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Alkanes as Stereoisomers. Enumeration by the Combination of Two Dichotomies for Three-Dimensional Trees

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Abstract

Alkanes as stereoisomers are categorized according to the dichotomy between centroidal and bicentroidal three-dimensional trees (3D-trees), which are distinctly counted by means of Fujita's proligand method (S. Fujita, *Theor. Chem. Acc.*, **113**, 73–79, 80–86 (2005); S. Fujita, *Theor. Chem. Acc.*, **115**, 37–53 (2006)). The centroidal 3D-trees are enumerated by using a tetrahedral skeleton of $\mathbf{T}_d$-symmetry, while the bicentroidal 3D-trees are enumerated by using a binuclear skeleton of $\mathbf{D}_{\infty h}$-symmetry. The enumerations based on the two skeletons are conducted by means of respective functional equations derived from cycle indices with chirality fittingness (CI-CFs), where the functions $a(x^d)$, $c(x^d)$, and $b(x^d)$ are substituted for three kinds of sphericity indices (SIs), i.e., a_d for homospheric cycles, c_d for enantiospheric cycles, and b_d for hemispheric cycles. The 3D-trees are alternatively counted by using the dichotomy between balanced and unbalanced 3D-trees. The two dichotomies are combined to categorize the 3D-trees into three categories, i.e., centroidal & unbalanced 3D-trees, bicentroidal & unbalanced 3D-trees, and bicentroidal & balanced 3D-trees, which are counted distinctly by using respective functional equations. These functional equations are programmed by means of the Maple programming language and executed to give respective stereoisomer numbers, which are collected in tabular forms up to carbon content 100. These numbers of stereoisomers obtained by Fujita's proligand method are compared with those of constitutional isomers (graphs) derived by using Pólya's theorem.

1 Introduction

Enumeration of alkanes is one of typical interdisciplinary problems which have variously been investigated by chemists and mathematicians, as described in books [1–4] and reviews [5–8]. Among their contributions, we should refer to the works done by Cayley [9, 10], Henze and Blair [11, 12], Pólya [13, 14], and Otter [15]. In particular, Pólya's theorem [13, 14] has been widely used in solving the enumeration problem as well as related ones, where Pólya's cycle indices (CIs) were used in connection with permutation groups. The dependence of Pólya's theorem upon permutation groups means that enumeration results were concerned with constitutional isomers, which were regarded as trees (graphs) in a mathematical context. Because the permutation groups disregarded inner structures of ligands, stereochemical problems such as pseudoasymmetry and *meso*-compounds were not treated properly. Later, Robinson et al. [16] reported the enumeration of alkanes as stereoisomers by modifying Pólya's cycle indices (CIs). Even their treatment, however, did not take account of problems due to the inner structures of ligands, e.g., pseudoasymmetry and *meso*-compounds.

By integrating permutation groups with point groups, we have developed the USCI (unit-subduced-cycle-index) approach [17], where we put emphasis on conjugate subgroups so as to give the concept of *sphericities of orbits*. The integration of the two branches of group theory has otherwise provided us with an additional approach named the *proligand method* [18–20], where we put emphasis on conjugacy classes so as to transform the concept of *sphericities of orbits* into the concept of *sphericities of cycles*. The concept of *sphericities of orbits* in Fujita's USCI approach [17] and the concept of *sphericities of cycles* in Fujita's proligand method [18–20] are both capable of treating the inner structures of ligands properly and of solving such problems as pseudoasymmetry and *meso*-compounds.

In this paper, we discuss the aforementioned enumeration of alkanes as a probe for testifying the versatility of Fujita's proligand method in comparison with Pólya's theorem. Thus, we enumerate alkanes as stereoisomers in contrast to alkanes as constitutional isomers, where we write and execute programs for counting them by using the Maple programming language after a succinct description of Fujita's proligand method. We discuss the enumeration on the basis of the dichotomy between centroidal and bicentroidal 3D-trees as well as the dichotomy between balanced and unbalanced 3D-trees. We show that the combination of the two dichotomies provides us with a versatile tool for counting alkanes as stereoisomers.

2 Two Dichotomies for Categorizing 3D-Trees

In the present paper, we adopt two dichotomies for categorizing trees (or 3D-trees), i.e., the dichotomy between centroidal and bicentroidal trees (or 3D-trees) and the dichotomy between balanced and unbalanced trees (or 3D-trees).

2.1 Centroidal and Bicentroidal 3D-Trees

A tree (or a 3D-tree) is defined usually as a graph (or a 3D-object) which has v vertices and e edges satisfying the relation $v = e + 1$. Let m be the number of vertices contained in the largest branch among the branches attaching to the vertex. According to Jordan [21], there are two cases:

1. A given tree (or 3D-tree) has an exceptional vertex (M) called a *centroid* if it satisfies the relationship $m < \frac{1}{2}v$. The tree (or 3D-tree) is called a *centroidal tree* (or *centroidal 3D-tree*).

2. A given tree (or 3D-tree) has two adjacent vertices (M_1 and M_2), each of which satisfies the relationship $m = \frac{1}{2}v$. The exceptional graph (M_1—M_2) composed of the two adjacent vertices and the relevant edge is called a *bicentroid*. The tree (or 3D-tree) is called a *bicentroidal tree* (or *bicentroidal 3D-tree*).

Thereby, trees (or 3D-trees) are classified into two categories, i.e., centroidal trees (or 3D-trees) and bicentroidal trees (or 3D-trees).

All of the vertices of the tree (or 3D-tree) other than the centroid or the bicentroid satisfy the relationship $m > \frac{1}{2}v$. There are no cases in which a given tree (or 3D-tree) has both a centroid and a bicentroid so that a kind of dichotomy takes place.

According to Jordan [21], there is another dichotomy for categorizing trees. i.e., the dichotomy between central and bicentral trees. To the best of our knowledge, this dichotomy has not been explicitly used for counting trees. Hence, we do not adopt the dichotomy between central and bicentral trees in the present paper.

2.2 Balanced and Unbalanced 3D-Trees

As a new dichotomy which is applicable to the enumeration of trees or 3D-trees, we have recently developed the dichotomy between balanced and unbalanced trees (or 3D-trees). Because we have submitted a paper on the new dichotomy to this journal as a successive paper, we will omit its detailed features in the present paper. However, we should refer to a minimum set of findings in order to discuss the combination of the two dichotomies, i.e., the dichotomy between centroidal and bicentroidal trees (or 3D-trees) and the dichotomy between balanced and unbalanced trees (or 3D-trees).

The crux of the new dichotomy is the absence or presence of a balance-edge, in which the two branch incident to the balance-edge are congruent to each other under the action of $\mathbf{D}_{\infty h}$ or more precisely under the action of the factor group $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$. A 3D-tree which has a balance-edge is called a *balanced 3D-tree*; otherwise a 3D-tree is called an *unbalanced 3D-tree*.

Such balanced 3D-trees are represented by X—X, p—p (paired with $\overline{\mathrm{p}}$—$\overline{\mathrm{p}}$), or p—$\overline{\mathrm{p}}$, where the symbol X represents an achiral proligand or ligand; the symbols p and $\overline{\mathrm{p}}$ represent a pair of enantiomeric proligands or ligands; and each linking bond is a balance-edge. As found easily, achiral balanced 3D-trees have the formula X—X or p—$\overline{\mathrm{p}}$, the latter of which corresponds to *meso*-compounds. On the other hand, chiral balanced 3D-trees are represented by the formula p—p paired with the corresponding enantiomeric formula $\overline{\mathrm{p}}$—$\overline{\mathrm{p}}$.

Bicentroidal 3D-trees other than the aforementioned balanced trees are represented by X—Y, X—p (paired with X—$\overline{\mathrm{p}}$), and p—q (paired with $\overline{\mathrm{p}}$—$\overline{\mathrm{q}}$). Note that the symbols X and Y represent achiral proligands or ligands, while the symbols p (or $\overline{\mathrm{p}}$) and q represent chiral proligands, where the pair of ligands in each bicentroidal 3D-tree, i.e., X and Y, X and p, or p and q, has the same carbon content.

3 Alkanes as Centroidal and Bicentroidal 3D-Trees

3.1 Alkyl Ligands as 3D-Components

To enumerate alkanes as stereoisomers, the enumeration data of alkyl ligands as components should be conducted as prerequisites. Although the derivation of the data is not described in detail, functional equations necessary to count alkyl ligands are described briefly.

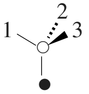
We use the symbols $a(x)$, $c(x)$, and $b(x)$ to represent generating functions for counting respective numbers:

$$a(x) = \sum_{k=0}^{\infty} \alpha_k x^k \tag{1}$$

$$c(x^2) = \sum_{k=0}^{\infty} \gamma_{2k} x^{2k} \tag{2}$$

$$b(x) = \sum_{k=0}^{\infty} \beta_k x^k, \tag{3}$$

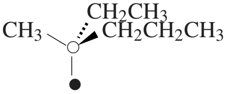
where the coefficient (α_k) of the term x^k in the counting series $a(x)$ represents the number of achiral alkyl ligands (or planted 3D-trees) of carbon content k; the coefficient (γ_{2k}) of the term x^{2k} in the counting series $c(x^2)$ represents the number of diploids of carbon content $2k$, in which an achiral alkyl ligand or a pair of enantiomeric alkyl ligands (or planted 3D-trees) is counted once; and finally the coefficient (β_k) of the term x^k in the counting series $b(x)$ represents the number of achiral and chiral alkyl ligands (or planted 3D-trees) of carbon content k, in which two enantiomers of each pair are separately counted. We put $\alpha_0 = 1$, $\gamma_0 = 1$, and $\beta_0 = 1$ to treat trivial cases of terminal vertices (or hydrogen atoms).



1

$\mathbf{C}_{3v}$-skeleton

($\mathbf{C}_{3v}(/\mathbf{C}_s)$)



2

alkyl ligand

planted 3D-tree

Figure 1: $\mathbf{C}_{3v}$-skeleton (**1**) with three substitution positions and an alkyl ligand (3-methylhex-3-yl ligand) as a planted 3D-tree (**2**). A solid circle (●) represents a root, while an open circle (○) represents a principal node, which is a carbon atom carrying three substitution positions.

Fujita's proligand method [18–20] is applied to this case, where we start from a methyl skeleton (**1**) belonging to $\mathbf{C}_{3v}$-point group. Any alkyl ligand can be regarded as a planted 3D-tree, which is constructed by substitution of inner alkyl ligands for the three positions (1–3) of the methyl skeleton (**1**), where the process of substitution has nested (recursive) nature. For example, a 3-methylhex-3-yl ligand (**2**) is regarded as a methyl skeleton having methyl, ethyl, and propyl ligands, each of which can be regarded as a methyl skeleton having respective inner alkyl ligands.

The three positions (1–3) of the methyl skeleton (**1**) construct an orbit governed by a coset representation (CR) $\mathbf{C}_{3v}(/\mathbf{C}_s)$. Each cycle contained in the permutations of the CR is characterized by sphericity so as to be categorized into a homospheric cycle, an enantiospheric cycle, or a hemispheric cycle. The sphericity is specified by a sphericity index (SI), i.e., a_d for a homospheric cycle, c_d for an enantiospheric cycle, or b_d for a hemispheric cycle. Then a product of SIs is assigned to each permutation of the CR according to its cycle structure. Such products of SIs are summed up to cover all of the symmetry operations of $\mathbf{C}_{3v}$ and then averaged by $|\mathbf{C}_{3v}| = 6$ so as to give the corresponding cycle indices with chirality fittingness (CI-CF). Other relevant CI-CFs for the $\mathbf{C}_{3v}$-skeleton are obtained according to Fujita's proligand method [18–20] and they are transformed into the following functional equations:

$$a(x) = 1 + xa(x)c(x^2) \tag{4}$$

$$c(x^2) = 1 + \frac{x^2}{3}\left(c(x^2)^3 + 2c(x^6)\right) \tag{5}$$

$$b(x) = 1 + \frac{x}{3}\left(b(x)^3 + 2b(x^3)\right), \tag{6}$$

where the sphericity indices (a_d, c_d, and b_d) of the CI-CFs are replaced by $a(x^d)$, $c(x^d)$, and $b(x^d)$. These equations have recursive nature.

Let B_k be the number of achiral and chiral alkyl ligands (planted promolecules) of carbon content k, where each pair of enantiomers is counted just once. Let C_k be the number of chiral alkyl ligands (planted promolecules) only, where each pair of enantiomers is counted just once. They are represented by the coefficients of the following generating functions:

$$B(x) = \sum_{k=0}^{\infty} B_k x^k \tag{7}$$

$$C(x) = \sum_{k=0}^{\infty} C_k x^k, \tag{8}$$

where we put $B_0 = 1$ and $C_0 = 0$ to treat a trivial case of carbon content 0. Because we can place $B_k = \alpha_k + C_k$ and $\beta_k = \alpha_k + 2C_k$, eq. 4 (for $a(x)$) and eq. 6 (for $b(x)$) are combined to give the following equations:

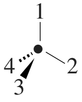
$$B(x) = \frac{1}{2}\left(a(x) + b(x)\right) \tag{9}$$

$$C(x) = \frac{1}{2}\left(b(x) - a(x)\right). \tag{10}$$

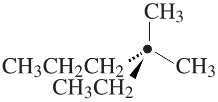
3.2 Enumeration of Centroidal 3D-Trees

3.2.1 CI-CFs for Centroidal 3D-Trees

The four substitution positions (numbered as 1–4) of a tetrahedral skeleton (**3**) construct an orbit governed by a CR $\mathbf{T}_d(/\mathbf{C}_{3v})$. They accommodate a set of ligands to give a centroidal derivative belonging to a subgroup of $\mathbf{T}_d$ in agreement with the sphericities of desymmetrized orbits. For example, 3,3-dimethylhexane (**3**) is a centroidal alkane derived by the substitution of two methyl, one ethyl, and one propyl ligands, where the longest branch (the propyl ligand) satisfies the relationship for centroidal 3D-trees, i.e., $3 < (1/2) \times 8$ in this case.



3



4

Figure 2: $\mathbf{T}_d$-skeleton (**3**) with four substitution positions and a centroidal alkane (3,3-dimethylhexane) as a 3D-tree (**4**). An solid circle (•) represents a centroid, which is a carbon atom carrying four substitution positions.

Following Fujita's proligand method [18–20], Theorem 1 of [20] is applied to the enumeration of tetrahedral promolecules under the action of $\mathbf{T}_d$ point group. Thereby, the cycle index with chirality fittingness (CI-CF) for counting achiral promolecules and enantiomeric pairs of chiral promolecules is calculated as follows:

$$\begin{aligned}&\text{CI-CF}(\mathbf{T}_d; a_d, b_d, c_d)\\ &= \frac{1}{24}(b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4),\end{aligned} \tag{11}$$

where each pair of enantiomers is counted just once in this enumeration.

Theorem 3 of [20] for the enumeration of ligands under the action of the maximum chiral subgroup (**T**) can be applied to this case for counting achiral promolecules and chiral promolecules. The following CI-CF is obtained:

$$\text{CI-CF}(\mathbf{T}; b_d) = \frac{1}{12}(b_1^4 + 3b_2^2 + 8b_1b_3), \tag{12}$$

where two enantiomers of each pair are counted separately.

The first proposition of Theorem 4 for the enumeration of achiral ligands [20] can be applied to this case for counting achiral promolecules only. The following CI-CF$_A$ is obtained:

$$\begin{aligned}&\text{CI-CF}_A(\mathbf{T}_d; a_d, b_d, c_d)\\ &= 2\text{CI-CF}(\mathbf{T}_d, a_d, b_d, c_d) - \text{CI-CF}(\mathbf{T}, b_d)\\ &= \frac{1}{2}(a_1^2c_2 + c_4).\end{aligned} \tag{13}$$

The second proposition of Theorem 4 for the enumeration of chiral ligands [20] can be applied to obtain the following CI-CF$_C$ for counting chiral promolecules only:

$$\begin{aligned}&\text{CI-CF}_C(\mathbf{T}_d; a_d, b_d, c_d)\\ &= \text{CI-CF}(\mathbf{T}; b_d) - \text{CI-CF}(\mathbf{T}_d; a_d, b_d, c_d)\\ &= \frac{1}{24}(b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 - 6c_4)\end{aligned} \tag{14}$$

where each pair of enantiomers is counted just once.

3.2.2 Functional Equations for Counting Centroidal 3D-Trees

Fujita's proligand method teaches us that eqs. 11–14 are used to count promolecules having various proligands as substituents. To enumerate alkanes as stereoisomers, such proligands are replaced by alkyl ligands represented by the generating functions (eqs. 1–3). These generating functions are in turn evaluated by using the functional equations (eqs. 4–6).

Let $\widehat{B}_k$ be the number of achiral and chiral centroidal 3D-trees (promolecules or alkanes) of carbon content k, where a pair of enantiomeric 3D-trees is counted just once. Let $\widehat{A}_k$ be the number of achiral centroidal 3D-trees (promolecules or alkanes) of carbon content k. Let $\widehat{C}_k$ be the number of chiral centroidal 3D-trees (promolecules or alkanes) of carbon content k, where a pair of enantiomeric 3D-trees is counted just once. In agreement with the definition of centroidal 3D-trees, the terms up to x^v are collected to give the following generating functions:

$$\widehat{B}(x) = \sum_{k=0}^{v} \widehat{B}_k x^k \tag{15}$$

$$\widehat{A}(x) = \sum_{k=0}^{v} \widehat{A}_k x^k \tag{16}$$

$$\widehat{C}(x) = \sum_{k=0}^{v} \widehat{C}_k x^k, \tag{17}$$

where v runs stepwise from 0 to infinite. Note that eq. 11 corresponds to eq. 15, eq. 13 to eq. 16, and eq. 14 to eq. 17.

