

# Systematic Comparison Between Three-Dimensional Structures and Graphs (Part 2). The Fate of Asymmetry and Pseudoasymmetry in the Enumeration of Alkanes

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## Abstract

Alkanes have been enumerated from two viewpoints, i.e., the first viewpoint of “3D structures with asymmetries and pseudoasymmetries” and the second viewpoint of “graphs with asymmetries”. After alkanes are categorized into Types I–V by means of stereoisograms (S. Fujita, *J. Org. Chem.*, **2004**, *69*, 3158–3165), non-recursive functional equations for counting alkanes of Types I–V (as 3D structures) are derived by using three functional equations i.e.,  $a(x, y, z)$  for enumerating achiral ligands,  $c(x^2, y^2, z^2)$  for enumerating diploids, and  $b(x, y, z)$  for enumerating achiral and chiral ligands as steric isomers. The resulting generating functions give isomer numbers from the first viewpoint, where each coefficient of the term  $x^k y^\ell z^m$  represents the number of respective objects with  $k$  carbons,  $\ell$  asymmetric carbons, and  $m$  pseudoasymmetric carbons. On the other hand, the non-recursive functional equations for counting Types I–V are reduced into the corresponding ones for counting alkanes as graphs, where a graph-reduction condition represented by  $a(x, y, z) = c(x, y, z) = b(x, y, z) = r(x, y)$  is employed. During this reduction, the non-recursive functional equations for counting Types II, III, and V vanish to zero. In particular, the variable  $z$  for characterizing pseudoasymmetric carbons disappear during the graph-reduction process, while the variable  $y$  for characterizing asymmetric carbons remains. The resulting non-recursive functional equations give isomer numbers from the

second viewpoint of “graphs with asymmetries”. The data from the two viewpoints are systematically compared with each other so that the fate of asymmetries and pseudoasymmetries are demonstrated. A stereochemical convention that the number of stereoisomers with  $\ell$  asymmetric carbons is equal to  $2^\ell$  has been examined by comparing the two viewpoints.

## 1 Introduction

There have been three epochs in the history of combinatorial enumeration of alkanes and related objects. The first epoch (on the 1970s) was made by Cayley, who investigated the enumeration of rooted trees [1] and trees [2, 3]. Cayley himself was aware that his enumeration of trees was applicable to chemical combinatorics (the enumeration of alkanes) [2]. His accomplishments on trees are concerned with graphs mathematically speaking, or with constitutional isomers chemically speaking.

The second epoch (on the 1930s) was formed by Pólya [4], who derived Pólya’s theorem and applied to the enumeration of alkanes as graphs. Earlier accomplishments before the second epoch as well as a lot of works done after the second epoch have been summarized in books [5–9] and reviews on the graph theory [10–13]. Among them, we should refer to pioneering works by Henze and Blair [14, 15], Otter [16], and Robinson et al. [17], because they prepared the next stage of chemical combinatorics.

The third epoch (the first decade of the 2000s) was marked by Fujita [18, 19], who investigated trees or alkanes as three-dimensional (3D) structures by employing Fujita’s prolignand method [20–22]. The method relied on the concepts of *sphericities* and *sphericity indices*, which were originally assigned to orbits (equivalence classes) in Fujita’s USCI (unit-subduced-cycle-index) approach [23–27]. These concepts were modified to be applied to cycles and combined with the concepts of *proligands* and *promolecules* [28] so as to formulate Fujita’s prolignand method. Several merits of Fujita’s prolignand method have been discussed in comparison with Pólya’s theorem in an article of his own [29]. Further applications of Fujita’s prolignand method to more detailed enumerations have been reported in the present journal [30–32] and other journals [33–35].

Recently, we have studied the effect of asymmetric and pseudoasymmetric centers on the enumerations of monosubstituted alkanes (as planted 3D trees) [36] and alkanes (as 3D trees) [37]. Throughout these studies, we have encountered difficulties in distinguishing between the term “asymmetric” and the closely related term “pseudoasymmetric”. These difficulties have been coped with in a practical manner so that we were able to evaluate the effect of asymmetric and pseudoasymmetric centers in 3D structures. However, more fundamental studies are necessary to grasp the gist of the effect with respect to the difference between graphs and 3D structures.

In contrast to 3D structures, graphs lack the concept of pseudoasymmetry, although the other concept of asymmetry has been employed in the enumeration of alkanes as graphs [4, 9]. This means that more understanding of pseudoasymmetry rather than asymmetry is crucial to throw a light to a question: how graphs are different from 3D structures. To answer this question, we have studied enumeration of monosubstituted alkanes as a representative example in Part 1 of this series. In a continuation of Part 1, the present paper will be devoted to examine the reduction of 3D structures into graphs and the fate of pseudoasymmetry during the reduction process, where we adopt the enumeration of alkanes as another representative example. In

particular, 3D structures discussed on the basis of point groups will be linked to such graphs discussed on the basis of permutation groups.

## 2 Centroidal and Bicentroidal Alkanes as 3D Structures

We have already reported the effects of asymmetric and pseudoasymmetric carbons in the enumeration of alkanes (3D trees) in a previous article appearing in this journal [37], where such alkanes were categorized into centroidal and bicentroidal alkanes as 3D structures. In the present paper, centroidal and bicentroidal alkanes as “3D structures with asymmetric and pseudoasymmetric carbons” will be compared with centroidal and bicentroidal alkanes as “graphs with asymmetric carbons”. To do this task, we first revisit the enumeration of 3D structures briefly and then discuss the reduction of 3D structures into graphs.

### 2.1 Enumeration of Centroidal Alkanes as 3D Structures

#### 2.1.1 Cycle Indices With Chirality Fittingness

In order to discuss the reduction of 3D structures into graphs, the present subsection is devoted to the brief introduction of previous results of centroidal alkanes (3D trees). Centroidal alkanes are generated by placing alkyl ligands on the four positions of a tetrahedral skeleton belonging to the *RS*-stereoisomeric group induced from the  $\mathbf{T}_d$ -point group. The cycle indices with chirality fittingness (CI-CFs) derived in the previous article (eqs. 29–33 of Ref. [37]) are cited here for the sake of convenience:

$$\text{CI-CF}^{(\text{I})}(\mathbf{T}_d; \$_d) = \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3) - \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \quad (1)$$

$$\text{CI-CF}^{(\text{II})}(\mathbf{T}_d; \$_d, b_d) = \frac{1}{2}(b_1^2b_2 + b_4) - \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \quad (2)$$

$$\begin{aligned} \text{CI-CF}^{(\text{III})}(\mathbf{T}; \$_d, b_d) &= \frac{1}{12}(b_1^4 + 3b_2^2 + 8b_1b_3) - \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3) - \frac{1}{2}(b_1^2b_2 + b_4) \\ &\quad - \frac{1}{2}(a_1^2c_2 + c_4) + (a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \end{aligned} \quad (3)$$

$$\text{CI-CF}^{(\text{IV})}(\mathbf{T}_d; \$_d) = \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \quad (4)$$

$$\text{CI-CF}^{(\text{V})}(\mathbf{T}_d; \$_d) = \frac{1}{2}(a_1^2c_2 - a_1^2a_2) - \frac{1}{2}(a_2c_2 - a_2^2), \quad (5)$$

where the symbol  $\$_d$  is used in place of  $a_d, b_d$ .

Suppose that alkyl ligands attaching to a centroid are characterized to be proligands stored in the following warehouse:

$$\mathbf{L} = \{A, B, X, Y, p, \bar{p}; q, \bar{q}; r, \bar{r}; s, \bar{s}\}, \quad (6)$$

where the symbols A, B, X, and Y represent achiral proligands in isolation, while  $p/\bar{p}$ ,  $q/\bar{q}$ ,  $r/\bar{r}$ , and  $s/\bar{s}$  represent pairs of enantiomeric (enantiomorphic) ligands in isolation. Fujita’s proligand method [20–22] requires the following ligand inventories:

$$a_d = A^d + B^d + X^d + Y^d \quad (7)$$

$$b_d = A^d + B^d + X^d + p^d + \bar{p}^d + q^d + \bar{q}^d + r^d + \bar{r}^d + s^d + \bar{s}^d \quad (8)$$

$$c_d = A^d + B^d + X^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} + 2r^{d/2}\bar{r}^{d/2} + 2s^{d/2}\bar{s}^{d/2}. \quad (9)$$

By introducing the ligand inventories into eqs. 1–5, we are able to obtain the numbers of achiral and chiral objects of Types I–V on the basis of the warehouse represented by eq. 6. Note again that each proligand contained in  $\mathbf{L}$  is selected from monosubstituted alkanes (or alkyl ligands) in the present context.

Because alkanes (3D trees) of Types I–III are chiral, two enantiomers of each pair are counted separately in eqs. 1–3. These equations for Types I–III are divided by two and summed up together with those for Types IV and V (eqs. 4 and 5) so as to provide the total number of alkanes as 3D structures:

$$\begin{aligned} \text{CI-CF}(\mathbf{T}_d; \$d, b_d) &= \frac{1}{2} \{ \text{CI-CF}^{(I)}(\mathbf{T}_I; \$d) + \text{CI-CF}^{(II)}(\mathbf{T}_{\bar{\sigma}}; \$d, b_d) + \text{CI-CF}^{(III)}(\mathbf{T}; \$d, b_d) \} \\ &\quad + \text{CI-CF}^{(IV)}(\mathbf{T}_d; \$d) + \text{CI-CF}^{(V)}(\mathbf{T}_d; \$d) \\ &= \frac{1}{24} (b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4), \end{aligned} \quad (10)$$

where each pair of enantiomers is counted once, just as each achiral alkane is counted once.

On the other hand, the summing-up of the equations for Types I to V gives the total number of steric isomers as 3D structures:

$$\begin{aligned} \text{CI-CF}(\mathbf{T}; b_d) &= \text{CI-CF}^{(I)}(\mathbf{T}_I; \$d) + \text{CI-CF}^{(II)}(\mathbf{T}_{\bar{\sigma}}; \$d, b_d) + \text{CI-CF}^{(III)}(\mathbf{T}; \$d, b_d) \\ &\quad + \text{CI-CF}^{(IV)}(\mathbf{T}_d; \$d) + \text{CI-CF}^{(V)}(\mathbf{T}_d; \$d) \\ &= \frac{1}{12} (b_1^4 + 3b_2^2 + 8b_1b_3), \end{aligned} \quad (11)$$

where two enantiomers of each pair are counted separately.

### 2.1.2 Functional Equations for Counting Centroidal Alkanes as 3D Structures

In the present paper, we postulate that the ligand inventories represented by eqs. 7–9 have been obtained as generating functions for counting alkyl ligands of carbon content  $k$ , which have  $\ell$  asymmetric centers and  $m$  pseudoasymmetric centers.

$$a(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \alpha_{k\ell m} z^m \right) y^{\ell} \right) x^k \quad (12)$$

$$c(x^2, y^2, z^2) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \gamma_{k\ell m} z^{2m} \right) y^{2\ell} \right) x^{2k} \quad (13)$$

$$b(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \beta_{k\ell m} z^m \right) y^{\ell} \right) x^k, \quad (14)$$

where we place  $\alpha_{000} = 1$ ,  $\gamma_{000} = 1$ , and  $\beta_{000} = 1$  for trivial cases of hydrogens. The series represented by eqs. 12–14 have been already noted in previous articles [36, 37].

