

A mathematical problem in isomerism and radicality of acyclic conjugated polyenes

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The interplay of radicality and resonance structures in conjugated π bonds is explored by graph theory. Radicality dominates substitution effect in polyenes. As a first step, non-radical and radical acyclic polyenes are sorted and enumerated through generating monosubstituted derivatives. The generating function is determined by the growth pattern of trees embedded in hexagonal lattice. Each substitution site of a polyene is characterized as either singly or doubly bonded. Doubly bonded sites are favored energetically. Growth pattern leads to the derivation of recurrence relations. The generating function consists of two parts intertwined, resulting in two coupled equations. Geometric and constitutional isomerisms of polyenes are treated. For the former, equations are solved either analytically or by iteration. For the latter, only numerical solution is obtained.

KEY WORDS: acyclic polyenes, substitution reaction, isomer enumeration, radicality

AMS subject classification: 05A15, 05C05

1. Introduction

Free radicals are reactive molecules. Resonance is often alluded as a mechanism for a molecule to achieve stability. These two seemingly opposite properties appear simultaneously in polyenes. In this article, graph theory shows a natural connection between radicality and resonance, both leading to the generation and sorting of polyene structures.

In 1857, Cayley [1] pioneered the study of tree structure as a new analytical form. In 1874, he treated acyclic chemical structures [2] as a subset of trees and started a new interdisciplinary subject between mathematics and chemistry: chemical graph theory. Ever since then, it has left us pondering how far this merging would push. Counter to the assertions of the local nature of any physical subject, quantum mechanics has discredited many hypotheses and theories that are based on locality. However, chemical graph theory [3,4] survives and thrives in the quantum era. Graph theory and chemistry prove to be mutually beneficial. Chemistry generates new mathematical problems in graph theory. Meanwhile, graph theory is handy for enumerating, classifying, en-

visioning chemical structures and storing chemical information, despite that chemical structures do not meet strict definition of mathematical graphs [5]. The following is an illustration of these two aspects using polyenes as an example.

2. Acyclic polyenes

Acyclic polyenes of the formula C_nH_{n+2} are tree-shaped chemical structures with three links or less evenly spaced at triangular corners of each node. Nodes short of three links are padded with hydrogens. All nodes are equivalent. Quantum mechanically (in Hückel sense) all links are equivalent but classically they are differentiated into single and double bonds. This model accounts for isomerism of polyenes but fails to differentiate isomers by radicality. To remedy, we shall revert to classical picture of chemical bonds. With the condition that double bonds are conjugated, a polyene strives for stability by acquiring a maximal number of double bonds. If double bonds are less than half the number of carbons, the structure is radical and often called polyenoid. Multiple configurations with the same number of conjugated double bonds corresponding to one polyenoid species are possible; they are resonant structures. An example is the three structures of trimethylenemethane diradical, C_4H_6 . We follow quantum-theoretical sense not to differentiate these configurations but adopt classical notation to sort isomers by radicality.

Acyclic polyenes without being sorted by radicality are treated in Cyvin et al. [6], where complete mathematical expression of generating function is given. Yeh [7] rationalizes this result by using Polya's scheme, namely, by building the cycle index with the symmetry of trees embedded in 2-D hexagonal lattice. Bytautas and Klein [8] further treat radicality as a parameter and have obtained an algorithm for isomer enumeration.

Radicality reflects chemical reactivity. Precisely, radicality is the number of nodes not linked to a double bond. These nodes are can always be set at tips of a tree structure. Discrepancy between the maximum possible and the actual number of double bonds amounts to radicality. Suppose that d is the number of double bonds and n is total number of carbon atoms in polyene, then radicality is $r = n - 2d$. Here are two interesting points about the radicality of acyclic polyenes. First, radicality concurs with the resonance of structures; even though they oppose each other in affecting energy. For example, the diradical trimethylenemethane has three resonant structures. That resonance comes along with radicality in acyclic polyenes does not imply a logical induction between the two concepts, but both result from the conjugation of double bonds. The energy raised by radicality by far exceeds the energy lowered by resonance, hence net energy is raised. Second, radicality is upper bounded by the number of branching in a polyene. Linear polyenes [9] can have at most a radicality of one: $r = 0$ for even n and 1 for odd n . Higher radicality exists only in branched structures. Three types of structural units are associated with radicality, all of which contain tip(s) not linked to a double bond, are shown in figure 1. One is the allyl fragment $CH_2-CH=CH-$; the other two are fragments of Y-shaped trimethylenemethanyl radical C_4H_5- . Molecular properties

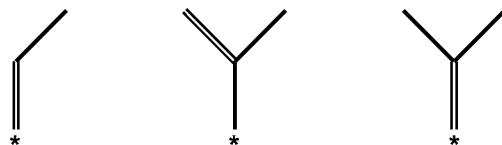


Figure 1. Three basic units associated with radicality. Star designates the root.

of polyenes [10–12] and their derivatives [13,14] have been subject to computations and experiments because many chemical reactions involve free radicals.

The same principle should apply in sorting and enumerating polyenes whether radicality is included as a factor or not. Non-radical and radical acyclic polyenes of all categories are constructed through the generating function of monosubstituted derivatives. The term ‘monosubstituted derivative’ is generic and includes free radicals formed with a hydrogen stripped off (not to be confused with radical parent species). For geometric isomers of polyenes indistinctly of their radicality, the generating function obeys

$$A(x) = 1 + x[A(x)]^2.$$

In this paper, we modify the above equation to accommodate radicality. Through the use of dummy variables x and y , monosubstituted polyenes of size n and radicality r are grouped together, by form of $x^n y^r$ in the generating function $A(x, y)$. Expansion coefficient of $A(x, y)$ in the term $x^n y^r$ is the isomer count of polyenes. Specifically, at $y = 0$, $A(x, y)$ is a set of terms representing polyenes of zero radicality; at $y = 1$, those of all radicalities. Through formulating recurrence relations, we shall construct polyenoid structures with distinct radicalities while disregarding difference between resonant structures.

