] \tag{36}$$

Finally, one obtains the geometric isomer count for a given *N* by summing over all diameters (at least up to the diameter after which there is no contribution in the count for the desired *N* in the polynomial series):

$$P(t) \equiv \sum_D P_D(t) \tag{37}$$

The results for the enumeration of two kinds of geometric isomers for polyenes up to $N = 44$ are given in Table 1. Here the geometric isomer counts for *cis*/*trans* arrangements around a C=C bond only are given explicitly, while the counts of *cis*/*trans* arrangements about both single and double bonds are used to compute the mean number of conformations per isomer, $\langle \#_{\mathrm{conf}} \rangle_N$, identified as

$$\langle \#_{\mathrm{conf}} \rangle_N \ = (\#_N^{(\mathrm{geo})})/(\#_N^{(\mathrm{str})}) \tag{38}$$

where $(\#_N^{(\mathrm{geo})})$ is the "isomer" count distinguishing rotation about both C=C and C—C bonds, and $(\#_N^{(\mathrm{str})})$ is the *N*-atom structural isomer count.

3 Radical (and poly-radical) polyenoid enumeration

The work by Cyvin et al. [14, 15] and Yeh [16] provided a nice result for the enumeration of acyclic polyenoid structural isomers, such as including both the non-radical polyenes as well as related radical species without separating them. The natural next questions of chemical interest are: what portions of these counts are due to radicals? Or, more generally, what portions of N-carbon isomer structures are due to the radicals of the n th degree? Or, what is the average degree of radicalicity? Or, what proportions of different radical species have different overall spin multiplicities? We seek answers to such questions in this section.

3.1 *Enumeration of poly-radicals*

The technique of generating functions used in the previous sections provides a nice tool for answering these questions in a relatively straightforward manner, only in this case we deal with the polynomial functions

$$F(t,s) \equiv \sum_{N,n} \#_{N,n} t^N s^n \tag{39}$$

containing two variables, variable t (for carbon atoms) and variable s (for the degree of "radicality"). Here the coefficient $P_{N,n}$ represents the count of polyenoid isomers that have N carbons in the structure (rooted or unrooted tree) and have a degree n of "radicality". Similar notational symbols are used for our generating functions, although they do not have precisely the same meaning as before. Again, we start by specifying the generating functions representing the structures with dangling bonds (rooted trees), for the single bond, $S_g(t,s)$, and for the double bond, $D_g(t,s)$. In building a $(g+1)$-generation structure out of two lower generation structures by connecting them to a single carbon center, the total number of radical sites can remain unchanged or increase depending on the bond character of these two structures. We define generating functions and give the recursion relations as indicated in Fig. 6. For a dangling single-bond structure polynomial $S_{g+1}(t,s)$ we have

$$S_{g+1}(t,s) = (\text{term-1}) + (\text{term-2}) \tag{40}$$

where

$$\begin{aligned}(\text{term-1}) = t\Big\{&S_g(t,s)D_{<g}(t,s) + S_{<g}(t,s)D_g(t,s)\\ &+ S_g(t,s)D_g(t,s)\Big\}\end{aligned} \tag{41}$$

$$\begin{aligned}(\text{term-2}) = (ts)\Big\{&(1/2)[(D_g(t,s))^2 + D_g(t^2,s^2)]\\ &+ D_{<g}(t,s)D_g(t,s)\Big\}\end{aligned} \tag{42}$$

For a double-bond polynomial, the recursion relations are (Fig. 6)

$$\begin{aligned}D_{g+1}(t,s) = t\Big\{&(1/2)[(S_g(t,s))^2 + S_g(t^2,s^2)]\\ &+ S_{<g}(t,s)S_g(t,s)\Big\}\end{aligned} \tag{43}$$

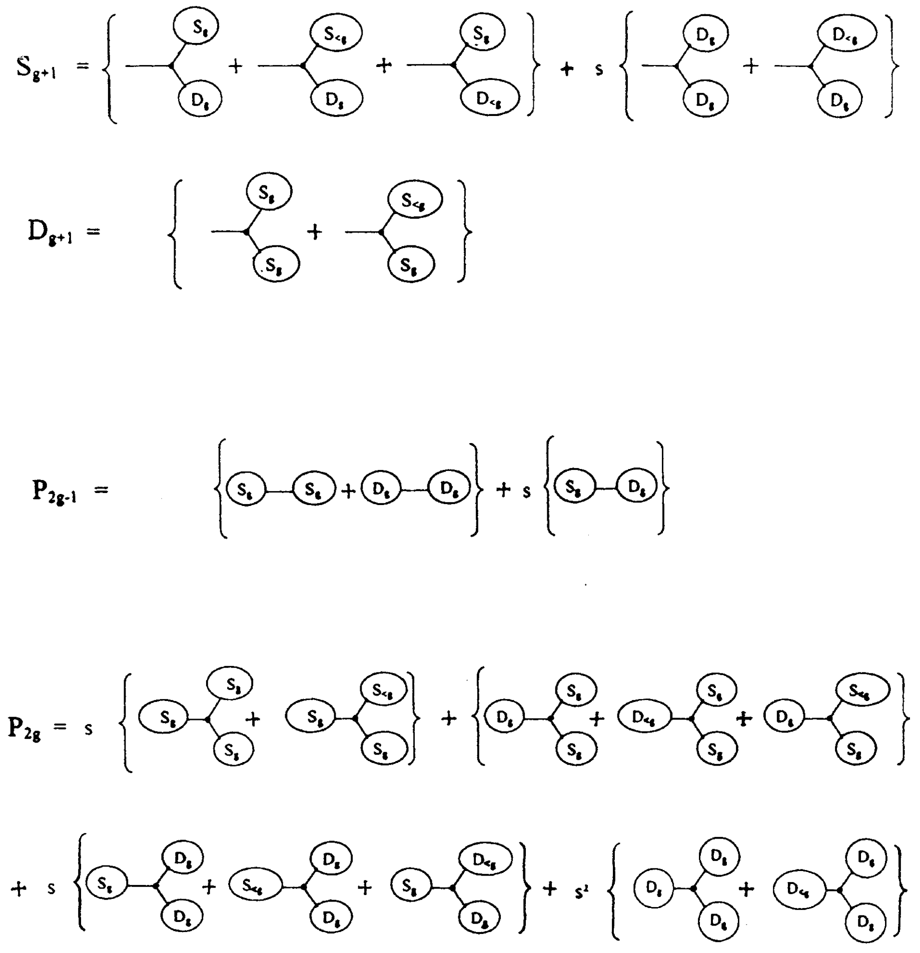

Fig. 6. Pictorial representation of computational schemes for the generating functions $S_{g+1}(t,s)$, $D_{g+1}(t,s)$,$P_{2g-1}(t,s)$, and $P_{2g}(t,s)$ relevant for the enumeration of polyenoids with varying degrees of radicality. The function arguments t and s are suppressed for the sake of brevity

Note that the symbol (S_g or D_g) for the generating functions above is not very important; the real significance lies in the way we build the polyenoids out of them, i.e. in this process we must sure that all possibilities are taken into account and none of the isomer structures are repeated in the enumeration. As in the previous sections, each polyenoid has either a center bond or a center site (see Fig. 6). For the even-diameter generating function involving a central site

$$P_{2g}(t,s) = (\text{term-I}) + (\text{term-II}) + (\text{term-III}) + (\text{term-IV}) \tag{44}$$

where

$$(\text{term-I}) = (ts)\Big\{(1/6)[(S_g(t,s))^3 + 3S_g(t^2,s^2)S_g(t,s) + 2S_g(t^3,s^3)] + S_{<g}(t,s)(1/2)\left[((S_g(t,s))^2 + S_g(t^2,s^2)\right]\Big\} \tag{45}$$

$$(\text{term-II}) = t\Big\{D_g(t,s)S_g(t,s)S_{<g}(t,s) + [D_g(t,s) + D_{<g}(t,s)] \cdot (1/2)\left[(S_g(t,s))^2 + S_g(t^2,s^2)\right]\Big\} \tag{46}$$

$$(\text{term-III}) = (ts)\Big\{S_g(t,s)D_g(t,s)D_{<g}(t,s) + (S_g(t,s) + S_{<g}(t,s))(1/2)[(D_g(t,s))^2 + D_g(t^2,s^2)]\Big\} \tag{47}$$

$$(\text{term-IV}) = (ts^2)\Big\{(1/6)[(D_g(t,s))^3 + 3D_g(t^2,s^2)D_g(t,s) + 2D_g(t^3,s^3)] + D_{<g}(t,s)(1/2)[(D_g(t,s))^2 + D_g(t^2,s^2)]\Big\} \tag{48}$$