By using eqs. 12–14, centroidal alkanes as 3D structures have been enumerated by considering the numbers of asymmetric and pseudoasymmetric carbons [37], where relevant functional equations were noted to count centroidal alkanes of Types I–V. The functional equations (eqs. 36–40 of Ref. [37]) are cited below:

$$\begin{aligned}\widehat{B}^{(I)}(x, y, z) &= \frac{xy}{12} \{a(x, y, z)^4 + 3c(x^2, y^2, z^2)^2 + 8a(x, y, z)a(x^3, y^3, z^3)\} \\ &\quad - \frac{xy}{2} \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) \\ &\quad \quad - a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4)\} \end{aligned} \quad (15)$$

$$\begin{aligned}\widehat{B}^{(II)}(x, y, z) &= \frac{x}{2} \{b(x, y, z)^2b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\ &\quad - \frac{x}{2} \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) \\ &\quad \quad - a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4)\} \end{aligned} \quad (16)$$

$$\begin{aligned}\widehat{B}^{(III)}(x, y, z) &= \frac{xy}{12} \{b(x, y, z)^4 + 3b(x^2, y^2, z^2)^2 + 8b(x, y, z)b(x^3, y^3, z^3)\} \\ &\quad - \frac{xy}{12} \{a(x, y, z)^4 + 3c(x^2, y^2, z^2)^2 + 8a(x, y, z)a(x^3, y^3, z^3)\} \\ &\quad - \frac{xy}{2} \{b(x, y, z)^2b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\ &\quad - \frac{xy}{2} \{a(x, y, z)^2c(x^2, y^2, z^2) + c(x^4, y^4, z^4)\} \\ &\quad + xy \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) \\ &\quad \quad - a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4)\} \end{aligned} \quad (17)$$

$$\begin{aligned}\widehat{B}^{(IV)}(x, y, z) &= \frac{x}{2} \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) \\ &\quad \quad - a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4)\} \end{aligned} \quad (18)$$

$$\begin{aligned}\widehat{B}^{(V)}(x, y, z) &= \frac{xz}{2} \{a(x, y, z)^2c(x^2, y^2, z^2) - a(x, y, z)^2a(x^2, y^2, z^2)\} \\ &\quad - \frac{xz}{2} \{a(x^2, y^2, z^2)c(x^2, y^2, z^2) - a(x^2, y^2, z^2)^2\}, \end{aligned} \quad (19)$$

These equations can be evaluated by introducing the generating functions eqs. 12–14.

In a similar way to the derivation of eq. 10, we use eqs. 15–19 to derive the following functional equation:

$$\begin{aligned}\widehat{B}(x, y, z) &= \frac{1}{2} \{\widehat{B}^{(I)}(x, y, z) + \widehat{B}^{(II)}(x, y, z) + \widehat{B}^{(III)}(x, y, z)\} + \widehat{B}^{(IV)}(x, y, z) + \widehat{B}^{(V)}(x, y, z) \\ &= \frac{xy}{24} \{b(x, y, z)^4 + 3b(x^2, y^2, z^2)^2 + 8b(x, y, z)b(x^3, y^3, z^3)\} \\ &\quad - \frac{xy}{4} \{b(x, y, z)^2b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\ &\quad - \frac{xy}{4} \{a(x, y, z)^2c(x^2, y^2, z^2) + c(x^4, y^4, z^4)\} \\ &\quad + \frac{xy}{4} \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) - a(x^2, y^2, z^2)^2 \\ &\quad \quad + c(x^4, y^4, z^4)\} \\ &\quad + \frac{x}{4} \{b(x, y, z)^2b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\ &\quad + \frac{x}{4} \{a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2) \\ &\quad \quad - a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4)\} \end{aligned}$$

$$\begin{aligned}
 & + \frac{xz}{2} \{a(x, y, z)^2 c(x^2, y^2, z^2) - a(x, y, z)^2 a(x^2, y^2, z^2)\} \\
 & - \frac{xz}{2} \{a(x^2, y^2, z^2) c(x^2, y^2, z^2) - a(x^2, y^2, z^2)^2\}, \tag{20}
 \end{aligned}$$

which has been already noted in part (eq. 45 of Ref. [37]), where the expanded form given in the latter half of eq. 20 has not been reported.

By following the procedure described in Ref. [37], eq. 20 is evaluated stepwise by using eqs. 12–14. The result is summarized to give a generating function:

$$\widehat{B}(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \widehat{B}_{k\ell m} z^m \right) y^{\ell} \right) x^k, \tag{21}$$

where the coefficient  $\widehat{B}_{k\ell m}$  of the term  $x^k y^{\ell} z^m$  represents the number of centroidal alkanes of carbon content  $k$  which have  $\ell$  asymmetric carbons and  $m$  pseudoasymmetric carbons.

The numbers of steric isomers, where two enantiomers (3D structures) of each pair are counted separately and each achiral 3D structure is counted once, are evaluated by summing up the functional equations for Types I–V (eqs. 15–19).

$$\begin{aligned}
 \widehat{S}(x, y, z) &= \widehat{B}^{(I)}(x, y, z) + \widehat{B}^{(II)}(x, y, z) + \widehat{B}^{(III)}(x, y, z) + \widehat{B}^{(IV)}(x, y, z) + \widehat{B}^{(V)}(x, y, z) \\
 &= \frac{xy}{12} \{b(x, y, z)^4 + 3b(x^2, y^2, z^2)^2 + 8b(x, y, z)b(x^3, y^3, z^3)\} \\
 &\quad - \frac{xy}{2} \{b(x, y, z)^2 b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\
 &\quad - \frac{xy}{2} \{a(x, y, z)^2 c(x^2, y^2, z^2) + c(x^4, y^4, z^4)\} \\
 &\quad + \frac{xy}{2} \{a(x, y, z)^2 a(x^2, y^2, z^2) + a(x^2, y^2, z^2) c(x^2, y^2, z^2) - a(x^2, y^2, z^2)^2 \\
 &\quad + c(x^4, y^4, z^4)\} \\
 &\quad + \frac{x}{2} \{b(x, y, z)^2 b(x^2, y^2, z^2) + b(x^4, y^4, z^4)\} \\
 &\quad + \frac{xz}{2} \{a(x, y, z)^2 c(x^2, y^2, z^2) - a(x, y, z)^2 a(x^2, y^2, z^2)\} \\
 &\quad - \frac{xz}{2} \{a(x^2, y^2, z^2) c(x^2, y^2, z^2) - a(x^2, y^2, z^2)^2\}. \tag{22}
 \end{aligned}$$

By following the procedure described in Ref. [37], eq. 22 is evaluated stepwise by using eqs. 12–14. The result is summarized to give a generating function:

$$\widehat{S}(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \widehat{S}_{k\ell m} z^m \right) y^{\ell} \right) x^k, \tag{23}$$

where the coefficient  $\widehat{S}_{k\ell m}$  of the term  $x^k y^{\ell} z^m$  represents the number of centroidal alkanes of carbon content  $k$  which have  $\ell$  asymmetric carbons and  $m$  pseudoasymmetric carbons.

### 2.1.3 Programming and Implementation for Counting Alkanes as 3D Structures

For the purpose of comparing them with the present data of alkanes as graphs, previous data reported in [37] are recalculated by using the following program (3DAlkaneCB.mpl), where the multiple recursive processes of the previous programs (Alkyl11-30zfinal9.mpl of [36] and

Alkane1-30b.mpl of [37]) are simplified into a single do loop by using the Maple command subs. For the sake of convenience, the calculation of bicentroidal alkanes (see below) is programmed together with the calculation of centroidal alkanes. Thereby, the total numbers of alkanes are obtained as data of 3D structures (Table 1), which can be directly compared with the data of graphs (Table 6).

```
#3DAalkaneCB.mpl
"Alkyl Ligands as Planted 3D-Trees";
axyz := 1 + x*a1*a2 + x*z*(a1*c2 - a1*a2);
cxyz := 1 + x^2*c2*c4 + x^2*z^2*(a2*c4-a2*a4)
+ (1/3)*x^2*y^2*c2^3 + (2/3)*x^2*y^2*c6
- x^2*y^2*c2*c4 - x^2*y^2*(a2*c4-a2*a4);
bxyz := 1 + x*b1*b2 + x*z*(a1*c2 - a1*a2)
+ (1/3)*x*y*b1^3 + (2/3)*x*y*b3
- x*y*b1*b2 - x*y*(a1*c2 - a1*a2);

"Alkanes as Centroidal 3D-Trees";
typeI := (x*y/12)*(a1^4 + 3*c2^2 + 8*a1*a3)
- (x*y/2)*(a1^2*a2 + a2*c2 - a2^2 + c4);
typeII := (x/2)*(b1^2*b2 + b4)
- (x/2)*(a1^2*a2 + a2*c2 - a2^2 + c4);
typeIII := (x*y/12)*(b1^4 + 3*b2^2 + 8*b1*b3)
- (x*y/12)*(a1^4 + 3*c2^2 + 8*a1*a3)
- (x*y/2)*(a1^2*c2 + c4) - (x*y/2)*(b1^2*b2 + b4)
+ x*y*(a1^2*a2 + a2*c2 - a2^2 + c4);
typeIV := (x/2)*(a1^2*a2 + a2*c2 - a2^2 + c4);
typeV := (x*z/2)*(a1^2*c2 - a1^2*a2) - (x*z/2)*(a2*c2 - a2^2);
Bxh := (1/2)*(typeI + typeII + typeIII) + typeIV + typeV;

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

"Initial Values";
a1 := 1; a2 := 1; a3 := 1; a4 := 1;
c2 := 1; c4 := 1; c6 := 1;
b1 := 1; b2 := 1; b3 := 1; b4 := 1;
Bh := x; Bt := 0;

"Recursive Calculation";
kmax := 15;
for k from 1 to kmax by 1 do
Cbxyz := expand(coeff(bxyz, x^k));
Caxyz := expand(coeff(axyz, x^k));
Ccxyz := expand(coeff(cxyz, x^(k*2)));
b1 := b1 + Cbxyz*x^k;
b2 := subs({x=x^2, y=y^2, z=z^2}, b1);
b3 := subs({x=x^3, y=y^3, z=z^3}, b1);
b4 := subs({x=x^4, y=y^4, z=z^4}, b1);
a1 := a1 + Caxyz*x^k;
a2 := subs({x=x^2, y=y^2, z=z^2}, a1);
a3 := subs({x=x^3, y=y^3, z=z^3}, a1);
a4 := subs({x=x^4, y=y^4, z=z^4}, a1);
c2 := c2 + Ccxyz*x^(2*k);
c4 := subs({x=x^2, y=y^2, z=z^2}, c2);
c6 := subs({x=x^3, y=y^3, z=z^3}, c2);
Bt := Bt + coeff(expand(Bxt), x^(2*k)) * x^(2*k);
q := 2*k + 1;
Bh := Bh + coeff(expand(Bxh), x^q) * x^q
end do;
```

```

+ coeff(expand(Bxh), x^(q+1)) * x^(q+1) :
end do:

"Print Out";
for k from 1 to 2*kmax by 1 do
BhBt := sort(collect(expand(coeff(Bh+Bt, x^k)), y),
[z, y], ascending) * x^k;
Total := subs({y=1, z=1}, expand(coeff(Bh+Bt, x^k)));
end do;

```

The symbols `typeI`–`typeV` denote the functional equations represented by  $\widehat{B}^{(I)}(x, y, z)$  (eq. 15)– $\widehat{B}^{(V)}(x, y, z)$  (eq. 19). The symbol `Bxh` declares the functional equation  $B(x, y, z)$  (eq. 20), where the resulting series is stored in `Bh`. The symbols `BtypeII` and `BtypeIV` represent the functional equations for bicentroidal alkanes described below:  $\widetilde{B}^{(II)}(x, y, z)$  (eq. 26) and  $\widetilde{B}^{(IV)}(x, y, z)$  (eq. 27). The symbol `Bxt` declares the functional equation  $\widetilde{B}(x, y, z)$  (eq. 28), where the resulting series is stored in `Bt`.