We sort acyclic polyenes through graph-theoretical techniques and hope to see some trends of these species. In section 3, how to generate geometric isomers of monosubstituted polyenes is presented as a mathematical problem. In sections 4 and 5, we seek solution in parallel with the scheme outlined in [7] as follows.

1. Sort monosubstituted polyenes into singly and doubly bonded ones.
2. Build monosubstituted polyenes through recurrence relations.
3. Build single-node labeled polyenes, single-link labeled polyenes and polyenes with centered link.
4. Based on the dissimilarity characteristic theorem, build and enumerate parent species.

In section 6, constitutional isomers are treated similarly.

3. Nature of problem: generating function

Our theme topic is a mathematical problem per se. Assume that a function $A(x, y) = \sum b_{nr} x^n y^r$ with positive integer expansion coefficients b_{nr} is met with two

conditions. On the one hand when $y = 0$, $A(x, y)$ generates all non-radical polyenes. Each double bond is a building block on which three distinct links may grow from a root: geminal, *cis* and *trans*. In the Polya formulation [5], the function generates itself through the cycle index as

$$A(x, 0) = 1 + 2x^2[A(x, 0)]^3,$$

where the exponent 3 represents the three distinct links of each building block and the multiplication factor 2 depicts the two geometric isomers that may grow from each link. On the other hand with all radicalities ($y = 1$), there is no distinction between single and double bonds. The function becomes

$$A(x, 1) = 1 + x[A(x, 1)]^2.$$

Our problem is to find $A(x, y)$. Some remarks about the generating function $A(x, y)$ are worth mentioning before pursuing solution.

First, this generating function is determined by the growth pattern of trees embedded in hexagonal lattice. Recurrence relations of this function are derived in compliance with the symmetry in 2-D space. Monosubstituted polyenes are generated while embedded in 2-D space. Analogous to those in 3-D space, chiral structures in 2-D space (not superimposable with the image in 1-D mirror) form enantiomeric pairs. These chiral pairs become indistinguishable in 3-D space and hence are overly counted. Redundant counts of both monosubstituted and parent polyenes caused by the expansion of space dimension need to be corrected.

Second, the two conditions posted for $A(x, y)$ are themselves recurrence relations, which by default are solvable by successive approximation. Starting from $A(x, 0) = 1$, iteration gives $A(x, 0) = 1 + 2x^2 + 12x^4 + 96x^6 + 880x^8 + 8736x^{10} + \dots$. Similarly, $A(x, 1) = 1 + x + 2x^2 + 5x^3 + 14x^4 + 42x^5 + 132x^6 + 429x^7 + 1430x^8 + \dots$. Not only coefficients of $A(x, 0)$ or $A(x, 1)$ are counts of monosubstituted polyenes sorted by size but each term symbolically represents a chemical structure. In other words, the iteration is a growth process for tree-shaped chemical structures. Generating function could generate distinct symbols to identify each chemical structure, a subject we shall not elaborate here. Note that $A(x, y)$ has the same number of terms as $A(x, 1)$ and splits acyclic polyenes further through radicality.

Third, passage from $A(x, 0)$ to $A(x, 1)$ represents the solution $A(x, y)$. Although $A(x, 1)$ is a bigger set (has more terms) than $A(x, 0)$, simply by adding extra term involving y at right-hand side of the recurrence relation of $A(x, 0)$, $A = 1 + 2x^2A^3$, does not give $A(x, y)$ but invariably yields something bigger. How a cubic equation of $A(x, 0)$ turns into quadratic equation of $A(x, 1)$ is intriguing.

Fourth, symmetry of a species is not diecasted. Different symmetries may apply to a species in accordance with categorization. In general, the symmetry used in geometric isomerism of acyclic polyenes, C_3 , is less than that in constitutional isomerism, $C_3 \times C_2$.

Fifth, the terms chirality and enantiomericity refer to those in 2-D space. All polyenes are achiral in 3-D space.

4. Solution: geometric isomers of monosubstituted acyclic polyenes

Bytautas and Klein [8] have studied the problem and found recurrence relations in algorithmic form. Initiated by these authors' work, we seek close-form formulation of their solution. We follow their notations (S and D) but drop the parameter of the generation number g , a simplification that renders closeness of formulation.

We start by sorting monosubstituted polyenes. A polyene (except for the first member, methyl radical) has several distinct substitution sites, each yielding a monosubstituted derivative. Once sorted, monosubstituted derivatives are in turn used to determine parent polyene. They are sorted by characterizing substitution sites of polyenes. There are two kinds of substitution sites. In the first kind, substitution lowers radicality and the substituent will be called *doubly bonded* because a double bond can be unambiguously assigned to the site. The other kind will be called *singly bonded* although the bond order is not decisively single but always given some double bond character by resonance structures. This dichotomy is evident by screening through structures of monosubstituted polyenes (see figure 3). The same rule as applied to parent species is used to decide the bond order at substitution site: double bonds are conjugated and their number is maximized. Consequently, configuration of polyene is irreversibly changed in doubly bonded substitution; either the places of single and double bonds are interchanged or the bonds of ambiguous bond order are now decisively assigned. This is due to lowered radicality. In singly bonded substitution, configuration stays the same.