Note that in the expressions above we write, for example, (1/2) $[(S_g(t,s))^2 + S_g(t^2,s^2)]$ instead of $(S_g(t,s))^2$ in order to avoid counting structures of the form A-B and B-A as distinct, and so on (e.g. see [23] for details). Similarly, for the odd-diameter generating function involving a central bond

$$P_{2g-1}(t,s) = \Big\{(1/2)[(S_g(t,s))^2 + S_g(t^2,s^2)] + (1/2)[(D_g(t,s))^2 + D_g(t^2,s^2)] + s[D_g(t,s)S_g(t,s)]\Big\} \tag{49}$$

The graphical representation of the terms listed above is given in Fig. 6. Finally, one obtains the structural isomer count for given N and n by summing over all diameters [at least up to the diameter $D_{\min}(N,n)$, after which there is no contribution in the count for these N and n in the polynomial series]:

$$P(t,s) \equiv \sum_D P_D(t,s) \tag{50}$$

Table 2 contains the computational result of these enumerations (omitting the zero th degree polyenoids that constitute the non-radical isomers) up to $N = 30$ and $n = 10$. The summation of all n th order radical counts (from 0 to $n = 10$) for a given N produces the total number of structural isomers reported by Yeh [16]. It is evident that the fraction of non-radical isomers in polyenoids falls quite rapidly (in fact, exponentially in the many-atom limit, as will be shown later on in the asymptotics section) with increasing N. At the end of the next subsection (in Table 3) we report some additional (average) characteristics of these radicaloid polyenoids.

3.2 Spin multiplicity for di-radical isomers

Although di-radical species in general exhibit a higher reactivity compared to non-radical species, di-radicals have received considerable attention in organic chemistry, as evidenced in the book edited by Borden [25]. Now such di-radical species can be of different ground-state spin multiplicity. It appears [17] that if for the di-radical structure the two unpaired electrons are located at carbon sites which are "alike" in that either both are "starred" (**) or both are "unstarred" (00), then the electronic ground state for that structure is triplet, whereas if these unpaired sites can be characterized as unlike "starred-unstarred" (*0), then the ground state is expected to be a singlet. Thus, for a given number N of carbons it is of interest to enumerate di-radical structures that have triplet ground states and, separately, those that have singlet ground states. This is accomplished by enumerating all structures for a given N that are like (** = 00) and those that are unlike (*0). To achieve this count we first obtain the total number of di-radical structures and the difference between the number $\#_N(**)$ of like and the number $\#_N(*0)$ of unlike. The starting point of the analysis is to select a single carbon-center as the reference point for determining the character of the structure (unrooted tree) or substructure (rooted tree). In the generation of the substructures of $(g+1)$-generations with dangling bonds it is convenient to choose the carbon center to which one attaches the substructures of generation g (or $<g$) as the reference point. By convention we identify a sign "+" to a substructure if the reference center and the unpaired electron site are like (**), otherwise [i.e. if we have unlike (*0) sites] the sign "−" is assigned. The addition of all contributions to the generating function [$S_g(t)$ or $D_g(t)$] gives the difference: $\Delta = \#(**) - \#(*0)$. Finally, at the stage the isomer structures are constructed all we need to do is keep track of the relative character of the sites being joined. The situation depends on whether the isomer structure has a center bond or a site.

The starting point is to specify the generating functions and recursion relations for structures with dangling single and double bonds [$S_g(t)$ and $D_g(t)$]. The degree of radicality n, now ranging from 0 to 2, is specified with an appropriate superscript: for example, $S_g^{(0)}(t)$, $S_g^{(1)}(t)$, $S_g^{(2)}$ (t) represent generating functions for structures with a dangling single bond and n = 0, 1, or 2 unpaired electrons [similarly for $D_g(t)$]. The recursion relations for

Table 2. Enumeration of *n*-fold radicals of polyenoids

N/n	1	2	3	4	5	6	7	8	9	10
1	1									
2										
3	1									
4		1								
5	2									
6		2								
7	5		1							
8		7								
9	14		4							
10		24		2						
11	45		21							
12		95		10						
13	159		103		3					
14		385		71						
15	582		524		26					
16		1644		441		6				
17	2238		2627		233					
18		7111		2701		73				
19	8836		13195		1802		13			
20		31383		15905		795				
21	35691		65906		12991		208			
22		139794		91610		7246		31		
23	146638		328276		88118		2702			
24		628385		516077		59993		618		
25	611162		1629366		572419		28612		73	
26		2842003		2860409		459106		9303		
27	2576518		8065525		3590739		267580		1867	
28		12922947		15633343		3318400		111663		194
29	10969176		39825133		21913766		2281608		32067	
30		59011164		84473620		22918778		1163875		5761

these generating functions are indicated by the constructions of Fig. 7, though here we omit the non-radical case. For $S_g(t)$ with $n = 1$ one obtains

$$\begin{aligned} S^{(1)}_{g+1}(t) = \sigma t\Big\{ & [S^{(0)}_g(t)D^{(1)}_{<g}(t) + S^{(0)}_{<g}(t)D^{(1)}_g(t) \\ & + S^{(0)}_g(t)D^{(1)}_g(t)] + [S^{(1)}_g(t)D^{(0)}_{<g}(t) \\ & + S^{(1)}_{<g}(t)D^{(0)}_g(t) + S^{(1)}_g(t)D^{(0)}_g(t)] \\ & + [D^{(0)}_g(t)D^{(0)}_{<g}(t) + Z[D^{(0)}_g; t]\Big\} \end{aligned} \tag{51}$$

For $n = 2$ we have

$$\begin{aligned} S^{(2)}_{g+1}(t) = t\Big\{ & [S^{(0)}_g(t)D^{(2)}_{<g}(t) + S^{(0)}_{<g}(t)D^{(2)}_g(t) \\ & + S^{(0)}_g(t)D^{(2)}_g(t)] + [S^{(2)}_g(t)D^{(0)}_{<g}(t) \\ & + S^{(2)}_{<g}(t)D^{(0)}_g(t) + S^{(2)}_g(t)D^{(0)}_g(t)] \\ & + [S^{(1)}_g(t)D^{(1)}_{<g}(t) + S^{(1)}_{<g}(t)D^{(1)}_g(t) \\ & + S^{(1)}_g(t)D^{(1)}_g(t)] + [D^{(1)}_g(t)D^{(0)}_{<g}(t) \\ & + D^{(1)}_{<g}(t)D^{(0)}_g(t) + D^{(1)}_g(t)D^{(0)}_g(t)]\Big\} \end{aligned} \tag{52}$$

For a dangling double bond we have:

$$\begin{aligned} D^{(1)}_{g+1}(t) = \sigma t\Big\{ & S^{(1)}_g(t)S^{(0)}_{<g}(t) + S^{(1)}_{<g}(t)S^{(0)}_g(t) \\ & + S^{(1)}_g(t)S^{(0)}_g(t)\Big\} \end{aligned} \tag{53}$$

and

$$\begin{aligned} D^{(2)}_{g+1}(t) = t\Big\{ & [S^{(0)}_g(t)S^{(2)}_{<g}(t) + S^{(0)}_{<g}(t)S^{(2)}_g(t) \\ & + S^{(0)}_g(t)S^{(2)}_g(t)] + (S^{(1)}_g(t)S^{(1)}_{<g}(t) + Z[S^{(1)}_g; t])\Big\} \end{aligned} \tag{54}$$

Next, polyenoid isomers for di-radicals can be constructed (see Fig. 7) by obtaining $P^{(2)}_{2g}(t)$ and $P^{(2)}_{2g-1}(t)$ polynomial functions for diameters $D = 2g$ and $D = 2g - 1$, correspondingly

$$\begin{aligned} P^{(2)}_{2g-1}(t) = \Big\{ & (S^{(0)}_g(t)S^{(2)}_g t + \sigma Z[S^{(1)}_g; t]) + (D^{(0)}_g(t)D^{(2)}_g(t) \\ & + \sigma Z[D^{(1)}_g; t]) + \sigma D^{(0)}_g(t)S^{(1)}_g(t) + D^{(1)}_g(t)S^{(0)}_g(t)\Big\} \end{aligned} \tag{55}$$

and

$$\begin{aligned} P^{(2)}_{2g}(t) = \{ & (\text{term-I}) + (\text{term-II}) \\ & + (\text{term-III}) + (\text{term-IV})\} \end{aligned} \tag{56}$$

where

$$\begin{aligned} (\text{term-I}) = \sigma t\Big\{ & (S^{(1)}_{<g}(t) + S^{(1)}_g(t)) \cdot Z[S^{(0)}_g; t] \\ & + (S^{(0)}_{<g}(t)S^{(0)}_g(t)S^{(1)}_g(t))\Big\} \end{aligned} \tag{57}$$