After escaping from the `do` loop for  $k$ , the last part (“Print Out of ...”) of the program shows the print-out of the calculation result (`BhBt`) which is the sum of the two series stored in `Bh` and `Bt`. The result is collected in Table 1. The coefficient of the term  $x^k y^\ell z^m$  represents the number of alkanes (as 3D structures) of carbon content  $k$  which are characterized by  $\ell$  asymmetric carbons or  $m$  pseudoasymmetric carbons. The data collected in Table 1 are confirmed by summing up Table 8 (for centroidal alkanes in Ref. [37]) and Table 11 (for bicentroidal alkanes in Ref. [37]), where these previous data of tabular forms (concerning  $k$ ,  $\ell$ , an  $m$ ) should be converted into generating functions concerning  $x^k y^\ell z^m$ .

By putting  $y = 1$  and  $z = 1$ , we are able to obtain the total number of alkanes (as 3D structures) of carbon content  $k$ , where the calculated values are stored in `Total` and shown in the rightmost column of Table 1. The values collected in the `Total`-column of Table 1 are identical to those obtained previously by taking no account of  $y$  and  $z$  (Table 4 of Ref. [19]).

The generating function (eq. 21) for counting centroidal alkanes as 3D structures is stored in the series `Bh`. The results are identical with those collected in Table 8 of Ref. [37].

To evaluate the numbers of centroidal steric isomers, eq. 22 is declared by adding the code:

```
Sxh := typeI + typeII + typeIII + typeIV + typeV;
```

to the program “3DAlkaneCB.mpl” together with related descriptions. Thereby, the corresponding generating function (eq. 23) is obtained, as shown in Table 2.

## 2.2 Enumeration of Bicentroidal Alkanes as 3D Structures

### 2.2.1 Cycle Indices With Chirality Fittingness

Bicentroidal alkanes are generated by placing alkyl ligands on the two positions of a dumbbell-like skeleton belonging to the *RS*-stereoisomeric group which can be equalized to the factor group  $\mathbf{K} = \mathbf{D}_{\infty h} / \mathbf{C}_{\infty h}$ . The cycle indices with chirality fittingness (CI-CFs) derived in one of the previous reports (eqs. 74 and 75 of Ref. [37]) are cited here for the sake of convenience:

$$\text{CI-CF}^{(II)}(\mathbf{K}; \$_d) = \frac{1}{2}(b_1^2 + b_2 - a_1^2 - c_2) \quad (24)$$

$$\text{CI-CF}^{(IV)}(\mathbf{K}; \$_d) = \frac{1}{2}(a_1^2 + c_2). \quad (25)$$



Table 1: Numbers of Alkanes (Centroidal and Bicentroidal 3D Structures) with Considering Asymmetric and Pseudoasymmetric Carbons<sup>a)</sup>

The term $\left(\sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}(\widehat{B}_{k\ell m} + \widetilde{B}_{k\ell m})y^{\ell}z^m\right)x^k$ (cf. eq. )	Total
$x$	1
$x^2$	1
$x^3$	1
$2x^4$	2
$3x^5$	3
$5x^6$	5
$(7 + 2y)x^7$	9
$(13 + 4y + 2y^2)x^8$	19
$(20 + 12y + 6y^2)x^9$	38
$(35 + 28y + (23 + 2z)y^2)x^{10}$	88
$(55 + 67y + (67 + 2z)y^2 + 12y^3)x^{11}$	203
$(96 + 143y + (196 + 12z)y^2 + 56y^3 + 6y^4)x^{12}$	509
$(156 + 313y + (518 + 16z)y^2 + 258y^3 + 38y^4)x^{13}$	1299
$(267 + 647y + (1341 + 54z)y^2 + 912y^3 + (230 + 4z)y^4 + 4y^5)x^{14}$	3459
$(438 + 1337y + (3296 + 80z)y^2 + 3034y^3 + (1070 + 4z)y^4 + 88y^5)x^{15}$	9347
$(747 + 2688y + (7917 + 214z)y^2 + 9158y^3 + (4466 + 32z)y^4 + 648y^5 + 20y^6)x^{16}$	25890
$(1239 + 5372y + (18447 + 338z)y^2 + 26402y^3 + (16591 + 40z)y^4 + 3844y^5 + 232y^6)x^{17}$	72505
$(2099 + 10557y + (42146 + 784z)y^2 + (72258 + 204z)y^3 + (57016 + 426z + 3z^2)y^4 + (18304 + 56z)y^5 + (1992 + 8z)y^6 + 24y^7)x^{18}$	205877
$(3498 + 20627y + (94307 + 1290z)y^2 + (191204 + 440z)y^3 + (184238 + 976z + 7z^2)y^4 + (79045 + 296z)y^5 + (13120 + 24z)y^6 + 540y^7)x^{19}$	589612
$(5912 + 39840y + (207717 + 2734z)y^2 + (489342 + 1362z)y^3 + (565173 + 3542z + 28z^2)y^4 + (308036 + 1524z + z^2)y^5 + (72488 + 256z)y^6 + 5548y^7 + 72y^8)x^{20}$	1703575
(omitted)	

<sup>a)</sup>The coefficient of each term  $y^{\ell}z^m x^k$  represents the number of alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers and  $m$  carbons are pseudoasymmetric centers.

Table 2: Numbers of Centroidal Alkanes as Steric Isomers with Considering Asymmetric and Pseudoasymmetric Carbons<sup>a)</sup>

The term $\left(\sum_{\ell=0}^{\infty}(\sum_{m=0}^{\infty}\widehat{S}_{k\ell m}z^m)y^{\ell}\right)x^k$ (cf. eqs. 22 and 23)	Total
$x$	1
0	0
$x^3$	1
$x^4$	1
$3x^5$	3
$2x^6$	2
$(7+4y)x^7$	11
$(7+2y)x^8$	9
$(20+24y+11y^2)x^9$	55
$(20+26y+(22+2z)y^2)x^{10}$	70
$(55+134y+(130+2z)y^2+24y^3)x^{11}$	345
$(60+158y+(216+12z)y^2+48y^3)x^{12}$	494
$(156+626y+(1024+16z)y^2+516y^3+74y^4)x^{13}$	2412
$(162+734y+(1562+54z)y^2+1024y^3+(240+4z)y^4+8y^5)x^{14}$	3788
$(438+2674y+(6559+80z)y^2+6068y^3+(2128+4z)y^4+176y^5)x^{15}$	18127
$(471+3260y+(9762+214z)y^2+11140y^3+(5232+32z)y^4+688y^5)x^{16}$	30799
$(1239+10744y+(36811+338z)y^2+52804y^3+(33131+40z)y^4+7688y^5+460y^6)x^{17}$	143255
$(1319+13158y+(53530+706z)y^2+91332y^3+(71108+176z)y^4+22608y^5+(2360+8z)y^6+48y^7)x^{18}$	256353
$(3498+41254y+(188416+1290z)y^2+(382408+880z)y^3+(368299+1708z+7z^2)y^4+(158090+592z)y^5+(26208+40z)y^6+1080y^7)x^{19}$	1173770
$(3767+51080y+(270614+2474z)y^2+(637364+964z)y^3+(730422+3346z+18z^2)y^4+(392360+1864z+2z^2)y^5+(89160+368z)y^6+6360y^7)x^{20}$	2190163
(omitted)	

<sup>a)</sup>The coefficient of each term  $y^{\ell}z^m x^k$  represents the number of alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers and  $m$  carbons are pseudoasymmetric centers.

## 2.2.2 Functional Equations for Counting Bicentroidal Alkanes as 3D Structures

Bicentroidal alkanes as 3D structures have been enumerated by considering the numbers of asymmetric and pseudoasymmetric carbons Ref. [37], where relevant functional equations were noted to count bicentroidal alkanes of Types II and IV. The functional equations (eqs. 78 and 79 of Ref. [37]) are cited below:

$$\tilde{B}^{(II)}(x, y, z) = \frac{1}{2} \{b(x, y, z)^2 + b(x^2, y^2, z^2) - a(x, y, z)^2 - c(x^2, y^2, z^2)\} \quad (26)$$

$$\tilde{B}^{(IV)}(x, y, z) = \frac{1}{2} \{a(x, y, z)^2 + c(x^2, y^2, z^2)\}. \quad (27)$$

The functional equation for calculating total numbers (eq. 82 of Ref. [37]) is also cited as follows:

$$\begin{aligned} \tilde{B}(x, y, z) &= \frac{1}{2} \tilde{B}^{(II)}(x, y, z) + \tilde{B}^{(IV)}(x, y, z) \\ &= \frac{1}{4} \{b(x, y, z)^2 + b(x^2, y^2, z^2) + a(x, y, z)^2 + c(x^2, y^2, z^2)\}, \end{aligned} \quad (28)$$

where a pair of enantiomers is counted once, just as each achiral alkane (3D tree) is counted once.

By following the procedure described in Ref. [37], eq. 28 is evaluated recursively by using eqs. 12–14. The result is summarized to give a generating function:

$$\tilde{B}(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{B}_{k\ell m} z^m \right) y^{\ell} \right) x^k, \quad (29)$$

where the coefficient  $\tilde{B}_{k\ell m}$  of the term  $x^k y^{\ell} z^m$  represents the number of bicentroidal alkanes of carbon content  $k$  which have  $\ell$  asymmetric carbons and  $m$  pseudoasymmetric carbons.

The total numbers of bicentroidal steric isomers, where 3D structures are counted separately, are evaluated by summing up eqs. 26 and eqs. 27:

$$\begin{aligned} \tilde{S}(x, y, z) &= \tilde{B}^{(II)}(x, y, z) + \tilde{B}^{(IV)}(x, y, z) \\ &= \frac{1}{2} \{b(x, y, z)^2 + b(x^2, y^2, z^2)\}. \end{aligned} \quad (30)$$

By following the procedure described in Ref. [37], eq. 30 is evaluated recursively by using eqs. 12–14. The result is summarized to give a generating function:

$$\tilde{S}(x, y, z) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{S}_{k\ell m} z^m \right) y^{\ell} \right) x^k, \quad (31)$$

where the coefficient  $\tilde{S}_{k\ell m}$  of the term  $x^k y^{\ell} z^m$  represents the number of bicentroidal alkanes of carbon content  $k$  which have  $\ell$  asymmetric carbons and  $m$  pseudoasymmetric carbons.

## 2.2.3 Programming and Implementation for Counting Bicentroidal Alkanes as 3D Structures

The generating function (eq. 29) for counting bicentroidal alkanes as 3D structures is stored in the series `Bt` of the program “3DAlkaneCB.mpl”. The results are identical with those collected in Table 11 of Ref. [37].

Table 3: Numbers of Bicentroidal Alkanes as Steric Isomers with Considering Asymmetric and Pseudoasymmetric Carbons<sup>a)</sup>

The term $\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\tilde{S}_{k\ell m}z^m\right)y^{\ell}\right)x^k$ (cf. eqs. 30 and 31)	Total
$x^2$	1
$x^4$	1
$3x^6$	3
$(6 + 6y + 3y^2)x^8$	15
$(15 + 30y + 21y^2)x^{10}$	66
$(36 + 128y + 168y^2 + 64y^3 + 10y^4)x^{12}$	406
$(105 + 560y + 1100y^2 + 800y^3 + 210y^4)x^{14}$	2775
$(276 + 2116y + 6026y^2 + 7176y^3 + 3662y^4 + 608y^5 + 36y^6)x^{16}$	19900
$(780 + 7956y + (30660 + 78z)y^2 + (53184 + 408z)y^3 + (42799 + 500z + 3z^2)y^4 + (14000 + 112z)y^5 + 1596y^6)x^{18}$	152076
$(2145 + 28600y + (144600 + 260z)y^2 + (341320 + 1760z)y^3 + (399558 + 2928z + 10z^2)y^4 + (223712 + 1184z)y^5 + (55668 + 64z)y^6 + 4736y^7 + 136y^8)x^{20}$	1206681
(omitted)	

<sup>a)</sup>The coefficient  $\tilde{S}_{k\ell m}$  of each term  $x^k y^{\ell} z^m$  represents the number of alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers and  $m$  carbons are pseudoasymmetric centers.