With above understanding, we sort monosubstituted polyenes $A(x, y)$ into two parts; those with singly bonded substitution site are grouped in $S(x, y)$ and others in $D(x, y)$. Naturally we assume that monosubstituted polyenes are expressed in the same format $x^n y^r$ as parent species. This makes $A(x, y)$ a superset of the generating function for parent polyenes. Consequently, terms from both $S(x, y)$ and $D(x, y)$ may converge to the same parent species. Based on this assumption, $D(x, y)$ is necessarily accompanied by a factor y , which reflects the radicality lost by the parent species. Thus,

$$A(x, y) = S(x, y) + yD(x, y).$$

The functions $S(x, y)$ and $D(x, y)$ are used in two places, first in this section for self-growth, namely, to build the recurrence relation, and then in the next section for building single-node labeled, single-link labeled, and parent polyenes.

That each substitution site can be characterized as singly or doubly bonded is not only the key point in sorting polyenes but also has implications in chemical reactivity of radical polyenes. Doubly bonded substitution lowers radicality and hence is energetically favorable. For example, allyl radical C_3H_5 , has three sites: doubly bonded sites at both ends and a singly bonded site at middle. See figure 3. A carbene group CH_2 : would favor attaching to one end of allyl radical but not the center. Substitution groups of doubly bonding tendency less than carbene, such as halogens, nonetheless would follow the same regioselectivity.

How to tackle the problem posted in section 3? The idea is to draw an analogy from the special case $y = 1$. We start from the recurrence relation of $A(x, 1)$, rewrite it

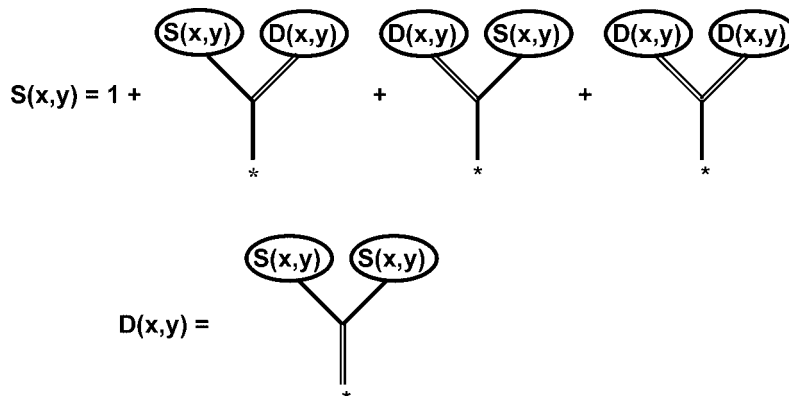


Figure 2. Pictorial representation of the recurrence relation for the functions $S(x, y)$ and $D(x, y)$. Star designates the root.

as $S(x, 1) + D(x, 1) = 1 + x[S(x, 1) + D(x, 1)]^2$, and then split into two parts, each of which is generalized in seeking recurrence relations of $S(x, y)$ and $D(x, y)$, with the notion that result should fit the special case $A(x, 0) = S(x, 0) = 1 + 2x^2[S(x, 0)]^3$. The result is a pair of coupled equations for functions $S(x, y)$ and $D(x, y)$. Their construction is rationalized as follows. We need only concern the growth at the root. A root is a node that is singled out by bonding to substituent or by labeling. Out of the two branches that can grow, each represented by $S(x, y)$ or $D(x, y)$, form three possible patterns: $S(x, y)D(x, y)$, $[D(x, y)]^2$, and $[S(x, y)]^2$. The first two patterns lead to the species with singly bonded substituent. The third leads to those with doubly bonded substituent. Pictorial representation of these recurrence relations is shown in figure 2. In the first pattern, the interchange of $S(x, y)$ and $D(x, y)$ yields enantiomeric isomers in 2-D space and doubles the count, hence a factor 2 is affixed. In the second, of which both branches are made of $D(x, y)$, yields a structure with two double bonds cramming the root node. To remedy the situation, we alternate sequence at one branch (double bonds replaced by single bonds and vice versa). Re-sequencing causes a double bond to disappear and raises radicality, hence a factor y is affixed. Species with singly bonded substituent are determined by the two patterns together as

$$S(x, y) = 1 + 2xS(x, y)D(x, y) + xy[D(x, y)]^2.$$

The third pattern is responsible for species with doubly bonded substituent,

$$D(x, y) = x[S(x, y)]^2.$$

In all but the null term, 1, a factor x is added to account for the root.

The above two coupled equations can be solved analytically or through iteration to obtain $A(x, y)$. When combined, the two equations yield the quartic equation for $S(x, y)$, $S = 1 + 2x^2S^3 + x^3yS^4$, which can be solved analytically. Final solution is given by $A(x, y) = S + yxS^2$. 3-dimensional plot of $A(x, y)$ could show a path of how

the cubic curve $A(x, 0)$ evolves into the quadratic curve $A(x, 1)$.¹ On the other hand, iterative approach starting from $S(x, y) = 1$ and $D(x, y) = 0$ gives explicit expression as

$$\begin{aligned} S(x, y) &= 1 + 2x^2 + yx^3 + 12x^4 + 14yx^5 + (96 + 4y^2)x^6 + 180yx^7 \\ &\quad + (880 + 110y^2)x^8 + (2288y + 22y^3)x^9 + \dots, \\ D(x, y) &= x + 4x^3 + 2yx^4 + 28x^5 + 32yx^6 + (240 + 9y^2)x^7 + 440yx^8 \\ &\quad + (2288 + 264y^2)x^9 + \dots \end{aligned}$$

Members of $S(x, y)$ and $D(x, y)$ are shown concisely in figure 3, where all 3-D mono-substituted species are shown; only one of each 2-D enantiomeric pair is shown. Obviously, a structure is in $S(x, y)$ if the substituent * is connected by a single bond or $D(x, y)$ if doubly bonded.