Table 3. Some characteristics of structural isomers of polyenoids

N	# Triplet diradicals	# Singlet diradicals	Non-radical Fraction	$\langle \#_{\mathrm{u}} \rangle_N$
1				1.000
2	0	0	1.000	0.000
3			0	1.000
4	1	0	0.500	1.000
5			0	1.000
6	1	1	0.500	1.000
7			0	1.333
8	5	2	0.364	1.273
9			0	1.444
10	15	9	0.297	1.514
11			0	1.636
12	62	33	0.222	1.704
13			0	1.823
14	238	147	0.174	1.909
15			0	2.018
16	1014	630	0.132	2.111
17			0	2.213
18	4278	2833	0.103	2.311
19			0	2.412
20	18659	12724	0.079	2.511
21			0	2.612
22	81900	57894	0.062	2.712
23			0	2.812
24	364214	264171	0.048	2.912
25			0	3.013
26	1630372	1211631	0.037	3.114
27			0	3.214
28	7350161	5572786	0.029	3.315
29			0	3.416
30	33304028	25707136	0.022	3.517
31			0	3.618
32	151601642	118853791	0.017	3.719
33			0	3.820
34	692702427	550654222	0.013	3.921
35			0	4.022

(term-II)

$$\begin{aligned}
&= t\Big[\Big\{(D^{(2)}_{<g}(t) + D^{(2)}_{g}(t)) \cdot Z[S^{(0)}_{g}; t] \\
&\quad + (D^{(2)}_{g}(t)S^{(0)}_{g}(t)S^{(0)}_{<g}(t))\Big\} \\
&\quad + \Big\{(D^{(0)}_{g}(t)S^{(2)}_{g}(t)S^{(0)}_{g}(t)) + (D^{(0)}_{<g}(t)S^{(2)}_{g}(t)S^{(0)}_{g}(t)) \\
&\quad + (D^{(0)}_{g}(t)S^{(2)}_{<g}(t)S^{(0)}_{g}(t)) + (D^{(0)}_{g}(t)S^{(2)}_{g}(t)S^{(0)}_{<g}(t))\Big\} \\
&\quad + \Big\{(D^{(1)}_{g}(t)S^{(1)}_{g}(t)S^{(0)}_{g}(t)) + (D^{(1)}_{<g}(t)S^{(1)}_{g}(t)S^{(0)}_{g}(t)) \\
&\quad + (D^{(1)}_{g}(t)S^{(1)}_{<g}(t)S^{(0)}_{g}(t)) + (D^{(1)}_{g}(t)S^{(1)}_{g}(t)S^{(0)}_{<g}(t))\Big\} \\
&\quad + \Big\{(D^{(0)}_{<g}(t) + D^{(0)}_{g}(t)) \cdot Z[S^{(1)}_{g}; t] \\
&\quad + (D^{(0)}_{g}(t)S^{(1)}_{g}(t)S^{(1)}_{<g}(t))\Big\}\Big]
\end{aligned} \tag{58}$$

(term-III)

$$\begin{aligned}
&= t\Big[\Big\{(S^{(1)}_{<g}(t) + S^{(1)}_{g}(t)) \cdot Z[D^{(0)}_{g}; t] \\
&\quad + (S^{(1)}_{g}(t)D^{(0)}_{g}(t)D^{(0)}_{<g}(t))\Big\} + \Big\{(S^{(0)}_{g}(t)D^{(1)}_{g}(t)D^{(0)}_{g}(t)) \\
&\quad + (S^{(0)}_{<g}(t)D^{(1)}_{g}(t)D^{(0)}_{g}(t)) + (S^{(0)}_{g}(t)D^{(1)}_{<g}(t)D^{(0)}_{g}(t)) \\
&\quad + (S^{(0)}_{g}(t)D^{(1)}_{g}(t)D^{(0)}_{<g}(t))\Big\}\Big]
\end{aligned} \tag{59}$$

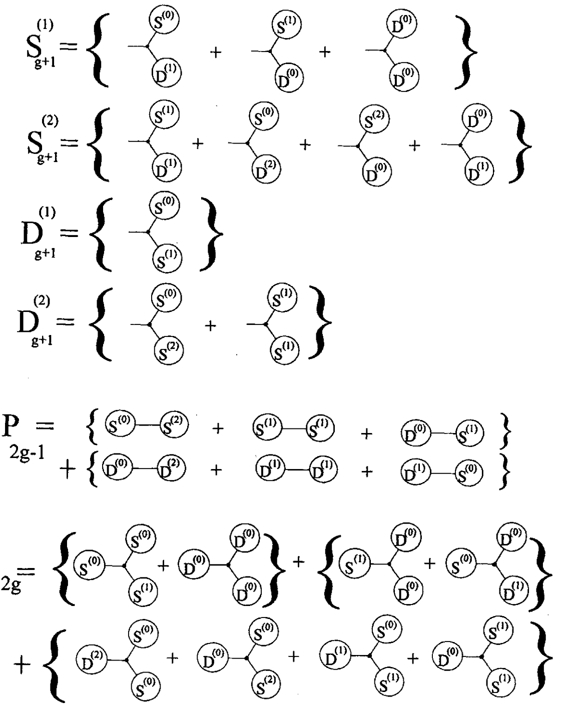

Fig. 7. Pictorial representation of the computational schemes for the six generating functions relevant in the enumeration of different types of di-radical polyenoids

and

(term-IV)

$$\begin{aligned}
&= t\Big[(1/6)\Big\{(D^{(0)}_{g}(t))^3 + 3(D^{(0)}_{g}(t^2)(D^{(0)}_{g}(t)) \\
&\quad + 2(D^{(0)}_{g}(t^3)\Big\} + D^{(0)}_{<g}(t) \cdot Z[D^{(0)}_{g}; t]\Big]
\end{aligned} \tag{60}$$

Above, the symbol σ can assume only two values: "$+1$" and "-1". In particular, the choice of the sign $\sigma = -1$ leads to the "difference" generating functions yielding the counts $\Delta = \{\#(**) - \#(*0)\}$, while the use of $\sigma = +1$ leads to total counts $\#_{\mathrm{di}} = \{\#(**) + \#(*0)\}$ of di-radicals. Also, the symbol $Z[f; t]$ has a slightly different form than that used in the previous sections. Here one has

$$Z[f; x] \equiv (1/2)[(f(x))^2 + |f(x^2)|] \tag{61}$$

where term $|f(x^2)|$ indicates that the polynomial coefficients $\#_{2N}$ for x^{2N} in $f(x^2)$ are equal to the absolute values of the coefficients $\#_N$ for x^N in $f(x)$ function. Equations (51)–(60) thence allow us to obtain the desired results.

Finally, the summation over all diameters yields the desired enumerative generating functions for di-radicals:

$$P(\Delta; t) = P^{(2)}(\Delta; t) = \sum_D P_D(\Delta; t) \tag{62}$$

and

$$P(t) = P^{(2)}(t) = \sum_D P_D(t) \tag{63}$$

The numerical results are listed in Table 3, where also are reported at each N the fraction of the polyenoids which are not radicals and the mean number $\langle \#_{\mathrm{u}} \rangle_N$ of unpaired electrons in each polyenoid. The non-radical fractions at each odd N are of course 0, and are not listed. However, for even N one sees the fraction which are not radicals (i.e., the fraction which are stable species) rapidly decreases. Moreover, the predominantly radical species become on-the-average ever higher-order radicals (i.e., with ever more radicaloid unpaired electrons per polyenoid structure) as N increases. That is, for the most part the polyenoids should be quite highly reactive, and for most of the remaining discussion we focus on the "stable" polyenes.

4 Recursive property computation

Very little seems to have previously been done with average characteristics of isomer classes of molecular structures. Here we first develop some methodology to obtain such averages for several graph invariants, and second we consider the usage of these graph-invariant averages to estimate averages for a few selected molecular properties, restricting ourselves only to structural isomers of conjugated polyenes.

