Monosubstituted alkanes as stereoisomers, not as constitutional isomers, are regarded as planted three-dimensional (3D) trees, which are defined as a 3D extension of planted trees (graphs). They are thus recognized as 3D-objects (planted promolecules) and enumerated by Fujita’s proligand method (Fujita S (2005) Theor. Chem. Acc. 113:73–79, 113:80–86, Fujita S (2006) Theor. Chem. Acc. 115:37–53). By starting from three kinds of sphericity indices, i.e., $a_d$ for homospheric cycles, $c_d$ for enantiospheric cycles, and $b_d$ for hemispheric cycles, cycle indices with chirality fittingness (CI-CFs) are obtained to enumerate planted 3D-trees or equivalently monosubstituted alkanes as stereoisomers. Functional equations $a(x)$, $c(x^2)$, and $b(x)$ for recursive calculations are derived from the CI-CFs and programmed in three ways by means of the Maple programming language. The three recursive procedures for calculating the numbers of planted 3D-trees are executed to give identical results, which are collected up to 100 carbon content in a tabular form. The results are compared with the enumeration of planted trees (as graphs).

Keywords: Monosubstituted alkane, Stereoisomer, Enumeration, Sphericity

1 Introduction

Combinatorial enumeration of rooted trees as models of monosubstituted alkanes has been initiated by a mathematician Cayley [1, 2]. Henze and Blair [3] obtained the numbers of aliphatic alcohols of a given carbon content by means of recursive equations. Later, a more systematic method based on Pólya’s theorem [4, 5] was applied to the evaluation of the numbers of rooted trees, which was differently formulated as planted trees.

Although Pólya’s theorem [4, 5] has been widely applied to chemical combinatorics [6–11], enumerated objects in most cases are “graphs”, not as “three-dimensional objects”. Chemically speaking, they are constitutional (structural) isomers, but not stereoisomers. As pointed out in our recent reports [12–14], Pólya’s theorem lacks the concept of sphericities [15, 16] so as to be incapable of solving stereochemical problems. Although Robinson et al. [17] have reported the enumeration of monosubstituted alkanes by modifying Pólya’s cycle indices (CIs), their treatment also lacks the concept of sphericities.

Without the sphericity concept, in general, any methods are incapable of treating fundamental stereochemical problems such as meso-compounds and pseudoasymmetry. Because the stereochemical problems have been already solved in the last quarter of the 19th century in a descriptive or non-mathematical fashion [18–21], the present status of chemical combinatorics based on Pólya’s theorem does not properly reflect the advance of stereochemistry before and during the 20th century.

On the basis of the sphericity concept, we have developed a general method named the proligand method for enumerating stereoisomers [12–14]. To show the versatility of the proligand method, we have recently applied it to the enumeration of monosubstituted alkanes (planted 3D-trees) as 3D-objects [22].

The sphericity concept was originally proposed in the form of “the sphericities of orbits”, which provides us with various tools for combinatorics in connection with Fujita’s USCI (unit-subduced-cycle-index) approach [16]. Then, it was modified into the concept “the sphericities of orbits based on cyclic groups”, which gives a basis to other types of combinatorial tools [23–25]. Further, it was transformed into the concept “the sphericities of cycles”, which gives the proligand method [12–14].

As found by the short history described in the preceding paragraph, the original formulation [12–14] was too mathematical to assure chemists of the traceability of
the proligand method. However, there is a short cut to become practical in the usage of the proligand method without acquainting such mathematical formulation. The short cut is to study suitable examples which disclose the details of calculation procedures. We can safely say that understanding mathematics is usually different from implementing mathematics as a program for concrete calculation. In other words, “The proof of the pudding is in the eating. You can’t eat mathematics, but you can digest it,” as Pólya phrased it [10](page 68). Note that the word “eat” corresponds to “understand” and the word “digest” corresponds to “implement”.

As clarified in the preceding paragraphs, the aim of the present paper is to report the details of calculation procedures. We can safely say that the procedures for obtaining the numbers of monosubstituted alkanes as 3D-objects (stereoisomers), but not as graphs, where the procedures are implemented by the Maple programming language [26].

2 Enumeration of Monosubstituted Alkanes as Stereoisomers

2.1 Planted Promolecules and Their Nesting

A monosubstituted alkane is regarded as a planted 3D-tree of degree 4, where a principal vertex (a central carbon atom) is connected with a root (the mono-substituent) and three substituents (alkyl ligands or hydrogen atoms). Each one of the three substituents is called a proligand, which is regarded as being a hypothetical structureless object with chirality/achirality. By considering such proligands, the original monosubstituted alkane (or the planted 3D-tree) is regarded as a planted promolecule, which is a 3D-skeleton (a tetrahedral skeleton) having the root (\(\bullet\)) and the tree proligands on its vertices.

\[
\text{CH}_3 \xrightarrow{\text{1}} \text{CH}_2\text{CH}_3 \xrightarrow{\text{2}} \text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{B}} \text{A} \xrightarrow{p} \text{X}
\]

\(\text{mono-X-alkane}\)

\(\text{planted 3D-tree}\)

\(\text{planted promolecule}\)

Figure 1. Monosubstituted alkane as a planted 3D-tree and a planted promolecule

For example, let us examine a 3,4-dimethyl-3-X-hexane (1), which is selected from a set of four diastereomers. The mono-X-substituted alkane (1) is regarded as a planted 3D-tree with a root X. When the three substituents are replaced by proligands, i.e., \(A = \text{CH}_3\), \(B = \text{CH}_2\text{CH}_3\), and \(p = R\text{-CH(CH}_3\text{)}\text{CH}_2\text{CH}_3\), and when the X is replaced by a solid circle, the planted 3D-tree (1) is converted into a planted promolecule (2) with a root (\(\bullet\)). The proligands A and B are achiral, while the proligand p is chiral. Note that the \(S\)-configuration is tentatively assigned by considering a vacant bond (incident to the X originally) as the lowest priority (\(p > B > A > \bullet\)).

Each of the proligands can be further regarded as a planted promolecule, if a root is attached to its central vertex (as a new principal vertex). For example, the proligand \(p\) (i.e., a 2-butyl ligand) can be regarded as a planted promolecule, if a root is attached to the p through the vacant bond and the three achiral substituents (H, \(A = \text{CH}_3\), and \(B = \text{CH}_2\text{CH}_3\)) are replaced by the corresponding achiral proligands. The resulting planted promolecule is represented by \(\bullet \text{—CHAB}\), which has the same skeleton as the starting planted promolecule (2). The proligand B (i.e., an ethyl ligand) can be regarded as a planted promolecule, if a root is attached to the B through the vacant bond and the three achiral substituents (two H’s and \(A = \text{CH}_3\)) are replaced as above. The resulting planted promolecule is represented by \(\bullet \text{—CH}_2\text{A}\), which has the same skeleton as 2.