Enantiomeric isomer becomes identical in 3-D space. Each enantiomeric pair has two counts in $A(x, y)$ and one needs to be dropped. The net count $A_{3d}(x, y)$ is an average between the raw count $A(x, y)$ and the count of achiral species $A_s(x, y)$ in 2-D space. Achiral species are those in $A(x, y)$ that have two enantiomeric moieties. They are counted by $A_s(x, y) = 1 + yx[S(x^2, y^2) + D(x^2, y^2)]$, with the same rationalization as described in figure 2. Monosubstituted polyenes in 3-D space are generated by the function

$$\begin{aligned} A_{3d}(x, y) &= \frac{A(x, y) + A_s(x, y)}{2} \\ &= 1 + yx + x^2 + 3yx^3 + (6 + y^2)x^4 + 22yx^5 + (48 + 18y^2)x^6 \\ &\quad + (212y + 5y^3)x^7 + (440 + 275y^2)x^8 + (2295y + 143y^3)x^9 + \dots \end{aligned}$$

The first few structures of $A_{3d}(x, y)$ are shown in figure 3. For pentadienyl derivatives, the term $22yx^5$ gives 7 structures with singly bonded root and 15 with doubly bonded root.

5. Parent species

In order to build parent species, we need use monosubstituted polyenes and build three more homologous series: single-node labeled species, single-link labeled species, and species with centered link. Labeling is symbolic but could be made real by radioactive atoms. The essential idea is to work backward: first find derivatives and labeled species and then set them free from substituents and labels. To do this, we use dissimilarity characteristic theorem [15,16], which is briefly delineated in the following. Each polyene contains a number of distinct nodes. The number is total number of nodes if there is no similar nodes (no symmetry in a structure) and less otherwise. It is also the number of single-node labeled species derived from a parent polyene. Analogously,

¹ There is no unique way of turning $A(x, 0)$ into $A(x, 1)$. Any combination of $A(x, y) = S(x, y) + y^m D(x, y)$ with $m > 0$ gives a possible path.