To evaluate the numbers of bicentroidal steric isomers, eq. 30 is declared by adding the code:

```
Sxt := BtypeII + BtypeIV;
```

and related descriptions to the program "3DAkaneCB.mpl". Thereby, the corresponding generating function (eq. 31) is obtained, as shown in Table 3.

## 3 Centroidal and Bicentroidal Alkanes as Graphs

### 3.1 Enumeration of Centroidal Alkanes as Graphs

#### 3.1.1 Cycle Indices Without Chirality Fittingness

If we do not take account of sphericities, we are able to adopt a graph-reduction condition:

$$a_d = b_d = c_d = r_d. \quad (32)$$

The graph-reduction condition (eq. 32) is introduced into eqs. 1–5 so as to give the following CIs:

$$\text{CI}^{(1)}(\mathcal{S}^{[4]}, r_d) = \frac{1}{12}(r_1^4 + 3r_2^2 + 8r_1r_3) - \frac{1}{2}(r_1^2r_2 + r_4) \quad (33)$$

$$\text{CI}^{(\text{II})}(\mathcal{S}^{[4]}, r_d) = \frac{1}{2}(r_1^2 r_2 + r_4) - \frac{1}{2}(r_1^2 r_2 + r_2^2 - r_2^2 + r_4) = 0 \quad (34)$$

$$\begin{aligned} \text{CI}^{(\text{III})}(\mathcal{A}^{[4]}, r_d) &= \frac{1}{12}(r_1^4 + 3r_2^2 + 8r_1 r_3) - \frac{1}{12}(r_1^4 + 3r_2^2 + 8r_1 r_3) - \frac{1}{2}(r_1^2 r_2 + r_4) \\ &\quad - \frac{1}{2}(r_1^2 r_2 + r_4) + (r_1^2 r_2 + r_2 r_2 - r_2^2 + r_4) = 0 \end{aligned} \quad (35)$$

$$\text{CI}^{(\text{IV})}(\mathcal{S}^{[4]}, r_d) = \frac{1}{2}(r_1^2 r_2 + r_4) \quad (36)$$

$$\text{CI}^{(\text{V})}(\mathcal{S}^{[4]}, r_d) = \frac{1}{2}(r_1^2 r_2 - r_1^2 r_2) - \frac{1}{2}(r_2^2 - r_2^2) = 0. \quad (37)$$

On a similar line to the derivation of eq. 10, equations (eqs. 33–35) for Types I to III are divided by two and summed up together with those for Types IV and V (eqs. 36 and 37) so as to provide the total number of monosubstituted alkanes as graphs:

$$\begin{aligned} \text{CI}(\mathcal{S}^{[4]}, r_d) &= \frac{1}{2} \left\{ \text{CI}^{(\text{I})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{II})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{III})}(\mathcal{A}^{[4]}, r_d) \right\} \\ &\quad + \text{CI}^{(\text{IV})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{V})}(\mathcal{S}^{[4]}, r_d) \\ &= \frac{1}{2} \text{CI}^{(\text{I})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{IV})}(\mathcal{S}^{[4]}, r_d) \\ &= \frac{1}{24}(r_1^4 + 3r_2^2 + 8r_1 r_3 + 6r_1^2 r_2 + 6r_4). \end{aligned} \quad (38)$$

This equation is alternatively derived by introducing the graph-reduction condition (eq. 32) into eq. 10.

On a similar line to the derivation of eq. 11, the summing-up of the equations for Types I to V gives the total number of steric isomers as graphs:

$$\begin{aligned} \text{CI}(\mathcal{A}^{[4]}, r_d) &= \text{CI}^{(\text{I})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{II})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{III})}(\mathcal{A}^{[4]}, r_d) \\ &\quad + \text{CI}^{(\text{IV})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{V})}(\mathcal{S}^{[4]}, r_d) \\ &= \frac{1}{12}(r_1^4 + 3r_2^2 + 8r_1 r_3) \end{aligned} \quad (39)$$

This equation is alternatively derived by introducing the graph-reduction condition (eq. 32) into eq. 11.

According to the equation  $b_2 = c_2$  of the graph-reduction condition, two enantiomeric ligands can be equalized so that we put  $p = \bar{p} = p_g$ ,  $q = \bar{q} = q_g$ ,  $r = \bar{r} = r_g$ , and  $s = \bar{s} = s_g$ . As a result, the warehouse represented by eq. 6 is reduced into the following warehouse:

$$\mathbf{L}' = \{A, B, X, Y; p_g, q_g, r_g, s_g\}. \quad (40)$$

Then, the three ligand inventories (eqs. 7–9) are reduced into the following single inventory:

$$r_d = A^d + B^d + X^d + Y^d + p_g^d + q_g^d + r_g^d + s_g^d. \quad (41)$$

The ligand inventory (eq. 41) is effective so as to be applied to eqs. 38 and 39. Cycle indices equivalent to eqs. 38 and 39 have been once noted by Pólya (Section 21 of [4]). It should be emphasized, however, that the present approach uses the the graph-reduction condition (eq. 32) so as to clarify the importance of the conceptual reduction from 3D structures to graphs. Thus, Pólya's method (Section 21 of [4]) can be regarded as a special case of the present formulation in terms of the graph-reduction condition (eq. 32).

### 3.1.2 Functional Equations for Counting Centroidal Alkanes as Graphs

In order that the reduction of 3D structures to graphs is applied to the enumeration of alkanes (3D trees), the graph-reduction condition (eq. 32) is modified to be applicable to the functional equations:

$$a(x^d, y^d, z^d) = b(x^d, y^d, z^d) = c(x^d, y^d, z^d) = r(x^d, y^d). \quad (42)$$

The graph-reduction condition (eq. 42) is introduced into eqs. 15–19. And we put the left hand-sides as follows:  $\widehat{B}_g^{(I)}(x, y) = \widehat{B}^{(I)}(x, y, z)$  (T = I, II, ... V). The function  $r(x^d, y^d)$  etc. are used in place of  $a(x^d, y^d, z^d)$  etc., because the terms depending on the variable  $z$  (Type V) vanishes to zero, as found in the following results:

$$\begin{aligned} \widehat{B}_g^{(I)}(x, y) &= \frac{xy}{12} \{r(x, y)^4 + 3r(x^2, y^2)^2 + 8r(x, y)r(x^3, y^3)\} \\ &\quad - \frac{xy}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\} \end{aligned} \quad (43)$$

$$\begin{aligned} \widehat{B}_g^{(II)}(x, y) &= \frac{x}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\} \\ &\quad - \frac{x}{2} \{r(x, y)^2r(x^2, y^2) + r(x^2, y^2)r(x^2, y^2) \\ &\quad \quad - r(x^2, y^2)^2 + r(x^4, y^4)\} = 0 \end{aligned} \quad (44)$$

$$\begin{aligned} \widehat{B}_g^{(III)}(x, y, z) &= \frac{xy}{12} \{r(x, y)^4 + 3r(x^2, y^2)^2 + 8r(x, y)r(x^3, y^3)\} \\ &\quad - \frac{xy}{12} \{r(x, y)^4 + 3r(x^2, y^2)^2 + 8r(x, y)r(x^3, y^3)\} \\ &\quad - \frac{xy}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\} \\ &\quad - \frac{xy}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\} \\ &\quad + xy \{r(x, y)^2r(x^2, y^2) + r(x^2, y^2)r(x^2, y^2) \\ &\quad \quad - r(x^2, y^2)^2 + r(x^4, y^4)\} = 0 \end{aligned} \quad (45)$$

$$\widehat{B}_g^{(IV)}(x, y) = \frac{x}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\} \quad (46)$$

$$\begin{aligned} \widehat{B}_g^{(V)}(x, y) &= \frac{xz}{2} \{r(x, y)^2r(x^2, y^2) - r(x, y)^2r(x^2, y^2)\} \\ &\quad - \frac{xz}{2} \{r(x^2, y^2)r(x^2, y^2) - r(x^2, y^2)^2\} = 0. \end{aligned} \quad (47)$$

It should be emphasized that the functional equations of Types II, III, and V vanishes to zero so as to leave the functional equations of Types I and IV effective.

We introduce the graph-reduction condition (eq. 42) into eq. 20 so that we are able to derive the following functional equation for evaluating the total number of graphs:

$$\begin{aligned} \widehat{B}_g(x, y) &= \frac{1}{2} \left\{ \widehat{B}^{(I)}(x, y) + \widehat{B}_g^{(II)}(x, y) + \widehat{B}_g^{(III)}(x, y) \right\} + \widehat{B}_g^{(IV)}(x, y) + \widehat{B}_g^{(V)}(x, y) \\ &= \frac{1}{2} \widehat{B}^{(I)}(x, y) + \widehat{B}_g^{(IV)}(x, y) \\ &= \frac{xy}{24} \{r(x, y)^4 + 3r(x^2, y^2)^2 + 8r(x, y)r(x^3, y^3) - 6r(x, y)^2r(x^2, y^2) - 6r(x^4, y^4)\} \\ &\quad + \frac{x}{2} \{r(x, y)^2r(x^2, y^2) + r(x^4, y^4)\}, \end{aligned} \quad (48)$$

which is alternatively obtained by summing up eqs. 43–47. We should evaluate eq. 48 to give a generating function:

$$\widehat{B}_g(x, y) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \widehat{B}_{gk\ell} y^{\ell} \right) x^k, \quad (49)$$

where the coefficient  $\widehat{B}_{gk\ell}$  of the term  $x^k y^{\ell}$  represents the number of centroidal alkanes (as graphs) of carbon content  $k$  which have  $\ell$  asymmetric carbons.

To do this task, we use the function  $r(x, y)$  evaluated recursively in Part 1 of this series as a generating function:

$$r(x, y) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} R_{k\ell} y^{\ell} \right) x^k. \quad (50)$$

In the recursive process of calculating eq. 50, we adopt an intermediate generating function evaluated up to  $k = \mu$ , i.e.,  $r(x, y)^{(\mu)} = \sum_{k=0}^{\mu} \left( \sum_{\ell=0}^{\infty} R_{k\ell} y^{\ell} \right) x^k$ . After the value  $\mu$  is tentatively fixed, the series  $r(x, y)^{(\mu)}$  is introduced into eq. 48 so as to give an equation  $\widehat{B}_g^{(\mu)}(x, y)$ . Let the symbol  $\text{coeff}(\widehat{B}_g^{(\mu)}(x, y), x^{2\mu+1})$  etc. represent the coefficient of the term  $x^{2\mu+1}$  etc. appearing in the equation  $\widehat{B}_g^{(\mu)}(x, y)$  after expansion. Note that the coefficient is a polynomial containing  $y^{\ell}$ . Then, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty} \widehat{B}_{g(2\mu+1)\ell} y^{\ell} = \text{coeff}(\widehat{B}_g^{(\mu)}(x, y), x^{2\mu+1}) \quad (51)$$

for odd carbon contents as well as the following coefficients:

$$\sum_{\ell=0}^{\infty} \widehat{B}_{g(2\mu+2)\ell} y^{\ell} = \text{coeff}(\widehat{B}_g^{(\mu)}(x, y), x^{2\mu+2}) \quad (52)$$

for even carbon contents. Note that the powers of  $y$  is equal to or less than  $2\mu + 2$ . These requirements should be considered in the following programming. The results shown in eqs. 51 and 52 have been alternatively noted by Pólya, where the equivalent equations were obtained by an alternative formulation based on the symmetric group  $S^{[4]}$  and the alternating group  $\mathcal{A}^{[4]}$  (eq. 2.52 of Ref. [4]). The present formulation shows that the Pólya formulation can be regarded as a special case derived by the graph-reduction procedure (cf. eq. 42).