Because eq. 11 corresponds to eq. 15, the SIs a_d, c_d, and b_d involved in eq. 11 are replaced by the terms $a(x^d)$, $c(x^d)$, and $b(x^d)$ respectively. Thereby we obtain the following functional equation:

$$\widehat{B}(x) = \frac{x}{24}\left\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3) + 6a(x)^2c(x^2) + 6c(x^4)\right\}, \tag{18}$$

where the multiplying by x is necessary because eq. 11 ignores the centroid of the $\mathbf{T}_d$ skeleton tentatively.

Because eq. 13 corresponds to eq. 16, a similar substitution gives the following functional equation:

$$\widehat{A}(x) = \frac{x}{2}\left(a(x)^2c(x^2) + c(x^4)\right). \tag{19}$$

By the correspondence of eq. 14 to eq. 17, we obtain the following functional equation:

$$\widehat{C}(x) = \frac{x}{24}\left\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3) - 6a(x)^2c(x^2) - 6c(x^4)\right\}. \tag{20}$$

Our target is to evaluate eqs. 18–20 by using eqs. 4–6 under the criterion for centroidal 3D-trees. We should examine the coefficient of the term x^v appearing in series generated from eq. 18, 19, or 20. The criterion for centroidal 3D-trees means that the maximum number (m), which is the number of non-terminal vertices in the largest proligand, is restricted to satisfy the following condition:

$$\frac{1}{2}v - 1 \leq m < \frac{1}{2}v \tag{21}$$

or equivalently

$$2m < v \leq 2m + 2 \tag{22}$$

Suppose that eqs. 4–6 have been evaluated up to the term x^m. They are introduced into the right-hand sides of eqs. 18–20 and the resulting equations are expanded to give respective series for $\widehat{B}(x)$ (eq. 15), $\widehat{A}(x)$ (eq. 16), and $\widehat{C}(x)$ (eq. 17). Because of eq. 22, the coefficients of the terms x^{2m+1} and x^{2m+2} in the series are effective to determine $\widehat{B}_{2m+1}$ and $\widehat{B}_{2m+2}$; $\widehat{A}_{2m+1}$ and $\widehat{A}_{2m+2}$; as well as $\widehat{C}_{2m+1}$ and $\widehat{C}_{2m+2}$.

It should be noted that eqs. 15–17 are evaluated by eqs. 18–20 only if the relationship of eq. 22 is satisfied. Strictly speaking, eqs. 18–20 up to the term x^{2m+2} are only effective to evaluate the coefficients of the terms x^{2m+1} and x^{2m+2} appearing in eqs. 15–17. Suppose that we have obtained $a(x) = \sum_{k=0}^{m} \alpha_k x^k$, $c(x^2) = \sum_{k=0}^{m} \gamma_{2k} x^{2k}$, and $b(x) = \sum_{k=0}^{m} \beta_k x^k$, where m is tentatively fixed. They are introduced into eqs. 18–20 to give $\widehat{B}(x)^{(m)}$, $\widehat{A}(x)^{(m)}$, and $\widehat{C}(x)^{(m)}$, respectively. Let the symbol coeff$(\widehat{B}(x)^{(m)}, x^{2m+1})$ etc. represent the coefficient of the term x^{2m+1} appearing in the equation $\widehat{B}(x)^{(m)}$ etc. after expansion. Then, we obtain the following coefficients:

$$\begin{aligned}
\widehat{B}_{2m+1} &= \mathrm{coeff}(\widehat{B}(x)^{(m)}, x^{2m+1}) \qquad (23)\\
\widehat{A}_{2m+1} &= \mathrm{coeff}(\widehat{A}(x)^{(m)}, x^{2m+1}) \qquad (24)\\
\widehat{C}_{2m+1} &= \mathrm{coeff}(\widehat{C}(x)^{(m)}, x^{2m+1}) \qquad (25)
\end{aligned}$$

for odd carbon contents as well as the following coefficients:

$$\begin{aligned}
\widehat{B}_{2m+2} &= \mathrm{coeff}(\widehat{B}(x)^{(m)}, x^{2m+2}) \qquad (26)\\
\widehat{A}_{2m+2} &= \mathrm{coeff}(\widehat{A}(x)^{(m)}, x^{2m+2}) \qquad (27)\\
\widehat{C}_{2m+2} &= \mathrm{coeff}(\widehat{C}(x)^{(m)}, x^{2m+2}) \qquad (28)
\end{aligned}$$

for even carbon contents. These requirements should be considered in the following programming.

3.2.3 Implementation and Calculations for Counting Centroidal 3D-Trees

By using the Maple programming language [22], we wrote a program for evaluating $a(x)$ (by eq. 4), $c(x^2)$ (by eq. 5), and $b(x)$ (by eq. 6) and for obtaining the coefficients $\widehat{B}_k$ (eq. 15), $\widehat{A}_k$ (eq. 16), and $\widehat{C}_k$ (eq. 17). The program was stored in a file named "Centroid1-100A.mpl", which was executed by by inputting as follows:

```
read "Centroid1-100A.mpl";
```

The results are shown in Table 1, where the values of $\widehat{B}_k$ for centroidal 3D-trees, those of $\widehat{A}_k$ for achiral centroidal 3D-trees, and those of $\widehat{C}_k$ for chiral centroidal 3D-trees are collected up to carbon content $k = 100$.

Maple program for counting centroidal 3D-trees, "Centroid1-100A.mpl":

```
"Functional Equations for Alkyl Ligands";
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;

"Alkanes as Centroidal 3D-Trees";
Bxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 + 6*a1^2*c2 + 6*c4):
Axh := (x/2)*(a1^2*c2 + c4):
Cxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 - 6*a1^2*c2 - 6*c4):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;
Bh := x; Ah := x; Ch := 0;
```

```
"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 +Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m +1:
Bh := Bh + coeff(Bxh,x^n)*x^n + coeff(Bxh,x^(n+1))*x^(n+1):
Ah := Ah + coeff(Axh,x^n)*x^n + coeff(Axh,x^(n+1))*x^(n+1):
Ch := Ch + coeff(Cxh,x^n)*x^n + coeff(Cxh,x^(n+1))*x^(n+1):
end do:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Bh,x^m), coeff(Ah,x^m), coeff(Ch,x^m));
end do;
```

The first paragraph of this code “Functional Equations for Alkyl Ligands” declares the functional equations: `ax` for $a(x)$ (by eq. 4), `cx` for $c(x^2)$ (by eq. 5), and `bx` for $b(x)$ (by eq. 6). The second paragraph of this code “Alkanes as Centroidal 3D-Trees” declares the functional equations: `Bxh` for $\widehat{B}(x)$ (eq. 18), `Axh` for $\widehat{A}(x)$ (eq. 19), and `Cxh` for $\widehat{C}(x)$ (eq. 20). The third paragraph “Initial Values” sets initial values for recursive calculations. The fourth paragraph “Recursive Calculation” shows a `do` loop for recursive calculations of the functional equations described above. The variables `Bh`, `Ah`, and `Ch` are used to store the series represented by eqs. 15–17, whose coefficients (for eqs. 23–25 and eqs. 26–28) are printed out in the last paragraph “Print-Out”.

Note that the `do` loop of the fourth paragraph moves m from 1 to 50 in oder to calculate $\widehat{B}_k$ (eq. 15), $\widehat{A}_k$ (eq. 16), and $\widehat{C}_k$ (eq. 17) up to carbon content 100. This stems from the condition represented by eq. 22 due to the criterion of centroidal 3D-trees.

3.3 Enumeration of Bicentroidal 3D-Trees

3.3.1 CI-CFs or Bicentroidal 3D-Trees

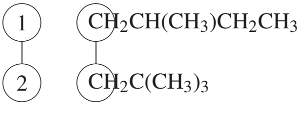
In order to enumerate bicentroidal 3D-trees, we consider a dumbbell skeleton (**5**) with two substitution positions, which construct an orbit governed by a CR $\mathbf{K}(/\mathbf{K}')$. Note that we take account of a factor group $\mathbf{K} = \mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ and its subgroup $\mathbf{K}' = \mathbf{D}_{\infty h}/\mathbf{C}_{\infty v}$. The two positions accommodate a set of ligands to give a bicentroidal derivative belonging to a subgroup of $\mathbf{D}_{\infty h}$ or $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ in agreement with the sphericities of desymmetrized orbits. For example, 2,2,4-trimethylheptane (**6**) is a bicentroidal alkane derived by the substitution of two alkyl ligands of the same carbon content 5, which satisfies the relationship for bicentroidal 3D-trees, i.e., $5 = (1/2) \times 10$ in this case.

Because the CR $\mathbf{K}(/\mathbf{K}')$ is isomorphic to $\mathbf{C}_{2v}(/\mathbf{C}_s)$, the use of Theorem 1 of [20] gives the following CI-CF:

$$\text{CI-CF}(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d) = \frac{1}{4}\left(b_1^2 + b_2 + a_1^2 + c_2\right). \tag{29}$$

Table 1: Numbers of Centroidal Alkanes as Stereoisomers

k	$\widehat{B}_k$ (Total)	$\widehat{A}_k$ (Achiral)	$\widehat{C}_k$ (Chiral)
1	1	1	0
2	0	0	0
3	1	1	0
4	1	1	0
5	3	3	0
6	2	2	0
7	9	7	2
8	8	7	1
9	38	21	17
10	46	22	24
11	203	61	142
12	283	72	211
13	1299	186	1113
14	2004	220	1784
15	9347	567	8780
16	15758	717	15041
17	72505	1755	70750
18	129281	2209	127072
19	589612	5454	584158
20	1098656	7149	1091507
21	4954686	17070	4937616
22	9576645	22476	9554169
23	42671509	53628	42617881
24	84998202	72656	84925546
25	374749447	169175	374580272
26	765965475	229676	765735799
27	3344714436	535267	3344179169
28	6992429665	743026	6991686639
29	30264120901	1698322	30262422579
30	64538102227	2361476	64535740751
31	277096805630	5400908	277091404722
32	601441729659	7642893	601434086766
33	2563418291362	17211368	2563401079994
34	5652900424627	24394779	5652876029848
35	23931052067297	54947147	23930997120150
36	53534903586744	79009726	53534824577018
37	225226025743122	175702378	225225850040744
38	510446528635659	252964410	510446275671249
39	2135109239262173	562645937	2135108676616236
40	4896889667780240	819922295	4896888847857945
41	20372876580255143	1804088396	20372874776166747
42	47238614063478058	2631820744	47238611431657314
43	195544793394384827	5791497722	195544787602887105
44	457999560484205773	8536377160	457999551947828613
45	1886989279103128211	18611821161	1886989260491307050
46	4461040396950967790	27458156708	4461040369492811082
47	18298681742426380229	59870273288	18298681682556106941
48	43636081544149901047	89120741244	43636081455029159803
49	178246302614039769705	192762694240	178246302421277075465
50	428497965173462968567	287167536146	428497964886295432421
51	1743475977870305954708	621145058010	1743475977249160896698
52	4222957579213874326998	932636649624	4222957578281237677374
53	17118606500538110493165	2003060193783	17118606498535050299382
54	41757573020631974557921	3009644412440	41757573017622330145481
55	168676827177458246245600	6464001746606	168676827170994244498994
56	414192406700454644211608	9780036558542	414192406690674607653066
57	1667507044106396700614662	20873421744449	1667507044085523278870213
58	4120269449060079231919190	31600908341722	4120269449028478323577468
59	16535111535321800418856805	67445191538640	16535111535254355227318165
60	41098222466126905529132145	102743321459580	41098222466024162207672565
61	164431691004690928193898010	218049903481679	164431691004472878290416331
62	410979018222119235952994626	332350277618212	410979018221786885675376414
63	1639544206288762558253253718	705330165952872	1639544206288057228087300846
64	4119529788256533749220428115	1081087049647181	4119529788255452662170780934
65	16388819934893627771459167067	2282686396696017	16388819934891345085062471050
66	41385225782249836799266208327	3500478814410329	41385225782246336320451797998
67	164207682036849477130738064324	7391016289967130	164207682036842086114448097194
68	416635607643584641443966956505	11391634034768010	416635607643573249809932188495
69	1648923729893987703415359750119	23941657967808209	1648923729893963761757391941910
70	4202708638020682863979777378556	36917161577580590	4202708638020645946818199797966
71	16592589875613236090913193392688	77586381466034947	16592589875613158504531727357741
72	42473372537692324926023951462175	120189309691294216	42473372537692204736714260167959
73	167295424464204241785279087528744	251528935349306793	167295424464203990256343738221951
74	430006772381311411463428100669081	389800782399677001	430006772381311021662645700992080
75	1689911835064564750230170718349855	815741140338068227	1689911835064563934489030380281628
76	4360786726830840048241690321351540	1269537925991351156	4360786726830838778703764330000384
77	17100609751074144217174560807768366	2646489896299591485	17100609751074141570684664508176881
78	44294354185222186820769124153521749	4120240983149128308	44294354185222182700528141004393441
79	173335468778163767515568474781956550	8588824555686539622	173335468778163758926743919095416928
80	450600427378156845559982800702584531	13423903573385498107	450600427378156832136079227317086424
81	1759767313496477955950136185436237113	27882748457230290862	1759767313496477928067387728205946251
82	4590528948690471604616529471778183215	43593968512517811907	4590528948690471561022560959260371308
83	17892924987803326824799846194126147310	90545956172141260398	17892924987803326734253890021984886912
84	46830869858741159259966803464456963334	142077351102286455091	46830869858741159117889452362170508243
85	182194157793655704794237473891139390912	294122275423916054352	182194157793655704500115198467223336560
86	478379522345454679309871516802458372263	461655253463248942128	478379522345454678848216263339209430135
87	1857742280338673467557442653721200301589	955666449267540395221	1857742280338673466601776204453659906368
88	4892807796459916529261704647629075403302	1505041735231994609714	4892807796459916527756662912397080793588
89	18967377099179003868970637596678249069674	3105981799108470323147	18967377099179003865864655797569778746527
90	50103146420285113739818866280484547768367	4892884042870228987320	50103146420285113734925982237614318781047
91	193898555422930447001151675263478441556235	10097190706324159336800	193898555422930446991054484557154282219435
92	513654043751710294733679292054184446263260	15955816379863267567356	513654043751710294717723475674321178695904
93	1984557489015003230954102094778322440355924	32832697580700874763572	1984557489015003230921269397197621565592352
94	5271743914770706258012825906425310485383995	51896703593122831089656	5271743914770706257960929202832187654294339
95	20335387509472990198674865937576370042014764	106785552739916704811839	20335387509472990198568080384836453337202925
96	54162175051500719402424219621363121075002053	169281344462058446325058	54162175051500719402254938276901062628676995
97	208602785663318655583000176804691552968239008	347387515383940750498193	208602785663318655582652789289307612217740815
98	557028727906484285339493725195492553290993302	550829851333133859420094	557028727906484285338942895344159419431573208
99	2142136450298921147961693542530974370563522319	1130336590391716286395368	2142136450298921147960563205940582654277126951
100	5734313151200075267210640593555000980047907239	1797192677522993383492050	5734313151200075267208843400877477986664415189



5 **6**

Figure 3: $\mathbf{D}_{\infty h}$-skeleton or $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$-skeleton (**5**) with two substitution positions and a bicentroidal alkane (2,2,4-trimethylheptane) as a 3D-tree (**6**). An two open circles represent a bicentroid.

An equation equivalent to eq. 29 has been reported previously on the basis of Fujita's USCI approach [23].

By following Fujita's proligand method [20], we obtain other relevant CI-CFs as follows:

$$\begin{aligned} &\text{CI-CF}(\mathbf{D}_{\infty}/\mathbf{C}_{\infty}; b_d) \\ &\quad = \frac{1}{2}\left(b_1^2 + b_2\right), \qquad (30) \\ &\text{CI-CF}_A(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d) \\ &\quad = 2\text{CI-CF}(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d) - \text{CI-CF}(\mathbf{D}_{\infty}/\mathbf{C}_{\infty}; b_d) \\ &\quad = \frac{1}{2}\left(a_1^2 + c_2\right), \qquad (31) \\ &\text{CI-CF}_C(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d) \\ &\quad = \text{CI-CF}(\mathbf{D}_{\infty}/\mathbf{C}_{\infty}; b_d) - \text{CI-CF}(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d) \\ &\quad = \frac{1}{4}\left(b_1^2 + b_2 - a_1^2 - c_2\right). \qquad (32) \end{aligned}$$

The $\text{CI-CF}(\mathbf{D}_{\infty}/\mathbf{C}_{\infty}; b_d)$ (eq. 30) is derived by using Theorem 3 of Fujita's proligand method [20] in order to count achiral promolecules and chiral promolecules, where two enantiomers of each pair are counted separately. The $\text{CI-CF}_A(\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}; a_d, c_d, b_d)$ (eq. 31) which is derived by using the first proposition of Theorem 4 for the enumeration of achiral ligands [20], counts achiral promolecules only, where each pair of enantiomers is counted just once. The $\text{CI-CF}_C(\mathbf{D}_{\infty h}; a_d, c_d, b_d)$ (eq. 32) is derived by using the second proposition of Theorem 4 for the enumeration of chiral ligands [20] so as to counts chiral promolecules only, where each pair of enantiomers is counted just once.