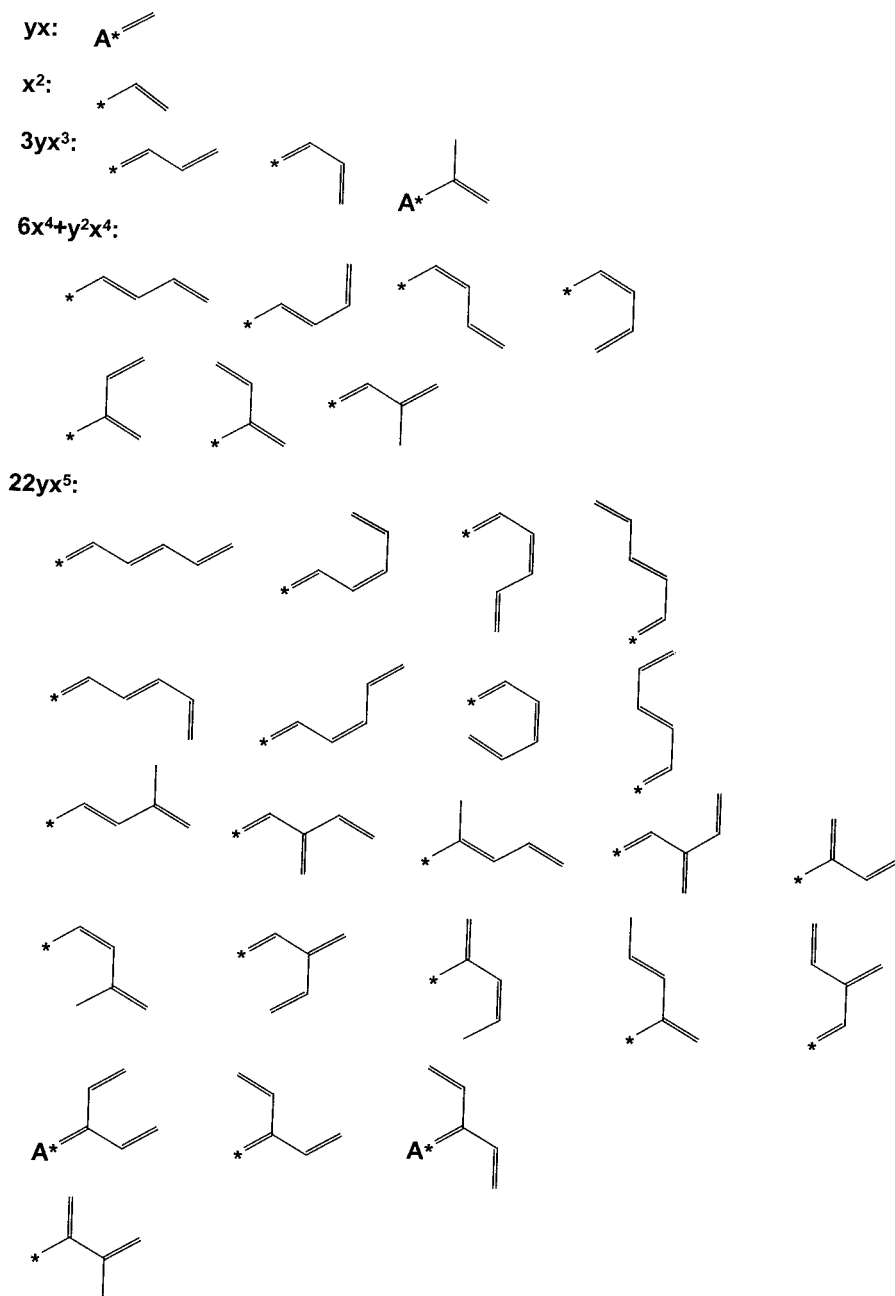


Figure 3. $A_{3d}(x, y)$: geometric isomers of monosubstituted polyenes $C_nH_{n+1}X$. Star designates the substituent. Only one resonant structure for each isomer is shown. Structures labeled with A at the root are 2-D achiral; the rest are chiral. This figure can also be used to visualize $S(x, y)$ and $D(x, y)$ if enantiomers of all 2-D chiral structures are added. Structures with singly and doubly bonded substituent are designated as members of $S(x, y)$ and $D(x, y)$, respectively.

each polyene derives a number of single-link labeled species. Since for each acyclic polyene nodes exceed links by one, single-node labeled species outnumber single-link labeled species by one. In other words, each parent polyene as one count is the difference between total single-node labeled species and single-link species. Summing over single-node labeled species and single-link labeled species separately and finding the difference, we should reach the number of parent species. Expression is shown below. This is why we need to build the first two said series. If some species have a symmetric, centered link, the set of single-link labeled species is over-counted and should be cancelled against the species with centered link, hence the third series.

Each single-node labeled polyene is made of a labeled node with three branches. We denote $P(x, y)$ as enumerating function of these polyenes. Each of the three branches is represented by $A(x, y)$. The construction of $P(x, y)$ is analogous to that of monosubstituted polyenes, only now each species has three growing branches, instead of two and a substituent. Generating functions of three branches are multiplied, not straightforwardly but dictated by the symmetry of a node in hexagonal lattice, in the form of Pólya's cycle index as $P(x, y) = (x/3)\{[A(x, y)]^3 + 2A(x^3, y^3)\}$. Besides, when $S(x, y)$ and $D(x, y)$ are fed into the cycle index, it is not a direct substitution with $A(x, y) = S(x, y) + yD(x, y)$, but each term should be modified to comply with radicality. $[A(x, y)]^3$ produces four terms. Only the term $3[S(x, y)]^2 D(x, y)$, corresponding to two single bonds and a double bond, does not upset existing radicality; other terms have to be adjusted. Again, classical picture of chemical bonds is used. The term $[S(x, y)]^3$ corresponds to a node with three single bonds which are readjusted by the conjugation of double bonds and give a new radicality, hence a y is affixed. A node with a single bond and two double bonds belongs to the term $3S(x, y)[D(x, y)]^2$, also affixed with y (section 4). The term $[D(x, y)]^3$ corresponds to a node of three double bonds that needs to be adjusted twice, resulting in an attachment of y^2 . $S(x^3, y^3)$ and $D(x^3, y^3)$ are treated the same way as $[S(x, y)]^3$ and $[D(x, y)]^3$. Final form of $P(x, y)$ for geometric isomers of node-labeled polyenes becomes

$$P(x, y) = \frac{x}{3} \{ y[S(x, y)]^3 + 3[S(x, y)]^2 D(x, y) + 3yS(x, y)[D(x, y)]^2 + y^2[D(x, y)]^3 + 2[yS(x^3, y^3) + y^2 D(x^3, y^3)] \}.$$

A single-link labeled polyene is synthesized by eliminating substituents from two monosubstituted species. In place of two substituents, a link is formed. Enumerating function is

$$Q(x, y) = \frac{1}{2} \{ [A(x, y) - 1]^2 + A(x^2, y^2) - 1 \},$$

where the null tree, 1, is rejected because linking to a null branch does not give new species. When two monosubstituted species are combined, three situations arise: two singly bonded roots are linked to each other, two doubly bonded roots are linked to each other, and a singly bonded root is linked to a doubly bonded one. In the first two combinations, there are no radicality changes. In the last situation, a reconcilia-

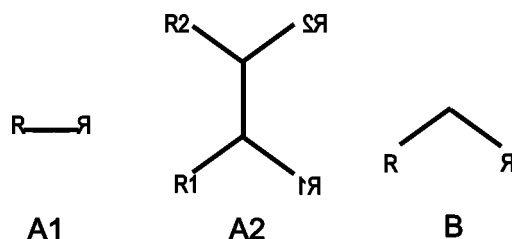


Figure 4. Three types of 2-D achiral polyenes.

tion of bond character at the link gives an extra radicality factor y . The term becomes $y[S(x, y) - 1]D(x, y)$. The net result is

$$Q(x, y) = \frac{1}{2} \{ [S(x, y) - 1]^2 + 2y[S(x, y) - 1]D(x, y) + [D(x, y)]^2 + S(x^2, y^2) - 1 + D(x^2, y^2) \}.$$