### 3.1.3 Programming and Implementation for Counting Centroidal Alkanes as Graphs

Suppose that the functional equation  $r(x, y)$  (eq. 50), has been recursively calculated and stored in a series concerning  $x^k y^{\ell}$  up to carbon content  $k = \mu$ . The resulting series  $r(x, y)^{(\mu)}$  is introduced into eq. 48 to count centroidal alkanes as graphs. Among the terms appearing in the expanded functional equations, the terms corresponding to  $x^{2\mu+1}$  and  $x^{2\mu+2}$  are adopted as new entries according to the definition of centroidal alkanes eqs. 51 and 52.

The procedure described in the preceding paragraph is programmed by using the Maple programming language and stored with the name “GraphAlkaneC-1.mpl”. Although the upper limit (`kmax`) of the carbon content ( $k$ ) is tentatively fixed to be 15, it can be freely selected as far as the capacity of a computer permits. The numbers of centroidal alkanes up to 32 ( $= 2 \times 15 + 2$ ) are obtained according to the maximum 15 of carbon content.

```

#GraphAlkaneC-1.mpl
#Centroidal Alkanes as Graphs
"Functional Equations for Alkyls";
rxy := 1 + x*r1*r2 + (1/6)*x*y*(r1^3 + 2*r3 - 3*r1*r2);
"Functional Equations for Alkanes as Centroidal Graphs";
BCgxy := (x*y/24)*(r1^4 + 3*r2^2 + 8*r1*r3 - 6*r1^2*r2 - 6*r4)
+(x/2)*(r1^2*r2 + r4);

"Initial Values";
r1 := 1: r2 := 1: r3 := 1: r4 := 1:
BCg := x:
"Recursive Calculation";
kmax:= 15;
for k from 1 to kmax by 1 do
Crx := expand(coeff(rxy,x^k)):
r1 := r1 + Crx*x^k:
r2 := subs({x=x^2,y=y^2},r1);
r3 := subs({x=x^3,y=y^3},r1);
r4 := subs({x=x^4,y=y^4},r1);
q := 2*k+1;
BCg := BCg + coeff(BCgxy,x^q)*x^q
+ coeff(BCgxy,x^(q+1))*x^(q+1);
end do:

"Print Out";
for k from 1 to 2*kmax by 1 do
NBCg := sort(expand(coeff(BCg,x^k)), [y], ascending)*x^k;
TBCg := subs({y=1},expand(coeff(BCg,x^k)));
end do;

```

The above program named “GraphAlkaneC-1.mpl” uses an abbreviated symbol  $r1$  for the functional equation  $r(x,y)$ , which serves as a series for storing the stepwise data of alkyl ligands (monosubstituted alkanes). The first part “Functional Equations for Alkyls” declares a functional equation  $rxy$  of calculating  $r(x,y)$ , which is recursively calculated by using  $r1$  and so on. The second part “Functional Equations for Alkanes as Centroidal Graphs” declares a functional equation  $BCgxy$  for  $\widehat{B}_g(x,y)$  (eq 48), which exhibit no recursive nature. In the third part “Initial Values”, the initial values are set for the initial (trivial) stage. The fourth part (“Recursive Calculation”) of the program shows a `do` loop with respect to carbon content  $k$ , in which the next coefficients are calculated by using a Maple command `coeff` and added to the end of respective functional equations so as to generate intermediate generating functions. The series  $BCg$  stores coefficients calculated stepwise by eqs. 51 and 52. After escaping from the `do` loop for  $k$ , the last part (“Print Out of ...”) of the program shows the print-out of the calculation results.

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

```

> restart;
> read "GraphAlkaneC-1.mpl";

```

The results are collected in Table 4, where the coefficient of the term  $x^k y^\ell$  represents the number of centroidal alkanes (as graphs) of carbon content  $k$  which are characterized by  $\ell$  asymmetric carbons.



Table 4: Numbers of Centroidal Alkanes as Graphs with Considering Asymmetric Carbons<sup>a)</sup>

The term $(\sum_{\ell=0}^{\infty} B_{gk\ell} y^{\ell}) x^k$ (cf. eqs. 51 and 52)	Total
$x$	1
0	0
$x^3$	1
$x^4$	1
$3x^5$	3
$2x^6$	2
$(7 + 2y)x^7$	9
$(7 + y)x^8$	8
$(20 + 12y + 3y^2)x^9$	35
$(20 + 13y + 6y^2)x^{10}$	39
$(55 + 67y + 34y^2 + 3y^3)x^{11}$	159
$(60 + 79y + 57y^2 + 6y^3)x^{12}$	202
$(156 + 313y + 263y^2 + 65y^3 + 5y^4)x^{13}$	802
$(162 + 367y + 404y^2 + 130y^3 + 15y^4)x^{14}$	1078
$(438 + 1337y + 1668y^2 + 766y^3 + 133y^4 + 5y^5)x^{15}$	4347
$(471 + 1630y + 2494y^2 + 1415y^3 + 326y^4 + 18y^5)x^{16}$	6354
$(1239 + 5372y + 9308y^2 + 6664y^3 + 2072y^4 + 232y^5 + 7y^6)x^{17}$	24894
$(1319 + 6579y + 13559y^2 + 11530y^3 + 4446y^4 + 688y^5 + 36y^6)x^{18}$	38157
$(3498 + 20627y + 47476y^2 + 48211y^3 + 23141y^4 + 4917y^5 + 406y^6 + 8y^7)x^{19}$	148284
$(3767 + 25540y + 68272y^2 + 80426y^3 + 45897y^4 + 12213y^5 + 1382y^6 + 44y^7)x^{20}$	237541
(omitted)	

<sup>a)</sup>The coefficient of each term  $y^{\ell}x^k$  represents the number of centroidal alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers.

## 3.2 Enumeration of Bicentroidal Alkanes as Graphs

### 3.2.1 Cycle Indices Without Chirality Fittingness

The graph-reduction condition (eq. 32) is introduced into eqs. 24 and 25 so as to give the following CIs:

$$CI^{(II)}(S^{[2]}; r_d) = \frac{1}{2}(r_1^2 + r_2 - r_1^2 - r_2) = 0 \quad (53)$$

$$CI^{(IV)}(S^{[2]}; r_d) = \frac{1}{2}(r_1^2 + r_2). \quad (54)$$

Because Type-II alkanes are chiral and two enantiomers of each pair are counted separately, the functional equation eq. 53 for Types II is divided by two and summed up together with eq. 54 for Types IV so as to provide the total number of alkanes as graphs:

$$CI(S^{[2]}; r_d) = \frac{1}{2}CI^{(II)}(S^{[4]}; r_d) + CI^{(IV)}(S^{[4]}; r_d)$$

$$= \frac{1}{2}(r_1^2 + r_2). \quad (55)$$

The summing-up of the equations for Types II and IV gives the total number of steric isomers as graphs. The resulting equation is equal to eq. 55:

$$\begin{aligned} \text{CI}(\mathcal{A}^{[2]}, r_d) &= \text{CI}^{(\text{II})}(\mathcal{S}^{[4]}, r_d) + \text{CI}^{(\text{IV})}(\mathcal{S}^{[4]}, r_d) \\ &= \frac{1}{2}(r_1^2 + r_2). \end{aligned} \quad (56)$$

Because the discussions described for eq. 40 hold true for this case, the ligand inventory (eq. 41) is effective so as to be applied to eqs. 55 and 56.

An equivalent cycle index to eq. 55 have been noted by Pólya (Section 21 of [4]). On the other hand, eq. 56 is different from the counterpart ( $\text{CI}(\mathcal{A}^{[2]}, r_d) = r_1^2$ ) derived by Pólya. Note that, when two achiral ligands A and B are considered, Pólya's formulation gives  $A^2$ ,  $B^2$ , AB, and BA, while eq. 56 gives  $A^2$ ,  $B^2$ , and AB. It should be emphasized that the present approach uses the the graph-reduction condition (eq. 32) so as to clarify the importance of the conceptual reduction from 3D structures to graphs. Pólya's method (Section 21 of [4]) can be regarded as a special case of the present formulation in terms of the graph-reduction condition (eq. 32) except eq. 56. Although eq. 56 is tentatively assigned to  $\mathcal{A}^{[2]}$ , such an exception (eq. 56) should be studied in the future.

### 3.2.2 Functional Equations for Counting Bicentroidal Alkanes as Graphs

We apply the graph-reduction condition (eq. 42) to eqs. 26 and 27 and we put the left hand-sides as follows:  $\tilde{B}_g^{(\text{T})}(x, y) = \tilde{B}^{(\text{T})}(x, y, z)$  (T = II and IV). The function  $r(x^d, y^d)$  etc. are used in place of  $a(x^d, y^d, z^d)$  etc., because the terms depending on the variable  $z$  (Type V) do not contained.

$$\tilde{B}_g^{(\text{II})}(x, y) = \frac{1}{2} \{r(x, y)^2 + r(x^2, y^2) - r(x, y)^2 - r(x^2, y^2)\} = 0 \quad (57)$$

$$\tilde{B}_g^{(\text{IV})}(x, y) = \frac{1}{2} \{r(x, y)^2 + r(x^2, y^2)\}. \quad (58)$$

Obviously, we obtain the following functional equation:

$$\tilde{B}_g(x, y) = \frac{1}{2} \tilde{B}_g^{(\text{II})}(x, y) + \tilde{B}_g^{(\text{IV})}(x, y) = \frac{1}{2} \{r(x, y)^2 + r(x^2, y^2)\}. \quad (59)$$

This equation is alternatively obtained by applying the graph-reduction condition (eq. 42) to eq. 28. We should evaluate eq. 59 to give a generating function:

$$\tilde{B}_g(x, y) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \tilde{B}_{gk\ell} y^\ell \right) x^k, \quad (60)$$

where the coefficient  $\tilde{B}_{gk\ell}$  of the term  $x^k y^\ell$  represents the number of bicentroidal alkanes (as graphs) of carbon content  $k$  which have  $\ell$  asymmetric carbons.

Suppose that we have obtained  $r(x, y)^{(\mu)} = \sum_{k=0}^{\mu} (\sum_{\ell=0}^{\infty} \alpha_{k\ell} y^\ell) x^k$ , where  $\mu$  is tentatively fixed. This series is introduced into eq. 59 so as to give an equation  $\tilde{B}_g^{(\mu)}(x, y)$ . Let the symbol  $\text{coeff}(B_g^{(\mu)}(x, y), x^{2\mu})$  represent the coefficient of the term  $x^{2\mu}$  appearing in the equation  $\tilde{B}_g^{(\mu)}(x, y)$

after expansion. Note that the coefficient is a polynomial containing  $y^\ell$ . Then, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty} \widetilde{B}_{g(2\mu+1)\ell} y^\ell = \text{coeff}(\widetilde{B}_g^{(\mu)}(x, y), x^{2\mu}). \quad (61)$$

The results shown in eqs. 59 and 61 have been alternatively noted by Pólya, where the equivalent equations were obtained by an alternative formulation based on the symmetric group  $S^{[2]}$  (eq. 2.47 of Ref. [4]). The present formulation shows that the Pólya formulation can be regarded as a special case derived by the graph-reduction procedure (cf. eq. 42).

### 3.2.3 Programming and Implementation for Counting Bicentroidal Alkanes as Graphs

Once the functional equation  $r(x, y)^{(\mu)}$  (cf. eq. 50) is recursively calculated up to carbon content  $k = \mu$ , it is introduced into eq. 59 for the enumeration of bicentroidal alkanes so that terms for carbon content  $2\mu$  are picked up by following eq. 61.