3.3.2 Functional Equations for Bicentroidal 3D-Trees

Let $\widetilde{B}_k$ be the number of achiral bicentroidal promolecules plus enantiomeric pairs of chiral bicentroidal promolecules of carbon content k; let $\widetilde{A}_k$ be the number of achiral bicentroidal promolecules of carbon content k; and let $\widetilde{C}_k$ be the number of chiral bicentroidal promolecules of carbon content k, where each pair of enantiomers is counted just once. Then, they appear as the coefficients of the following generating functions:

$$\widetilde{B}(x) = \sum_{k=0}^{v} \widetilde{B}_k x^k \qquad (33)$$

$$\widetilde{A}(x) = \sum_{k=0}^{v} \widetilde{A}_k x^k \tag{34}$$

$$\widetilde{C}(x) = \sum_{k=0}^{v} \widetilde{C}_k x^k, \tag{35}$$

each of which contains the terms up to v, where the v runs stepwise from 0 to infinite.

Our target is to calculate the numbers $\widetilde{B}_k$, $\widetilde{A}_k$, and $\widetilde{C}_k$ (eqs. 33–35) which satisfy the criterion of bicentroidal 3D-trees. To do this task, we use Theorem 6 of Fujita's proligand method [20] after the selection of the CI-CFs (eqs. 29, 31, and 32).

To evaluate the counting series represented by eqs. 33–35, we derive functional equations by substituting $a(x^d)$, $c(x^d)$, and $b(x^d)$ for the SIs (a_d, c_d, and b_d) appearing in the CI-CFs (eqs. 29, 31, and 32). Thereby, we obtain the following functional equations:

$$\widetilde{B}(x) = \frac{1}{4}\left(b(x)^2 + b(x^2) + a(x)^2 + c(x^2)\right) \tag{36}$$

$$\widetilde{A}(x) = \frac{1}{2}\left(a(x)^2 + c(x^2)\right) \tag{37}$$

$$\widetilde{C}(x) = \frac{1}{4}\left(b(x)^2 + b(x^2) - a(x)^2 - c(x^2)\right). \tag{38}$$

Because we have evaluated $a(x)$, $c(x)$, and $b(x)$ by using eqs. 4–6, they are introduced into eqs. 36–38 to evaluate $\widetilde{B}(x)$, $\widetilde{A}(x)$, and $\widetilde{C}(x)$ under the criterion for bicentroidal 3D-trees, which requires the relationship:

$$m = \frac{1}{2}v \tag{39}$$

or

$$2m = v. \tag{40}$$

Suppose that we have obtained $a(x)$, $c(x)$, and $b(x)$ (eqs. 4–6) up to $k = m$. They are introduced into eqs. 36–38. The resulting equations are expanded to give generating functions, which contain no terms having powers larger than $2m$, because each of eqs. 4–6 contain no terms having powers larger than m. Obviously, the term x^{2m} appearing in each of eqs. 36–38 comes from the largest term x^m appearing in each of eqs. 4–6.

Strictly speaking, eqs. 36–38 up to the term x^{2m} are only effective to evaluate the coefficients of the term x^{2m} appearing in eqs. 33–35. This means that eqs. 33–35 are evaluated by eqs. 36–38 only if the relationship of eq. 40 is satisfied. Suppose that we have obtained $a(x) = \sum_{k=0}^{m} \alpha_k x^k$, $c(x^2) = \sum_{k=0}^{m} \gamma_{2k} x^{2k}$, and $b(x) = \sum_{k=0}^{m} \beta_k x^k$, where m is tentatively fixed. They are introduced into eqs. 36–38 to give $\widetilde{B}(x)^{(m)}$, $\widetilde{A}(x)^{(m)}$, and $\widehat{C}(x)^{(m)}$, respectively. Let the symbol $\mathrm{coeff}(\widetilde{B}(x)^{(m)}, x^{2m})$ etc. represent the coefficient of the term x^{2m} appearing in the equation $\widetilde{B}(x)^{(m)}$ etc. after expansion. Then, we obtain the following coefficients:

$$\widetilde{B}_{2m} = \mathrm{coeff}(\widetilde{B}(x)^{(m)}, x^{2m}) \tag{41}$$

$$\widetilde{A}_{2m} = \mathrm{coeff}(\widetilde{A}(x)^{(m)}, x^{2m}) \tag{42}$$

$$\widetilde{C}_{2m} = \mathrm{coeff}(\widetilde{C}(x)^{(m)}, x^{2m}). \tag{43}$$

Hence, the following programming should take account of these requirements.

More strictly speaking, the substitution of $a(x^d) - 1$, $c(x^d) - 1$, and $b(x^d) - 1$ for the SIs (a_d, c_d, and b_d) in the CI-CFs (eqs. 29–32) should be considered instead of the derivation of eqs. 36–38. However, the requirements shown in eqs. 41–43 permit the use of such simplified equations as shown in eqs. 36–38.

3.3.3 Implementation and Calculations for Counting Bicentroidal 3D-Trees

The same code for evaluating $a(x)$ (by eq. 4), $c(x^2)$ (by eq. 5), and $b(x)$ (by eq. 6) was followed by the code for evaluating $\widetilde{B}_k$ (eq. 33), $\widetilde{A}_k$ (eq. 34), and $\widetilde{C}_k$ (eq. 35). The following program was stored in a file named "Bicentroid1-100A.mpl", which was executed on the Maple system. The results are shown in Table 2, where the values of $\widetilde{B}_k$ for bicentroidal 3D-trees, those of $\widetilde{A}_k$ for achiral bicentroidal 3D-trees, and those of $\widetilde{C}_k$ for chiral bicentroidal 3D-trees are collected up to carbon content $k = 100$.

Maple program for counting bicentroidal 3D-trees, "Bicentroid1-100A.mpl":

```
"Functional Equations for Alkyl Ligands";
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;

"Alkanes as Bicentroidal 3D-Trees";
Bxt := (1/4)*(b1^2 + b2 + a1^2 + c2):
Axt := (1/2)*(a1^2 + c2):
Cxt := (1/4)*(b1^2 + b2 - a1^2 - c2):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;

Bt := 0; At := 0; Ct := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 +Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m:
Bt := Bt + coeff(Bxt,x^n)*x^n:
At := At + coeff(Axt,x^n)*x^n:
Ct := Ct + coeff(Cxt,x^n)*x^n:
end do:

"Print-Out";
for m from 2 to 100 by 2 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Bt,x^m), coeff(At,x^m), coeff(Ct,x^m));
end do;
```

3.4 Total Number of 3D-Trees

3.4.1 Summation for Obtaining Total Numbers of 3D-Trees

Because we have evaluated the values of $\widehat{B}_k$, $\widehat{A}_k$, and $\widehat{C}_k$ for centroidal 3D-trees in Subsection 3.2 as well as those of $\widetilde{B}_k$, $\widetilde{A}_k$, and $\widetilde{C}_k$ for bicentroidal 3D-trees in Subsection 3.3, the corresponding total numbers are obtained by their summations. Let $B_k^{(\mathrm{T})}$ be the total number of achiral 3D-trees plus enantiomeric pairs of chiral 3D-trees of carbon content k; let $A_k^{(\mathrm{T})}$ be the total number

Table 2: Numbers of Bicentroidal Alkanes as Stereoisomers

k	$\widetilde{B}_k$ (Total)	$\widetilde{A}_k$ (Achiral)	$\widetilde{C}_k$ (Chiral)
2	1	1	0
4	1	1	0
6	3	3	0
8	11	7	4
10	42	18	24
12	226	46	180
14	1455	135	1320
16	10132	364	9768
18	76596	1116	75480
20	604919	3157	601762
22	4925463	9660	4915803
24	41182288	28048	41154240
26	351540477	87198	351453279
28	3052718874	257498	3052461376
30	26911575651	807024	26910768627
32	240342103858	2416930	240339686928
34	2171043239281	7615957	2171035623324
36	19810929594366	23049846	19810906544520
38	182415941988708	72998375	182415868990333
40	1693333948230414	222772878	1693333725457536
42	15834518487216684	708229602	15834517778987082
44	149058123647139706	2176253909	149058121470885797
46	1411693345198989804	6940071788	1411693338258918016
48	13444259000085324450	21447095265	13444258978638229185
50	128691508729059112011	68575115832	128691508660483996179
52	1237676126576594750782	212938845214	1237676126363655905568
54	11955155210701470446671	682361154964	11955155210019109291707
56	115946610493627953674082	2127595209954	115946610491500358464128
58	1128738527380959873010625	6830764951225	1128738527374129108059400
60	11026844701965874529190922	21374156991589	11026844701944500372199333
62	108076850325929347339118106	68735616099846	108076850325860611723018260
64	1062546355974859184433303907	215750350143463	1062546355974643434083160444
66	10476479815331791402908804773	694810203326143	10476479815331096592705478630
68	103576425125386740139551603997	2186885259231139	103576425125384553254292372858
70	1026636422872860993299342917081	7051608612790801	1026636422872853941690730126280
72	10200477451834298878750661296831	22248706566076681	10200477451834276630044095220150
74	101581672299213473582179782664595	71821230998745295	101581672299213401760948783919300
76	1013791682525676228576683088291396	227098401776737991	1013791682525676001478281311553405
78	10138463629083017972808924946341975	733830838917910260	10138463629083017238978086028431715
80	101587632316921574251763999702477485	2324913064252782235	101587632316921571926850935449695250
82	1019796001920058521542882241719699280	7519313772353585910	1019796001920058514023568469366113370
84	10255363028472401480641863051040385436	23864756535236123646	10255363028472401456777106515804261790
86	103304260659529997894882067280991825026	77246762086123054349	103304260659529997817635305194868770677
88	1042273130631919368189895707650012227320	245559550069814892615	1042273130631919367944336157580197334705
90	10531975749055818891917647391993815769431	795425023466713343636	10531975749055818891122222368527102425795
92	106579600371335056375718032870298888591898	2532284335946868011910	106579600371335056373185748534352020579988
94	1080057924052835851977837463100215491985144	8208157600050190035463	1080057924052835851969629305500165301949681
96	10959815284871517870373418435789451751642966	26166292215009183994466	10959815284871517870347252143574442567648500
98	111357307668915457889370368365383883484840146	84867504834430057342222	111357307668915457889285500860549453427497924
100	1132846394716372419231583119434015949776511616	270878332458926178189871	1132846394716372419231312241101557023598321745

of achiral 3D-trees of carbon content k; and let $C_k^{(\mathrm{T})}$ be the total number of achiral and chiral 3D-trees of carbon content k, where each pair of enantiomers is counted just once. Then, they appear as the coefficients of the following generating functions:

$$B(x)^{(\mathrm{T})} = \sum_{k=0}^{\infty} B_k^{(\mathrm{T})} x^k \tag{44}$$

$$A(x)^{(\mathrm{T})} = \sum_{k=0}^{\infty} A_k^{(\mathrm{T})} x^k \tag{45}$$

$$C(x)^{(\mathrm{T})} = \sum_{k=0}^{\infty} C_k^{(\mathrm{T})} x^k \tag{46}$$

By means of eqs. 15–17 and eqs. 33–35, we obtain the following relationships:

$$B_k^{(\mathrm{T})} = \widehat{B}_k + \widetilde{B}_k \tag{47}$$

$$A_k^{(\mathrm{T})} = \widehat{A}_k + \widetilde{A}_k \tag{48}$$

$$C_k^{(\mathrm{T})} = \widehat{C}_k + \widetilde{C}_k \tag{49}$$

It should be noted that the functional equations $\widehat{B}(x)$, $\widehat{A}(x)$, and $\widehat{C}(x)$ (eqs. 18–20) for centroidal 3D-trees (Subsection 3.2) cannot be added to the functional equations $\widetilde{B}(x)$, $\widetilde{A}(x)$, and

$\widetilde{C}(x)$ (eqs. 36–38) for bicentroidal 3D-trees (Subsection 3.3). Simple summations of the functional equations (eqs. 18–20) and the functional equations (eqs. 36–38) give erroneous results, because the integer m runs according to eq. 22 for the former set and differently according to eq. 40 for the latter set.

3.4.2 Implementation and Calculations of Total Numbers

We used the same code for evaluating $a(x)$ (by eq. 4), $c(x^2)$ (by eq. 5), and $b(x)$ (by eq. 6). Then, the functional equations derived in Subsections 3.2 and 3.3 were programmed. The resulting program was stored in a file named “Total1-100A.mpl”, which was executed on the Maple system. The results are shown in Table 3, where the total values of $B_k^{(\mathrm{T})}$ for 3D-trees, those of $A_k^{(\mathrm{T})}$ for achiral 3D-trees, and those of $C_k^{(\mathrm{T})}$ for chiral 3D-trees are collected up to carbon content $k = 100$.

Maple program for counting 3D-trees “Total1-100A.mpl”:

```
"Functional Equations for Alkyl Ligands";
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;

"Alkanes as Centroidal 3D-Trees";
Bxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 + 6*a1^2*c2 + 6*c4):
Axh := (x/2)*(a1^2*c2 + c4):
Cxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 - 6*a1^2*c2 - 6*c4):

"Alkanes as Bicentroidal 3D-Trees";
Bxt := (1/4)*(b1^2 + b2 + a1^2 + c2):
Axt := (1/2)*(a1^2 + c2):
Cxt := (1/4)*(b1^2 + b2 - a1^2 - c2):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;
Bh := x; Ah := x; Ch := 0;
Bt := 0; At := 0; Ct := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 +Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m +1:
Bh := Bh + coeff(Bxh,x^n)*x^n + coeff(Bxh,x^(n+1))*x^(n+1):
Ah := Ah + coeff(Axh,x^n)*x^n + coeff(Axh,x^(n+1))*x^(n+1):
Ch := Ch + coeff(Cxh,x^n)*x^n + coeff(Cxh,x^(n+1))*x^(n+1):
nn := 2*m:
Bt := Bt + coeff(Bxt,x^nn)*x^nn:
At := At + coeff(Axt,x^nn)*x^nn:
Ct := Ct + coeff(Cxt,x^nn)*x^nn:
end do:

"Total Numbers";
TB := Bh + Bt:
```