Species with centered link, $R(x, y)$, are special cases of $Q(x, y)$ where two branches linked at the center are enantiomeric to each other:

$$R(x, y) = S(x^2, y^2) - 1 + D(x^2, y^2).$$

According to the dissimilarity characteristic theorem, parent species are counted by

$$F(x, y) = P(x, y) - Q(x, y) + R(x, y).$$

However, these parent species are counted in 2-D space. When extended to 3-D space, structures merge and redundancy occurs. Redundancy is removed by deleting half of chiral structures from total counts. Or equivalently, we add 2-D achiral structures, as counted by $F_{3s}(x, y)$, to total count and divide the sum by two. Net count in 3-D space is

$$F_{3d}(x, y) = \frac{1}{2} [F(x, y) + F_{3s}(x, y)].$$

It is more cumbersome to figure out 2-D achiral structures in parent species than in monosubstituted species. Achiral polyenes are divided into three categories, A1, A2, and B, as shown in figure 4. The first two categories are more tedious. First, we consider the situation $y = 1$ (no breakdown by radicality). The A1 and A2 categories combined are counted by the function $A(x^2, 1) - 1$. This result is explained as follows. The structures that are common to both A1 and A2 categories have the symmetries of both categories and belong to D_{2h} group in 3-D space. Because their twin center nodes are connected to either four equivalent achiral side groups or two pairs of enantiomeric chiral side groups, these structures are counted by $x^2 A(x^4, 1)$. On the other hand, each category is counted by $(1/2)x^2 \{ [A(x^2, 1)]^2 + A(x^4, 1) \}$, for the same reason that single-link labeled species as represented by $Q(x, 1)$ are counted by $(1/2) \{ [A(x, 1) - 1]^2 + A(x^2, 1) - 1 \}$. Only now the size of each achiral structure (the exponent of x) reflects not two polyenyl

groups but four divided into two pairs. The x^2 factor corresponds to the two center nodes. The net count of 2-D achiral polyenes in A1 and A2 categories is obtained by subtracting common members from the sum of A1 and A2, resulting in $x^2[A(x^2, 1)]^2 = A(x^2, 1) - 1$.

Next, we extend the expression to include the radicality variable y . The two categories A1 and A2 combined would have been counted by $S(x^2, y^2) - 1 + D(x^2, y^2)$, however, radicality complicates outcome. $S(x^2, y^2)$ and $D(x^2, y^2)$ represent 2-D achiral polyenes with single bond and double bond at middle link, respectively. Note that for radical species the single bond at middle link has partial double bond character. For $D(x^2, y^2)$, there is no complication. $S(x^2, y^2)$ is split according to the relation $S(x, y) = 1 + 2xS(x, y)D(x, y) + yx[D(x, y)]^2$, which is modified by radicality and size-doubling as

$$S(x^2, y^2) \Rightarrow 1 + (1 + y^2)x^2S(x^2, y^2)D(x^2, y^2) + y^2x^2[D(x^2, y^2)]^2.$$

That is, achiral species with single bond as center link may have two kinds of composition, consisting of either a pair of singly bonded branch plus a pair of doubly bonded branch as represented by $x^2S(x^2, y^2)D(x^2, y^2)$ or two pairs of doubly bonded branches as represented by $x^2[D(x^2, y^2)]^2$. In the $x^2S(x^2, y^2)D(x^2, y^2)$ term, the moiety R in A1 structures (figure 4) is branched into one singly bonded root as represented by $S(x, y)$ and one doubly bonded root as represented by $D(x, y)$. Note that every achiral structure in A1 category has a corresponding structure in A2. As A1 is mapped into A2, two double bonds are lost upon the readjustment to conjugation and radicality is raised by two, hence a factor y^2 is attached. This is why the pre-factor 2 of $x^2S(x^2, y^2)D(x^2, y^2)$ turns into $1 + y^2$. The appearance of the pre-factor y^2 in the $x^2[D(x^2, y^2)]^2$ term is explained similarly. See figure 5.

Each structure in category B bears a centered node with two enantiomeric branches and belongs to either $xS(x^2, y^2)$ or $xD(x^2, y^2)$, both readjusted to a new radicality formed at center node. Hence category B is counted by $xy[S(x^2, y^2) + D(x^2, y^2)]$.

Summarily, 2-D achiral polyenes are counted by

$$F_{3s}(x, y) = (1 + y^2)x^2S(x^2, y^2)D(x^2, y^2) + y^2x^2[D(x^2, y^2)]^2 + D(x^2, y^2) + xy[S(x^2, y^2) + D(x^2, y^2)].$$

Figure 5 gives graphical interpretation of each term in $F_{3s}(x, y)$.

The final count of polyenes is explicitly expressed as

$$F_{3d}(x, y) = yx + x^2 + yx^3 + (2 + y^2)x^4 + 4yx^5 + (9 + 3y^2)x^6 + (26y + y^3)x^7 + (50 + 32y^2)x^8 + (214y + 14y^3)x^9 + \dots$$

Each term $x^n y^r$ corresponds to a structure that is converged from a mutually exclusive set of images shown in figure 3. In other words, $F_{3d}(x, y)$ is a subset of $A(x, y)$, as rooted graphs must be a superset of (many-to-one mapping to) free graphs.