This procedure is repeated to reach terminal vertices of the original monosubstituted alkane (or the planted 3D-tree). Thereby, the original monosubstituted alkane (or the planted 3D-tree) is recognized to have a nested structure of such planted promolecules.

2.2 Sphericities of Cycles

It is to be noted that each planted promolecule contained in a nested fashion is a 3D-object (not a graph) which has a common skeleton belonging to \(C_{3s}\). Hence, such planted promolecules can be enumerated by means of Fujita’s proligand method [12–14].

\[
\begin{align*}
3a. & \quad \sigma_v(1) \\
& \quad (1)(2)(3), b_1^3 \\
3b. & \quad C_3 \quad (1 2 3), b_3 \\
3c. & \quad C_3^2 \quad (1 3 2), b_3 \\
3d. & \quad \sigma_d(1) \\
& \quad (1)(2 3), a_1c_2 \\
3e. & \quad \sigma_d(2) \\
& \quad (1 3)(2), a_1c_2 \\
3f. & \quad \sigma_d(3) \\
& \quad (1 2)(3), a_1c_2 
\end{align*}
\]

Figure 2. Symmetry operations for a \(C_{3v}\)-skeleton (3). The identity operation (1) converts 3 into itself, where the resulting skeleton is denoted as 3a.
For this purpose, we examine the three positions of the \( C_{3v} \)-skeleton under all operations of \( C_{3v} \). In terms of the USCI approach [16], the three positions other than the root construct an orbit governed by a right coset representation (RCR) represented as \( \{ C_s \} \backslash C_{3v} \), whose concrete form is shown as a product of cycles as follows:

\[
(C_s \backslash C_{3v}) = \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2)\}
\]

The numbering used in the RCR \( \{ C_s \} \backslash C_{3v} \) corresponds to the numbering shown in the skeleton (3), where the product of cycles corresponding to each improper rotation \( \sigma_{v(1)}, \sigma_{v(2)}, \text{ or } \sigma_{v(3)} \) is attached by an overbar, which shows the inverse of chirality.

The sphericity of each cycle is determined according to its shape, so that a sphericity index (SI) is assigned to it, where the subscript \( d \) is assigned to it. The sphericity index of a homospheric cycle permits the transitivity of achiral (pro)ligands only.

1. A cycle belonging to an improper rotation is determined to be homospheric, if the length \( d \) is odd; and a sphericity index \( a_d \) is assigned to it. The chirality fittingness of a homospheric cycle permits the transitivity of achiral (pro)ligands only.

2. If the length \( d \) is even, on the other hand, the cycle in an improper rotation is determined to be enantiospheric; and a sphericity index \( c_d \) is assigned to it. The chirality fittingness of an enantiospheric cycle permits the transitivity of achiral (pro)ligands or the transitivity of pairs of enantiomeric ligands (i.e., \( d/2 \) of chiral (pro)ligands of the same kind and \( d/2 \) of their enantiomeric (pro)ligands).

3. Any cycle belonging to a proper rotation is determined to be hemispheric and a sphericity index \( b_d \) is assigned to it, where the subscript \( d \) is the length of the cycle. The chirality fittingness of a hemispheric cycle permits the transitivity of achiral and chiral (pro)ligands.

Thereby, each symmetry operation acting on the skeleton is characterized by a product of such sphericity indices, as collected along with the corresponding product of cycles in Figure 2.

To count achiral planted promolecules and enantiomeric pairs of chiral planted promolecules, we apply Theorem 2 of [14] to the enumeration of planted promolecules without any modification. Hence, the cycle index with chirality fittingness (CI-CF) for this case is calculated by using the product of SIs collected in Figure 2:

\[
\text{CI-CF}(C_{3v}; a_d, c_d, b_d) = \frac{1}{6}(b_1^3 + 2b_3 + 3a_1c_2).
\]

To count achiral and chiral planted promolecules, Theorem 3 of [14] for the enumeration of ligands under the action of the maximum chiral subgroup is applied to this case so as to derive the following CI-CF:

\[
\text{CI-CF}(C_3; b_d) = \frac{1}{3}(b_1^3 + 2b_3),
\]

To count achiral planted promolecules only, the first proposition of Theorem 4 for the enumeration of achiral ligands [14] is applied to this case so as to derive the following CI-CF:

\[
\text{CI-CF}_A(C_{3v}; a_d, c_d, b_d) = 2\text{CI-CF}(C_{3v}; a_d, c_d, b_d) - \text{CI-CF}(C_3; b_d) = a_1c_2.
\]

To count chiral planted promolecules only, the second proposition of Theorem 4 for the enumeration of chiral ligands [14] is applied to obtain the following CI-CF:

\[
\text{CI-CF}_C(C_{3v}; a_d, c_d, b_d) = a_1c_2.
\]

### 2.3 Recursive Procedures

By using eq. 3, let us consider the enumeration of achiral and chiral planted promolecules, where two enantiomers of each pair are counted separately. For this purpose, the SI appearing in the right-hand side of eq. 3 is replaced by the following ligand inventory:

\[
b(x^d) = b_d = \sum_{k=0}^{\infty} \beta_kx^{dk},
\]

where achiral and chiral (pro)ligands for substitution are itemized by their carbon contents \( k \) (\( k = 1 \) to \( \infty \)) and we put \( \beta_0 = 1.0 \). If the ligand inventory is introduced into eq. 3, the resulting equation is a generating function for counting achiral and chiral planted promolecules. The generating function can be regarded as a new ligand inventory for the hemispheric cycle. This means that this process is recursive, so that we can obtain the following functional equation:

\[
b(x) = 1 + \frac{x}{3}(b(x)^3 + 2b(x^3)),
\]

where the principal node of the parent planted promolecule is taken into consideration by multiplying by \( x \) and the initial (trivial) planted promolecule is considered by adding 1. This type of equation was first noted by Pólya [4, 5], although the sphericity concept was not taken into consideration.

According to the chirality fittingness of an enantiospheric cycle, diploids (ordered pairs) of achiral
(pro)ligands or enantiomeric ligands satisfy the following ligand inventory:

\[ c(x^d) = c_d = \sum_{k=0}^{\infty} \gamma_k x^{dk} \]  

(8)

where achiral and chiral prolignands for substitution are itemized by their carbon contents \( k \) (\( k = 1 \) to \( \infty \)) and we put \( \gamma_0 = 1 \). The concept of diploid is here used without definition, which will be reported elsewhere [22]. Because the diploids for this case are characterized by \( C_3 \), we modify eq. 7 into the following functional equation:

\[ c(x^2) = 1 + \frac{x^2}{3}(c(x^2)^3 + 2c(x^6)) \]  

(9)

where the principal nodes of the parent planted promolecules contained in a diploid are characterized by multiplying by \( x^2 \) and the initial (trivial) planted promolecule is taken into consideration by adding 1.