Table 3: Total Numbers of Alkanes as Stereoisomers

k	$B_k^{(\mathrm{T})} = \widehat{B}_k + \widetilde{B}_k$ (Total)	$A_k^{(\mathrm{T})} = \widehat{A}_k + \widetilde{A}_k$ (Achiral)	$C_k^{(\mathrm{T})} = \widehat{C}_k + \widetilde{C}_k$ (Chiral)
1	1	1	0
2	1	1	0
3	1	1	0
4	2	2	0
5	3	3	0
6	5	5	0
7	9	7	2
8	19	14	5
9	38	21	17
10	88	40	48
11	203	61	142
12	509	118	391
13	1299	186	1113
14	3459	355	3104
15	9347	567	8780
16	25890	1081	24809
17	72505	1755	70750
18	205877	3325	202552
19	589612	5454	584158
20	1703575	10306	1693269
21	4954686	17070	4937616
22	14502108	32136	14469972
23	42671509	53628	42617881
24	126180490	100704	126079786
25	374749447	169175	374580272
26	1117505952	316874	1117189078
27	3344714436	535267	3344179169
28	10045148539	1000524	10044148015
29	30264120901	1698322	30262422579
30	91449677878	3168500	91446509378
31	277096805630	5400908	277091404722
32	841783833517	10059823	841773773694
33	2563418291362	17211368	2563401079994
34	7823943663908	32010736	7823911653172
35	23931052067297	54947147	23930997120150
36	73345833181110	102059572	73345731121538
37	225226025743122	175702378	225225850040744
38	692862470624367	325962785	692862144661582
39	2135109239262173	562645937	2135108676616236
40	6590223616010654	1042695173	6590222573315481
41	20372876580255143	1804088396	20372874776166747
42	63073132550694742	3340050346	63073129210644396
43	195544793394384827	5791497722	195544787602887105
44	607057684131345479	10712631069	607057673418714410
45	1886989279103128211	18611821161	1886989260491307050
46	5872733742149957594	34398228496	5872733707751729098
47	18298681742426380229	59870273288	18298681682556106941
48	57080340544235225497	110567836509	57080340433667388988
49	178246302614039769705	192762694240	178246302421277075465
50	557189473902522080578	355742651978	557189473546779428600
51	1743475977870305954708	621145058010	1743475977249160896698
52	5460633705790469077780	1145575494838	5460633704644893582942
53	17118606500538110493165	2003060193783	17118606498535050299382
54	53712728231333445004592	3692005567404	53712728227641439437188
55	168676827177458246245600	6464001746606	168676827170994244498994
56	530139017194082597885690	11907631768496	530139017182174966117194
57	1667507044106396700614662	20873421744449	1667507044085523278870213
58	5249007976441039104929815	38431673292947	5249007976402607431636868
59	16535111535321800418856805	67445191538640	16535111535254355227318165
60	52125067168092780058323067	124117478451169	52125067167968662579871898
61	164431691004690928193898010	218049903481679	164431691004472878290416331
62	519055868548048583292112732	401085893718058	519055868547647497398394674
63	1639544206288762558253253718	705330165952872	1639544206288057228087300846
64	5182076144231392933653732022	1296837399790644	5182076144230096096253941378
65	16388819934893627771459167067	2282686396696017	16388819934891345085062471050
66	51861705597581628202175013100	4195289017736472	51861705597577432913157276628
67	164207682036849477130738064324	7391016289967130	164207682036842086114448097194
68	520212032768971381583518560502	13578519293999149	520212032768957803064224561353
69	1648923729893987703415359750119	23941657967808209	1648923729893963761757391941910
70	5229345060893543857279120295637	43968770190371391	5229345060893499888508929924246
71	16592589875613236090913193392688	77586381466034947	16592589875613158504531727357741
72	52673849989526623804774612759006	142438016257370897	52673849989526481366758355388109
73	167295424464204241785279087528744	251528935349306793	167295424464203990256343738221951
74	531588444680524885045607883333676	461622013398422296	531588444680524423423594484911380
75	1689911835064564750230170718349855	815741140338068227	1689911835064563934489030380281628
76	5374578409356516276818373409642936	1496636327768089147	5374578409356514780182045641553789
77	17100609751074144217174560807768366	2646489896299591485	17100609751074141570684664508176881
78	54432817814305204793578049099863724	4854071822067038568	54432817814305199939506227032825156
79	173335468778163767515568474781956550	8588824555686539622	173335468778163758926743919095416928
80	552188059695078419811746800405062016	15748816637638280342	552188059695078404062930162766781674
81	1759767313496477955950136185436237113	27882748457230290862	1759767313496477928067387728205946251
82	5610324950610530126159411713497882495	51113282284871397817	5610324950610530075046129428626484678
83	17892924987803326824799846194126147310	90545956172141260398	17892924987803326734253890021984886912
84	57086232887213560740608666515497348770	165942107637522578737	57086232887213560574666558877974770033
85	182194157793655704794237473891139390912	294122275423916054352	182194157793655704500115198467223336560
86	581683783004984677204753584083450197289	538902015549371996477	581683783004984676665851568534078200812
87	1857742280338673467557442653721200301589	955666449267540395221	1857742280338673466601776204453659906368
88	5935080927091835897451600355279087630622	1750601285301809502329	5935080927091835895700999069977278128293
89	18967377099179003868970637596678249069674	3105981799108470323147	18967377099179003865864655797569778746527
90	60635122169340932631736513672478363537798	5688309066336942330956	60635122169340932626048204606141421206842
91	193898555422930447001151675263478441556235	10097190706324159336800	193898555422930446991054484557154282219435
92	620233644123045351109397324924483334855158	18488100715810135579266	620233644123045351090909224208673199275892
93	1984557489015003230954102094778322440355924	32832697580700874763572	1984557489015003230921269397197621565592352
94	6351801838823542109990663369525525977369139	60104861193173021125119	6351801838823542109930558508332352956244020
95	20335387509472990198674865937576370042014764	106785552739916704811839	20335387509472990198568080384836453337202925
96	65121990336372237272797638057152572826645019	195447636677067630319524	65121990336372237272602190420475505196325495
97	208602785663318655583000176804691552968239008	347387515383940750498193	208602785663318655582652789289307612217740815
98	668386035575399743228864093560876436775833448	635697356167563916762316	668386035575399743228228396204708872859071132
99	2142136450298921147961693542530974370563522319	1130336590391716286395368	2142136450298921147960563205940582654277126951
100	6867159545916447686442223712989016929824418855	2068071009981919561681921	6867159545916447686440155641979035010262736934

```
TA := Ah + At:
TC := Ch + Ct:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(TB,x^m), coeff(TA,x^m), coeff(TC,x^m));
end do;
```

4 Alkanes as Balanced and Unbalanced 3D-Trees

The enumeration of 3D-trees by a single use of the new dichotomy between balanced and unbalanced 3D-trees will be reported in an accompanying paper submitted to this journal. Hence this subsection is devoted to a brief description of functional equations which are necessary to the enumeration by the combination of the new dichotomy with the conventional one between centroidal and bicentroidal 3D-trees.

4.1 Balanced 3D-Trees and Balance-Edge

As found easily, each balanced 3D-tree is represented by X—X, p—p (paired with $\overline{\mathrm{p}}$—$\overline{\mathrm{p}}$) or p—$\overline{\mathrm{p}}$, among which X—X and p—$\overline{\mathrm{p}}$ are achiral, while p—p (paired with $\overline{\mathrm{p}}$—$\overline{\mathrm{p}}$) is chiral. Hence, they are respectively ascribed to the following CI-CFs:

$$\mathrm{X}\text{—}\mathrm{X},\ \mathrm{p}\text{—}\mathrm{p}\ (\overline{\mathrm{p}}\text{—}\overline{\mathrm{p}}),\ \mathrm{p}\text{—}\overline{\mathrm{p}} \ :\ \frac{1}{2}(b_2+c_2) \tag{50}$$

$$\mathrm{X}\text{—}\mathrm{X},\ \mathrm{p}\text{—}\overline{\mathrm{p}} \ :\ \frac{1}{2}(a_2+c_2) \tag{51}$$

$$\mathrm{p}\text{—}\mathrm{p}\ (\overline{\mathrm{p}}\text{—}\overline{\mathrm{p}}) \ :\ \frac{1}{2}(b_2-a_2). \tag{52}$$

Let $B_k^{\mathrm{(AC)}}$ be the number of achiral balanced 3D-trees plus enantiomeric pairs of chiral balanced 3D-trees of carbon content k; let $B_k^{\mathrm{(A)}}$ be the number of achiral balanced 3D-trees of carbon content k; and let $B_k^{\mathrm{(C)}}$ be the number of achiral and chiral balanced 3D-trees of carbon content k, where each pair of enantiomers is counted just once. Then, they appear as the coefficients of the following series:

$$B(x)^{\mathrm{(AC)}} = \sum_{k=1}^{\infty} B_k^{\mathrm{(AC)}} x^k \tag{53}$$

$$B(x)^{\mathrm{(A)}} = \sum_{k=1}^{\infty} B_k^{\mathrm{(A)}} x^k \tag{54}$$

$$B(x)^{\mathrm{(C)}} = \sum_{k=1}^{\infty} B_k^{\mathrm{(C)}} x^k, \tag{55}$$

where the coefficient of x^k is equal to 0 if k is odd.

To evaluate the counting series represented by eqs. 53–55, we derive functional equations by substituting $a(x^d)-1$, $c(x^d)-1$, and $b(x^d)-1$ for the SIs (a_d, c_d, and b_d) appearing in the CI-CFs (eqs. 50–52). Thereby, we obtain the following functional equations:

$$B(x)^{\mathrm{(AC)}} = \frac{1}{2}\{(b(x^2)-1)+(c(x^2)-1)\} \tag{56}$$

$$B(x)^{(A)} = \frac{1}{2}\{(a(x^2)-1)+(c(x^2)-1)\} \quad (57)$$

$$B(x)^{(C)} = \frac{1}{2}\{(b(x^2)-1)-(a(x^2)-1)\} \quad (58)$$

Because we have already obtained the coefficients of every terms of eqs. 1–3, they are introduced into eqs. 56–58. The resulting equations are expanded to give $B_k^{(AC)}$, $B_k^{(A)}$, and $B_k^{(C)}$.

4.2 Unbalanced 3D-Trees as Residuals

The numbers of unbalanced 3D-trees, i.e., $U_k^{(AC)}$, $U_k^{(A)}$, and $U_k^{(C)}$, can be obtained by dual recognition of 3D-trees as uninuclear 3D-trees and binuclear ones, although the detailed procedure will be discussed in an accompanied paper submitted to this journal.

Because the total numbers of 3D-trees have been obtained in the present enumeration, the values of $U_k^{(AC)}$, $U_k^{(A)}$, and $U_k^{(C)}$ are alternatively obtained as follows:

$$U_k^{(AC)} = B_k^{(T)} - B_k^{(AC)} \quad (59)$$

$$U_k^{(A)} = A_k^{(T)} - B_k^{(A)} \quad (60)$$

$$U_k^{(C)} = C_k^{(T)} - B_k^{(C)}, \quad (61)$$

where the coefficients appearing in the right-hand sides are obtained by using eqs. 47–49 and eqs. 53-55.

5 Combination of Two Dichotomies

5.1 Three Categories of 3D-Trees Due to the Two Dichotomies

The combination of the conventional dichotomy between centroidal and bicentroidal 3D-trees with the new dichotomy between balanced and unbalanced 3D-trees provides us with a versatile tool for categorizing 3D-trees, as shown in Fig. 4. Among the four possible categories, there appear three categories, i.e., centroidal & unbalanced, bicentroidal & unbalanced, and bicentroidal & balanced. Note that the category of “centroidal & balanced” is not permitted because of the definitions of the two dichotomies, as shown in Section 2.

The numbers of centroidal & unbalanced 3D-trees of carbon content k are equal to those of centroidal 3D-trees of carbon content k, i.e., $\widehat{B}_k$ (total), $\widehat{A}_k$ (achiral), and $\widehat{C}_k$ (chiral). The numbers of bicentroidal & balanced 3D-trees of carbon content k are equal to those of balanced 3D-trees of carbon content k, i.e., $B_k^{(AC)}$ (total), $B_k^{(A)}$ (achiral), and $B_k^{(C)}$ (chiral). It follows that the numbers of bicentroidal & unbalanced 3D-trees of carbon content k are calculated as follows:

$$\widetilde{U}_k^{(AC)} = \widetilde{B}_k - B_k^{(AC)} \quad (62)$$

$$\widetilde{U}_k^{(A)} = \widetilde{A}_k - B_k^{(A)} \quad (63)$$

$$\widetilde{U}_k^{(C)} = \widetilde{C}_k - B_k^{(C)}, \quad (64)$$

where the symbol $\widetilde{U}_k^{(AC)}$ represents the number of achiral and chiral bicentroidal & unbalanced 3D-trees of carbon content k; the symbol $\widetilde{U}_k^{(A)}$ represents the number of achiral bicentroidal & unbalanced 3D-trees of carbon content k; and the symbol $\widetilde{U}_k^{(C)}$ represents the number of chiral bicentroidal & unbalanced 3D-trees of carbon content k.

Total 3D-trees itemized by two dichotomies

	unbalanced 3D-trees ($U_k^{(\mathrm{AC})}$)	balanced 3D-trees ($B_k^{(\mathrm{AC})}$)
centroidal 3D-trees ($\widehat{B}_k$)	$\widehat{B}_k = U_k^{(\mathrm{AC})} - (\widetilde{B}_k - B_k^{(\mathrm{AC})})$	none
bicentroidal 3D-trees ($\widetilde{B}_k$)	$\widetilde{B}_k - B_k^{(\mathrm{AC})}$	$B_k^{(\mathrm{AC})}$

Achiral 3D-trees itemized by two dichotomies

	unbalanced 3D-trees ($U_k^{(\mathrm{A})}$)	balanced 3D-trees ($B_k^{(\mathrm{A})}$)
centroidal 3D-trees ($\widehat{A}_k$)	$\widehat{A}_k = U_k^{(\mathrm{A})} - (\widetilde{A}_k - B_k^{(\mathrm{A})})$	none
bicentroidal 3D-trees ($\widetilde{A}_k$)	$\widetilde{A}_k - B_k^{(\mathrm{A})}$	$B_k^{(\mathrm{A})}$

Chiral 3D-trees itemized by two dichotomies

	unbalanced 3D-trees ($U_k^{(\mathrm{C})}$)	balanced 3D-trees ($B_k^{(\mathrm{C})}$)
centroidal 3D-trees ($\widehat{C}_k$)	$\widehat{C}_k = U_k^{(\mathrm{C})} - (\widetilde{C}_k - B_k^{(\mathrm{C})})$	none
bicentroidal 3D-trees ($\widetilde{A}_k$)	$\widetilde{C}_k - B_k^{(\mathrm{C})}$	$B_k^{(\mathrm{C})}$

Figure 4: Three categories of 3D-trees on the basis of two dichotomies

The numbers of bicentroidal & unbalanced 3D-trees of carbon content k are alternatively calculated as follows:

$$\widetilde{U}_k^{(\mathrm{AC})} = U_k^{(\mathrm{AC})} - \widehat{B}_k \tag{65}$$

$$\widetilde{U}_k^{(\mathrm{A})} = U_k^{(\mathrm{A})} - \widehat{A}_k \tag{66}$$

$$\widetilde{U}_k^{(\mathrm{C})} = U_k^{(\mathrm{C})} - \widehat{C}_k. \tag{67}$$

5.2 Implementation and Calculations Based on Two Dichotomies

5.2.1 Alkanes as Bicentroidal/Unbalanced 3D-trees

The functional equation for counting bicentroidal & unbalanced 3D-trees (eq. 62) was programmed and stored in a file named "CBUBtotal1-100.mpl". According to the two dichotomies, the procedures for counting centroidal & unbalanced 3D-trees (the same as eq. 18) and for counting bicentroidal & balanced 3D-trees (eq. 36) were also stored in this file.

Maple program for counting alkanes, "CBUBtotal1-100.mpl":

```
"Functional Equations for Alkyl Ligands";
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;

"Alkanes as Centroidal 3D-Trees";
Bxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 + 6*a1^2*c2 + 6*c4):

"Alkanes as Bicentroidal 3D-Trees";
```

Table 4: Total Numbers of Alkanes as 3D-Trees Categorized by Two Dichotomies

k	$\widehat{B}_k$ (Centroidal & unbalanced)	$\widetilde{U}_k^{(\mathrm{AC})}$ (Bicentroidal & unbalanced)	$B_k^{(\mathrm{AC})}$ (Bicentroidal & balanced)
1	1	0	0
2	0	0	1
3	1	0	0
4	1	0	1
5	3	0	0
6	2	1	2
7	9	0	0
8	8	6	5
9	38	0	0
10	46	31	11
11	203	0	0
12	283	198	28
13	1299	0	0
14	2004	1381	74
15	9347	0	0
16	15758	9933	199
17	72505	0	0
18	129281	76045	551
19	589612	0	0
20	1098656	603366	1553
21	4954686	0	0
22	9576645	4921027	4436
23	42671509	0	0
24	84998202	41169456	12832
25	374749447	0	0
26	765965475	351502981	37496
27	3344714436	0	0
28	6992429665	3052608374	110500
29	30264120901	0	0
30	64538102227	26911247559	328092
31	277096805630	0	0
32	601441729659	240341123367	980491
33	2563418291362	0	0
34	5652900424627	2171040292392	2946889
35	23931052067297	0	0
36	53534903586744	19810920692475	8901891
37	225226025743122	0	0
38	510446528635659	182415914976422	27012286
39	2135109239262173	0	0
40	4896889667780240	1693333865930139	82300275
41	20372876580255143	0	0
42	47238614063478058	15834518235546121	251670563
43	195544793394384827	0	0
44	457999560484205773	149058122874978784	772160922
45	1886989279103128211	0	0
46	4461040396950967790	1411693342822695764	2376294040
47	18298681742426380229	0	0
48	43636081544149901047	13444258992752041696	7333282754
49	178246302614039769705	0	0
50	428497965173462968567	128691508706370656031	22688455980
51	1743475977870305954708	0	0
52	4222957579213874326998	1237676126506233507858	70361242924
53	17118606500538110493165	0	0
54	41757573020631974557921	11955155210482791181899	218679264772
55	168676827177458246245600	0	0
56	414192406700454644211608	115946610492946934994478	681018679604
57	1667507044106396700614662	0	0
58	4120269449060079231919190	1128738527378835030873075	2124842137550
59	16535111535321800418856805	0	0
60	41098222466126905529132145	11026844701959233190560208	6641338630714
61	164431691004690928193898010	0	0
62	410979018222119235952994626	108076850325908555335816270	20792003301836
63	1639544206288762558253253718	0	0
64	4119529788256533749220428115	1062546355974793990987131006	65193446172901
65	16388819934893627771459167067	0	0
66	41385225782249836799266208327	10476479815331586693555668856	204709353135917
67	164207682036849477130738064324	0	0
68	416635607643584641443966956505	103576425125386096473721765608	643665829838389
69	1648923729893987703415359750119	0	0
70	4202708638020682863979777378556	1026636422872858966837971093915	2026461371823166
71	16592589875613236090913193392688	0	0
72	42473372537692324926023951462175	10200477451834292491113398009478	6387637263287353
73	167295424464204241785279087528744	0	0
74	430006772381311411463428100669081	101581672299213453424633076856030	20157546705808565
75	1689911835064564750230170718349855	0	0
76	4360786726830840048241690321351540	1013791682525676164896492054480070	63680191033811326
77	17100609751074144217174560807768366	0	0
78	44294354185222186820769124153521749	10138463629083017771429048800953331	201379876145388644
79	173335468778163767515568474781956550	0	0
80	450600427378156845559982800702584531	101587632316921573614307703735698056	637456295966779429
81	1759767313496477955950136185436237113	0	0
82	4590528948690471604616529471778183215	1019796001920058519523183252345234581	2019698989374464699
83	17892924987803326824799846194126147310	0	0
84	46830869858741159259966803464456963334	10255363028472401474237063904003094785	6404799147037290651
85	182194157793655704794237473891139390912	0	0
86	478379522345454679309871516802458372263	103304260659529997874554326564470473464	20327740716521351562
87	1857742280338673467557442653721200301589	0	0
88	4892807796459916529261704647629075403302	1042273130631919368125327197348723120746	64568510301289106574
89	18967377099179003868970637596678249069674	0	0
90	50103146420285113739818866280484547768367	10531975749055818891712396562528443631155	205250829465372138276
91	193898555422930447001151675263478441556235	0	0
92	513654043751710294733679292054184446263260	106579600371335056375065102244975385922382	652930625323502669516
93	1984557489015003230954102094778322440355924	0	0
94	5271743914770706258012825906425310485383995	1080057924052835851975758946394434337237994	2078516705781154747150
95	20335387509472990198674865937576370042014764	0	0
96	54162175051500719402424219621363121075002053	10959815284871517870366797313442033145643730	6621122347418605999236
97	208602785663318655583000176804691552968239008	0	0
98	557028727906484285339493725195492553290993302	111357307668915457889349263170983554881575606	21105194400328603264540
99	2142136450298921147961693542530974370563522319	0	0
100	5734313151200075267210640593555000980047907239	1132846394716372419231515803866879770275428450	67315567136179501083166

```
Bxt := (1/4)*(b1^2 + b2 + a1^2 + c2):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;
Bh := x; Ah := x; Ch := 0;
Bt := 0; At := 0; Ct := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 + Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m +1:
Bh := Bh + coeff(Bxh,x^n)*x^n + coeff(Bxh,x^(n+1))*x^(n+1):
nn := 2*m:
Bt := Bt + coeff(Bxt,x^nn)*x^nn:
end do:

"Alkanes as Ballanced 3D-trees";
BxAC := (1/2)*((b2-1) + (c2-1)):

"Alkanes as Bicentroidal/Unbalanced 3D-trees":
BUxAC := Bt - BxAC:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Bh,x^m), coeff(BUxAC,x^m), coeff(BxAC,x^m));
end do;
```