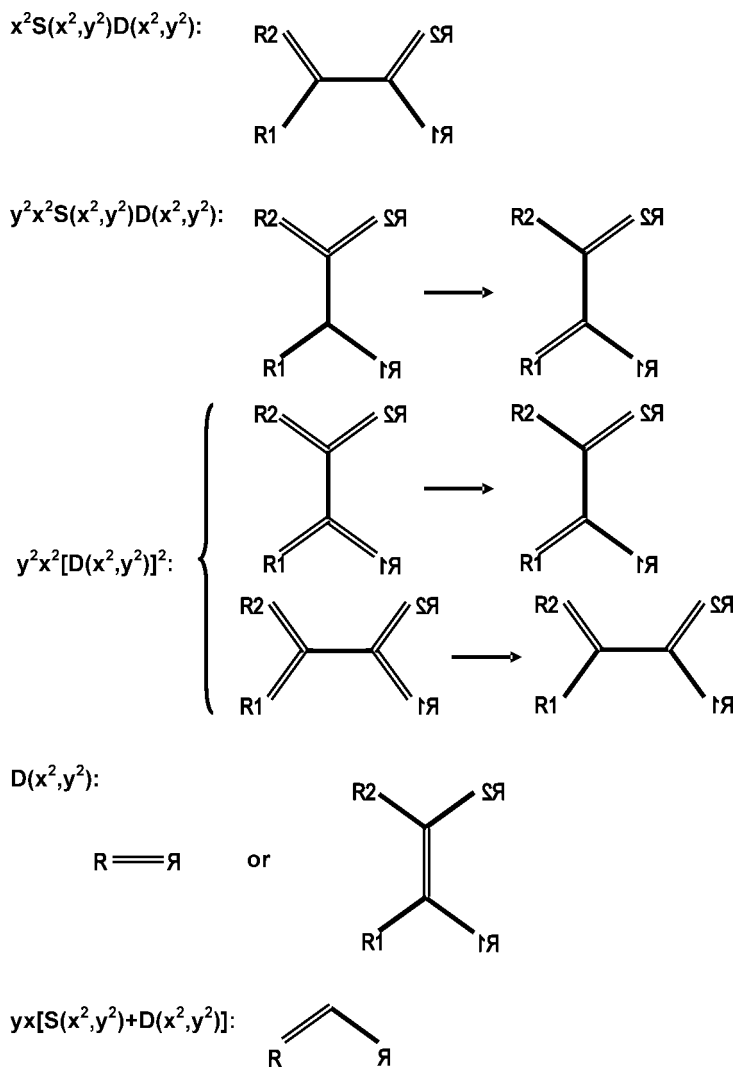


Figure 5. $F_{3S}(x, y)$: terms representing 2-D achiral polyenes. Only one resonant structure for each kind is shown.

6. Constitutional isomers

Constitutional isomers are in a one-to-many correspondence with geometric isomers. For acyclic polyenes, all geometric isomers that can be superimposed into one another through rotation around single or double bonds merge to a constitutional isomer. Now that all structures are achiral in 2-D sense, the treatment is simpler. No redundancy occurs when constitutional structures are extended to 3-D space. Derivations are parallel to those in geometric isomerism and briefly stated as follows. Monosubstituted species are generated by the function $a(x, y)$. Each species with size n and radicality r is a term

$x^n y^r$ in $a(x, y)$. Again, we rely on situations $y = 0$ (with no radicality) and $y = 1$ (with all radicalities but no discrimination among them) to build up overall situation. Recurrence relations can readily be derived from the Cayley–Polya scheme [1,5] as

$$a(x, 0) = 1 + \frac{x^2}{2} a(x, 0) \{ [a(x, 0)]^2 + a(x^2, 0) \},$$

$$a(x, 1) = 1 + \frac{x}{2} \{ [a(x, 1)]^2 + a(x^2, 1) \}.$$

The latter equation is listed as equation (4) in [7], where $f_2(x) = a(x, 1) - 1$ is used. Iteration of these recurrence relations gives $a(x, 0) = 1 + x^2 + 2x^4 + 6x^6 + 19x^8 + 67x^{10} + \dots$ and $a(x, 1) = 1 + x + x^2 + 2x^3 + 3x^4 + 6x^5 + 11x^6 + 23x^7 + 46x^8 + 98x^9 + \dots$. The coefficient of each term is the number of isomers with the size expressed by the exponent. Seeking a function $a(x, y)$ that incorporates both recurrence relations of $a(x, 0)$ and $a(x, 1)$, we separate it into two components, $s(x, y)$ and $d(x, y)$, each representing monosubstituted polyenes with singly and doubly bonded root, respectively. The same strategy as in geometric isomerism is used. Upon substituting $a(x, 1) = s(x, 1) + d(x, 1)$, the recurrence relation of $a(x, 1)$ is split into two parts, each of which is extrapolated to restore the discriminating factor y . Results are

$$s(x, y) = 1 + xs(x, y)d(x, y) + \frac{1}{2}xy \{ [d(x, y)]^2 + d(x^2, y^2) \},$$

$$d(x, y) = \frac{1}{2}x \{ [s(x, y)]^2 + s(x^2, y^2) \}.$$

As two branches of doubly bonded root grow from a singly bonded root, radicality raises by one (section 4). Therefore, the third term in the recurrence relation of $s(x, y)$ is affixed with a factor y . Unlike in geometric isomerism, the generating function $a(x, y)$ of constitutional isomers cannot be expressed in close algebraic form because the recurrence relations contain functionals. The recurrence relations must be solved by iteration, which gives

$$a(x, y) = 1 + yx + x^2 + 2yx^3 + (2 + y^2)x^4 + 6yx^5 + (6 + 5y^2)x^6$$

$$+ (21y + 2y^3)x^7 + (19 + 27y^2)x^8 + (82y + 16y^3)x^9 + \dots$$

Through dissimilarity characteristic theorem, parent species are expressed in terms of the three homologous series – single-node labeled species $p(x, y)$, single-link labeled species $q(x, y)$ and species with centered link $r(x, y)$ – as $f(x, y) = p(x, y) - q(x, y) + r(x, y)$. $p(x, y)$, $q(x, y)$ and $r(x, y)$ are, in turn, expressed in terms of monosubstituted species $a(x, y)$. Among the three series, only single-node labeled species $p(x, y)$ is formulated differently from the counterpart in geometric isomerism, whereas $q(x, y)$ and $r(x, y)$ are exact copies of their counterparts. For constitutional isomers, the symmetry at each node is $C_3 \times C_2$. Hence, the growth of single-node labeled polyenes is formulated in terms of cycle index as

$$p(x, 1) = \frac{x}{6} \{ [a(x, 1)]^3 + 3a(x, 1)a(x^2, 1) + 2a(x^3, 1) \}.$$

Table 1
Comparison between geometric and constitutional isomers.