4.1 Averages for graph invariants

First we consider the approach for counting carbon centers of different types: primary, secondary, and tertiary. Now, the generating functions $G_g(t;\alpha,\beta,\gamma)$ representing rooted and unrooted trees include the dependence also on the number of carbon center type. Here variable α represents "$=\mathrm{C}\langle$", β is for "$=\mathrm{C}-$", and γ is for type "$=\mathrm{C}$" centers. Instead of using a standard technique, one can simplify the procedure of enumeration of different-type carbon centers by taking the first derivative of the generating function $G_g(t;\alpha,\beta,\gamma)$ by the variable, say α, and then set all of the variables α, β, and γ to unity, thus obtaining the desired count of α-type centers in $G_g(t)$, i.e. function $G_g^{(\alpha)}(t;\alpha,\beta,\gamma=1) = G_g^{(\alpha)}(t)$ where the superscript (α) marks the first derivative by the α variable.

The recursion relations for generating functions $G_g(t;\alpha,\beta,\gamma)$ representing structures with dangling bonds (rooted trees) are

$$S_{g+1}(t;\alpha,\beta,\gamma) = t\alpha\Big\{S_g(\boldsymbol{t})D_{<g}(\boldsymbol{t}) + S_{<g}(\boldsymbol{t})D_g(\boldsymbol{t}) + S_g(\boldsymbol{t})D_g(\boldsymbol{t})\Big\} + t\beta\Big\{S_{\mathrm{H}}D_g(\boldsymbol{t})\Big\} \quad (64)$$

$$D_{g+1}(t;\alpha,\beta,\gamma) = t\alpha\Big\{S_g(\boldsymbol{t})S_{<g}(\boldsymbol{t}) + Z[S_g;\boldsymbol{t}]\Big\} + t\beta\Big\{S_{\mathrm{H}}S_g(\boldsymbol{t})\Big\} \quad (65)$$

[abbreviating the function arguments $(t;\alpha,\beta,\gamma)$ to just $\boldsymbol{t}$]. The functions $S_{<g+1}(\boldsymbol{t})$ and $D_{<g+1}(\boldsymbol{t})$ are obtained much as in Eq. (9), the symbol $S_{\mathrm{H}} = 1$ represents a dangling single bond to an H atom, and the current initial conditions are

$$S_{<1}(\boldsymbol{t}) = D_{<1}(\boldsymbol{t}) = S_1(\boldsymbol{t}) = 0$$

and

$$D_1(\boldsymbol{t}) = \gamma \quad (66)$$

For the generating functions $P_D(t)$ for polyene isomers we have:

$$P_{2g-1}(\boldsymbol{t}) = Z[S_g;\boldsymbol{t}] + Z[D_g;\boldsymbol{t}] \quad (67)$$

$$P_{2g}(\boldsymbol{t}) = t\Big\{\alpha\{(D_{<g}(\boldsymbol{t}) + D_g(\boldsymbol{t}))\cdot Z[S_g;\boldsymbol{t}] + D_g(\boldsymbol{t})S_g(\boldsymbol{t})S_{<g}(\boldsymbol{t})\} + \beta\{D_g(\boldsymbol{t})S_g(\boldsymbol{t})S_{\mathrm{H}}\}\Big\} \quad (68)$$

for center-bond and center-site structures, respectively. Now, taking the derivatives by the selected variable $\xi(\xi \equiv \alpha$, or β, or $\gamma)$ provides us with the necessary generating functions for enumeration of the carbon centers of the type ξ. This time dealing with the first derivatives $P_D{}^{(\xi)}(t;\alpha,\beta,\gamma=1) \equiv P_D{}^{(\xi)}(t)$ and maintaining only one variable t, one proceeds further in the essentially identical manner as we did before with functions $P_D(t)$. Finally, the summation over all diameters

$$P^{(\xi)}(t;\alpha,\beta,\gamma=1) \equiv P_D^{(\xi)}(t) = \sum_D P_D^{(\xi)}(t;\alpha,\beta,\gamma=1) \quad (69)$$

provides us with the desired count.

On the other hand, the alternative way is to consider the generating functions as depending on two variables t and α (instead of only a single variable t as in the case above) at a time, say $G_g(t;\alpha)$, and setting the remaining variables to unity from the very beginning. Then, the polynomial generating functions are, for rooted trees

$$G_g(t;\alpha) = \sum_g G_g^{(N,n)} t^N \alpha^n \quad (70)$$

and for unrooted trees

$$P_D(t;\alpha) = \sum_D P_D{}^{(N,n)} t^N \alpha^n \quad (71)$$

where the situation becomes mathematically identical to that in Sect. 3.1. Next, taking the first derivative of $G_g(t;\alpha)$ with respect to the variable $\alpha, G_g^{(\alpha)}(t;\alpha)$, and setting $\alpha = 1$, the addition of all terms for each N gives us the count of the carbon centers of type α for generation g. The same applies to unrooted-tree functions $P_D(t;\alpha)$ for the diameter D.

For standard deviation σ values we also need second derivatives of the generating functions $\left[G_g{}^{(\alpha,\alpha)}(t;\alpha)\right.$ or $\left.P_D{}^{(\alpha,\alpha)}(t;\alpha)\right]$, which are obtained in a similar manner, only this type differentiating the functions $\left[G_g(t;\alpha)\right.$ or $\left.P_D(t;\alpha)\right]$ twice with respect to the variable α. The mean counts of ξ-type carbon centers, $\langle \#(\xi) \rangle_N$, are obtained by dividing the total number of ξ-type carbon centers for a given N (summed over all isomers for a particular D, and then over all diameters D) by the total count of structural isomers of polyenes for N, $\#_N$. Also, for the structural isomers we compute the mean diameter for the isomer classes labeled by N as

$$\langle D \rangle_N = \sum_D [D \cdot \#_N(D)] / \sum_D \#_N(D) \quad (72)$$

where the sum is over all diameters that give a non-zero contribution to $\#_N(D)$. Finally, for the standard deviation $\sigma_N(\#(\xi))$ we have:

$$\sigma_N(\#(\xi)) = \left\{ \langle \#(\xi)^2 \rangle_N - (\langle \#(\xi) \rangle_N)^2 \right\}^{1/2} \tag{73}$$

where

$$\langle \#(\xi)^2 \rangle_N = \sum_D \left\{ \left[[P_D{}^{(\xi,\xi)}(N; \#(\xi)) + P_D{}^{(\xi)}(N; \#(\xi))]_{\xi=1} \right] / \#_N \right\} \tag{74}$$

The computed data are listed in Table 4. As expected, the diameter and the atom-type counts all increase with the number N of carbons. The corresponding standard deviations seem to increase more slowly. More quantitative statements of the leading functional dependencies are addressed in Sect. 5.

4.2 Averages for molecular property estimates

Next, the estimates of some mean properties of non-radical polyenes are sought. This is done by computing the mean characteristics of the structural isomers such as the types of carbon centers or types of bonds and utilizing the "group contribution" (or "cluster expansion") scheme as suggested by Cohen and Benson [26] for the heats of formation ΔH_f at $T = 298$ K, by Vogel et al. [27] for the molar refractive indices $Mn_\mathrm{D}^{(20)}$, and by Schmalz et al. [20] for magnetic susceptibilities χ_m. In all these cases for a property X having a value $X(G)$ for a molecular structure graph G we presume an expansion

$$X(G) = \sum_\gamma X^\tau(\gamma)\ \#(\gamma; G) \tag{75}$$

where $\#(\gamma; G)$ is the number of substructures of type γ occurring in G, and $X^\tau(\gamma)$ is a property-dependent expansion parameter. The γ-sum is limited to a subset of substructures, and presumably if extended to sufficiently large substructures would yield accurate results. In the present case, accurate results are evidently attainable with the limitation of the substructures γ to just different "types" of C atoms in the H-deleted structures G. Here these types simply refer to the numbers n of adjacent C atoms, this number being $n = 1$ (=C), $n = 2$ (=C—), or $n = 3$ (=C⟨).