The first paragraph “Functional Equations for Alkyl Ligands”, the second paragraph “Alkanes as Centroidal 3D-Trees”, the third paragraph “Alkanes as Bicentroidal 3D-Trees”, the fourth paragraph “Initial Values”, and the fifth paragraph “Recursive Calculation” are cited from the Maple program for counting 3D-trees “Total1-100A.mpl” described above. The six paragraph “Alkanes as Balanced 3D-trees” is cited from the paper accompanied with the present paper, where the symbol `BxAC` is used to designate $B(x)^{(\mathrm{AC})}$ for obtaining $B_k^{(\mathrm{AC})}$. The seventh paragraph “Alkanes as Bicentroidal/Unbalanced 3D-trees” is concerned with the enumeration of bicentroidal & unbalanced 3D-trees, where the `BUxAC` is used to designate $\widetilde{U}_k^{(\mathrm{AC})}$ (eq. 62). The last paragraph describes a print-out step.

The program “CBUBtotal1-100.mpl” was executed on the Maple system. The calculation results are summarized in Table 4. The summation of $\widehat{B}_k$-column (centroidal & unbalanced trees), $\widetilde{U}_k^{(\mathrm{AC})}$-column (bicentroidal & unbalanced trees), and $B_k^{(\mathrm{AC})}$-column (bicentroidal & balanced tree) gave the total values shown in the $B_k^{(\mathrm{T})}$-column of Table 3. The functional equation (eq. 65) for counting bicentroidal & unbalanced 3D-trees gave the same results as collected in Table 4.

5.2.2 Achiral Alkanes as Bicentroidal/Unbalanced 3D-trees

The functional equation (eq. 63) for counting achiral bicentroidal & unbalanced 3D-trees was programmed. The program stored in a file named “CBUBachiral1-100.mpl” is shown below.

According to the two dichotomies, the procedures for counting achiral centroidal & unbalanced 3D-trees (the same as eq. 19) and for counting achiral bicentroidal & balanced 3D-trees (eq. 37) were also stored in this file.

Maple program for counting achiral alkanes, “CBUBachiral1-100.mpl”:

```
"Functional Equaitons for Alkyl Ligands";
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;

"Alkanes as Centroidal 3D-Trees";
Axh := (x/2)*(a1^2*c2 + c4):

"Alkanes as Bicentroidal 3D-Trees";
Axt := (1/2)*(a1^2 + c2):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;
Bh := x; Ah := x; Ch := 0;
Bt := 0; At := 0; Ct := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 + Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m +1:
Ah := Ah + coeff(Axh,x^n)*x^n + coeff(Axh,x^(n+1))*x^(n+1):
nn := 2*m:
At := At + coeff(Axt,x^nn)*x^nn:
end do:

"Achiral Alkanes as Ballanced 3D-trees";
BxA := (1/2)*((a2-1) + (c2-1)):

"Achiral Alkanes as Bicentroidal/Unbalanced 3D-trees";
BUxA := At - BxA:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Ah,x^m), coeff(BUxA,x^m), coeff(BxA,x^m));
end do;
```

The first paragraph “Functional Equations for Alkyl Ligands” to the fifth paragraph “Recursive Calculation” are cited from the Maple program for counting 3D-trees “Total1-100A.mpl” described above. The six paragraph “Achiral Alkanes as Balanced 3D-trees” is cited from the paper accompanied with the present paper, where the symbol `BxA` is used to designate $B(x)^{(\mathrm{A})}$ for obtaining $B_k^{(\mathrm{A})}$. The seventh paragraph “Achiral Alkanes as Bicentroidal/Unbalanced 3D-trees” is concerned with the enumeration of bicentroidal & unbalanced 3D-trees, where the `BUxA` is used to designate $\widetilde{U}_k^{(\mathrm{A})}$ (eq. 63). The last paragraph describes a print-out step.

The program “CBUBachiral1-100.mpl” was executed on the Maple system to give the results summarized in Table 5. The summation of $\widehat{A}_k$-column (achiral centroidal & unbalanced

Table 5: Numbers of Achiral Alkanes Categorized by Two Dichotomies

k	$\widehat{A}_k$ (Centroidal & unbalanced)	$\widetilde{U}_k^{(A)}$ (Bicentroidal & unbalanced)	$B_k^{(A)}$ (Bicentroidal & balanced)
1	1	0	0
2	0	0	1
3	1	0	0
4	1	0	1
5	3	0	0
6	2	1	2
7	7	0	0
8	7	3	4
9	21	0	0
10	22	10	8
11	61	0	0
12	72	28	18
13	186	0	0
14	220	91	44
15	567	0	0
16	717	253	111
17	1755	0	0
18	2209	820	296
19	5454	0	0
20	7149	2346	811
21	17070	0	0
22	22476	7381	2279
23	53628	0	0
24	72656	21528	6520
25	169175	0	0
26	229676	68265	18933
27	535267	0	0
28	743026	201930	55568
29	1698322	0	0
30	2361476	642411	164613
31	5400908	0	0
32	7642893	1925703	491227
33	17211368	0	0
34	24394779	6140760	1475197
35	54947147	0	0
36	79009726	18595851	4453995
37	175702378	0	0
38	252964410	59486778	13511597
39	562645937	0	0
40	819922295	181613211	41159667
41	1804088396	0	0
42	2631820744	582377256	125852346
43	5791497722	0	0
44	8536377160	1790143530	386110379
45	18611821161	0	0
46	27458156708	5751871140	1188200648
47	59870273288	0	0
48	89120741244	17780359600	3666735665
49	192762694240	0	0
50	287167536146	57230718681	11344397151
51	621145058010	0	0
52	932636649624	177757925626	35180919588
53	2003060193783	0	0
54	3009644412440	573020987311	109340167653
55	6464001746606	0	0
56	9780036558542	1787084924878	340510285076
57	20873421744449	0	0
58	31600908341722	5768342184165	1062422767060
59	67445191538640	0	0
60	102743321459580	18053484671778	3320672319811
61	218049903481679	0	0
62	332350277618212	58339609048020	10396007051826
63	705330165952872	0	0
64	1081087049647181	183153617487435	32596732656028
65	2282686396696017	0	0
66	3500478814410329	592455509546916	102354693779227
67	7391016289967130	0	0
68	11391634034768010	1865052313774653	321832945456486
69	23941657967808209	0	0
70	36917161577580590	6038377871932071	1013230740858730
71	77586381466034947	0	0
72	120189309691294216	19054887836824378	3193818729252303
73	251528935349306793	0	0
74	389800782399677001	61742457470138910	10078773528606385
75	815741140338068227	0	0
76	1269537925991351156	195258305947375686	31840095829362305
77	2646489896299591485	0	0
78	4120240983149128308	633140900282570001	100689938635340259
79	8588824555686539622	0	0
80	13423903573385498107	2006184915267847485	318728148984934750
81	27882748457230290862	0	0
82	43593968512517811907	6509464275862265941	1009849496491319969
83	90545956172141260398	0	0
84	142077351102286455091	20662356958503263256	3202399576732860390
85	294122275423916054352	0	0
86	461655253463248942128	67082891722070880846	10163870364052173503
87	955666449267540395221	0	0
88	1505041735231994609714	213275294908843788720	32284255160971103895
89	3105981799108470323147	0	0
90	4892884042870228987320	692799608715415455555	102625414751297888081
91	10097190706324159336800	0	0
92	15955816379863267567356	2205819023251906595676	326465312694961416234
93	32832697580700874763572	0	0
94	51896703593122831089656	7168899247099742388600	1039258352950447646863
95	106785552739916704811839	0	0
96	169281344462058446325058	22855731041192979799716	3310561173816204194750
97	347387515383940750498193	0	0
98	550829851333133859420094	74314907634072993022128	10552597200357064320094
99	1130336590391716286395368	0	0
100	1797192677522993383492050	237220548890492029224300	33657783568434148965571

trees), $\widetilde{U}_k^{(A)}$-column (achiral bicentroidal & unbalanced trees), and $B_k^{(A)}$-column (achiral bicentroidal & balanced trees) gave the total values shown in the $A_k^{(T)}$-column of Table 3. The functional equation (eq. 66) for counting achiral bicentroidal & unbalanced 3D-trees gave the same results as collected in Table 5.

5.2.3 Chiral Alkanes as Bicentroidal/Unbalanced 3D-trees

A program for executing the functional equation (eq. 64) for counting chiral bicentroidal & unbalanced 3D-trees (named "CBUBchiral1-100.mpl") is shown below. To show the correspondence to the two dichotomies, the procedures for counting chiral centroidal & unbalanced 3D-trees (the same as eq. 20) and for counting chiral bicentroidal & balanced 3D-trees (eq. 38) were also programmed in this code.

Maple program for counting chiral alkanes, "CBUBchiral1-100.mpl":

```
"Functional Equations for Alkyl Ligands";
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;

"Alkanes as Centroidal 3D-Trees";
Cxh := (x/24)*(b1^4 + 3*b2^2 + 8*b1*b3 - 6*a1^2*c2 - 6*c4):

"Alkanes as Bicentroidal 3D-Trees";
Cxt := (1/4)*(b1^2 + b2 - a1^2 - c2):

"Initial Values";
a1 := 1; a2 := 1;
b1 := 1; b2 := 1; b3 := 1;
c2 := 1; c4 := 1; c6 := 1;

Bh := x; Ah := x; Ch := 0;
Bt := 0; At := 0; Ct := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Cbx:= coeff(bx,x^m):
Cax:= coeff(ax,x^m):
Ccx:= coeff(cx,x^(m*2)):
a1 := a1 + Cax*x^m:
a2 := a2 + Cax*x^(m*2):
b1 := b1 + Cbx*x^m:
b2 := b2 + Cbx*x^(m*2):
b3 := b3 + Cbx*x^(m*3):
c2 := c2 + Ccx*x^(m*2):
c4 := c4 + Ccx*x^(m*4):
c6 := c6 + Ccx*x^(m*6):
n := 2*m +1:
Ch := Ch + coeff(Cxh,x^n)*x^n + coeff(Cxh,x^(n+1))*x^(n+1):
nn := 2*m:
Ct := Ct + coeff(Cxt,x^nn)*x^nn:
end do:

"Chiral Alkanes as Ballanced 3D-trees";
BxC := (1/2)*((b2-1) - (a2-1)):

"Chiral Alkanes as Bicentroidal/Unbalanced 3D-trees":
BUxC := Ct - BxC:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Ch,x^m), coeff(BUxC,x^m), coeff(BxC,x^m));
end do;
```

Table 6: Numbers of Chiral Alkanes Categorized by Two Dichotomies

k	$\widehat{C}_k$ (Centroidal & unbalanced)	$\widetilde{U}_k^{(C)}$ (Bicentroidal & unbalanced)	$B_k^{(C)}$ (Bicentroidal & balanced)
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0	0	0
6	0	0	0
7	2	0	0
8	1	3	1
9	17	0	0
10	24	21	3
11	142	0	0
12	211	170	10
13	1113	0	0
14	1784	1290	30
15	8780	0	0
16	15041	9680	88
17	70750	0	0
18	127072	75225	255
19	584158	0	0
20	1091507	601020	742
21	4937616	0	0
22	9554169	4913646	2157
23	42617881	0	0
24	84925546	41147928	6312
25	374580272	0	0
26	765735799	351434716	18563
27	3344179169	0	0
28	6991686639	3052406444	54932
29	30262422579	0	0
30	64535740751	26910605148	163479
31	277091404722	0	0
32	601434086766	240339197664	489264
33	2563401079994	0	0
34	5652876029848	2171034151632	1471692
35	23930997120150	0	0
36	53534824577018	19810902096624	4447896
37	225225850040744	0	0
38	510446275671249	182415855489644	13500689
39	2135108676616236	0	0
40	4896888847857945	1693333684316928	41140608
41	20372874776166747	0	0
42	47238611431657314	15834517653168865	125818217
43	195544787602887105	0	0
44	457999551947828613	149058121084835254	386050543
45	1886989260491307050	0	0
46	4461040369492811082	1411693337070824624	1188093392
47	18298681682556106941	0	0
48	43636081455029159803	13444258974971682096	3666547089
49	178246302421277075465	0	0
50	428497964886295432421	128691508649139937350	11344058829
51	1743475977249160896698	0	0
52	4222957578281237677374	1237676126328475582232	35180323336
53	17118606498535050299382	0	0
54	41757573017622330145481	11955155209909770194588	109339097119
55	168676827170994244498994	0	0
56	414192406690674607653066	115946610491159850069600	340508394528
57	1667507044085523278870213	0	0
58	4120269449028478323577468	1128738527373066688688910	1062419370490
59	16535111535254355227318165	0	0
60	41098222466024162207672565	11026844701941179705888430	3320666310903
61	164431691004472878290416331	0	0
62	410979018221786885675376414	108076850325850215726768250	10395996250010
63	1639544206288057228087300846	0	0
64	4119529788255452662170780934	1062546355974610837369643571	32596713516873
65	16388819934891345085062471050	0	0
66	41385225782246336320451797998	10476479815330994238046121940	102354659356690
67	164207682036842086114448097194	0	0
68	416635607643573249809932188495	103576425125384231421407990955	321832884381903
69	1648923729893963761757391941910	0	0
70	4202708638020645946818199797966	1026636422872852928460099161844	1013230630964436
71	16592589875613158504531727357741	0	0
72	42473372537692204736714260167959	10200477451834273436225561185100	3193818534035050
73	167295424464203990256343738221951	0	0
74	430006772381311021662645700992080	101581672299213391682175606717120	10078773177202180
75	1689911835064563934489030380281628	0	0
76	4360786726830838778703764330000384	1013791682525675969638186107104384	31840095204449021
77	17100609751074141570684664508176881	0	0
78	44294354185222182700528141004393441	10138463629083017138288148518383330	100689937510048385
79	173335468778163758926743919095416928	0	0
80	450600427378156832136079227317086424	101587632316921571608122788467850571	318728146981844679
81	1759767313496477928067387728205946251	0	0
82	4590528948690471561022560959260371308	1019796001920058513013718976482968640	1009849492883144730
83	17892924987803326734253890021984886912	0	0
84	46830869858741159117889452362170508243	10255363028472401453574706945499831529	3202399570304430261
85	182194157793655704500115198467223336560	0	0
86	478379522345454678848216263339209430135	103304260659529997807471434842399592618	10163870352469178059
87	1857742280338673466601776204453659906368	0	0
88	4892807796459916527756662912397080793588	1042273130631919367912051902439879332026	32284255140318002679
89	18967377099179003865864655797569778746527	0	0
90	50103146420285113734925982237614318781047	10531975749055818891019596953813028175600	102625414714074250195
91	193898555422930446991054484557154282219435	0	0
92	513654043751710294717723475674321178695904	106579600371335056372859283221723479326706	326465312628541253282
93	1984557489015003230921269397197621565592352	0	0
94	5271743914770706257960929202832187654294339	1080057924052835851968590047147334594849394	1039258352830707100287
95	20335387509472990198568080384836453337202925	0	0
96	54162175051500719402254938276901062628676995	10959815284871517870343941582400840165844014	3310561173602401804486
97	208602785663318655582652789289307612217740815	0	0
98	557028727906484285338942895344159419431573208	111357307668915457889274948263349481888553478	10552597199971538944446
99	2142136450298921147960563205940582654277126951	0	0
100	5734313151200075267208843400877477986664415189	11328463947163724192312785833179892782462041 50	33657783567745352117595

The first paragraph "Functional Equations for Alkyl Ligands" to the fifth paragraph "Recursive Calculation" are cited from the Maple program for counting 3D-trees "Total1-100A.mpl" described above. The six paragraph "Chiral Alkanes as Balanced 3D-trees" is cited from the paper accompanied with the present paper, where the symbol `BxC` is used to designate $B(x)^{(C)}$ for obtaining $B_k^{(C)}$. The seventh paragraph "Chiral Alkanes as Bicentroidal/Unbalanced 3D-trees" is concerned with the enumeration of chiral bicentroidal & unbalanced 3D-trees, where the `BUxC` is used to designate $\widetilde{U}_k^{(C)}$ (eq. 64). The last paragraph describes a print-out step.