	Geometric isomers	Constitutional isomers
Mono-substituted trees	$A(x, y) = S(x, y) + yD(x, y)$	$a(x, y) = s(x, y) + yd(x, y)$
Recurrence relations	$S(x, y) = 1 + 2xyS(x, y)D(x, y) + xy[D(x, y)]^2$ $D(x, y) = x[S(x, y)]^2$	$s(x, y) = 1 + xs(x, y)d(x, y) + \frac{1}{2}xy\{[d(x, y)]^2 + d(x^2, y^2)\}$ $d(x, y) = \frac{1}{2}x\{[s(x, y)]^2 + s(x^2, y^2)\}$
Single-node labeled trees	$P(x, y) = \frac{x}{3}\{y[S(x, y)]^3 + 3[S(x, y)]^2D(x, y) + 3yS(x, y)[D(x, y)]^2 + y^2[D(x, y)]^3 + 2[yS(x^3, y^3) + y^2D(x^3, y^3)]\}$	$p(x, y) = \frac{x}{6}\{y[s(x, y)]^3 + 3[s(x, y)]^2d(x, y) + 3ys(x, y)[d(x, y)]^2 + y^2[d(x, y)]^3 + 3ys(x, y)s(x^2, y^2) + 3ys(x, y)d(x^2, y^2) + 3s(x^2, y^2)d(x, y) + 3y^2d(x, y)d(x^2, y^2) + 2[ys(x^3, y^3) + y^2d(x^3, y^3)]\}$
Single-link labeled trees	$Q(x, y) = \frac{1}{2}\{[S(x, y) - 1]^2 + 2y[S(x, y) - 1]D(x, y) + [D(x, y)]^2 + S(x^2, y^2) - 1 + D(x^2, y^2)\}$	$q(x, y) = \frac{1}{2}\{[s(x, y) - 1]^2 + 2y[s(x, y) - 1]d(x, y) + [d(x, y)]^2 + s(x^2, y^2) - 1 + d(x^2, y^2)\}$
Trees with centered link	$R(x, y) = S(x^2, y^2) - 1 + D(x^2, y^2)$	$r(x, y) = s(x^2, y^2) - 1 + d(x^2, y^2)$
Free trees in 3-D space	$F_{3d}(x, y) = \frac{1}{2}\{P(x, y) - Q(x, y) + R(x, y) + (1 + y^2)x^2S(x^2, y^2)D(x^2, y^2) + y^2x^2[D(x^2, y^2)]^2 + D(x^2, y^2) + xy[S(x^2, y^2) + D(x^2, y^2)]\}$	$f(x, y) = p(x, y) - q(x, y) + r(x, y)$

With radicality taken into account (section 5), generating function of single-node labeled polyenes becomes:

$$\begin{aligned}
 p(x, y) = & \frac{x}{6} \{ y[s(x, y)]^3 + 3[s(x, y)]^2 d(x, y) \\
 & + 3ys(x, y)[d(x, y)]^2 + y^2[d(x, y)]^3 + 3ys(x, y)s(x^2, y^2) \\
 & + 3ys(x, y)d(x^2, y^2) + 3s(x^2, y^2)d(x, y) \\
 & + 3y^2d(x, y)d(x^2, y^2) + 2[ys(x^3, y^3) + y^2d(x^3, y^3)] \}.
 \end{aligned}$$

Results are summarized and compared with those of geometric isomers in table 1. Final counts of constitutional isomers are given in the explicit expression,

$$\begin{aligned}
 f(x, y) = & yx + x^2 + yx^3 + (1 + y^2)x^4 + 2yx^5 + (2 + 2y^2)x^6 + (5y + y^3)x^7 \\
 & + (4 + 7y^2)x^8 + (14y + 4y^3)x^9 + \dots
 \end{aligned}$$

7. Discussion and conclusion

Graph theory complements quantum mechanics for exploring chemical structures. This work presents close-form formulation and analytical solution of an enumeration problem that previously has been solved by algorithmic method. Through close-form formulation, we are able to interpret the growth pattern of acyclic polyenes in terms of tree structures embedded in hexagonal lattice. In addition, how a function $A(x, 0)$ of cubic equation evolves into $A(x, 1)$ of quadratic equation through continuous function $A(x, y)$ as a mathematical curiosity is rationalized. Function for generating polyenoids, $A(x, y)$, consists of two parts coupling to each other. Neither part alone, $S(x, y)$ or $D(x, y)$, generates the whole set of polyenoid structures. However, non-radical polyenes are generated by $S(x, 0)$ alone. The key to sort polyenes is to split $A(x, y)$ into parts based on two kinds of substitution sites. Sites of doubly bonded root counted by $D(x, y)$ are more stable than those of singly bonded root counted by $S(x, y)$. Each part has its characteristic growth pattern that dictates the recurrence relation. Growth patterns from these two kinds of root also determine node- and link-labeled derivatives, which are needed for generating parent species.

Constitutional isomerism of polyenes is expressed similarly in close form, but the equations thus derived cannot be solved analytically.

A similar problem is to count staggered conformers of alkanes. Structures are built from σ bonds and counted in 3-D space, instead of π bonds and 2-D space. This problem is less involved than ours in two aspects. One, the placement of alternating double bonds is not an issue and there is no radicality to muddle. Two, chirality stays in 3-D space and hence would not be the source of miscount. This problem is posed by Cyvin [17] and solved analytically by Wang, Cao and Li [18]. Their solution also uses coupled generating functions but can be simplified to a single function, yielding the recurrence relation $b = 1 + xb^3$.

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