The procedure described in the preceding paragraph is implemented by mean of the Maple programming language and stored with the name “GraphAlkaneB-1.mpl”. Although the upper limit (kmax) of the carbon content ( $k$ ) is tentatively fixed to be 15, it can be freely selected as far as the capacity of a computer permits. According to the fixed maximum (15), we are able to count bicentroidal alkanes up to carbon content 30.

```
#GraphAlkaneB-1.mpl
#Bicentroidal Alkanes as Graphs
"Functional Equations for Alkyls";
rxy := 1 + x*r1*r2 + (1/6)*x*y*(r1^3 + 2*r3 - 3*r1*r2);
"Functional Equations for Alkanes as Bicentroidal Graphs";
BBgxy := (1/2)*(r1^2 + r2);

"Initial Values";
r1 := 1: r2 := 1: r3 := 1: r4 := 1:
BBg := 0:
"Recursive Calculation";
kmax:= 15;
for k from 1 to kmax by 1 do
Crx := expand(coeff(rxy, x^k)):
r1 := r1 + Crx*x^k:
r2 := subs({x=x^2, y=y^2}, r1);
r3 := subs({x=x^3, y=y^3}, r1);
p := 2*k;
BBg := BBg + coeff(BBgxy, x^p)*x^p:
end do:

"Print Out";
for k from 1 to 2*kmax by 1 do
NBBg := sort(expand(coeff(BBg, x^k)), [y], ascending)*x^k;
TBBg := subs({y=1}, expand(coeff(BBg, x^k)));
end do;
```

The program named “GraphAlkaneB-1.mpl” is different from the above-mentioned program “GraphAlkaneC-1.mpl” in the calculation concerned with the series  $BBg$ , which stores coefficients calculated stepwise by using eq. 59 (and eq. 61). After escaping from the `do` loop for  $k$ , the last part (“Print Out”) of the program shows the print-out of the calculation results, which are collected in Table 5. The coefficient of the term  $x^k y^\ell$  represents the number of bicentroidal alkanes (as graphs) of carbon content  $k$  which are characterized by  $\ell$  asymmetric carbons.

Table 5: Numbers of Bicentroidal Alkanes as Graphs with Considering Asymmetric Carbons<sup>a)</sup>

The term $\left(\sum_{\ell=0}^{\infty} \widetilde{B}_{gk\ell} y^{\ell}\right) x^k$ (cf. eq. 61)	Total
$x^2$	1
$x^4$	1
$3x^6$	3
$(6 + 3y + y^2) x^8$	10
$(15 + 15y + 6y^2) x^{10}$	36
$(36 + 64y + 44y^2 + 8y^3 + y^4) x^{12}$	153
$(105 + 280y + 280y^2 + 100y^3 + 15y^4) x^{14}$	780
$(276 + 1058y + 1518y^2 + 897y^3 + 236y^4 + 19y^5 + y^6) x^{16}$	4005
$(780 + 3978y + 7710y^2 + 6699y^3 + 2730y^4 + 441y^5 + 28y^6) x^{18}$	22366
$(2145 + 14300y + 36270y^2 + 42885y^3 + 25225y^4 + 7028y^5 + 887y^6 + 37y^7 + y^8) x^{20}$	128778
(omitted)	

<sup>a)</sup>The coefficient of each term  $y^{\ell} x^k$  represents the number of bicentroidal alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers.

### 3.3 Total Numbers of Alkanes as Graphs

Because the numbers of centroidal alkanes (as graphs) and those of bicentroidal alkanes (as graphs) have been evaluated (Tables 4 and 5), they are summed up to give the total numbers of alkanes (as graphs), as shown in Table 6.

By putting  $y = 1$  in each row of Table 6, we are able to obtain the total number of alkanes (as graphs) of carbon content  $k$ , which appears as the coefficient of the term  $x^k$  and is collected in the rightmost column of Table 6.

## 4 Discussions on Reduction of 3D Structures into Graphs

### 4.1 Meso-Compounds and Pseudoasymmetric Cases

#### 4.1.1 Meso-Compounds

By comparing between Table 6 and Table 1, the listed polynomials up to carbon content  $k = 7$  are equal to each other. Moreover, constant terms (in the term  $y^0 x^k$ : no asymmetric carbons) and coefficient of  $y^1$  (in the term  $y^1 x^k$ : with one asymmetric carbon) in Table 6 (for graphs) are identical to the counterparts collected in Table 1 (for 3D structures), because each pair of enantiomers (3D structures) is counted once.

The comparison of the term  $(13 + 4y + y^2) x^8$  in Table 6 with the term  $(13 + 4y + 2y^2) x^8$  in Table 1 shows the lowest case in which two asymmetric carbons cause different effects on isomer numbers as graphs and as 3D structures. Note that the former term  $(13 + 4y + y^2) x^8$  (Table 6) is the sum of  $(7 + y) x^8$  (Table 4) and  $(6 + 3y + y^2) x^8$  (Table 5). Hence, the term  $x^8 y^2$  is concerned with bicentroidal alkanes, which are depicted in Fig. 1. The three stereoisomers (**1** and **2/2'**) are regarded as a single graph (a single constitutional isomer) which is counted once as graphs ( $x^8 y^2$ ). From the viewpoint of 3D structures, on the other hand, they are regarded as

Table 6: Numbers of Alkanes as Graphs with Considering Asymmetric Carbons<sup>a)</sup>

The term $\left(\sum_{\ell=0}^{\infty} (B_{gk\ell} + \bar{B}_{gk\ell})y^{\ell}\right) x^k$ (cf. eq. 61)	Total
$x$	1
$x^2$	1
$x^3$	1
$2x^4$	2
$3x^5$	3
$5x^6$	5
$(7 + 2y)x^7$	9
$(13 + 4y + y^2)x^8$	18
$(20 + 12y + 3y^2)x^9$	35
$(35 + 28y + 12y^2)x^{10}$	75
$(55 + 67y + 34y^2 + 3y^3)x^{11}$	159
$(96 + 143y + 101y^2 + 14y^3 + y^4)x^{12}$	355
$(156 + 313y + 263y^2 + 65y^3 + 5y^4)x^{13}$	802
$(267 + 647y + 684y^2 + 230y^3 + 30y^4)x^{14}$	1858
$(438 + 1337y + 1668y^2 + 766y^3 + 133y^4 + 5y^5)x^{15}$	4347
$(747 + 2688y + 4012y^2 + 2312y^3 + 562y^4 + 37y^5 + y^6)x^{16}$	10359
$(1239 + 5372y + 9308y^2 + 6664y^3 + 2072y^4 + 232y^5 + 7y^6)x^{17}$	24894
$(2099 + 10557y + 21269y^2 + 18229y^3 + 7176y^4 + 1129y^5 + 64y^6)x^{18}$	60523
$(3498 + 20627y + 47476y^2 + 48211y^3 + 23141y^4 + 4917y^5 + 406y^6 + 8y^7)x^{19}$	148284
$(5912 + 39840y + 104542y^2 + 123311y^3 + 71122y^4 + 19241y^5 + 2269y^6 + 81y^7 + y^8)x^{20}$	366319
(omitted)	

<sup>a)</sup>The coefficient of each term  $y^{\ell}x^k$  represents the number of alkanes of carbon content  $k$  (as graphs) among which  $\ell$  carbons are asymmetric centers.

an achiral compound (**1**, a *meso*-compound) and a pair of enantiomers (**2/2**), so that they give a value 2 as 3D structures ( $2x^8y^2$ ).

Let us next examine the coefficient of the term  $x^9y^2$  relevant to carbon content 9, which is contained in the term  $(20 + 12y + 3y^2)x^9$  in Table 6 (graphs) or in the term  $(20 + 12y + 6y^2)x^9$  in Table 1 (3D structures). The coefficient 6 of the term  $x^9y^2$  for 3D structures (Table 1) corresponds to one achiral compound (**5**, a *meso*-compound) and five pairs of enantiomers (**3/3**, **4/4**, **6/6**, **7/7**, and **8/8**), which are listed in Fig. 2. Because each of the three rows (**3/3**, **4/4**), [**5**, **6/6**], and [**7/7**, **8/8**]) represents a single graph, we are able to confirm the coefficient 3 of the term  $x^9y^2$  for graphs (Table 6).

The achiral compound (**5**) corresponds to the term  $x^9y^2$  appearing at the intersection of the ( $k = 9$ )-row and the ( $m = 2$ )-column of Table 6 of Ref. [37], which is concerned with achiral centroidal alkanes. On the other hand, the remaining five pairs of enantiomers (**3/3**, **4/4**, **6/6**, **7/7**, and **8/8**) correspond to the term  $5x^9y^2$  appearing at the intersection of the ( $k = 9$ )-row and the ( $m = 2$ )-column of Table 7 of Ref. [37], which is concerned with chiral centroidal alkanes.

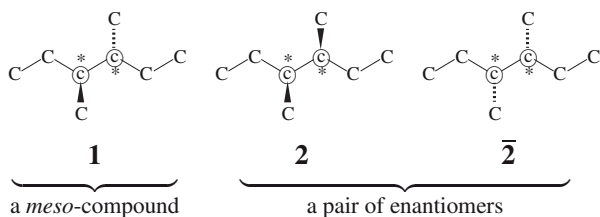


Figure 1: Stereoisomers of 3,4-dimethylhexane corresponding to the term  $x^8y^2$  (two asymmetric carbons). The symbol \* represents an asymmetric carbon. The symbol  $\odot\text{---}\odot$  represents a bicentroid.

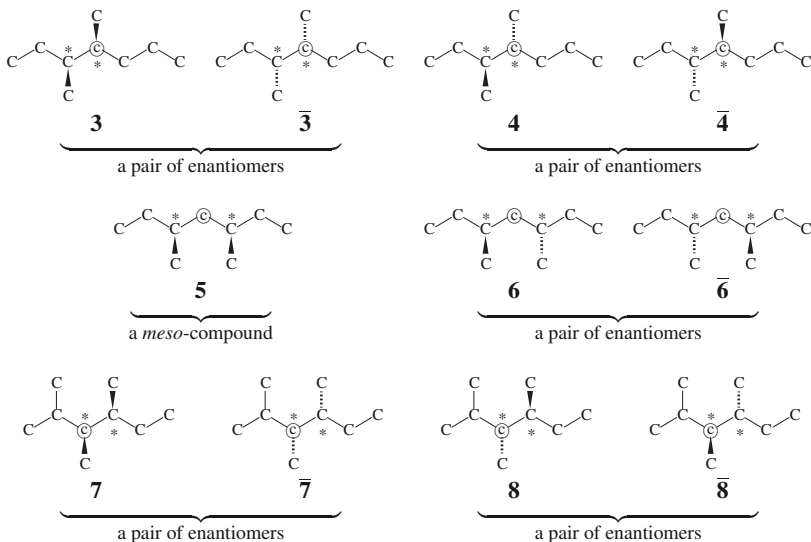


Figure 2: Alkanes corresponding to the term  $x^9y^2$  (two asymmetric carbons), where each row represents a single graph. The symbol \* represents an asymmetric carbon. The symbol  $\odot$  represents a centroid.

### 4.1.2 Fate of Pseudoasymmetry

The comparison of the term  $(35 + 28y + 12y^2)x^{10}$  in Table 6 (graphs) with the corresponding term  $(35 + 28y + (23 + 2z)y^2)x^{10}$  in Table 1 (3D structures) shows the lowest case in which one pseudoasymmetric carbon as well as two asymmetric carbons participates. The coefficient 2 of the term  $x^{10}y^2z$  for 3D structures indicates the presence of **9** and **10** (Fig. 3), which are both achiral and exhibit pseudoasymmetry. Thus, the central atoms of them (identical to their centroids  $\textcircled{C}$ ) show pseudoasymmetry ( $\dagger$ ) so that **9** and **10** are interchanged by permutation, but not interchangeable by reflection.