By using eq. 4, we are able to enumerate achiral planted promolecules only. Thus, the SI appearing in the right-hand side of eq. 4 is replaced by the following ligand inventory:

\[ a(x^d) = a_d = \sum_{k=0}^{\infty} \alpha_k x^{dk} \]  

(10)

where achiral and chiral prolignands for substitution are itemized by their carbon contents \( k \) (\( k = 1 \) to \( \infty \)) and we put \( \alpha_0 = 1 \). Therefore, the generating function can be regarded as a new ligand inventory for the homospheric molecules only. Because the generating function can be considered to be a new ligand inventory for the homospheric cycle, this process is recognized to be recursive, so that we obtain the following functional equation:

\[ a(x) = 1 + x a(x)c(x^2) \]  

(11)

where the principal node of the parent planted promolecule is taken into consideration by multiplying by \( x \) and the initial (trivial) planted promolecule is considered by adding 1. Although this type of equation was first noted by Robinson et al. [17], their treatment did not take the sphericity concept into consideration.

Let \( B(x) \) be a generating function for counting achiral and chiral planted promolecules, where each pair of enantiomers is counted just once. Let \( C(x) \) be a generating function for counting chiral planted promolecules only, where each pair of enantiomers is counted just once. They are represented by the following equations:

\[ B(x) = \sum_{k=0}^{\infty} B_k x^k \]  

(12)

\[ C(x) = \sum_{k=0}^{\infty} C_k x^k \]  

(13)

where we put \( B_0 = 1 \) and \( C_0 = 0 \). Because we can place \( B_k = \alpha_k + C_k \) and \( \beta_k = \alpha_k + 2C_k \), eq. 7 (for \( b(x) \)) and eq. 11 (for \( a(x) \)) give the following equations:

\[ B(x) = \frac{1}{2} (a(x) + b(x)) \]  

(14)

\[ = 1 + \frac{x}{6} (b(x)^3 + 2b(x^3) + 3\alpha \gamma_2) \]  

(15)

\[ C(x) = \frac{1}{2} (b(x) - a(x)) \]  

(16)

\[ = \frac{x}{6} (b(x)^3 + 2b(x^3) - 3\alpha \gamma_2) \]  

(17)

It should be noted that \( a(x) \) (eq. 10), \( c(x^2) \) (eq. 9), and \( b(x) \) (eq. 7) have recursive nature, while \( B(x) \) (eq. 14 or eq. 15) and \( C(x) \) (eq. 16 or eq. 17) have no recursive nature.

### 2.4 Preliminary Calculations for Implementation

To collect data for implementing the process of recursive calculation, suppose that the coefficients of \( x^k \) (\( k \leq 5 \)) have been already calculated to give intermediate generating functions as follows:

\[ a(x) = 1 + x + x^2 + 2x^3 + 3x^4 + 5x^5 + \alpha_6 x^6 + \alpha_7 x^7 + \alpha_8 x^8 \]  

(18)

\[ c(x^2) = 1 + x^2 + x^4 + 2x^5 + 5x^8 + 11x^{10} + \gamma_6 x^{12} + \gamma_7 x^{14} + \gamma_8 x^{16} \]  

(19)

\[ b(x) = 1 + x + x^2 + 2x^3 + 5x^4 + 11x^5 + \beta_6 x^6 + \beta_7 x^7 + \beta_8 x^8 \]  

(20)

where we add the coefficients of the terms \( x^6 \), \( x^7 \), and \( x^8 \) for calculation and omit the terms for \( k \geq 9 \) tentatively. The intermediate generating functions (eqs. 18–20) are introduced into the respective right-hand sides of eqs. 11, 9, and 7. The resulting equations are expanded to give the following equations:

\[ a(x) = 1 + x + x^2 + 2x^3 + 3x^4 + 5x^5 + 8x^6 + (6 + \alpha_6) x^7 + (9 + \alpha_7) x^8 + \cdots \]  

(21)

\[ c(x^2) = 1 + x^2 + x^4 + 2x^5 + 5x^8 + 11x^{10} + 28x^{12} + (46 + \gamma_6) x^{14} + (60 + 2 \gamma_6 + \gamma_7) x^{16} + \cdots \]  

(22)

\[ b(x) = 1 + x + x^2 + 2x^3 + 5x^4 + 11x^5 + 28x^6 + (46 + \beta_6) x^7 + (60 + 2 \beta_6 + \beta_7) x^8 + \cdots \]  

(23)

which are compared with eqs. 18–20. Thereby, the coefficients of the terms \( x^6 \) (for \( a(x) \) and \( b(x) \)) or \( x^{12} \) (for \( c(x) \)) give the following relationships:

\[ \alpha_6 = 8 \]  

(24)

\[ \gamma_6 = 28 \]  

(25)

\[ \beta_6 = 28, \]  

(26)
which show that they are determined as distinct numbers, if the generating functions up to $x^8$ (for $a(x)$ and $b(x)$) or to $x^{10}$ (for $c(x)$) are given.

**Rule 1**: In general, if such generating functions up to $x^n$ (for $a(x)$ and $b(x)$) or to $x^m$ (for $c(x)$) are given, the coefficients $(\alpha_{n+1}, \gamma_{n+1}, \text{and} \beta_{n+1})$ are recursively generated as distinct numbers.

Comparison of the coefficients of the terms $x^7$ (for $a(x)$ and $b(x)$) or $x^{14}$ (for $c(x)$) gives the following relationships:

\[
\begin{align*}
\alpha_7 &= 6 + \alpha_6 = 14 \\
\gamma_7 &= 46 + \gamma_6 = 74 \\
\beta_7 &= 46 + \beta_6 = 74.
\end{align*}
\]

These equations (eqs. 27–29) mean that the coefficients $(\alpha_7, \gamma_7, \text{and} \beta_7)$ can be calculated by using the coefficients $(\alpha_6, \gamma_6, \text{and} \beta_6)$, which have been already obtained by eqs. 24–26.

**Rule 2**: In general, if such generating functions up to $x^n$ (for $a(x)$ and $b(x)$) or to $x^{2m}$ (for $c(x)$) are given, the coefficients $(\alpha_{n+2}, \gamma_{n+2}, \text{and} \beta_{n+2})$ are recursively calculated by using the generated coefficients $(\alpha_{n+1}, \gamma_{n+1}, \text{and} \beta_{n+1})$.

Comparison of the coefficients of the terms $x^8$ (for $a(x)$ and $b(x)$) or $x^6$ (for $c(x)$) gives the following relationships:

\[
\begin{align*}
\alpha_8 &= 9 + \alpha_7 = 23 \\
\gamma_8 &= 69 + 2\gamma_7 + \gamma_7 = 199 \\
\beta_8 &= 69 + 2\beta_7 + \beta_7 = 199.
\end{align*}
\]

These equations (eqs. 30–32) mean that the coefficients $(\alpha_8, \gamma_8, \text{and} \beta_8)$ can be calculated by using the coefficients $(\gamma_7, \beta_7)$ and the coefficients $(\alpha_7, \gamma_7, \text{and} \beta_7)$, which have been already obtained by eqs. 25 and 26 as well as eqs. 27–29.