The program "CBUBchiral1-100.mpl" was executed on the Maple system to give the results summarized in Table 6. The summation of $\widehat{C}_k$-column (chiral centroidal & unbalanced trees), $\widetilde{U}_k^{(C)}$-column (chiral bicentroidal & unbalanced trees), and $B_k^{(C)}$-column (chiral bicentroidal & balanced trees) gave the total values shown in the $C_k^{(T)}$-column of Table 3. The functional equation (eq. 67) for counting chiral bicentroidal & unbalanced 3D-trees gave the same results as collected in Table 6.

6 Alkanes as Constitutional Isomers

The enumeration problems discussed in this section have once been discussed by Pólya [13, 14] by using Pólya's theorem. In this section, we shall discuss these enumeration problems as special cases of Fujita's proligand method [18–20]. The comparison of the two methodologies demonstrates that the sphericity concept contained in Fujita's proligand method is, in fact, what Pólya's theorem is deficient in for stereoisomer enumeration.

6.1 Constitutional Isomers as Graphs

6.1.1 Alkyl Ligands as Planted Trees

In contrast to Subsection 3.1 which has discussed alkyl ligands as 3D-components, this subsection is devoted to the treatment of alkyl ligands as planted trees, which are graphs in a mathematical context and in turn constitutional isomers in a chemical context.

In place of the generating functions for counting alkyl ligands as 3D-components (eqs. 1–3), we use the symbols $r(x)$ for counting planted trees and $s(x)$ for counting steric planted trees as follows:

$$r(x) = \sum_{k=0}^{\infty} \rho_k x^k \tag{68}$$

$$s(x) = \sum_{k=0}^{\infty} \sigma_k x^k, \tag{69}$$

where the coefficient (ρ_k) of the term x^k of $r(x)$ represents the number of alkyl ligands (or planted trees) of carbon content k; and the coefficient (σ_k) of the term x^k of $s(x)$ represents the number of steric alkyl ligands (or planted 3D-trees) of carbon content k, in which two enantiomers of each pair are separately counted. We put $\rho_0 = 1$ and $\sigma_0 = 1$ to treat trivial cases of terminal vertices (or hydrogen atoms).

By introducing eqs. 4–6 into eq. 9, we obtain the following functional equation:

$$B(x) = 1 + \frac{x}{6}\left(b(x)^3 + 2b(x^3) + 3a(x)c(x^2)\right). \tag{70}$$

When we put $B(x) = r(x)$ and $a(x^d) = b(x^d) = c(x^d) = r(x^d)$, the functional equation (eq. 70) derived by Fujita's proligand method is converted into the following functional equation for $r(x)$. By putting $b(x) = s(x)$, eq. 6 is converted into the following equation function for $s(x)$:

$$\begin{aligned} r(x) &= 1+\frac{x}{6}\left(r(x)^3+2r(x^3)+3r(x)r(x^2)\right) && (71)\\ s(x) &= 1+\frac{x}{3}\left(s(x)^3+2s(x^3)\right). && (72) \end{aligned}$$

The functional equations (eqs. 71 and 72) have recursive nature so as to be capable of calculating the coefficients ρ_k and σ_k appearing in eq. 68 and eq. 69.

The derivation of these equations implies the omission of sphericities so that the CR $\mathbf{C}_{3v}(/\mathbf{C}_s)$ is reduced into the symmetric group of degree 3 ($\mathcal{S}^{[3]}$) and the CR $\mathbf{C}_3(/\mathbf{C}_1)$ is reduced into the alternating group of degree 3 ($\mathcal{A}^{[3]}$). The equations (eqs. 71 and 72) were first noted by Pólya [13, 14], who directly used $\mathcal{S}^{[3]}$ and $\mathcal{A}^{[3]}$. Thus, according to Pólya's treatment [13, 14], the three positions of the methyl skeleton are permuted by the symmetric group of degree 3 (i.e., $\mathcal{S}^{[3]}$) or by the alternating group of degree 3 (i.e., $\mathcal{A}^{[3]}$), where they are characterized by the corresponding cycle indices (CIs). The CIs are transformed into the functional equations (eqs. 71 and 72), which have now been obtained alternatively by the omission of sphericities. These results mean that Fujita's proligand method contains Pólya's theorem as a special case, where the latter lacks the sphericity concept.

6.1.2 Alkanes as Centroidal Trees

The CI-CFs for $\mathbf{T}_d$ (eq. 11) and for $\mathbf{T}$ (eq. 12), which are derived by Fujita's proligand method, can be converted into the following CIs:

$$\begin{aligned} \mathrm{CI}(\mathcal{S}^{[4]}; r_d) &= \frac{1}{24}(r_1^4+3r_2^2+8r_1r_3+6r_1^2r_2+6r_4), && (73)\\ \mathrm{CI}(\mathcal{A}^{[4]}; s_d) &= \frac{1}{12}(s_1^4+3s_2^2+8s_1s_3), && (74) \end{aligned}$$

where we put $r_d = a_d = b_d = c_d$ and $s_d = b_d$ by omitting the sphericities of cycles. The derivation of these equations with the omission of sphericities means that the CR $\mathbf{T}_d(/\mathbf{C}_{3v})$ is reduced into the symmetric group of degree 4 ($\mathcal{S}^{[4]}$) and the CR $\mathbf{T}(/\mathbf{C}_3)$ is reduced into the alternating group of degree 4 ($\mathcal{A}^{[4]}$). These equations (eqs. 73 and 74) were first noted by Pólya [13, 14], who directly used $\mathcal{S}^{[4]}$ and $\mathcal{A}^{[4]}$.

Let $\widehat{R}_k$ be the number of centroidal trees (alkanes as constitutional isomers) of carbon content k. Let $\widehat{S}_k$ be the number of steric centroidal trees carbon content k. In agreement with the definition of centroidal trees, the terms up to x^ν are collected to give the following generating functions:

$$\begin{aligned} \widehat{R}(x) &= \sum_{k=0}^{\nu} \widehat{R}_k x^k && (75)\\ \widehat{S}(x) &= \sum_{k=0}^{\nu} \widehat{S}_k x^k && (76) \end{aligned}$$

where ν runs stepwise from 0 to infinite.

To evaluate these generating functions, the dummy variable r_d (in eq. 73) and s_d (in eq. 74) are replaced by the terms $r(x^d)$ and $s(x^d)$, respectively. Thereby we obtain the following functional equations:

$$\widehat{R}(x) = \frac{x}{24}\left\{r(x)^4 + 3r(x^2)^2 + 8r(x)r(x^3) + 6r(x)^2 r(x^2) + 6r(x^4)\right\} \quad (77)$$

$$\widehat{S}(x) = \frac{x}{12}\left\{s(x)^4 + 3s(x^2)^2 + 8s(x)s(x^3)\right\}, \quad (78)$$

where the multiplying by x is required to take account of the centroid of the $\mathcal{S}^{[4]}$- or $\mathcal{A}^{[4]}$-skeleton. Obviously, eq. 77 is a special case of eq. 18 and eq. 78 is a special case of the functional equation in which the b_d of eq. 12 is replaced by $b(x^d)$. Because we have evaluated $r(x)$ (eq. 71) and $s(x)$ (eq. 72), we are able to evaluate the functional equations (eqs. 77 and 78) under the condition represented by eq. 22 due to the criterion of centroidal trees.

6.1.3 Alkanes as Bicentroidal Trees

The CI-CFs for the factor group $\mathbf{D}_{\infty h}/\mathbf{C}_\infty$ (eq. 29) and for the factor group $\mathbf{D}_\infty/\mathbf{C}_\infty$ (eq. 30), which are derived by Fujita's proligand method, can be converted into the following CIs by omitting the sphericities of cycles:

$$\mathrm{CI}(\mathcal{S}^{[2]}; r_d) = \frac{1}{2}\left(r_1^2 + r_2\right) \quad (79)$$

$$\mathrm{CI}(\mathcal{S}^{[2]}; s_d) = \frac{1}{2}\left(s_1^2 + s_2\right), \quad (80)$$

where we place $r_d = a_d = c_d = b_d$ and $s_d = b_d$.

Let $\widetilde{R}_k$ be the number of bicentroidal trees of carbon content k (alkanes as constitutional isomers). Let $\widetilde{S}_k$ be the number of steric bicentroidal trees carbon content k. In agreement of the definition of bicentroidal trees, the terms up to x^v are collected to give the following generating functions:

$$\widetilde{R}(x) = \sum_{k=0}^{v} \widetilde{R}_k x^k \quad (81)$$

$$\widetilde{S}(x) = \sum_{k=0}^{v} \widetilde{S}_k x^k \quad (82)$$

where v runs stepwise from 0 to infinite.

To evaluate the counting series represented by eqs. 81 and 82, we derive functional equations by substituting $r(x^d)$ and $s(x^d)$ for the dummy variable (r_d and s_d) appearing in the CIs (eqs. 79 and 80). Thereby, we obtain the following functional equations:

$$\widetilde{R}(x) = \frac{1}{2}\left(r(x)^2 + r(x^2)\right) \quad (83)$$

$$\widetilde{S}(x) = \frac{1}{2}\left(s(x)^2 + s(x^2)\right) \quad (84)$$

Because we have evaluated $r(x)$ (eq. 71) and $s(x)$ (eq. 72), the functional equations (eqs. 83 and 84) can be evaluated under the condition represented by eq. 40 due to the criterion of bicentroidal trees.

6.1.4 Total Number of Alkanes as Constitutional Isomers

Because we have evaluated the values of $\widehat{R}_k$ and $\widehat{S}_k$ for centroidal trees as well as those of $\widetilde{R}_k$ and $\widetilde{S}_k$ for bicentroidal trees, the corresponding total numbers are obtained by their summations. Let $R_k^{(\mathrm{T})}$ be the total number of trees of carbon content k. Let $S_k^{(\mathrm{T})}$ be the total number of steric trees of carbon content k. By means of eqs. 75 and 76 and of eqs. 81 and 82, we obtain the following relationships:

$$R_k^{(\mathrm{T})} = \widehat{R}_k + \widetilde{R}_k \tag{85}$$

$$S_k^{(\mathrm{T})} = \widehat{S}_k + \widetilde{S}_k \tag{86}$$

6.2 Implementation and Calculations of Trees

The functional equations derived in Subsection 6.1 were programmed by using Maple programming language. The resulting program was stored in a file named "Graph1-100.mpl", which was executed on the Maple system. The results are shown in Table 7, where the values of $R_k^{(\mathrm{T})}$ and those of $S_k^{(\mathrm{T})}$ are collected up to carbon content 100.

Maple program for counting alkanes as graphs, "Graph1-100.mpl":

```
"Functional Equaitons
for Alkyl Ligands as Graphs";
rx := 1 + (1/6)*x*r1^3 + (1/3)*x*r3 + (1/2)*x*r1*r2;;
sx := 1 + (1/3)*x*s1^3 + (2/3)*x*s3;

"Alkanes as Centroidal Trees or Steric Trees";
Rx := (x/24)*(r1^4 + 3*r2^2 + 8*r1*r3 + 6*r1^2*r2 + 6*r4):
Sx := (x/12)*(s1^4 + 3*s2^2 + 8*s1*s3):

"Alkanes as Bicentroidal Trees or Steric Trees";
Rxb := (1/2)*(r1^2 + r2):
Sxb := (1/2)*(s1^2 + s2):

"Initial Values";
r1 := 1; r2 := 1; r3 := 1; r4 := 1;
s1 := 1; s2 := 1; s3 := 1;
Rc := x; Sc := x;
Rb := 0; Sb := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Crx:= coeff(rx,x^m):
Csx:= coeff(sx,x^m):
r1 := r1 + Crx*x^m:
r2 := r2 + Crx*x^(m*2):
r3 := r3 + Crx*x^(m*3):
r4 := r4 + Crx*x^(m*4):
s1 := s1 + Csx*x^m:
s2 := s2 + Csx*x^(m*2):
s3 := s3 + Csx*x^(m*3):
n := 2*m +1:
Rc := Rc + coeff(Rx,x^n)*x^n + coeff(Rx,x^(n+1))*x^(n+1):
Sc := Sc + coeff(Sx,x^n)*x^n + coeff(Sx,x^(n+1))*x^(n+1):
nn := 2*m:
Rb := Rb + coeff(Rxb,x^nn)*x^nn:
Sb := Sb + coeff(Sxb,x^nn)*x^nn:
end do:

"Total Numbers";
TR := Rc + Rb:
TS := Sc + Sb:
```

Table 7: Total Numbers of Alkanes as Constitutional Isomers

k	$R_k^{(\mathrm{T})} = \widehat{R}_k + \widetilde{R}_k$ (Constitutional isomers)	$S_k^{(\mathrm{T})} = \widehat{S}_k + \widetilde{S}_k$ (Steric isomers)
1	1	1
2	1	1
3	1	1
4	2	2
5	3	3
6	5	5
7	9	11
8	18	24
9	35	55
10	75	136
11	159	345
12	355	900
13	802	2412
14	1858	6563
15	4347	18127
16	10359	50699
17	24894	143255
18	60523	408429
19	148284	1173770
20	366319	3396844
21	910726	9892302
22	2278658	28972080
23	5731580	85289390
24	14490245	252260276
25	36797588	749329719
26	93839412	2234695030
27	240215803	6688893605
28	617105614	20089296554
29	1590507121	60526543480
30	4111846763	182896187256
31	10660307791	554188210352
32	27711253769	1683557607211
33	72214088660	5126819371356
34	188626236139	15647855317080
35	493782952902	47862049187447
36	1295297588128	146691564302648
37	3404490780161	450451875783866
38	8964747474595	1385724615285949
39	23647478933969	4270217915878409
40	62481801147341	13180446189326135
41	165351455535782	40745751356421890
42	438242894769226	126146261761339138
43	1163169707886427	391089580997271932
44	3091461011836856	1214115357550059889
45	8227162372221203	3773978539594435261
46	21921834086683418	11745467449901686692
47	58481806621987010	36597363424982487170
48	156192366474590639	114160680977902614485
49	417612400765382272	356492605035316845170
50	1117743651746953270	1114378947449301509178
51	2994664179967370611	3486951955119466851406
52	8031081780535296591	10921267410435362660722
53	21557771913572630901	34237212999073160792547
54	57919180873148437753	107425456458974884441780
55	155745431857549699124	337353654348452490744594
56	419149571193411829372	1060278034376257564002884
57	1128939578361332867936	3335014088191919979484875
58	3043043571906827182530	10498015952843646536566683
59	8208615366863753915949	33070223070576155646174970
60	22158734535770411074184	104250134336061442638194965
61	59858097847706865855186	328863382009163806484314341
62	161805725349297357221898	1038111737095696080690507406
63	437671691526158936922623	3279088412576819786340554564
64	1184616185385310843585573	10364152288461489029907673400
65	3208285066181475821271463	32777639869784972856521638117
66	8694130712024868414002815	103723411195159061115332289728
67	23573796134448175745408811	328415364073691563245186161518
68	63955159527348138708694312	1040424065537929184647743121855
69	173603007393950249896865875	3297847459787951465172751692029
70	471484798515330363034639871	10458690121787043745788050219883
71	1281151315764638215613845510	33185179751226394595444920750429
72	3482965749140691245110434511	105347699979053105171532968147115
73	9473447386804490449091871124	334590848928408232041622825750695
74	25779306238954404972323916397	1063176889361049308469202368245056
75	70183211512214096492433058105	3379823670129128684719201098631483
76	191156381393249393027319384769	10749156818713031057000419051196725
77	520874195248906781713044332539	34201219502148285787859225315945247
78	1419908915343952137338409797325	108865635628610404733084276132688880
79	3872282575137005474139119076135	346670937556327526442312393877373478
80	10564476906946675106953415600016	1104376119390156823874676963171843690
81	28833609436277333169440806135431	3519534626992955884017523913642183364
82	78725585464391037293036629979444	11220649901221060201205541142124367173
83	215027809474796675607407513633870	35785849975606653559053736216111034222
84	587531723826577193455385789266377	114172465774427121315275225393472118803
85	1605913778494711520354663202536756	364388315587311409294352672358362727472
86	4391002908093323425994602631972445	1163367566009969353870605152617528398101
87	12010257907756938974208750945664835	3715484560677346934159218858174860207957
88	32861295558120887536942123568548502	11870161854183671793152599425256365758915
89	89940959024891576997396491928932689	37934754198358007734835293394248027816201
90	246245150242821439632304475956113295	121270244338681865257784718278619784744640
91	674391606297983432514229725117306224	387797110845860893992206159820632723775670
92	1847515048012613337782670842346319120	1240467288246090702200306549133156534131050
93	5062818112121161180862827915688625902	3969114978030006461875371491975944005948276
94	13877857529584521384324419956411729295	12703603677647084219921221877857878933613159
95	38051836070803837001309074456088423358	40670775018945980397242946322412823379217689
96	104363664561059273927704242814298678658	130243980672744474545399828477628078022970514
97	286312976836850192359345859166390622180	417205571326637311165652966093999165185979823
98	785684759853087702778573182234297830503	1336772071150799486457092489765585309634904580
99	2156596319845084996862701478402986311496	4284272900597842295922256748471557024840649270
100	5921072038125809849884993369103538010139	13734319091832895372882379354968051940087155789

```
"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d  \\\\ \n",
m, coeff(TR,x^m), coeff(TS,x^m));
end do;
```

In this code, the first paragraph "Functional Equations for Alkyl Ligands as Graphs" declares the functional equations for counting alkyl ligands as graphs (eqs. 71 and 72). The symbols `rx` and `sx` are used to designate $r(x)$ and $s(x)$. The second paragraph "Alkanes as Centroidal Trees or Steric Trees" declares the functional equations for counting centroidal trees or steric centroidal trees (eqs. 77 and 78). The symbols `Rx` and `Sx` are used to designate $\widehat{R}(x)$ and $\widehat{S}(x)$. The third paragraph "Alkanes as Bicentroidal Trees or Steric Trees" declares the functional equations for counting bicentroidal trees or steric bicentroidal trees (eqs. 83 and 84). The symbols `Rxb` and `Sxb` are used to designate $\widetilde{R}(x)$ and $\widetilde{S}(x)$. The fourth paragraph "Initial Values" sets initial values for recursive calculations. The fifth paragraph "Recursive Calculation" is composed of a `do` loop for recursive calculations. We use the following symbols: `Rc` for storing $\widehat{R}_k$ (eq. 75), `Sc` for storing $\widehat{S}_k$ (eq. 76), `Rb` for storing $\widetilde{R}_k$ (eq. 81), and `Sb` for storing $\widetilde{S}_k$ (eq. 82). The six paragraph "Total Numbers" involves `TR` for calculation by means of eq. 85 and `TS` for calculation by means of eq. 86. The last paragraph "Print-Out" is to print out the calculation results.