	X^τ	=C	=C—	=C⟨	Units	Ref.
1.	$Mn_\mathrm{D}^{(20)^\tau}$	17.555	20.115	22.675	g/mol	[27]
2.	ΔH_f^τ	6.27	8.55	10.19	kcal/mol	[26]
3.	χ_m^τ	10.265	7.055	4.365	-10^{-13} J/G^2 mol	[20]

Actually the contribution for the molar indices of refraction are not directly of the same form in Vogel et al. [27], where the full graph including H atoms is imagined and the only substructural contributions are for atoms (C and H) and double bonds (C=C). Then evidently for our current polyenes

$$\begin{aligned} \#(\mathrm{C}) &= \#(=\mathrm{C}) + \#(=\mathrm{C}—) + \#(=\mathrm{C}\langle) \\ \#(\mathrm{H}) &= 2\#(=\mathrm{C}) + \#(=\mathrm{C}—) \\ \#(\mathrm{C}=\mathrm{C}) &= \{\#(=\mathrm{C}) + \#(=\mathrm{C}—) + \#(=\mathrm{C}\langle)\}/2 \end{aligned} \tag{76}$$

so that the current cluster-expansion coefficients may be expressed in terms of those of Vogel et al. [27]:

$$\begin{aligned} Mn_\mathrm{D}^{(20)^\tau}(=\mathrm{C}) &= Mn_\mathrm{D}^{(20)^\tau}(\mathrm{C}) + 2Mn_\mathrm{D}^{(20)^\tau}(\mathrm{H}) \\ &\quad + (1/2)Mn_\mathrm{D}^{(20)^\tau}(\mathrm{C}=\mathrm{C}) \\ Mn_\mathrm{D}^{(20)^\tau}(=\mathrm{C}—) &= Mn_\mathrm{D}^{(20)^\tau} + Mn_\mathrm{D}^{(20)^\tau}(\mathrm{H}) \\ &\quad + (1/2)Mn_\mathrm{D}^{(20)^\tau}(\mathrm{C}=\mathrm{C}) \\ Mn_\mathrm{D}^{(20)^\tau}(=\mathrm{C}\langle) &= Mn_\mathrm{D}^{(20)^\tau}(\mathrm{C}) + (1/2)Mn_\mathrm{D}^{(20)^\tau}(\mathrm{C}=\mathrm{C}) \end{aligned} \tag{77}$$

Table 4. Mean characteristics of conjugated polyene isomers[a]

N	$\langle D \rangle_N$	$\langle \#_\mathrm{t} \rangle_N$	$\langle \#_\mathrm{s} \rangle_N$	$\langle \#_\mathrm{p} \rangle_N$
2	1.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	2.00 ± 0.00
4	3.00 ± 0.00	0.00 ± 0.00	2.00 ± 0.00	2.00 ± 0.00
6	4.50 ± 0.50	0.50 ± 0.50	3.00 ± 1.00	2.50 ± 0.50
8	5.75 ± 0.83	1.00 ± 0.71	4.00 ± 1.41	3.00 ± 0.71
10	6.91 ± 1.08	1.55 ± 0.78	4.91 ± 1.56	3.55 ± 0.78
12	8.03 ± 1.17	2.03 ± 0.84	5.93 ± 1.67	4.03 ± 0.84
14	9.07 ± 1.33	2.56 ± 0.90	6.87 ± 1.80	4.56 ± 0.90
16	10.04 ± 1.46	3.08 ± 0.95	7.84 ± 1.90	5.08 ± 0.95
18	10.97 ± 1.61	3.60 ± 1.00	8.79 ± 2.01	5.60 ± 1.00
20	11.85 ± 1.74	4.12 ± 1.05	9.75 ± 2.11	6.12 ± 1.05
22	12.71 ± 1.87	4.65 ± 1.11	10.70 ± 2.21	6.65 ± 1.11
24	13.52 ± 1.99	5.17 ± 1.15	11.66 ± 2.31	7.17 ± 1.15
26	14.31 ± 2.11	5.70 ± 1.20	12.61 ± 2.40	7.70 ± 1.20
28	15.07 ± 2.23	6.22 ± 1.25	13.56 ± 2.50	8.22 ± 1.25
30	15.81 ± 2.34	6.75 ± 1.29	14.51 ± 2.58	8.75 ± 1.29
32	16.53 ± 2.45	7.27 ± 1.33	15.46 ± 2.67	9.27 ± 1.33
34	17.23 ± 2.56	7.80 ± 1.38	16.41 ± 2.75	9.80 ± 1.38
36	17.90 ± 2.67	8.32 ± 1.42	17.36 ± 2.83	10.32 ± 1.42
38	18.57 ± 2.77	8.85 ± 1.46	18.31 ± 2.91	10.85 ± 1.46
40	19.21 ± 2.87	9.37 ± 1.49	19.26 ± 2.99	11.37 ± 1.49
42	19.84 ± 2.97	9.90 ± 1.53	20.21 ± 3.06	11.90 ± 1.53
44	20.46 ± 3.07	10.42 ± 1.57	21.15 ± 3.13	12.42 ± 1.57

[a] Each entry represents the quantity $\langle Y \rangle_N \pm \sigma_N$, where $\sigma_N =$ a standard deviation

To determine the refractive indices $n_D^{(20)}$ one devides $Mn_D^{(20)}$ by the molecular weight of the compound (C_NH_{N+2}).

Next we obtain the mean properties of non-radical polyenes by adding the products of $\langle\#(\xi)\rangle_N$ and $X^\tau(\xi)$ for atom type ξ and obtain isomer-averaged property estimates

$$\langle X\rangle_N = \sum_{\xi}\left\{(\langle\#(\xi)\rangle_N \cdot X^\tau(\xi))\right\} \qquad (78)$$

with X^τ values from the above tabulation.

Finally, we also compute the standard deviation σ for the mean characteristics and properties of non-radical polyenes to get some insight on how the properties of different classes of isomers labeled by N differ from each other. Note that for the average values of $Mn_D^{(20)}$ the standard deviations σ are 0, since in the group function scheme utilized here every isomer within the isomer class labeled by N has the same value of $Mn_D^{(20)}$, and the values $Mn_D^{(20)}$ are different for different isomer classes. This implies that there is no overlap between different isomer classes for $Mn_D^{(20)}$. The computed results for the three considered properties are plotted in Figs. 8–10. There the mean values are connected by a curve. In Figs. 8 and 9 points above and below these mean values are displaced up and down by one standard deviation.

5 Isomer asymptotics

Asymptotic behaviors of isomer counts or isomer properties do not seem to have been previously considered for conjugated polyenes and polyenoids, though asymptotics for alkane isomer counts have (e.g. see paper by Polya [8, 9] and Otter [28]). Though these particular mathematical arguments presumably extend to isomer counts for conjugated polyenes and polyenoids, we here take a slightly different approach which seems to us more readily understandable. We focus on asymptotics of polyenoid structural isomer counts as well as those for structural and geometric isomers of polyenes. Besides the isomer counts for a given N, the asymptotic behavior of certain properties that are averaged over all conformations seem to be of chemical interest as well. Such properties considered here are: the average diameter $\langle D\rangle_N$, the mean number of primary ("=C"), secondary ("=C—"), and tertiary ("=C⟨") carbon centers per (structural) isomer; also, the mean number of conformations per (structural) isomer $\langle\#_{\mathrm{conf}}\rangle_N$ defined as the ratio of geometric isomer count to that of structural isomer; non-radical fraction of polyenoids; and the mean number of radical (unpaired electrons) sites per isomer $\langle\#_{\mathrm{u}}\rangle_N$ as $N \to \infty$.

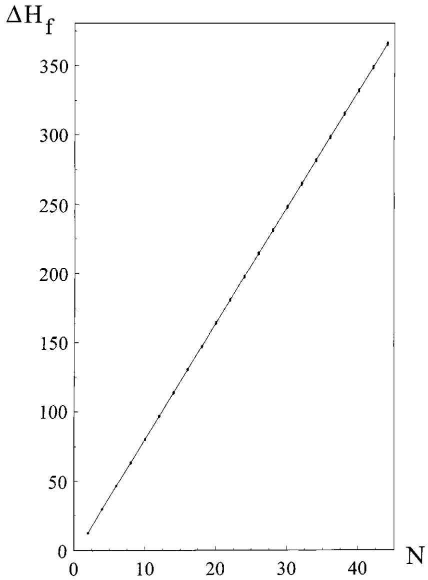

Fig. 8. The graphical representation of $\langle\Delta H_f\rangle$ data

5.1 Asymptotic forms

The method used to deduce the asymptotic forms for isomer counts and isomer properties mentioned above can be understood on the basis of the following line of