**Rule 3**: In general, if such generating functions up to $x^n$ (for $a(x)$ and $b(x)$) or to $x^{m}$ (for $c(x)$) are given, the coefficients $(\alpha_{n+3}, \gamma_{n+3}, \text{and} \beta_{n+3})$ are recursively calculated by using the generated coefficients $(\gamma_{n+1}, \beta_{n+1})$ and the calculated coefficients $(\alpha_{n+2}, \gamma_{n+2}, \text{and} \beta_{n+2})$.

### 2.5 Implementation and Results

In the preceding subsection, we have obtained three rules, each of which is capable of working as a basis of recursive calculation.

First, we implement Rule 1 as a Maple program for calculating the numbers of planted 3D-trees (monosubstituted alkanes) which are itemized with respect to carbon content (1 to 100). The upper limit of the carbon content (ccntt ) is tentatively fixed to be 100, but it is freely selected.

Maple program for Rule 1, "EnumAlkyl1-100RR.mpl":

```maple
ax := 1 + x^a1*c2;
cx := (1/3)*x^2*c2^3 + (2/3)*x^2*c6;
bx := 1 + (1/3)*x*b1*3 + (2/3)*x*b3;

"Initial Values":
a1 := 1;
c2 := 1;
b1 := 1;
b3 := 1;
c6 := 1;

for ccntt from 1 to 100 by 1 do
  CCx := (1/2)*(a1 - c1):
  BBx := (1/2)*(a1 + c1):
  bx := 1 + (1/3)*x*b1*3 + (2/3)*x*b3:
  cx := 1+ (1/3)*x^2*c2^3 + (2/3)*x^2*c6:
  for c1 := 1 to 100 do
    bx := bx + (1/3)*x*b1*3 + (2/3)*x*b3:
    cx := cx + (1/3)*x^2*c2^3 + (2/3)*x^2*c6:
  end do;
  printf("%d & %d & %d & %d \\
", BBx, CCx, bx, cx):
  end do;
  "Comparison of the coefficients of the terms x^7 (for a(x) and b(x)) or x^6 (for c(x)) gives the following relationships:

\[
\begin{align*}
\alpha_7 &= 6 + \alpha_6 = 14 \\
\gamma_7 &= 46 + \gamma_6 = 74 \\
\beta_7 &= 46 + \beta_6 = 74.
\end{align*}
\]

These equations (eqs. 27–29) mean that the coefficients $(\alpha_7, \gamma_7, \text{and} \beta_7)$ can be calculated by using the coefficients $(\alpha_6, \gamma_6, \text{and} \beta_6)$, which have been already obtained by eqs. 24–26.

**Rule 2**: In general, if such generating functions up to $x^n$ (for $a(x)$ and $b(x)$) or to $x^{2m}$ (for $c(x)$) are given, the coefficients $(\alpha_{n+2}, \gamma_{n+2}, \text{and} \beta_{n+2})$ are recursively calculated by using the generated coefficients $(\alpha_{n+1}, \gamma_{n+1}, \text{and} \beta_{n+1})$.

Comparison of the coefficients of the terms $x^8$ (for $a(x)$ and $b(x)$) or $x^6$ (for $c(x)$) gives the following relationships:

\[
\begin{align*}
\alpha_8 &= 9 + \alpha_7 = 23 \\
\gamma_8 &= 69 + 2\gamma_7 + \gamma_7 = 199 \\
\beta_8 &= 69 + 2\beta_7 + \beta_7 = 199
\end{align*}
\]

These equations (eqs. 30–32) mean that the coefficients $(\alpha_8, \gamma_8, \text{and} \beta_8)$ can be calculated by using the coefficients $(\gamma_7, \beta_7)$ and the coefficients $(\alpha_7, \gamma_7, \text{and} \beta_7)$, which have been already obtained by eqs. 25 and 26 as well as eqs. 27–29.

**Rule 3**: In general, if such generating functions up to $x^n$ (for $a(x)$ and $b(x)$) or to $x^{m}$ (for $c(x)$) are given, the coefficients $(\alpha_{n+3}, \gamma_{n+3}, \text{and} \beta_{n+3})$ are recursively calculated by using the generated coefficients $(\gamma_{n+1}, \beta_{n+1})$ and the calculated coefficients $(\alpha_{n+2}, \gamma_{n+2}, \text{and} \beta_{n+2})$.

This code is stored in a file named "EnumAlkyl1-100RR.mpl" tentatively. In this code, the abbreviated symbols for functional equations are used as follows: a1 for $a(x)$, c2 for $c(x^2)$, c6 for $c(x^6)$, b1 for $b(x)$, and b3 for $b(x^3)$. Such symbols as a1 and c2 are used to remember that such functions as $a(x)$ and $c(x^2)$ correspond to the SIs $a_1$, $c_2$, and so on. The first paragraph of this code declares three functional equations (eqs. 11, 9, and 7). In the 2nd paragraph, the initial values $a(x) = 1$, $c(x^2) = 1$, and $b(x) = 1$ are set by encoding $a1 := 1; c2 := 1; ... c6 := 1;$, which means that we put $c_1 = 1$, $c_2 = 1$, and $b_0 = 1$ for the initial (trivial) planted promolecule. The 3rd paragraph of the code shows a do loop, in which the next coefficients are calculated by using a Maple command coeff and added to the end of respective functional equations so as to generate intermediate generating functions. After escaping from the do loop, the 4th paragraph declares the calculation of $B(x)$ (eq. 14) and $C(x)$ (eq. 16). The 5th paragraph of the code (the final do loop) shows the print-out of the calculation results.

We execute the code by inputting the following command on the Maple inputting window:

```
read "EnumAlkyl1-100RR.mpl";
```
<table>
<thead>
<tr>
<th>$k$</th>
<th>$\alpha_k$ (Chiral)</th>
<th>$\beta_k$ (Chiral + Achiral)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1. Numbers of Monosubstituted Alkanes as Stereoisomers$^a$

$^a$In each value of $C_\alpha$ (Chiral) or $B_\beta$ (Chiral + Achiral), each enantiomeric pair is counted just once for chiral monosubstituted alkanes.
Thereby, we obtain the coefficients $a_k$ (eq. 10) for $a(x)$ (eq. 11), $B_k$ (eq. 12) for $B(x)$ (eq. 14), and $C_k$ (eq. 13) for $C(x)$ (eq. 16), as collected in Table 1.

Rule 2 is implemented as a Maple program for calculating the numbers of planted 3D-trees (monosubstituted alkanes), which are itemized with respect to carbon content (1 to 100).

**Maple program for Rule 2, "Enum2by1-100RR.mpl":**

ax := 1 + x*a1*c2;
cx := 1 + (1/3)*x^2*c2^3 + (2/3)*x^2*c6;
bx := 1 + (1/3)*x*b1^3 + (2/3)*x*b3;
a1 := 1 + x + x^2;
c2 := 1 + x^2 + x^4;
b1 := 1 + x + x^2;
b3 := 1 + x^3 + x^6;
c6 := 1 + x^6 + x^12;
for ccntt from 3 to 100 by 2 do
  ccntt:
  ccntt1:=ccntt+1:
  Cbx:= coeff(bx,x^ccntt):
  Cax:= coeff(ax,x^ccntt):
  Ccx:= coeff(cx,x^(ccntt*2)):
  Cbxn:= Cbx + coeff(bx,x^ccntt1):
  Caxn:= Cax + coeff(ax,x^ccntt1):
  Ccxn:= Ccx + coeff(cx,x^(ccntt1*2)):
  a1 := a1 + Cax*x^ccntt + Caxn*x^ccntt1:
  c2 := c2 + Ccx*x^(ccntt*2) + Ccxn*x^(ccntt1*2):
  b1 := b1 + Cbx*x^ccntt + Cbxn*x^ccntt1:
  b3 := b3 + Cbx*x^(ccntt1*3) + Cbxn*x^(ccntt1*3):
  c6 := c6 + Ccx*x^(ccntt*6) + Ccxn*x^(ccntt1*6):
end do:
BBx := (1/2)*(a1 + b1):
CCx := (1/2)*(b1 - a1):
for ccntt from 1 to 100 by 1 do
  printf("%d & %d & %d & %d \\
", ccntt, coeff(a1,x^ccntt), coeff(CCx,x^ccntt),
coeff(BBx,x^ccntt));
end do;

We execute this code to obtain the coefficients $a_k$ (eq. 10) for $a(x)$ (eq. 11), $B_k$ (eq. 12) for $B(x)$ (eq. 14), and $C_k$ (eq. 13) for $C(x)$ (eq. 16), which are identical with those collected in Table 1.

3 Enumeration of Monosubstituted Alkanes as Graphs

It is worthwhile to mention the difference between the present work and previous results based on Pólya’s theorem. For this purpose, we implement the Pólya’s treatment [4, 5](Section 40) by using the Maple programming language on the same line as the present treatment based on Fujita’s proligand method.

3.1 Implementation of Pólya’s Treatment

Pólya’s treatment has been implicitly based on the condition that substituents for a given skeleton are limited to atoms (or graphs), because it uses the following functional equation:

\[
b_3 := 1 + x^3 + x^6 + 2x^9;
b_6 := 1 + x^6 + x^{12} + 2x^{18};\]

for ccntt from 4 to 100 by 3 do
  ccntt:
  ccntt1:=ccntt+1:
  ccntt2:=ccntt+2:
  Cbx:= coeff(bx,x^ccntt):
  Cax:= coeff(ax,x^ccntt):
  Ccx:= coeff(cx,x^((ccntt*2))):
  Cbxn:= 2*Cbx + Cbxn + coeff(bx,x^ccntt2):
  Caxn:= Caxn + coeff(ax,x^ccntt2):
  Ccxn:= 2*Ccx + Ccxn + coeff(cx,x^((ccntt2*2))):
  a1 := a1 + Cax*x^ccntt + Caxn*x^ccntt1 + Caxn*x^ccntt2:
  c2 := c2 + Ccx*x^((ccntt*2)) + Ccxn*x^((ccntt1*2)) + Ccxn*x^((ccntt2*2)):
  b1 := b1 + Cbx*x^ccntt + Cbxn*x^ccntt1 + Cbxn*x^ccntt2:
  b3 := b3 + Cbx*x^((ccntt1*3)) + Cbxn*x^((ccntt1*3)) + Cbxn*x^((ccntt2*3)):
  c6 := c6 + Ccx*x^((ccntt6)) + Ccxn*x^((ccntt1*6)) + Ccxn*x^((ccntt2*6)):
end do:
BBx := (1/2)*(a1 + b1):
CCx := (1/2)*(b1 - a1):
for ccntt from 1 to 100 by 1 do
  printf("%d & %d & %d & %d \\
", ccntt, coeff(a1,x^ccntt), coeff(CCx,x^ccntt),
coeff(BBx,x^ccntt));
end do;
<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
<th>$k_4$</th>
<th>$k_5$</th>
<th>$k_6$</th>
<th>$k_7$</th>
<th>$k_8$</th>
<th>$k_9$</th>
<th>$k_{10}$</th>
<th>$k_{11}$</th>
<th>$k_{12}$</th>
<th>$k_{13}$</th>
<th>$k_{14}$</th>
<th>$k_{15}$</th>
<th>$k_{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>4</td>
<td>11</td>
<td>17</td>
<td>74</td>
<td>199</td>
<td>551</td>
<td>1553</td>
<td>4436</td>
<td>1238</td>
<td>1282</td>
<td>3746</td>
<td>7639</td>
<td>11050</td>
<td>72160922</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td>199</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td>551</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td>1553</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td>4436</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td>1238</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td>1282</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td>3746</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td>7639</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td>11050</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td>72160922</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Numbers of Monosubstituted Alkanes as Graphs
\[ r(x) = 1 + \frac{x}{6} (r(x)^3 + 2r(x^3) + 3r(x)r(x^2)) \]

(33)

in place of eq. 15. Obviously, eq. 33 is a special case of eq. 15, where we put \( r(x) = t(x) \) in the left-hand side and \( r(x) = b(x) = a(x) = c(x) \) in the right-hand side. As a result, eq. 33 turns out to have recursive nature. The functional equation eq. 33 was first noted by Pólya [4] by using the symmetric group of degree 3 \( (S^3) \), where an equation equivalent to eq. 7 was also derived by using the alternating group of degree 3 \( (A^3) \).

We implement the functional equation (eq. 33) as a Maple program for calculating the numbers of planted trees (monosubstituted alkanes as graphs), which are itemized with respect to carbon content (1 to 100).

Maple program for counting planted trees, "EnumPTr1-100RR.mpl":

```maple
bx := 1 + (1/3)*x*b1^3 + (2/3)*x*b3;
rx := 1 + (1/6)*x*r1^3 + (1/3)*x*r3 + (1/2)*x*r1*r2;