6.3 Combination of Two Dichotomies for Categorizing Trees

6.3.1 Three Categories of Trees

The combination of the two dichotomies described in Section 5 is also effective to itemize trees as graphs, where the sphericities for describing 3D-trees are omitted in accord with the shift of a viewpoint from 3D-objects to graphs (Fig. 5). Hence, there appear three categories, i.e., centroidal & unbalanced trees, bicentroidal & unbalanced trees, and bicentroidal & balanced trees, where the category of "centroidal & balanced" is not permitted because of the definitions of the two dichotomies.

	unbalanced trees ($U_k^{(G)}$)	balanced trees ($B_k^{(G)}$)
centroidal trees ($\widehat{R}_k$)	$\widehat{R}_k = U_k^{(G)} - (\widetilde{R}_k - B_k^{(G)})$	none
bicentroidal trees ($\widetilde{R}_k$)	$\widetilde{R}_k - B_k^{(G)}$	$B_k^{(G)}$

Figure 5: Alkanes as trees (graphs) categorized by two dichotomies

The number of centroidal & unbalanced trees of carbon content k is equal to that of centroidal trees of carbon content k, i.e., $\widehat{R}_k$. The number of bicentroidal & balanced trees of carbon content k is equal to that of balanced trees of carbon content k, where the number is denoted by the symbol $B_k^{(G)}$. It follows that the number of bicentroidal & unbalanced tree of carbon content k is calculated as follows:

$$\widetilde{U}_k^{(G)} = \widetilde{R}_k - B_k^{(G)}, \tag{87}$$

where the symbol $\widetilde{U}_k^{(G)}$ represents the number of bicentroidal & unbalanced trees of carbon content k.

6.3.2 Implementation for Itemized Calculations

The functional equation for counting bicentroidal & unbalanced trees (eq. 87) was programmed and stored in a file named “CBUBgraph1-100.mpl”.

Maple program for counting alkanes, “CBUBgraph1-100.mpl”:

```
"Functional Equations for Alkyl Ligands as Graphs";
rx := 1 + (1/6)*x*r1^3 + (1/3)*x*r3 + (1/2)*x*r1*r2:

"Alkanes as Centroidal Trees or Steric Trees";
Rx := (x/24)*(r1^4 + 3*r2^2 + 8*r1*r3 + 6*r1^2*r2 + 6*r4):

"Alkanes as Bicentroidal Trees or Steric Trees";
Rxb := (1/2)*(r1^2 + r2):

"Initial Values";
r1 := 1; r2 := 1; r3 := 1; r4 := 1;
Rc := x; Rb := 0;

"Recursive Calculation";
for m from 1 to 50 by 1 do
m:
Crx:= coeff(rx,x^m):
r1 := r1 + Crx*x^m:
r2 := r2 + Crx*x^(m*2):
r3 := r3 + Crx*x^(m*3):
r4 := r4 + Crx*x^(m*4):
n := 2*m +1:
Rc := Rc + coeff(Rx,x^n)*x^n + coeff(Rx,x^(n+1))*x^(n+1):
nn := 2*m:
Rb := Rb + coeff(Rxb,x^nn)*x^nn:
end do:

"Alkanes as Balanced Trees";
BxG := r2-1:
"Bicentroidal and Balanced Trees";
BUxG := Rb - BxG:

"Print-Out";
for m from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\\ \n",
m, coeff(Rc,x^m), coeff(BUxG,x^m), coeff(BxG,x^m));
end do;
```

As found easily, the paragraphs “Functional Equations for Alkyl Ligands as Graphs” to “Recursive Calculation” in the program “CBUBgraph1-100.mpl” are composed of codes selected adequately from the program shown in Subsection 6.2 (CBUBtotal1-100.mpl). The subsequent paragraph “Alkanes as Balanced Trees” is added to calculate the number of bicentroidal & balanced trees, where the symbol $B_k^{(G)}$ is abbreviated as `BxG`. The paragraph “Bicentroidal and Balanced Trees” aims at calculating the number of bicentroidal & unbalanced trees, where the symbol $\widetilde{U}_k^{(G)}$ (eq. 87) is represented by `BUxG`.

The calculation results are shown in Table 8, where the numbers of trees are itemized as follows: $\widehat{R}_k$ (centroidal & unbalanced), $\widetilde{U}_k^{(G)}$ (bicentroidal & unbalanced), and $B_k^{(G)}$ (bicentroidal & balanced) (cf. Fig. 5).

Table 8: Numbers of Alkanes as Trees Categorized by Two Dichotomies

k	$\widehat{R}_k$ (Centroidal & unbalanced)	$\widetilde{U}_k^{(\mathrm{G})}$ (Bicentroidal & unbalanced)	$B_k^{(\mathrm{G})}$ (Bicentroidal & balanced)
1	1	0	0
2	0	0	1
3	1	0	0
4	1	0	1
5	3	0	0
6	2	1	2
7	9	0	0
8	8	6	4
9	35	0	0
10	39	28	8
11	159	0	0
12	202	136	17
13	802	0	0
14	1078	741	39
15	4347	0	0
16	6354	3916	89
17	24894	0	0
18	38157	22155	211
19	148284	0	0
20	237541	128271	507
21	910726	0	0
22	1511717	765703	1238
23	5731580	0	0
24	9816092	4671096	3057
25	36797588	0	0
26	64658432	29173341	7639
27	240215803	0	0
28	431987953	185098420	19241
29	1590507121	0	0
30	2917928218	1193869680	48865
31	10660307791	0	0
32	19910436898	7800691965	124906
33	72214088660	0	0
34	137041997938	51583917003	321198
35	493782952902	0	0
36	950665379038	344631378871	830219
37	3404490780161	0	0
38	6640556836540	2324188482045	2156010
39	23647478933969	0	0
40	46677743532346	15804051992886	5622109
41	165351455535782	0	0
42	329965311285835	108277568767578	14715813
43	1163169707886427	0	0
44	2344582517352728	746878455834976	38649152
45	8227162372221203	0	0
46	16737981626775790	5183852358085701	101821927
47	58481806621987010	0	0
48	120009045820117784	36183320385462370	269010485
49	417612400765382272	0	0
50	863868095187587242	253875555846799461	712566567
51	2994664179967370611	0	0
52	6241262372719148751	1789819405924154496	1891993344
53	21557771913572630901	0	0
54	45245054518087830547	12674126350025902378	5034704828
55	155745431857549699124	0	0
56	329032677134210143651	90116894045776567915	13425117806
57	1128939578361332867936	0	0
58	2399838836269611579515	643204735601349052146	35866550869
59	8208615366863753915949	0	0
60	17551563430795289730068	4607171104879129978828	95991365288
61	59858097847706865855186	0	0
62	128695623771737013477627	33110101577303010879765	257332864506
63	437671691526158936922623	0	0
64	945925190131843244233008	238690995252776670998460	690928354105
65	3208285066181475821271463	0	0
66	6968380624869684767461795	1725750087153325825189461	1857821351559
67	23573796134448175745408811	0	0
68	51443628833668465573508031	12511530693674670829579128	5002305607153
69	173603007393950249896865875	0	0
70	380542765558018188591703256	90942032957298688002860946	13486440075669
71	1281151315764638215613845510	0	0
72	2820326219075706272153640730	662639530064948568574363503	36404382430278
73	9473447386804490449091871124	0	0
74	20939917383878361076979181211	4839388855075945514565564903	98380779170283
75	70183211512214096492433058105	0	0
76	155736193991753950318739270766	35420187401495176550028113526	266158552000477
77	520874195248906781713044332539	0	0
78	1160126845612029859367497324697	259782069731921557162935641181	720807976831447
79	3872282575137005474139119076135	0	0
80	8655414899951377197004438074726	1909062006995295955946926863471	1954002050661819
81	28833609436277333169440806135431	0	0
82	64670244894100928025403542397928	14055340570290103965682395564453	5301950692017063
83	215027809474796675607407513633870	0	0
84	483866244117748414180271706010224	103665479708828764876122472116936	14398991611139217
85	1605913778494711520354663202536756	0	0
86	3625120436671718862353794041776817	765882471421604524503039838729876	39137768751465752
87	12010257907756938974208750945664835	0	0
88	27193795807444648606634691041759657	5667499750676238823841477868257380	106465954658531465
89	89940959024891576997396491928932689	0	0
90	204241134823246231673454450083001304	42004015419575207669008636766672578	289841389106439413
91	674391606297983432514229725117306224	0	0
92	1535747711108903353585330669197686679	311767336903709983407698055599536680	789642117549095761
93	5062818112121161180862827915688625902	0	0
94	11560551433785050267926870803673066949	2317306095799471114244734206767006790	2152814945971655556
95	38051836070803837001309074456088423358	0	0
96	87116273863058463335214480687627283623	17247390698000810586616536318310063081	5873225808361331954
97	286312976836850192359345859166390622180	0	0
98	657148274926370623920529007067537922228	128536484926717078842010679919202869201	16033495247557039074
99	2156596319845084996862701478402986311496	0	0
100	4961959128679789479667095353444545912459	959112909446020370174100460717054519920	43797554941937577760

7 Discussion

7.1 Effective Categorization by Two Dichotomies

In order to show the effectiveness of the two dichotomies in the enumeration of alkanes as 3D-trees, let us examine alkanes of carbon content 8. They are depicted in Fig. 6 (14 achiral alkanes) and Fig. 7 (5 chiral alkanes), where they are itemized with respect to the two dichotomies, i.e., the dichotomy of centroidal/bicentroidal 3D trees and the dichotomy of unbalanced/balanced 3D trees. The total numbers appear in Table 3, in which the $(k = 8)$-row indicates $B_8^{(T)} = \widehat{B}_8 + \widetilde{B}_8 = 19$ (total number), $A_8^{(T)} = \widehat{A}_8 + \widetilde{A}_8 = 14$ (the number of achiral alkanes), and $C_8^{(T)} = \widehat{C}_8 + \widetilde{C}_8 = 5$ (the number of chiral alkanes).

Among the fourteen achiral stereoisomers of alkanes of carbon content 8 shown in Fig. 6 (**7**–**20**), there exist seven achiral centroidal alkanes (**7**–**13**) in agreement with the number $\widehat{A}_8 = 7$ (Achiral) listed in the $(k = 8)$-row of Table 1. In addition, Fig. 6 involves seven achiral bicentroidal alkanes (**14**–**20**) in agreement with the number $\widetilde{A}_8 = 7$ (Achiral) listed in the $(k = 8)$-row of Table 2. The seven achiral bicentroidal alkanes (**14**–**20**) shown in Fig. 6 are categorized into three bicentroidal & unbalanced alkanes (**14**–**16**) and four bicentroidal & balanced alkanes (**17**–**20**) in agreement with the numbers ($\widetilde{U}_8^{(A)} = 3$ and $B_8^{(A)} = 4$) listed in the $(k = 8)$-row of Table 5.

Among the five chiral stereoisomers of alkanes of carbon content 8 shown in Fig. 7 (**21**–**25**), there exists one chiral centroidal alkane (**21**) in agreement with the number $\widehat{C}_8 = 1$ (Chiral) listed in the $(k = 8)$-row of Table 1. In addition, Fig. 7 involves four chiral bicentroidal alkanes (**22**–**25**) in agreement with the number $\widetilde{C}_8 = 4$ (Chiral) listed in the $(k = 8)$-row of Table 2. The four chiral bicentroidal alkanes (**22**–**25**) shown in Fig. 7 are categorized into three bicentroidal & unbalanced alkanes (**22**–**24**) and one bicentroidal & balanced alkane (**25**) in agreement with the numbers ($\widetilde{U}_8^{(C)} = 3$ and $B_8^{(C)} = 1$) listed in the $(k = 8)$-row of Table 6.

By combining Fig. 6 with Fig. 7, the total number of each category is confirmed to be equal to the value listed in Table 4, i.e., $\widehat{B}_8 = 8$ (centroidal & unbalanced alkanes: **7**–**13** and **21**), $\widetilde{U}_8^{(AC)} = 6$ (bicentroidal & unbalanced alkanes: **14**–**16** and **22**–**24**), and $B_8^{(AC)} = 5$ (bicentroidal & balanced alkanes: **17**–**20** and and **25**).

7.2 Stereoisomers vs. Constitutional Isomers

The number of alkanes of carbon content 8 is found to be $B_8^{(T)} = 19$ as stereoisomers (3D-trees or 3D-objects) in the $(k = 8)$-row of Table 3, while it is found to be $R_8^{(T)} = 18$ as constitutional isomers (trees or graphs) in the $(k = 8)$-row of Table 7. To examine the difference systematically, relevant values are picked up from Tables 4–6 and Table 8. They are listed in Fig. 8, where they are itemized in terms of the two dichotomies. By examining the data listed in Fig. 8, the difference, i.e., $B_8^{(T)} - R_8^{(T)} = 19 - 18 = 1$, is found to stem from the difference in the numbers of bicentroidal & balanced (3D)-trees, i.e., $B_8^{(AC)} - B_8^{(G)} = 5 - 4 = 1$.

The comparison between Fig. 6 and Fig. 7 indicates that the *meso*-form (**20**) and the chiral form (**25**) of 3,4-dimethylhexane coalesce to give a single constitutional isomer (a single graph) in agreement with the value $B_8^{(AC)} - B_8^{(G)} = 5 - 4 = 1$. Note that each pair of enantiomers is counted just once in the present enumeration, where the formula **25** is depicted as a representative of such a pair of enantiomers. Stereochemically speaking, the relationship between **20** and **25** is diastereomeric.

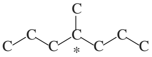
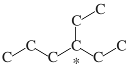
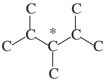
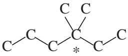
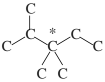
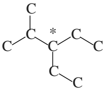
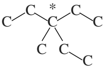
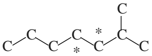
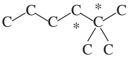
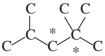
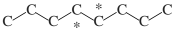
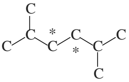
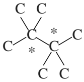
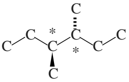
	Unbalanced 3D-trees (10)	Balanced 3D-trees (4)
Centroidal 3D-trees (7)	 **7**  **8**  **9**  **10**  **11**  **12**  **13**	(none)
Bicentroidal 3D-trees (7)	 **14**  **15**  **16**	 **17**  **18**  **19**  **20** (meso)

Figure 6: Fourteen achiral stereoisomers of alkanes of carbon content 8. They are itemized with respect to two kinds of dichotomies, i.e., the dichotomy of centroidal/bicentroidal 3D trees and the dichotomy of unbalanced/balanced 3D trees. A wedged edge is used to show the configuration of the carbon node if necessary. Each carbon with an asterisk is a centroid, while an adjacent pair of carbons with asterisks represents a bicentroid.

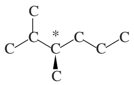
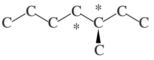
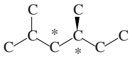
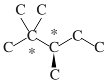
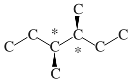
	Unbalanced 3D-trees (4)	Balanced 3D-trees (1)
Centroidal 3D-trees (1)	 **21**	(none)
Bicentroidal 3D-trees (4)	 **22**  **23**  **24**	 **25**

Figure 7: Five chiral stereoisomers of alkanes of carbon content 8. An appropriate enantiomer of each enantiomeric pair is depicted as a representative. The stereoisomers are itemized with respect to two kinds of dichotomies, i.e., the dichotomy of centroidal/bicentroidal 3D trees and the dichotomy of unbalanced/balanced 3D trees. A wedged edge is used to show the configuration of carbon nodes. Each carbon with an asterisk is a centroid, while an adjacent pair of carbons with asterisks represents a bicentroid.