A pair of enantiomers **11/11** listed in the second row of Fig. 3 are stereoisomers of **9** and **10**. Thus, the two achiral compounds **9** and **10** and the pair **11/11** are reduced into a single graph (a single constitutional isomer) so as to contribute the term  $12x^{10}y^2$  (in the term  $(35 + 28y + 12y^2)x^{10}$ ) by one. Note that the pair **11/11** contributes the term  $23x^{10}y^2$  (in the term  $(35 + 28y + (23 + 2z)y^2)x^{10}$ ) by one. Hence, the relevant coefficients satisfy the following relationship:  $(12 - 1) \times 2^{(2-1)} = 23 - 1 (= 22)$ .

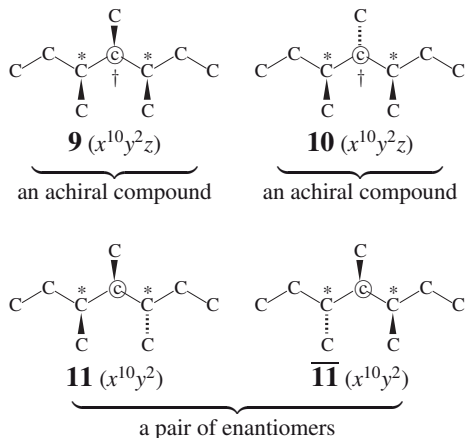


Figure 3: Stereoisomers of 3,4,5-trimethylheptane corresponding to the term  $x^{10}y^2z$  (two asymmetric carbons and one pseudoasymmetric carbon) or the term  $x^{10}y^2$  (two asymmetric carbons). The symbol \* represents an asymmetric carbon. The symbol  $\dagger$  represents a pseudoasymmetric carbon. The symbol  $\textcircled{C}$  represents a centroid.

### 4.2 Stepwise Tracing of Calculations

The achiral compounds **9** and **10** are generated by placing a hydrogen, a methyl ligand ( $C_1$ ), an *S*-1-methylpropyl ligand (*p*), and an *R*-1-methylpropyl ligand ( $\bar{p}$ ) on a central atom (a centroid), where the *R*- and *S*-configuration are assigned on the basis of a tentative priority sequence: a vacant valence > ethyl > methyl > hydrogen. This generation can be traced by using generating functions which serve as a basis of the present method. Suppose that eqs. 12–14 have been

evaluated up to carbon content 4 as follows:

$$a(x, y, z)^{(4)} = 1 + x + x^2 + 2x^3 + 3x^4 \quad (62)$$

$$c(x^2, y^2, z^2)^{(4)} = 1 + x^2 + x^4 + 2x^6 + (3 + 2y^2)x^8 \quad (63)$$

$$b(x, y, z)^{(4)} = 1 + x + x^2 + 2x^3 + (3 + 2y)x^4, \quad (64)$$

where the superscript (4) indicates that ligands of carbon content 4 or smaller ligands (or hydrogen) are used as substituents. These generating functions are introduced into eqs. 15–19 for counting centroidal alkanes of Types I–V so as to give the following generating functions:

$$\widehat{B}^{(I)}(x, y, z)^{(4)} = \dots + (14y)x^9 + (20y)x^{10} \quad (65)$$

$$\widehat{B}^{(II)}(x, y, z)^{(4)} = \dots + (10y + 2y^2)x^9 + (6y + 2y^2)x^{10} \quad (66)$$

$$\widehat{B}^{(III)}(x, y, z)^{(4)} = \dots + (8y^2)x^9 + (20y^2)x^{10} \quad (67)$$

$$\widehat{B}^{(IV)}(x, y, z)^{(4)} = \dots + (20 + y^2)x^9 + 20x^{10} \quad (68)$$

$$\widehat{B}^{(V)}(x, y, z)^{(4)} = \dots + (2y^2z)x^{10}, \quad (69)$$

where terms relevant to  $x^9$  and  $x^{10}$  are collected. The total numbers of centroidal alkanes of carbon contents 9 and 10 are obtained by using eq. 20 as follows:

$$\widehat{B}(x, y, z)^{(4)} = \dots + (20 + 12y + 6y^2)x^9 + (20 + 13y + (11 + 2z)y^2)x^{10} \quad (70)$$

There are no bicentroidal alkanes of odd carbon content. In order to enumerate bicentroidal alkanes of carbon content 10, we should evaluate eqs. 12–14 up to carbon content 5 as follows:

$$a(x)^{(5)} = 1 + x + x^2 + 2x^3 + 3x^4 + 5x^5 \quad (71)$$

$$c(x^2)^{(5)} = 1 + x^2 + x^4 + 2x^6 + (3 + 2y^2)x^8 + (5 + 6y^2)x^{10} \quad (72)$$

$$b(x)^{(5)} = 1 + x + x^2 + 2x^3 + (3 + 2y)x^4 + (5 + 6y)x^5 \quad (73)$$

These generating functions are introduced into eqs. 26 and 27 for counting bicentroidal alkanes of Types II and IV so as to give the following generating functions:

$$\widetilde{B}^{(II)}(x, y, z)^{(5)} = \dots + (30y + 18y^2)x^{10} \quad (74)$$

$$\widetilde{B}^{(IV)}(x, y, z)^{(5)} = \dots + (16 + y^2)x^{10}. \quad (75)$$

The total number of bicentroidal alkanes of carbon content 10 is obtained by using eq. 28 as follows:

$$\widetilde{B}(x, y, z)^{(5)} = \dots + (15 + 15y + 12y^2)x^{10} \quad (76)$$

By summing up eqs. 70 and 76, we obtain the total number of alkanes (centroidal and bicentroidal alkanes) of carbon contents 9 and 10 as follows:

$$\widehat{B}(x, y, z)^{(4)} + \widetilde{B}(x, y, z)^{(5)} = \dots + (20 + 12y + 6y^2)x^9 + (35 + 28y + (23 + 2z)y^2)x^{10}. \quad (77)$$

Each of the terms relevant to  $x^9$  and  $x^{10}$  is identical to the value collected in Table 1.

Because eqs. 12–14 are evaluated up to carbon content 4 as shown in eqs. 62–64, these are reduced into generating functions (ligand inventories) for counting graphs;

$$a(x, y, z)^{(4)'} = 1 + x + x^2 + 2x^3 + (3 + y)x^4 \quad (78)$$

$$c(x^2, y^2, z^2)^{(4)'} = 1 + x^2 + x^4 + 2x^6 + (3 + y^2)x^8 \quad (79)$$

$$b(x, y, z)^{(4)'} = 1 + x + x^2 + 2x^3 + (3 + y)x^4, \quad (80)$$



where each alkyl ligand is regarded as a graph selected from the warehouse (eq. 40) according to the ligand inventory represented by eq. 41. Thus, the term  $2y^2x^8$  in eq. 63 and the term  $2yx^4$  in eq. 64 are reduced into  $y^2x^8$  in eq. 79 and  $yx^4$  in eq. 80, respectively. Note that the coefficient of each  $y$  (or  $y^2$ ) is divided by 2 according to the graph-reduction condition (eq. 42). The three equations (eqs. 78–78) are essentially identical to each other so that they are reduced into a single ligand inventory for counting graphs (i.e.,  $r(x,y)$ ) which can be alternatively derived in Part 1 of this series. The equations (eqs. 78–80) are introduced into eqs. 15–19 so as to give the following generating functions:

$$\widehat{B}^{(I)}(x,y,z)^{(4)'} = \dots + (14y + 4y^2)x^9 + (20y + 10y^2)x^{10} \quad (81)$$

$$\widehat{B}^{(II)}(x,y,z)^{(4)'} = 0 \quad (82)$$

$$\widehat{B}^{(III)}(x,y,z)^{(4)'} = 0 \quad (83)$$

$$\widehat{B}^{(IV)}(x,y,z)^{(4)'} = \dots + (20 + 5y + y^2)x^9 + (20 + 3y + y^2)x^{10} \quad (84)$$

$$\widehat{B}^{(V)}(x,y,z)^{(4)'} = 0. \quad (85)$$

Note that the process of obtaining eqs. 81–85 is equivalent to an alternative way using eqs. 43–47. In other words, we can put  $\widehat{B}^{(I)}(x,y,z)^{(4)'} = \widehat{B}_g^{(I)}(x,y)^{(4)}$ ,  $\dots$ ,  $\widehat{B}^{(V)}(x,y,z)^{(4)'} = \widehat{B}_g^{(V)}(x,y)^{(4)}$ .

The total numbers of centroidal alkanes of carbon contents 9 and 10 are obtained by introducing eqs. 78–80 into eq. 20 as follows:

$$\widehat{B}(x,y,z)^{(4)'} = \dots + (20 + 12y + 3y^2)x^9 + (20 + 13y + 6y^2)x^{10}. \quad (86)$$

Note that the process of obtaining eq. 86 is equivalent to an alternative way using eq. 48. Thus, we can put  $\widehat{B}(x,y,z)^{(4)'} = \widehat{B}_g(x,y)^{(4)}$ . The values appearing in eq. 86 are identical to those collected in Table 4.

In order to enumerate bicentroidal alkanes of carbon content 10 (as graphs), eqs. 71–73 should be converted according to the graph-reduction condition (eq. 42). Thereby, we obtain the following equations:

$$a(x)^{(5)'} = 1 + x + x^2 + 2x^3 + (3 + y)x^4 + (5 + 3y)x^5 \quad (87)$$

$$c(x^2)^{(5)'} = 1 + x^2 + x^4 + 2x^6 + (3 + y^2)x^8 + (5 + 3y^2)x^{10} \quad (88)$$

$$b(x)^{(5)'} = 1 + x + x^2 + 2x^3 + (3 + y)x^4 + (5 + 3y)x^5 \quad (89)$$

The equations (eqs. 87–89) are eqs. 26 and 27 so as to give the following generating functions:

$$\widetilde{B}^{(II)}(x,y,z)^{(5)'} = 0 \quad (90)$$

$$\widetilde{B}^{(IV)}(x,y,z)^{(5)'} = \dots + (15 + 15y + 6y^2)x^{10} \quad (91)$$

The equations (eqs. 87–89) are introduced into eq. 28 so as to give the following generating function:

$$\widetilde{B}(x,y,z)^{(5)'} = \dots + (15 + 15y + 6y^2)x^{10} \quad (92)$$

The values appearing in eq. 92 are identical to those collected in Table 5.

The total numbers of alkanes of carbon contents 9 and 10 (as graphs) are obtained by summing up eqs. 86 and 92 as follows:

$$\widehat{B}(x,y,z)^{(4)'} + \widetilde{B}(x,y,z)^{(5)'} = \dots + (20 + 12y + 3y^2)x^9 + (35 + 28y + 12y^2)x^{10}. \quad (93)$$

The values appearing in eq. 93 are identical to those collected in Table 6.

The comparison of eqs. 65–69 (for alkanes as 3D structures) with eqs. 81–85 (for alkanes as graphs) provides us with a more concrete idea than the comparison of eqs. 15–19 with eqs. 43–47. In particular, the comparison of eq. 69 with eq. 85 indicates the fate of pseudoasymmetry, where the term  $2x^{10}y^2z$  in eq. 69 (3D structures) disappears in eq. 85 (graphs).

The data of eqs. 65–69 (for alkanes as 3D structures) are capable of categorizing the centroidal alkanes listed in Fig. 2. The term  $2x^9y^2$  appearing in  $\widehat{B}^{(II)}(x, y, z)^{(4)}$  (eq. 66) corresponds to **6** and  $\overline{6}$ , which are counted separately as centroidal alkanes of Type II; the term  $8x^9y^2$  appearing in  $\widehat{B}^{(III)}(x, y, z)^{(4)}$  (eq. 67) corresponds to **3/3**, **4/4**, **7/7**, and **8/8**, which are counted separately as centroidal alkanes of Type III; and the term  $x^9y^2$  appearing in  $\widehat{B}^{(IV)}(x, y, z)^{(4)}$  (eq. 68) corresponds to **5**, which is counted once as a centroidal alkane of Type IV.