"Initial Values";
b1 := 1;
b3 := 1;
r1 := 1;
r2 := 1;
r3 := 1;

for ccntt from 1 to 100 by 1 do
  ccntt:
  Cbx:= coeff(bx,x^ccntt):
  Crx:= coeff(rx,x^ccntt):
  b1 := b1 + Cbx*x^ccntt:
  b3 := b3 + Cbx*x^ccntt*3:
  r1 := r1 + Crx*x^ccntt:
  r2 := r2 + Crx*x^ccntt*2:
  r3 := r3 + Crx*x^ccntt*3:
end do:

for ccntt from 1 to 100 by 1 do
  printf("%d & %d & %d \\
   
", ccntt, coeff(b1,x^ccntt), coeff(r1,x^ccntt));
end do;
```

We execute this code to obtain the coefficients \( \beta_k \) for \( b(x) \) (eq. 7) and \( R_k \) for \( r(x) \) (eq. 33), as collected in Table 2. It should be noted that the two enantiomers of each pair are counted separately in the evaluation of \( \beta_k \), while structural isomers (constitutional isomers) are counted as graphs in the evaluation of \( R_k \). The results of \( R_k \) up to 20 are identical to those of Henze and Blair [3], the results from carbon content 21 to 30 are identical to those of Perry [27], and the results from carbon up to 50 are identical to those collected in [28](pages 153–154 of Vol. II).

4 Discussions

4.1 Stereoisomers vs. Graphs

Let us exemplify the difference between the enumeration results based on Fujita’s proligand method (Table 1) and those based on Pólya’s theorem (Table 2).
The k = 6 row of Table 1 indicates the presence of 8 achiral monosubstituted alkanes and of 10 enantiomeric pairs of chiral monosubstituted alkanes. The structural formulas of monosubstituted alkanes of carbon content 6 are shown in Figure 3, where either one selected from each pair of enantiomers is depicted as a representative, which is designated by an asterisk. In agreement with the calculation result shown in Table 1, there exist 8 achiral alkanes (4, 8, 11, 12, 13, 17, 19, and 21) and 10 enantiomeric pairs of chiral monosubstituted alkanes (5, 6, 7, 9, 10, 14, 15, 16, 18, and 20).

On the other hand, Table 2 (Rk = 17) indicates the presence of 17 monosubstituted alkanes as graphs (constitutional isomers). The difference between the value and the value of Table 1 (Rk = 18) comes from the presence of diastereoisomers. 14 and 15, which are equalized in the enumeration based on Pólya’s theorem so as to be counted once as one graph. Chemically speaking, 14 and 15 are so congruent as to be regarded as one constitutional (structural) isomer. The value βk = 28 in the k = 6 row of Table 2 can be calculated from the data collected in the k = 6 row of Table 1, i.e., 8 + 10 × 2 = 28, which are the number of stereoisomers, where enantiomers are counted separately.

The k = 7 row of Table 1 indicates the presence of 14 achiral monosubstituted alkanes and of 30 enantiomeric pairs of chiral monosubstituted alkanes. On the other hand, Table 2 indicates the presence of 39 monosubstituted alkanes as graphs. Manual enumeration shows that there are 14 achiral stereoisomers, 20 pairs of enantiomers with one asymmetric carbon, and 5 quartets of diastereomers with two asymmetric carbons. Thereby, we obtain the relationships 14 + 20 × 2 + 5 × 4 = 74 (= β7) and 14 + 20 + 5 = 39 (= R7). Note that β7 can be alternatively calculated by the data of Table 1, i.e., 14 + 30 × 2 = 74 (= β7).

The evaluation of R7 from B7 and C7 would require the evaluation of the number of diastereomeric quartets. In general, the evaluation of Rk from Bk and Ck requires the evaluation of the number of diastereomeric quartets and higher stereoisomeric sets. The latter evaluation is open to further investigation.

4.2 Comments on Earlier Works

Robinson et al. [17] reported the enumeration of monosubstituted alkanes by modifying Pólya’s cycle indices (CIs) as follows:

\[ B(x) = 1 + \frac{2}{6} (r(x)^3 + 2r(x^3) + 3p(x)r(x^3)) \]

(34)

where the \( r(x) \) in eq. 33 is replaced by \( p(x) \) for achiral ligands. However, the transitivity between a chiral ligand and its enantiomeric ligand is specified by the term \( r(x^3) \), which is the same as the term for two chiral ligands of the same chirality. By comparison between eq. 15 and eq. 34, the latter presumes \( p(x) = a(x) \) and \( r(x) = b(x) = c(x) \) in the present context, where the transitivity for \( p/p \) (or \( p/p \)) is mixed up with the transitivity for \( p/p \) (or \( p/p \)) if \( p \) and \( p \) represent a pair of enantiomeric proligands. In other words, their treatment also lacks the concept of sphericities.

An example of erroneous interpretation of transitivity by using eq. 34 is illustrated in Figure 4, where the term \( p(x)r(x^3) \) in eq. 34 corresponds to the action of the permutation (1)(2 3). When we put \( p = R-CH(CH_3)CH_2CH_2 \) and \( p = S-CH(CH_3)CH_2CH_2 \), the formula \( 22 \) represents pseudoasymmetry for carbon content 9. The action of the permutation (1)(2 3) converts \( 22 \) into its diastereomer \( 23 \). This means that \( 22 \) and \( 23 \) are equalized so as to be regarded as one isomer, which is counted just once.

On the other hand, \( 24 \) is converted into the same \( 24 \) by the action of the permutation (1)(2 3). This means that \( 24 \) is counted just once. In a similar way, its enantiomer \( 24 \) is converted into the same \( 24 \) by the action of the permutation (1)(2 3). Thereby, \( 24 \) is counted just once, independent of \( 24 \).

Consequently, in the enumeration based on eq. 34, individual isomers to be counted are \( 22 \) (or \( 23 \)), \( 24 \), and \( 24 \), which contribute by three to the coefficient of the term \( x^3 \). Obviously, the pseudoasymmetry between \( 22 \) and \( 23 \) is not treated properly.
Moreover, Robinson et al. [17] used the following functional equation:

\[ p(x) = 1 + xp(x)r(x^2) \]  
(35)
to enumerate achiral planted 3D-trees. Although this equation is akin to eq. 11, its connotation is entirely different from that of eq. 11. The misunderstanding connotation of eq. 35 stems from an unconscious assumption that the permutation \((1)(2\ 3)\) can be assigned to the reflection operation \(\sigma_{v(1)}\). The term \(r(x^2)\) in eq. 35 means that \(24\) is “achiral” and independently \(24\) is also “achiral” because the permutation \((1)(2\ 3)\) is erroneously assigned to the reflection operation \(\sigma_{v(1)}\), as shown in Figure 4. This means that the set of \(22\) and \(23\) is regarded as one isomer to be counted as “achiral” are \(24\) and \(24\), which contribute by two to the coefficient of the term \(x^9\).

By the same reason, we are forced to say that \(22\) and \(23\) are “chiral” so as to be “enantiomeric” to each other under the action of the permutation \((1)(2\ 3)\) \((\sim \sigma_{v(1)}\) erroneously). This means that the set of \(22\) and \(23\) is regarded as one isomer and counted just once as an “enantiomeric” pair of “chiral” stereoisomers. Note that the term pseudoasymmetry has been coined to explain this type of phenomenon \(22\) vs. \(23\). It can be said that chemical combinatorics based on eq. 35 using the criteria of Figure 4 still remains before the coinage of the term pseudoasymmetry.

In consequence, so long as we rely on eqs. 34 and 35, “achiral” and “chiral” are reversely recognized in cases of pseudoasymmetry, as shown in Figure 4.