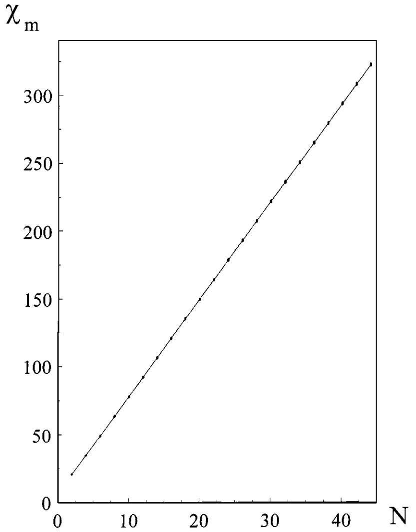

Fig. 9. The graphical representation of $\langle\chi_m\rangle$ data

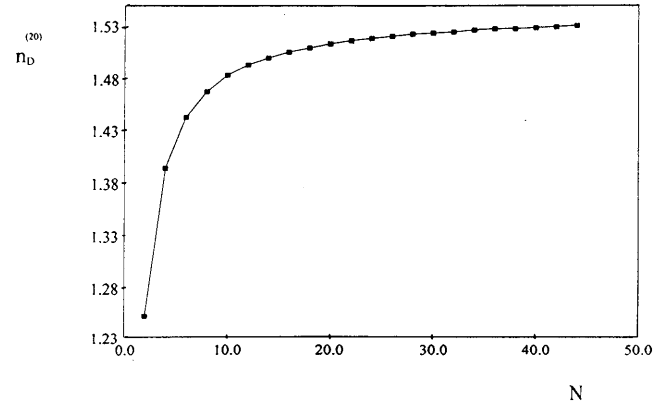

Fig. 10. The graphical representation of $\langle n_D^{(20)}\rangle$ data

thought. We begin with the simpler polyenoid case. For the structural isomers the generating function for rooted polyenoids

$$\phi(t) = \sum_{g \geq 0} \phi_g(t) = \sum_{N \geq 0} \#_N t^N \tag{79}$$

exhibits the recursion:

$$\phi(t) = 1 + (t/2)\{(\phi(t))^2 + \phi(t^2)\} \tag{80}$$

It is evident that the function $\phi(t)$ increases monotonically for $t > 0$. Furthermore, from Eq. (79) it is seen that $\phi(t)$ represents a convergent series in t if the t-variable is sufficiently small and the series diverges for sufficiently large values of t. Thus, there must exist some critical value t_c (*t-critical* in the range $0 < t < 1$) such that for any $t > t_c$ the function $\phi(t)$ diverges, and for any $t < t_c$ the function $\phi(t)$ converges. Now, defining the form

$$F(x) = a + bx^2 \tag{81}$$

one sees that Eq.(80) can be viewed as $\phi(t) = F(\phi(t))$ when Eq. (81) one takes $a = 1 + (t/2)\phi(t^2)$ and $b = t/2$. In Eq. (80) we incorporate the functional dependence of $\phi(t)$ on t-variable near t_c into the putative "constant" a, since for $t < 1$ one has $(t_c)^2 < t_c$ and with t near t_c the function $\phi(t^2)$ is well behaved, in the sense that $\phi(t^2)$ can be expanded in a nice low-order Taylor series expansion as $t \rightarrow t_c$.

Now, for a simultaneous plot of $y = F(x)$ and $y = x$, as in Fig. 11, with the constants a and b indicated above, a solution is obtained for $\phi(t)$ as an intersection of these two curves. Indeed, it is the first point of intersection. Furthermore, from Fig. 11 it is evident that as t-variable increases towards t_c, the curve $y = F(x)$ moves upwards until there is no intersection with $y = x$, whence there is no simultaneous solution for $y = F(x)$ and $y = x$, indicating that t has exceeded t_c. Thus, $t = t_c$ corresponds to the situation where the curves $y = F(x)$ and $y = x$ just touch at a single point, as in Fig. 11, thereby yielding a unique solution $\phi = \phi(t_c)$. Evidently at this critical point

$$dF(x)/dx = 1 \quad \text{and} \quad 1 = 2b_c\phi_c \tag{82}$$

where b_c is the b-constant value at $t = t_c$.

To obtain a quantitative description of how $\phi(t)$ varies with t near t_c we introduce deviations (from critical values): $\delta = t_c - t$ and $\varepsilon = \phi_c - \phi(t)$. Then via Taylor expansion at $t = t_c$, one (restricting to low-order terms) has

$$a = a_c - a'\delta + O(\delta^2) \tag{83}$$

$$b = b_c - b'\delta \tag{84}$$

where the first derivatives are $a' = (1/2)\{\phi(t_c^2) + 2(t_c^2)\,\phi'(t_c^2)\}$ and $b' = 1/2$. For ϕ one has (omitting higher-order terms)

$$\phi(t) \equiv \phi_c - \varepsilon \approx (a_c - a'\delta) + (b_c - b'\delta)(\phi_c - \varepsilon)^2 \tag{85}$$

After straightforward mathematical manipulation, noting that $\phi_c = a_c + b_c\phi_c^2$ and keeping in mind Eq. (82), while leaving out the higher terms, one obtains

$$\varepsilon^2 \approx \{(a' - b'\phi_c^2)/b_c\}\delta \tag{86}$$

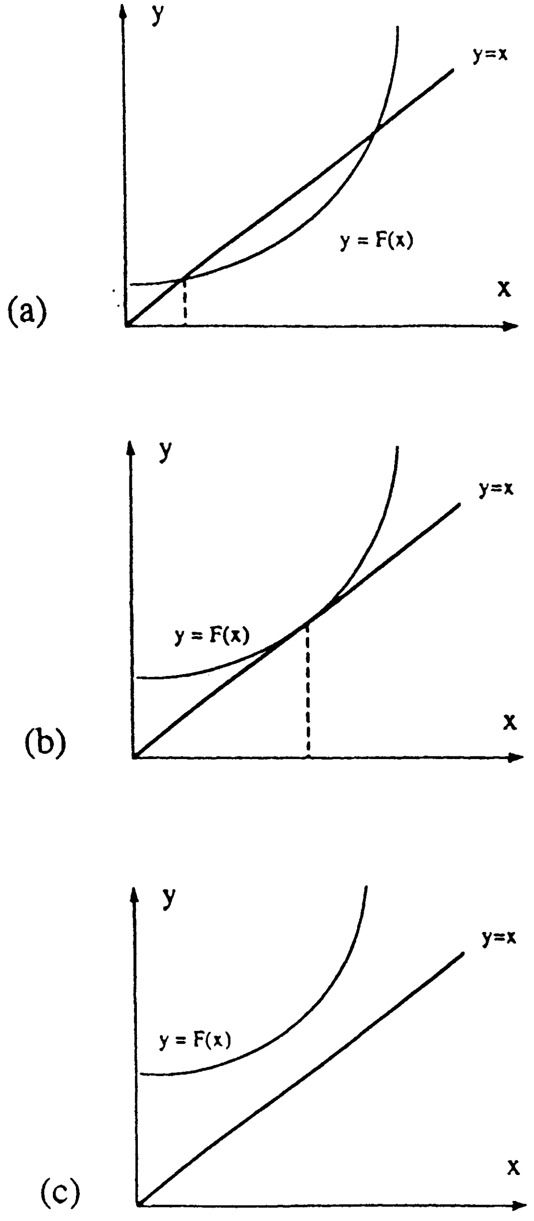

Fig. 11 a–c. Three possible types of result obtainable in analyzing for the critical behavior of $\phi(t)$. In **a** $t < t_c$, in **b** $t = t_c$, and in **c** $t > t_c$

which indicates that

$$\varepsilon \approx C(\delta)^{1/2} \tag{87}$$

with of course $C \equiv \{(a' - b'\phi_c^2)/b_c\}^{1/2}$. Now, keeping in mind Eq. (79), it is evident that the behavior of $\phi(t)$ near t_c leads to asymptotic behavior for coefficients $\#_N$ (counts of rooted trees). In particular, if we assume that the asymptotic behavior of $\#_N$ is described by the form

$$\#_N = N^{-\alpha}\kappa^N\left\{A + BN^{-1} + O(N^{-2})\right\} \tag{88}$$

then with restriction to the first two terms, one obtains

$$\begin{aligned}\phi(t) = 1 &+ \sum_{N \geq 1}\{\#_N - (A + BN^{-1})\}N^{-\alpha}\kappa^N t^N \\ &+ A\sum_{N \geq 1} N^{-\alpha}\kappa^N t^N + B\sum_{N \geq 1} N^{-1-\alpha}\kappa^N t^N\end{aligned} \tag{89}$$