The value $B_9^{(\mathrm{T})} = 38$ for alkanes of carbon content 9 as stereoisomers (3D-trees or 3D-objects) found in the ($k = 9$)-row of Table 3 is different by 3 from the value $R_9^{(\mathrm{T})} = 35$ as constitutional isomers (trees or graphs) found in the ($k = 9$)-row of Table 7. By examining Fig. 9 which lists relevant values, the difference stems from the difference in the numbers of centroidal & unbalanced (3D)-trees, because there are no bicentroidal (3D)-trees in this case.

Among the 38 alkanes as stereoisomers of carbon content 9, the formulas that cause the difference ($\widehat{B}_9 - \widehat{R}_9 = 38 - 35 = 3$) are depicted in Fig. 10.

1. The achiral form (**26**) of 3,5-dimethylheptane and the corresponding chiral form (**27**) have the same constitutional formula so that their coalescence takes place to give a single constitutional isomer. Stereochemically speaking, the relationship between them is diastereomeric. When we focus our attention on the centroid (marked with an asterisk) and we put p = R-$\mathrm{CH(CH_3)CH_2CH_3}$ and $\overline{\mathrm{p}}$ = S-$\mathrm{CH(CH_3)CH_2CH_3}$ (a linking bond is regarded as having lowest priority), the achiral form (**26**) is regarded as a promolecule $\mathrm{CH_2p\overline{p}}$, while the chiral form (**27**) is regarded as a promolecule $\mathrm{CH_2p_2}$ (paired with $\mathrm{CH_2\overline{p}_2}$). Because such a pair of proligands p and $\overline{\mathrm{p}}$ has the same constitutional formula, it generally causes a difference by 1 between the number of stereoisomers and the number of constitutional isomers (graphs).

2. Two chiral 3,4-dimethylheptanes which are diastereomeric, i.e., **28** (paired its enantiomer)

$(B_8^{(\mathrm{T})} = 19)$	Unbalanced 3D-trees	Balanced 3D-trees
Centroidal 3D-trees	$\widehat{A}_8 = 7$ $\widehat{C}_8 = 1$ $\widehat{B}_8 = 8$	none
Bicentroidal 3D-trees	$\widetilde{U}_8^{(\mathrm{A})} = 3$ $\widetilde{U}_8^{(\mathrm{C})} = 3$ $\widetilde{U}_8^{(\mathrm{AC})} = 6$	$B_8^{(\mathrm{A})} = 4$ $B_8^{(\mathrm{C})} = 1$ $B_8^{(\mathrm{AC})} = 5$

$(R_8^{(\mathrm{T})} = 18)$	Unbalanced trees	Balanced trees
Centroidal trees	$\widehat{R}_8 = 8$	none
Bicentroidal trees	$\widetilde{U}_8^{(\mathrm{G})} = 6$	$B_8^{(\mathrm{G})} = 4$

Figure 8: Itemized numbers of 3D-trees (left) vs. trees (right) for alkanes of carbon content 8.

$(B_9^{(\mathrm{T})} = 38)$	Unbalanced 3D-trees	Balanced 3D-trees
Centroidal 3D-trees	$\widehat{A}_9 = 21$ $\widehat{C}_9 = 17$ $\widehat{B}_9 = 38$	none
Bicentroidal 3D-trees	$\widetilde{U}_9^{(\mathrm{A})} = 0$ $\widetilde{U}_9^{(\mathrm{C})} = 0$ $\widetilde{U}_9^{(\mathrm{AC})} = 0$	$B_9^{(\mathrm{A})} = 0$ $B_9^{(\mathrm{C})} = 0$ $B_9^{(\mathrm{AC})} = 0$

$(R_9^{(\mathrm{T})} = 35)$	Unbalanced trees	Balanced trees
Centroidal trees	$\widehat{R}_9 = 35$	none
Bicentroidal trees	$\widetilde{U}_9^{(\mathrm{G})} = 0$	$B_9^{(\mathrm{G})} = 0$

Figure 9: Itemized numbers of 3D-trees (left) vs. trees (right) for alkanes of carbon content 9.

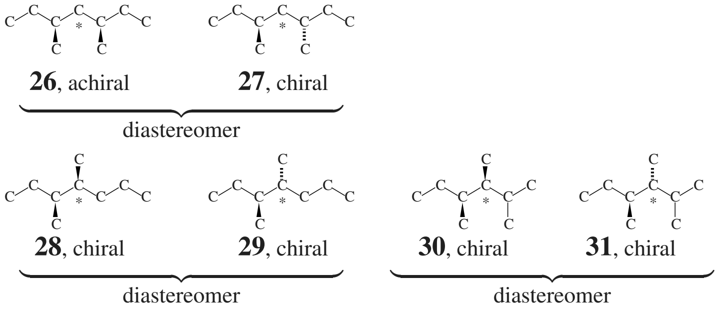
and **29** (paired with its enantiomer), coalesce to give a single constitutional isomer so that they contribute by 1 to the difference ($\widehat{B}_9 - \widehat{R}_9 = 38 - 35 = 3$).

3. On the same line, two chiral 2,3,4-trimethylpentanes (**30** paired its enantiomer and **31** paired with its enantiomer), cause a difference by 1 in the present enumeration.

Totally, the number 6 for stereoisomers (Fig. 10) are reduced into the number 3 for constitutional isomers in agreement with the aforementioned difference ($\widehat{B}_9 - \widehat{R}_9 = 38 - 35 = 3$).

The number of alkanes of carbon content 10 enumerated as stereoisomers $B_{10}^{(\mathrm{T})} = 88$ is larger by 13 than the value enumerated as constitutional isomers ($R_{10}^{(\mathrm{T})} = 75$). To examine the difference systematically, relevant values are collected from Tables 4–6 and Table 8 and listed in Fig. 11. By examining the data listed in Fig. 11, the difference by 13 is divided into three factors: $\widehat{B}_{10} - \widehat{R}_{10} = 46 - 39 = 7$ for the numbers of centroidal & unbalanced (3D)-trees; $\widetilde{U}_{10}^{(\mathrm{AC})} - \widetilde{U}_{10}^{(\mathrm{G})} = 31 - 28 = 3$ for the numbers of bicentroidal & unbalanced (3D)-trees; and $B_{10}^{(\mathrm{AC})} - B_{10}^{(\mathrm{G})} = 11 - 8 = 3$ for the numbers of bicentroidal & balanced (3D)-trees.

1. Among them, alkanes of pseudoasymmetric and *meso*-type cases are depicted in Fig. 12. Two diastereomers of 3,4,5-trimethylheptane, **32** and **33**, exhibit pseudoasymmetric nature. Together with the corresponding chiral stereoisomer (**34** paired with its enantiomer),



26, achiral

27, chiral

28, chiral

29, chiral

30, chiral

31, chiral

Figure 10: Stereoisomers as 3D-trees vs. constitutional isomers as trees. Respective sets of diastereomers are depicted with respect alkanes of carbon content 9. Wedged edges and boldfaced dashed edges are used to show the configurations of carbon nodes. Each carbon with an asterisk is a centroid.

($B^{(\mathrm{T})}_{10} = 88$)	Unbalanced 3D-trees	Balanced 3D-trees
Centroidal 3D-trees	$\widehat{A}_{10} = 22$ $\widehat{C}_{10} = 24$ $\widehat{B}_{10} = 46$	none
Bicentroidal 3D-trees	$\widetilde{U}^{(\mathrm{A})}_{10} = 10$ $\widetilde{U}^{(\mathrm{C})}_{10} = 21$ $\widetilde{U}^{(\mathrm{AC})}_{10} = 31$	$B^{(\mathrm{A})}_{10} = 8$ $B^{(\mathrm{C})}_{10} = 3$ $B^{(\mathrm{AC})}_{10} = 11$

($R^{(\mathrm{T})}_{10} = 75$)	Unbalanced trees	Balanced trees
Centroidal trees	$\widehat{R}_{10} = 39$	none
Bicentroidal trees	$\widetilde{U}^{(\mathrm{G})}_{10} = 28$	$B^{(\mathrm{G})}_{10} = 8$

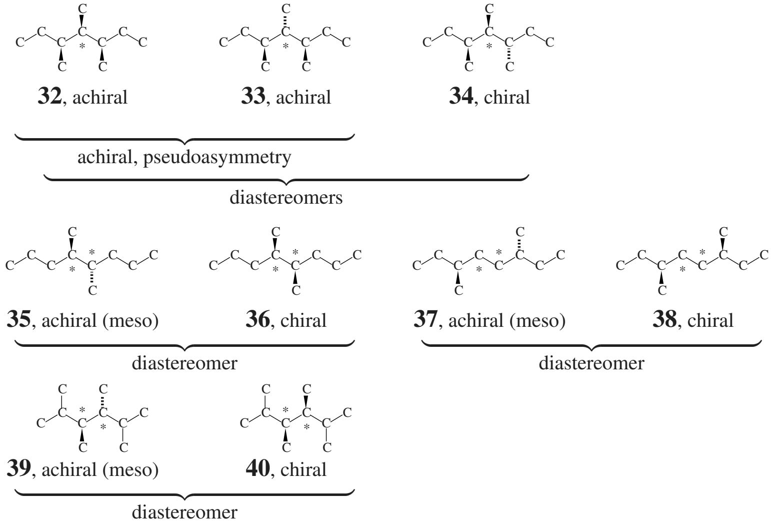
Figure 11: Itemized numbers of 3D-trees (left) vs. trees (right) for alkanes of carbon content 10.

they are regarded as a single constitutional isomer so that a difference by 2 ($= 3 - 1$) contributes to $\widehat{B}_{10} - \widehat{R}_{10} = 46 - 39 = 7$.

2. The remaining three sets of diastereomers depicted in Fig. 12 are concerned with *meso*-cases. For example, the achiral stereoisomer of 3,4-dimethyloctane (**35**) is a *meso*-compound, which is diastereomeric to the chiral stereoisomer (**36**). They are regarded as a single constitutional isomer so that a difference by 1 contributes to the difference $\widetilde{U}^{(\mathrm{AC})}_{10} - \widetilde{U}^{(\mathrm{G})}_{10} = 31 - 28 = 3$. On a similar line, the other sets of chiral diastereomers (**37** and **38** as well as **39** and **40**), each of which is regarded as a single constitutional isomer, contribute to the difference.

Consequently, the three sets of *meso*/chiral diastereomers shown in the second and third rows of Fig. 12 contribute to the whole of the difference $\widetilde{U}^{(\mathrm{AC})}_{10} - \widetilde{U}^{(\mathrm{G})}_{10} = 31 - 28 = 3$.

The remaining 8 sets of diastereomers contributing to $B^{(\mathrm{T})}_{10} - R^{(\mathrm{T})}_{10}$ ($= 13$) are depicted in Fig. 13, where each structure having two asymmetric carbons is a representative of an enantiomeric



32, achiral **33**, achiral **34**, chiral

achiral, pseudoasymmetry

diastereomers

35, achiral (meso) **36**, chiral **37**, achiral (meso) **38**, chiral

diastereomer diastereomer

39, achiral (meso) **40**, chiral

diastereomer

Figure 12: Stereoisomers as 3D-trees vs. constitutional isomers as Trees. Respective sets of diastereomers are depicted with respect to pseudoasymmetric cases and *meso*-cases of alkanes of carbon content 10. Wedged edges and boldfaced dashed edges are used to show the configurations of carbon nodes. Each carbon with an asterisk is a centroid, while an adjacent pair of carbons with asterisks represents a bicentroid.

pair.

1. Because each of the sets is counted just once as a single constitutional isomer (as a graph), it causes a difference by 1 to the value $B^{(\mathrm{T})}_{10} - R^{(\mathrm{T})}_{10}$. Among them, the five sets, i.e., **41/42**, **45/46**, **47/48**, **53/54**, and **55/56**, contribute to $\widehat{B}_{10} - \widehat{R}_{10} = 46 - 39 = 7$ for the numbers of centroidal & unbalanced (3D)-trees.

2. On the other hand, the three sets, i.e., **43/44**, **49/50**, and **51/52**, contribute to $\widetilde{U}^{(\mathrm{AC})}_{10} - \widetilde{U}^{(\mathrm{G})}_{10} = 31 - 28 = 3$ for the numbers of bicentroidal & unbalanced (3D)-trees.

Consequently, there are at least three cases that cause the difference between the number of stereoisomers and the number of constitutional isomers.

1. *Meso*-cases and related cases: A *meso*-promolecule represented by p—$\overline{\mathrm{p}}$ and the corresponding chiral promolecule p—p (paired with $\overline{\mathrm{p}}$—$\overline{\mathrm{p}}$) are counted separately as stereoisomers but regarded as a single constitutional isomer. See Fig. 12 (**35/36**, **37/38**, and **39/40**). The same situation holds true for an achiral promolecule $\mathrm{CH_2p\overline{p}}$ and the corresponding chiral promolecule $\mathrm{CH_2p_2}$ (paired with $\mathrm{CH_2\overline{p}_2}$). See Fig. 10 (**26/27**).

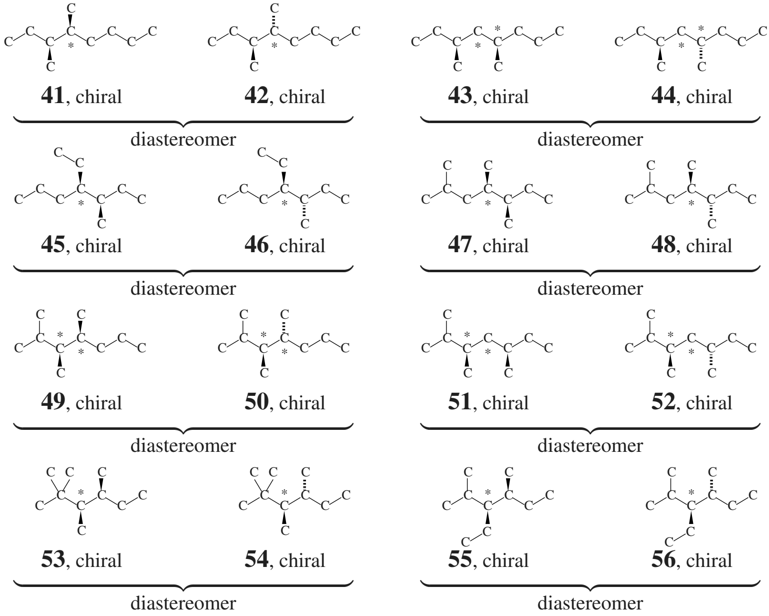


Figure 13: Stereoisomers as 3D-trees vs. constitutional isomers as trees (continued). Respective sets of diastereomers are depicted with respect to chiral alkanes of carbon content 10. Wedged edges and boldfaced dashed edges are used to show the configurations of carbon nodes. Each carbon with an asterisk is a centroid, while an adjacent pair of carbons with asterisks represents a bicentroid.

2. Pseudoasymmetric cases: Two achiral promolecules CXY$p\overline{p}$ and CXY$\overline{p}p$ (pseudoasymmetry) as well as the corresponding chiral promolecule CXYp_2 (paired with CXY$\overline{p}_2$) are counted separately as three stereoisomers but regarded as a single constitutional isomer. See Fig. 12 (**32/33/34** as one constitutional isomer)

3. Other chiral cases having two or more asymmetric carbons. See Fig. 13.

8 Conclusion

Alkanes are counted as 3D-trees or stereoisomers by means of Fujita's proligand method [18–20], where the 3D-trees are categorized according to the dichotomy between centroidal and bicentroidal 3D-trees. The centroidal 3D-trees are enumerated by using a tetrahedral skeleton of $\mathbf{T}_d$-symmetry under the criterion of defining such centroidal 3D-trees. On the other hand, the bicentroidal 3D-trees are enumerated by using a binuclear skeleton of $\mathbf{D}_{\infty h}$-symmetry under the criterion of defining such bicentroidal 3D-trees. Both the enumerations are based on functional equations derived from cycle indices with chirality fittingness (CI-CFs), where the functions $a(x^d)$, $c(x^d)$, and $b(x^d)$ (or their modifications) are substituted for three kinds of sphericity indices (SIs), i.e., a_d for homospheric cycles, c_d for enantiospheric cycles, and b_d for hemispheric cycles. In addition, 3D-trees are alternatively counted under the dichotomy between balanced and unbalanced 3D-trees. The two dichotomies are combined so as to provide a tool of enumeration using three categories, i.e., centroidal & unbalanced 3D-trees, bicentroidal & unbalanced 3D-trees, and bicentroidal & balanced 3D-trees, where the category of centroidal & balanced 3D-trees is not permitted. Respective functional equations based on the two dichotomies are programmed by means of the Maple programming language and executed to give respective stereoisomer numbers, which are collected in tabular forms up to carbon content 100. Thus, the combination of the two dichotomies provides us with a versatile tool for counting alkanes, which satisfies theoretical requirements as well as practical usabilities for personal-computer calculations. The numbers of stereoisomers obtained by Fujita's proligand method are compared with those of constitutional isomers (graphs) derived by using Pólya's theorem so that we derive the conclusion that Pólya's theorem lacks the sphericity concept.

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