In contrast to eqs. 34 and 35, the present enumeration based on Fujita’s proligand method uses eqs. 15 and 11. Because the permutation \((1)(2\ 3)\) is assigned to the reflection operation \(\sigma_{v(1)}\), the case of pseudoasymmetry described above is interpreted in agreement with geometry and point-group theory, as shown in Figure 5.

The action of the permutation \((1)(2\ 3)\) converts \(22\) into itself as shown in Figure 5, because the one-cycle \((1)\) is homospheric and the two-cycle \((2\ 3)\) is enantiospheric. This means that \(22\) is achiral so as to be regarded as one stereoisomer, which is counted just once. On the same line, \(23\) is converted into itself by the action of the permutation \((1)(2\ 3)\), so that it is achiral so as to be regarded as one stereoisomer, which is counted just once.

On the other hand, \(24\) is converted into its enantiomer \(24\) by the action of the permutation \((1)(2\ 3)\). This means that \(24\) and \(24\) are regarded as one pair of enantiomers, which is counted just once.

Consequently, in the enumeration based on eq. 15, individual isomers to be counted are \(22, 23, 24\) (as one enantiomeric pair with \(24\), which contribute by three to the coefficient of the term \(x_0\). Thus the pseudoasymmetry between \(22\) and \(23\) is treated properly.

In Fujita’s proligand method, the term \(c(x^2)\) in eq. 11 corresponds to the enantiosphericity, so that \(22\) is achiral and independently \(23\) is also achiral, because the permutation \((1)(2\ 3)\) is correctly assigned to the reflection operation \(\sigma_{v(1)}\), as found in Figure 5. Hence, in the enumeration based on eq. 11, individual isomers to be counted as being achiral are \(22\) and \(23\), which contribute by two to the coefficient of the term \(x^9\).

\[
\begin{align*}
H^1 & \quad P^1 & \quad P^1 \\
\text{achiral} & \quad \text{achiral} & \\
22 & \quad 22
\end{align*}
\]

\[
\begin{align*}
H^1 & \quad P^2 & \quad P^2 & \quad P^2 \\
\text{chiral} & \quad \text{achiral} & \\
23 & \quad 22
\end{align*}
\]

\[
\begin{align*}
H^1 & \quad P^2 & \quad P^2 & \quad P^2 \\
\text{chiral} & \quad \text{achiral} & \\
24 & \quad 24
\end{align*}
\]

Figure 5. Correct interpretation of transitivity which comes from the permutation \((1)(2\ 3)\) assigned properly to \(\sigma_{v(1)}\).

In the enumeration based on eq. 17, a set of \(24\) and \(24\) is counted just once as one pair of enantiomers, which contribute by one to the coefficient of the term \(x^9\).

The enumeration based on the modified Pólya’s CIs (eq. 34 etc.) fortunately gives the same isomer numbers as obtained by means of Fujita’s CI-CFs (eq. 15 etc.). Enumeration of the two types provides the apparently same contribution (e.g., three to the coefficient of the term \(x^9\)) because such a relationship between Figure 4 and Figure 5 holds true for any case of pseudoasymmetry. It should be noted, however, that the content of the former enumeration (cf. Figure 4) is quite different from the content of the latter enumeration (cf. Figure 5). Thus, the former enumeration erroneously shows the presence of one “chiral” isomer \(22\) (or \(23\)) and two “achiral” isomers \(24\) and \(24\), which contribute by three to the coefficient of the term \(x^9\) (Figure 4). The latter enumeration correctly shows the presence of two achiral isomers \(22\) and \(23\) and one chiral isomer \(24\) (as one enantiomeric pair with \(24\)).
which contribute by three to the coefficient of the term $x^9$ (Figure 5).

The discussions described in this section have clearly shown that Fujita’s proligand method [12–14] is concerned with the enumeration of stereoisomers (3D-objects), while Pólya’s theorem [4, 5] is concerned with the enumeration of constitutional isomers (graphs). The difference between the two methodologies stems from the presence/absence of the sphericity concept so that Fujita’s proligand method involves Pólya’s theorem as a special case without sphericity. Moreover, it has been shown that the modification of Pólya’s theorem by Robinson et al. [17] has failed in the proper treatment of pseudoasymmetric cases because of the lack of the sphericity concept.

4.3 Comments on a Stereochemical Convention

It is worthwhile to mention a stereochemical convention in comparison with the methodology adopted in the present approach. The IUPAC nomenclature (1996) [29] defines terms on stereoisomerism as follows:

1. (Def. 1) The term stereoisomerism is defined as “Isomerism due to differences in the spatial arrangement of atoms without any differences in connectivity or bond multiplicity between the isomers” [29](page 221). The related term stereoisomers is defined as “Isomers that possess identical constitution, but which differ in the arrangement of their atoms in space. See enantiomer, diastereoisomer, cis-trans isomers”.

2. (Def. 2) The term enantiomerism is defined as “The isomerism of enantiomers” [29](page 2207). The related term enantiomer is defined as “One of a pair of molecular entities which are mirror images of each other and non-superposable. See also enantiomorphism” [29](page 2207).

Because the term “stereoisomer” (Def. 1) is concerned with a relationship between two compounds (as 3D-objects), the relevant term “stereoisomer” is incapable of specifying a compound (a 3D-object) without another 3D-object stereoisomeric to it. For example, 22 is not a “stereoisomer” by itself; 22 can be called a “stereoisomer” just when 23 is taken into consideration. Thereby, we are able to say that the compounds 22 and 23 are “stereoisomers”. In a similar way, 24 cannot be a “stereoisomer” nor an “enantiomer” by itself; the 24 can be called a “stereoisomer” or an “enantiomer” just when 22 (or 23) and/or 24 is taken into consideration. In the literal sense of the word “stereoisomer” defined in Def. 1, therefore, the expression “the number of stereoisomers” is permitted if a reference compound (e.g., 22) is given or if a common skeleton for generating stereoisomers is specified. When there exist two or more skeletons to be considered, therefore, the consideration of “the number of stereoisomers” is unsuitable for a systematic approach so as to require complicated treatments of various cases. In particular, the present enumeration problem for counting monosubstituted alkanes must consider an infinite number of skeletons which grow in their varieties in accord with the increase of carbon contents from zero to infinite. Then, what is aimed at by the expression “Numbers of Monosubstituted Alkanes as Stereoisomers”?

Obviously, Def. 1 contains two viewpoints, i.e., one viewpoint to recognize differences which are referred to by the expression “the differences in the spatial arrangement of atoms” and the other viewpoint to recognize equivalences which are referred to by the expression “without any differences in connectivity or bond multiplicity”. However, a stereochemical convention tends to put emphasis on the viewpoint of “differences”. On the same line, Def. 2 is mostly used in a context that enantiomers are non-superposable (i.e., different) instead of referring to their mirror-image equivalence. So long as we obey the tendency of the stereochemical convention, it is difficult to count “different” objects, as found easily. In contrast, the present approach puts emphasis on equivalence classes (e.g., sets of compounds equivalent under Def. 1 or Def. 2) so that such equivalence classes can be counted by employing group theory.