From this it is evident that the convergence of the series $\phi(t)$ is equivalent to the requirement that $t \leq (1/\kappa)$, implying that $t_c = 1/\kappa$. Furthermore, the first summation terms gives a finite value (given $\alpha > 0$), and the remaining summations can be estimated using the Euler-McLaurin Formula, replacing these sums by the integrals over N. These integrals are of the general form [keeping in mind that $t = t_c - \delta = t_c(1 - \kappa\delta)$]:

$$\begin{aligned} I &= \int_0^\infty N^\beta (1-\gamma)^N \, dN \\ &= (\gamma)^{-\beta-1} \int_0^\infty x^\beta e^{-x} dx \\ &= (\beta!)\gamma^{-\beta-1} \end{aligned} \tag{90}$$

where $\gamma = \kappa\delta$ and $x = \kappa\delta N$, whence one obtains

$$I = (\beta!) \ \kappa^{-\beta-1} \ \delta^{-\beta-1} \tag{91}$$

Thus, as $t \to t_c$ (approaching from below) we have

$$\begin{aligned} \phi(t) \approx \text{constant} &+ A(-\alpha!)\kappa^{-\alpha-1} \ \delta^{-\alpha-1} \\ &+ \ B(-1-\alpha)! \, \kappa^{-\beta-1} \ \delta^{-\beta-1} \end{aligned} \tag{92}$$

Since $\phi(t) \equiv \phi_c - \varepsilon$, one can simply identify the constant as ϕ_c. Recalling that $\varepsilon = (\delta)^{1/2}$, from the second term in Eq. (92) it is evident that $1/2 = \alpha - 1$, so that $\alpha = 3/2$. That is, the asymptotic form of Eq. (88) is consistent with behavior of $\phi(t)$ near t_c. In fact there is a one-to-one correspondence between the asymptotics of $\#_N$ as expressed by Eq. (88) and the behavior of $\phi(t)$ near $t = t_c$, as in Eq. (92). This correspondence can be understood on the basis of the Cauchy relation:

$$\#_N = (N!/2\pi i) \oint \phi^{(N)}(t_c)(z - t_c)^{-N} dz \tag{93}$$

where $\phi^{(N)}(t_c)$ indicates the Nth derivatives of $\phi(t)$ with respect to t, as evaluated at $t = t_c$, and the contour of the integral is a cycle around t_c in the complex plane.

Once the asymptotic behavior for rooted tree counts is known, the asymptotic behavior of unrooted tree (polynoid isomer) counts can be deduced. A power series

$$\Phi(t) = \sum_{N \geq 0} \#_N^* t^N \tag{94}$$

for N-atom polyenoid isomer counts $\#_N{}^*$ can be defined, and with the use of the ideas about constructing unrooted trees from the rooted ones as has been discussed earlier, one can determine the relationship between $\Phi(t)$ and $\phi(t)$ in the many-atom limit. The result

$$\#_N^* = N^{-1-\alpha} \kappa^N \left\{ A + BN^{-1} + O(N^{-2}) \right\} \tag{95}$$

where α and κ are the same as in Eqs. (88) and (92), can be derived in a rigorous manner (e.g. see Harary et al. [29]), though it can be understood from rather general considerations without going through the formal derivation. Indeed, an N-atom polyenoid has $N + 2$ hydrogens and after removal of any of these hydrogens there results a rooted (tree) structure, though sometimes the removal of different H-atoms may yield the same rooted structure. Thus, in general, there can be no more than N possibilities to construct a rooted (tree) structure from it, and likewise there can be no fewer than N/s where s is a (maximum possible) symmetry number, which for typical structures should not be too large. On average, then, one expect that $\#_N \sim N\#_N^*$, which implies Eq. (95). Although, in this section, we restricted the analysis of the asymptotic forms to polyenoid structural isomer counts, the resulting asymptotic forms remain the same for polyene isomers as well.

Besides the asymptotic behavior of isomer counts, it is possible to make some comments regarding the asymptotic forms for average properties of isomer classes as well. For instance, the mean numbers of atom types ($\xi \equiv$ primary, secondary, or tertiary) per isomer at a given N are expected to be non-zero fractions of the total number of carbons

$$\langle \#_\xi \rangle_N \approx A_\xi \ N + B_\xi \tag{96}$$

where A_ξ is the (asymptotic) mean fraction of such sites, and B_ξ is a higher-order correction. Also, a similar expression is expected to hold for the mean numbers of radical sites per isomer $\langle \#_u \rangle_N$ asymptotic behavior.

The asymptotic form for the mean diameter $\langle D \rangle_N$ (through-bond) is somewhat different. Earlier polymer statistical results [30] indicate that the diameter averaged over all conformations is $\sim N^{1/2}$, so that by analogy for the current isomer averages we might expect that

$$\langle D \rangle_N \ \approx \ A_D(N)^{1/2} + B_D \tag{97}$$

where A_D and B_D are the certain constants. Now, we proceed with the numerics.

5.2 Asymptotic numerics

The asymptotic forms deduced in the preceding section can be used to fit the numerical data as listed in Tables 1–4. The first step in asymptotic numerics of isomer counts is the determination of the growth factor κ, which can be found with a rather high accuracy. We seek to determine the growth factor κ for three different counts: for structural isomers of polyenoids, for structural isomers of polyenes, and for geometric isomers (*cis/trans* about both C—C and C=C bonds) of polyenes. The result for geometric isomers of polyenes can be easily obtained in an analytic way, while the first two isomer types require a more numerical (but related) approach for the deduction of their κ (or t_c).

We begin with the (analytic) determination of t_c for geometric isomers of polyenes. It is evident from Eqs. (16), (17) and (27) that the generating functions of interest have the following forms

$$\sigma(t) = 1 + 2t \ \sigma(t) \ \delta(t) \tag{98}$$

$$\delta(t) = t \ (\sigma(t))^2 \tag{99}$$

for single and double dangling bonds, respectively. The substitution of Eq. (99) into Eq. (98) leads to the relation

$$\sigma(t) = 1 + 2t^2 \sigma(t)^3 \tag{100}$$

which is a cubic polynomial in $\sigma(t)$. This could be solved analytically and analyzed to yield the critical behavior. Following the arguments near Eq. (81) we define $F(x) = a + bx^3$, so that the solution to Eq. (100) is equivalent to the solution of $x = F(x)$ where $x = \sigma(t)$, $a = 1$, and $b = 2t^2$. Further, at $t = t_c$, $dF(x)/dx = 1$, whence it follows that $(\sigma(t_c))^2 = 1/6t_c{}^2$. Then after substitution into Eq. (100) one is lead to

$$\sigma(t_c) = 3/2 \quad \text{and} \quad t_c = (2/27)^{1/2} \tag{101}$$

which are quite neatly explicit.

The determination of t_c for structural isomers of polyenes and polyenoids, however does not seem to be quite so analytically soluble. The polyenoid case is simpler, and involves an overall generating function for rooted polyenoids, as already noted in Eq. (80):

$$\phi(t) = 1 + (t/2)\ \{(\phi(t))^2 + \phi(t^2)\} \tag{102}$$

Owing to the presence of the term $\phi(t^2)$, one cannot so straightforwardly use this equation to solve for t_c as we just did for the case of geometric isomers of polyenes. However, one can start from high power $z > 2^M$ of t where $t^z \approx 0$ and $\phi(t^z) \approx \phi(0) = 1$, and then recur downward, obtaining at the kth step $\phi(t^{z(k)})$, where $z(k) \equiv z_k = 2^{(M-k)}$, until at the Mth step we reach $\phi(t^1) = \phi(t)$. The choice of powers z for $t(0 < t < 1)$ is made with reference to a suitable small tolerance ε such that $t^z \ll \varepsilon$, so that $\phi(t^z) = 1 + O(\varepsilon)$ [while $\phi(t) = 1 + O(t)$].

The recursion at each step involves the solution of a polynomial (which here is a quadratic) equation for $\phi(t^{z(k)})$ in terms of t and higher-order $\phi(t^{z(k-1)})$ (which has already been obtained) where $z(k) = 2^{M-k}$ and $z(k-1) = 2^{(M-k+1)}$. Furthermore, if our guessed value for t was $t < t_c$, then the recursion procedure leads to a real polynomial root at the last step (where one has a situation as in Fig. 11a), otherwise if $t > t_c$ it does not (where one has a situation as in Fig. 11c). Thus within a chosen tolerance ε one can rather easily decide whether a given t is $> t_c$ or $< t_c$. Therefore, one can use the following procedures for deducing t_c:

1. Choose bounds $0 < t < 1$.
2. Guess value $t = 0.1$ and (a) if the resulting root is *real*, then increase t value by the step-size $\Delta t = 0.1$ and repeat this every time before reinitializing the recursion procedure until the root at some step (say, mth step) becomes imaginary, indicating that $t_{m-1} < t_c < t_m$; (b) on the other hand, if the root is *imaginary*, go to the step (with $t_{m-1} = 0$).
3. Now, start with $t = t_{m-1} + 0.01$ (one order smaller step-size), repeating essentially the same steps as in 2 but using this new step-size.