From a viewpoint of the group theory which the present approach employs, the emphasis of “differences” in the stereochemical convention implies that the alternating group of degree 3 ($A_3$) is used to recognize stereoisemical “equivalence”. Under the action of $A_3$, two enantiomers of each pair are different from each other, so that they are counted separately, as found in the $eta_2$-column of Table 2. Although the values collected in the $eta_{k2}$-column of Table 2 are adopted as “the numbers of stereoisomers” in terms of the stereochemical convention or as “the numbers of steric trees” in terms of the combinatorial enumeration by Pólya [4] and by Robinson et al. [17], we should mention several comments:

1. The use of $A_3$ is incapable of recognizing the chiral or achiral nature of each counted isomer. For example, the chirality of 22 (or 23) and the chirality of 24 are not recognized properly under the action of $A_3$. The recognition of chirality/chiarity necessitates subsequent manual examination by stereochemists.

2. The use of $A_3$ is incapable of recognizing enantiomeric relationships. For example, the enantiomeric relationship between 24 and 24 is not recognized properly under the action of $A_3$. The recognition of enantiomeric relationships again necessitates subsequent manual examination by stereochemists.
3. What is the subsequent manual examination described in the above-mentioned comments? In the stereochemical convention, the manual examination for recognizing achirality (e.g., \(22\) or \(23\)), chirality (e.g., \(24\) or \( \overline{24} \)), and enantiomeric relationship (e.g., between \(24\) and \( \overline{24} \)) is to consider the mirror image of each 3D-object. However, concrete processes of considering mirror images have not been fully formulated from the viewpoint of group theory.

4. Even if we adopt the symmetric group of degree 3 \(S^3\), the recognition of chirality/chirality and enantiomeric relationships has proved futile, as discussed in Section 3. The enumeration of this type has given the numbers of graphs, as shown in the \(R_k\)-column of Table 2.

5. Even by the attempt in which the symmetric group of degree 3 \(S^3\) was used after modification [17], insufficient interpretations on chirality/chirality and on enantiomeric relationships took place, as discussed in Subsection 4.2.

These comments reveal why the stereochemical convention has adopted the values \(\beta_k\) (Table 2) as the numbers of stereoisomers. That is to say, the stereochemical convention lacks a mathematical formulation for recognizing chirality/chirality and enantiomeric relationships so that the convention is forced to rely on the alternating group of degree 3 \(A^3\).

In contrast, the present approach puts emphasis on “equivalences” or more precisely on “equivalence classes”, which are frequently called orbits in a mathematical context. The crux of the present approach is to use RCRs \((C_4\backslash C_{3v})\) and \((C_1\backslash C_3)\) (cf. Figure 2) in place of \(S^3\) and \(A^3\). As shown in Figure 5, for example, the use of \(\{1\}(\{2,3\})\) assigned to \(\sigma_v(1)\) is capable of treating the achirality of \(22\) (or \(23\)), which is superposable on its mirror image so as to be self-enantiomeric. The use of \(\{1\}(\{2,3\})\) is also capable of treating the enantiomeric relationship between \(24\) and \( \overline{24} \), which is characterized as being in a mirror-image relationship. Thereby, the manual examinations described above are formulated by the RCR \((C_4\backslash C_{3v})\).

In terms of the present methodology, stereoisomer enumeration is concerned with the numbers of equivalence classes under the action of the RCR \((C_4\backslash C_{3v})\). Note that the achiral compound \(22\) (or \(23\)) constructs an equivalence class under the action of \((C_4\backslash C_{3v})\), where the achiral compound is counted just once. On the same line, the pair of \(24\) and \( \overline{24} \) constructs an equivalence class under the action of \((C_4\backslash C_{3v})\), where the pair is counted just once. It follows that each value in the \(C_k\)-column and the \(B_k\)-column of Table 1 represents the number in which each achiral compound is counted just once and each enantiomeric pair is counted just once.

Consequently, the expression “Numbers of Monosubstituted Alkanes as Stereoisomers” (i.e., the title of this article) is permissible if the phrase “as Stereoisomers” is used as a simplified expression of the phrase “under the criterion of stereoisomerism” (cf. Def. 1) or more precisely “under the criterion of enantiomerism” (cf. Def. 2). The phrase “under the criterion of enantiomerism” means the action of the RCR of a point group, e.g., \((C_4\backslash C_{3v})\). This viewpoint means that enumeration concerned with stereoisomers should be done on the basis of equivalence classes provided “under the criterion of stereoisomerism” (cf. Def. 1) or more precisely “under the criterion of enantiomerism” (cf. Def. 2). More mathematically speaking, the enumeration concerned with stereoisomers should be done on the basis of equivalence classes provided by point groups through such RCRs as \((C_4\backslash C_{3v})\).

When two enantiomers of each pair are counted separately according to the stereochemical convention, the value \(2C_k\) is used for counting chiral compounds; and the value \(C_k + C_k (= \beta_k)\) is used for counting achiral and chiral compounds. These values should be adopted under the implicit restrictions described above for the stereochemical convention.

5 Conclusion

Planted three-dimensional (3D) trees or equivalently monosubstituted alkanes as stereoisomers are regarded as planted promolecules, which are enumerated by Fujita’s proligand method [12–14]. Cycle indices with chirality fittingness (CI-CFs), which are composed of three kinds of sphericity indices (SIs), i.e., \(c_d\) for homospheric cycles, \(c_d\) for enantiospheric cycles, and \(b_d\) for hemispheric cycles, are used to obtain generating functions for calculating planted 3D-trees. Functional equations \(a(x), c(x^2)\), and \(b(x)\) for recursive calculations are derived from the CI-CFs and programmed by means of the Maple programming language. Thereby, recursive calculations of the numbers of planted 3D-trees (or equivalently those of monosubstituted alkanes as stereoisomers) are executed and collected up to 100 carbon content in a tabular form. The results are compared with the enumeration of planted trees (as graphs).

We gratefully acknowledge the financial support given to our recent project by the Japan Society for the Promotion of Science: Grant-in-Aid for Scientific Research B (No. 18300033, 2006).

http://www.sccj.net/publications/JCCJ/
References