Following this procedure, after (at the most) 10 × 10 steps one arrives at a t_c estimate within our chosen tolerance of $\varepsilon = 10^{-10}$. The obtained t critical value for polyenoid structural isomer counts is $t_c \cong 0.4026975036$, which surpasses Otter's [28] value of seven significant digits.

The procedure for obtaining t_c in the case of polyene structural isomers proceeds in essentially the same way, though the generating function involved is different. For rooted trees of structural isomers of polyenes we have [with $\sigma(t)$ and $\delta(t)$ representing dangling single and double bonds, respectively]:

$$\sigma(t) = 1 + t\sigma(t)\delta(t) \tag{103}$$

$$\delta(t) = (t/2)\{(\sigma(t))^2 + \sigma(t^2)\} \tag{104}$$

After the substitution of Eq. (104) into Eq. (103) one obtains

$$\sigma(t) = 1 + (t^2/2)\sigma(t^2)\sigma(t) + (t^2/2)(\sigma(t))^3 \tag{105}$$

Following the same steps as already outlined, one arrives at the recursion procedure (moving downwards from some high t powers). This procedure involves at each step the solution of a polynomial (which this time is cubic). Using this procedure with a tolerance of $\varepsilon = 10^{-10}$ the consequent estimate for t-critical is $t_c \cong 0.4573321739$.

Granted the growth factor $\kappa = 1/t_c$ for isomer classes and sub-classes mentioned above, the next step is the determination of the (A and B proportionality constants and exponents in the asymptotic forms for different quantities. These proportionality constants and exponents can be deduced from the examination of the numerical data listed in Tables 1–5. In particular, for a quantity Ξ with an asymptotic leading term ($\approx AN^\beta$) one can analyze for the exponent β. For instance, in the case $\langle D\rangle_N = \Xi_N$ the argument of the proceeding section indicates that $\beta = 1/2$, so that a plot of $\langle D\rangle_N/\sqrt{N}$ versus $1/\sqrt{N}$ should asymptotically yield a straight line with intercept A and slope B:

$$\langle D\rangle_N/(N)^{1/2} = A + B/N^{1/2} + C/N \tag{106}$$

Thence using our data for $\langle D\rangle_N$, a fit to this functional form yields values for A, B, and C. In the same way we

Table 5. Polyene and polyenoid asymptotics

Asymptotic form: $\Xi = N^\alpha\ (A + BN^{-\beta} + CN^{-2\beta})$

	Ξ	α	β	A	B	C
Conjugated polyene structural isomers						
1.	$\#^s_N/\kappa^N$	−5/2	1	1.2973	−3.22	20.7
2.	$\langle D\rangle_N$	1/2	1/2	4.233	−8.77	7.6
3.	$\langle\#_p\rangle_N$	1	1	0.26316	0.829	0.67
4.	$\langle\#_s\rangle_N$	1	1	0.4737	0.343	−1.33
5.	$\langle\#_t\rangle_N$	1	1	0.26316	−1.171	0.67
Conjugated polyene geometric isomers						
6.	$\#^g_N/\kappa^N$	−5/2	1	0.3456	−1.11	2.7
Polyenoid structural isomers						
7.	$\#^{s,p}_N/\kappa^N$	−5/2	1	1.266	−3.12	26.3
8.	$\langle\#_u\rangle_N$	1	1	0.10139	0.459	0.48

Asymptotic form: $\Xi = A\kappa^N$

	Ξ	A	κ
9.	$\langle\#_{conf}\rangle_N$	0.26639	1.68034
10.	$\langle Y^{nr}\rangle_N$	1.0247	0.880536

can deal with the other quantities of interest (isomer counts or properties). The numerical data we used includes isomer counts up to $N = 98$ carbon atoms (for structural isomers), up to $N = 66$ (for geometric isomers) of polyenes, and up to $N = 45$ for structural isomers of polyenoids. The data analysis of atom types (in polyene structural isomers) includes results up to just $N = 70$ carbon atoms, and for the mean number of radical sites per isomer up to $N = 45$ (in structural isomers of polyenoids); for $\langle D \rangle_N$ we include data up to $N = 110$. All the quantities Ξ mentioned here were found to have the following general form for the asymptotic behavior:

$$\langle \Xi \rangle_N / (N)^{\alpha} = A + B/N^{\beta} + C/(N)^{2\beta} \tag{107}$$

where A, B, and C are fitting constants, and α and β are exponents.

The other asymptotic form that is suitable for the quantities such as the non-radical fraction of polyenoids $(Y^{\mathrm{nr}})_N$ or the mean number of conformations $\langle \#_{\mathrm{conf}} \rangle_N$ easily follows from the behavior of the asymptotic forms for the components which we have already obtained. In particular, for $(Y^{\mathrm{nr}})_N$ one has (restricting only to the leading term):

$$\begin{aligned}(Y^{\mathrm{nr}})_N &= (\#^{\mathrm{nr}})_N / (\#^{\mathrm{all}})_N \\ &= (A_1 N^{-5/2} \kappa_1^N)/(A_2 N^{-5/2} \kappa_2^N)\end{aligned} \tag{108}$$

which leads to

$$(Y^{\mathrm{nr}})_N = (A_1/A_2) \cdot (\kappa_1/\kappa_2)^N \tag{109}$$

where $(\#^{\mathrm{nr}})_N$ is the non-radical (polyene) count, $(\#^{\mathrm{all}})_N$ is the total count of polyenoid isomers for a given N, and subscript "1" marks the constants for polyenes, "2" for polyenoids. Here we restrict ourselves to structural isomers only. On the basis of Eq. (109) one is easily led to the asymptotic form for $(Y^{\mathrm{nr}})_N$:

$$\ln(Y^{\mathrm{nr}})_N = a + bN \tag{110}$$

where $a = \ln(A_1/A_2)$ and $b = \ln(\kappa_1/\kappa_2)$. The same argument applies to the mean number of conformations $\langle \#_{\mathrm{conf}} \rangle_N$.

The procedure of fitting is based on the weighted least-squares technique where the weights are determined by the presumed next leading term in the power series expansion. In fitting a quantity Z_N to a functional form $f(N)$, one minimizes a least-squares error

$$\Omega \equiv \sum_N \{Z_N - f(N)\}^2 w_N \tag{111}$$

Here

$$f(N) = \sum_i a_i f_i(N) \tag{112}$$

where $f_i(N)$ are basis functions, the a_i are parameters, and the w_N are weights. Then taking derivatives with respect to each a_j and setting them to 0, one obtains

$$\sum_N \left\{ Z_N - \left[\sum_i a_i f_i(N) \right] \right\}^2 f_j(N) w_N = 0 \tag{113}$$

This procedure allows one to obtain fairly accurate asymptotic values of the constants A, B, and C, as are listed in Table 5.

6 Conclusions

The present work on isomer combinatorics of fully conjugated acyclic polyenes, and to some extent of polyenoids, yields results on a wide variety of quantities that are of interest for chemistry. A variety of numerical results for individual numbers N of carbons are found in Tables 1–4. Special attention has been paid to the separation of the polyenoid counts (already reported by Cyvin et al. [14, 15] and Yeh [16]) into subsets labeled by the different degrees of radicality, and for the di-radical case a further subdivision into spin-singlet and spin-triplet di-radicals has been made. The fraction of polyenoids which are non-radical diminishes exponentially fast as the carbon number N increases. On the other hand, it was exhibited how the average number of conformations per structural isomer (defined as the ratio of the geometric isomer counts to that of structural isomers) in polyenes increases exponentially with N (as N approaches ∞). The average degree of radicality of the polyenoids appears to increase in proportion to N. A variety of quantitative asymptotic behaviors are summarized in Table 5.

Another novel development here is the tabulated average conjugated- polyene properties, including: heats of formation, indices of refraction, and magnetic susceptibilities as functions of the carbon atom number N. In addition, the property Figs. 8 and 9 indicate standard deviations, all utilizing the "group contribution" scheme to estimate properties. The comparison of the standard deviations to differences of averages for neighboring isomer classes provides a measure of how the isomer properties overlap between different isomer classes. In particular, from the Figs. 8 and 9 representing data for ΔH_f and χ_m one observes no overlap with the averages of the nearest neighbor classes. But this overlap slowly increases with increasing N, though even at $N = 70$ there is no overlap with the averages of nearest neighbors. The data for the standard deviations is consistent with these deviations scaling $\sim N^{1/2}$, and one might surmise that a normal distribution for the considered properties is approached for large-N isomer classes (much as the distribution of net displacements for a forward-biased random walk).

An interesting and hopefully useful formal combinatoric chemistry beyond the classical enumerations seems possible.

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