The data of eqs. 81–85 (for alkanes as graphs) alternatively categorize the centroidal alkanes listed in Fig. 2. The term  $4x^9y^2$  appearing in  $\widehat{B}^{(I)}(x, y, z)^{(4)'$  (eq. 81) should be divided by 2, as implied in the derivation of eq. 86 (cf. eq. 59). Note that this process is an embodiment of the reduction of **L** (eq. 6) into **L'** (eq. 40), where an *S*-1-methylpropyl ligand (**p**) and an *R*-1-methylpropyl ligand ( $\overline{p}$ ) coalesce into a single ligand as a graph (**p<sub>g</sub>**). The coefficient 2 of the resulting term  $2x^9y^2$  corresponds to a set of 3D structures [**3/3**, **4/4**] and another set of 3D structures [**7/7**, **8/8**], where four molecules of each set coalesce, giving a single graph as bundled together by a pair of brackets. The coefficient 1 of the term  $x^9y^2$  appearing in  $\widehat{B}^{(IV)}(x, y, z)^{(4)'$  (eq. 84) corresponds to a set of **5** and **6/6**, which is regarded as a single graph after coalescence.

### 4.3 Systematic Comparison Between Graphs and 3D Structures

#### 4.3.1 Two Viewpoints for Characterizing Stereoisomerism

A stereochemical convention, which is called here *the viewpoint of “graphs with asymmetries”*, teaches us that if a graph (corresponding to a constitutional isomer) has  $\ell$  asymmetric carbons, there exist  $2^\ell$  stereoisomers maximum. Accordingly, the replacement of the variable  $y$  by  $2y$  in a generating function for counting graphs gives a generating function for evaluating the number of possible stereoisomers of carbon content  $k$ . For example, eq. 49 for counting centroidal graphs and eq. 60 for counting bicentroidal graphs are converted into the following generating functions:

$$\widehat{B}_g(x, 2y) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \widehat{B}_{gk\ell}(2y)^\ell \right) x^k = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} 2^\ell \widehat{B}_{gk\ell} y^\ell \right) x^k \quad (94)$$

$$\widetilde{B}_g(x, 2y) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \widetilde{B}_{gk\ell}(2y)^\ell \right) x^k = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} 2^\ell \widetilde{B}_{gk\ell} y^\ell \right) x^k, \quad (95)$$

where the the factor  $2^\ell$  is consistent with the viewpoint of “graphs with asymmetries”.

On the other hand, the present approach, which emphasizes pseudoasymmetries together with asymmetries, is referred to as *the viewpoint of “3D structures with asymmetries and pseudoasymmetries”*. From this viewpoint, the numbers of centroidal alkanes (steric isomers) have been evaluated by the generating function  $\widehat{S}(x, y, z)$  (eq. 23, cf. Table 2), while the numbers of bicentroidal alkanes (steric isomers) have been evaluated by the generating function  $\widetilde{S}(x, y, z)$  (eq. 31, cf. Table 3).

Such enumerations from the two viewpoints give different values, although they are concerned with the same set of centroidal or bicentroidal alkanes (steric isomers). Hence, the

difference between the two viewpoints can be systematically detected by comparing between  $\widehat{B}_g(x, 2y)$  and  $\widehat{S}(x, y, z)$  for centroidal steric alkanes or between  $\widetilde{B}_g(x, 2y)$  and  $\widetilde{S}(x, y, z)$  for bicentroidal steric alkanes. Thereby, we are able to demonstrate what happens in the over-estimation due to the formula  $2^{\ell}$  of the stereochemical convention.

### 4.3.2 Centroidal Alkanes From Two Viewpoints for Characterizing Stereoisomerism

Because  $\widehat{B}_g(x, 2y)$  (eq. 94) and  $\widehat{S}(x, y, z)$  (eq. 23) are concerned with the same set of centroidal alkanes, their difference is useful to detect the difference between the two viewpoints:

$$\begin{aligned} & \widehat{B}_g(x, 2y) - \widehat{S}(x, y, z) \\ &= y^2x^9 + (2 - 2z)y^2x^{10} + (6 - 2z)y^2x^{11} + (12 - 12z)y^2x^{12} \\ & \quad + ((28 - 16z)y^2 + 4y^3 + 6y^4)x^{13} + ((54 - 54z)y^2 + 16y^3 - 4zy^4 - 8y^5)x^{14} \\ & \quad + ((113 - 80z)y^2 + 60y^3 - 4zy^4 - 16y^5)x^{15} \\ & \quad + ((214 - 214z)y^2 + 180y^3 + (-16 - 32z)y^4 - 112y^5)x^{16} \\ & \quad + ((421 - 338z)y^2 + 508y^3 + (21 - 40z)y^4 - 264y^5 - 12y^6)x^{17} \\ & \quad + ((706 - 706z)y^2 + 908y^3 + (28 - 176z)y^4 \\ & \quad \quad - 592y^5 + (-56 - 8z)y^6 - 48y^7)x^{18} \\ & \quad + ((1488 - 1290z)y^2 + (3280 - 880z)y^3 + (1957 - 1708z - 7z^2)y^4 \\ & \quad \quad + (-746 - 592z)y^5 + (-224 - 40z)y^6 - 56y^7)x^{19} \\ & \quad + ((2474 - 2474z)y^2 + (6044 - 964z)y^3 + (3930 - 3346z - 18z^2)y^4 \\ & \quad \quad + (-1544 - 1864z - 2z^2)y^5 + (-712 - 368z)y^6 - 728y^7)x^{20} + \dots \quad (96) \end{aligned}$$

**Centroidal Alkanes of Carbon Content 9** The first term  $x^9y^2$  appearing in the right-hand side of eq. 96 corresponds to a set of stereoisomers **5**, **6**, and **6** depicted in the middle row of Fig. 2. Because of the presence of two asymmetric carbons, the viewpoint of “graphs with asymmetries” shows 4 ( $= 2^2$ ) possibilities which contribute to the generating function  $\widehat{B}_g(x, 2y)$  in the form of the term  $4x^9y^2$ . From the viewpoint of “3D structures with asymmetries and pseudoasymmetries”, on the other hand, there exist three stereoisomers (i.e., **5**, **6**, and **6**) which contribute to the generating function  $\widehat{S}(x, y, z)$  in the form of the term  $3x^9y^2$ . Hence, the difference  $x^9y^2$  ( $= 4x^9y^2 - 3x^9y^2$ ) appears in eq. 96.

It should be noted, the achiral isomer **5** is a *meso*-compound in which two chiral moieties of opposite configurations compensate each other. Such a *meso*-compound is generally represented by the formula  $P-\textcircled{A}_2-\overline{P}$ , where P and  $\overline{P}$  are ligands with opposite configurations. In this case, the ligand P (or  $\overline{P}$ ) is selected from a pair of enantiomeric ligands of carbon content 4 (when A = H for **5** of Table 2; cf. Table 6 of Part 1 of this series). When a ligand P of carbon content  $k$  has one asymmetric carbon, there appears the term  $x^{2k+1+2\alpha}y^2$  where  $\alpha$  represents the carbon content of the ligand A.

**Centroidal Alkanes of Carbon Content 10** The second term  $(2 - 2z)y^2x^{10}$  appearing in eq. 96 detects the pseudoasymmetric case shown in Fig. 3, i.e., two achiral stereoisomers (**9** and

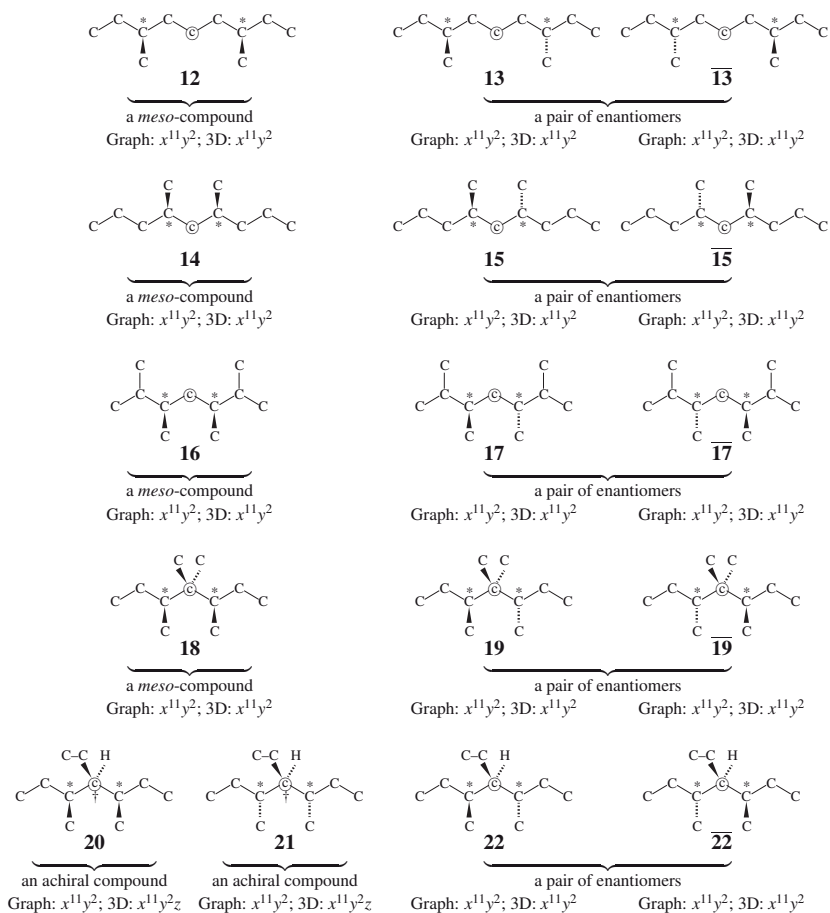


Figure 4: Centroidal alkanes corresponding to the term  $(6 - 2z)y^2x^{11}$  appearing in eq. 96 where each row represents a single graph. The symbol \* represents an asymmetric carbon and the symbol † represents a pseudoasymmetric carbon. The symbol © represents a centroid.

**10**) and two enantiomers of a pair (i.e., **11/11**), where the two achiral stereoisomers (**9** and **10**) exhibit pseudoasymmetry. These four stereoisomers are characterized by the term  $4x^{10}y^2$  (in  $\widehat{B}_g(x, 2y)$ ) from the viewpoint of “graphs with asymmetries”. From the viewpoint of “3D structures with asymmetries and pseudoasymmetries”, on the other hand, the two achiral stereoisomers (**9** and **10**) correspond to  $2x^{10}y^2z$ , while the two enantiomers of a pair (i.e., **11/11**) are characterized by  $2x^{10}y^2$ . As a result, the term  $2x^{10}y^2z + 2x^{10}y^2$  appears in  $\widehat{S}(x, y, z)$ . It follows that their difference  $4x^{10}y^2 - (2x^{10}y^2z + 2x^{10}y^2)$  is calculated to give  $(2 - 2z)y^2x^{10}$ .

A typical pseudoasymmetric case is represented by  $P-\textcircled{C}(AB)-\overline{P}$ , where P and  $\overline{P}$  are enantiomers of a pair where A and B are achiral ligands. In this case, the ligand P (or  $\overline{P}$ ) is selected from a pair of enantiomeric ligands of carbon content 4 (when A = CH<sub>3</sub> and B = H for Fig. 3; cf. Table 6 of Part 1 of this series). When a ligand P of carbon content  $k$  has one asymmetric carbon, there appears the term  $(2 - 2z)y^2x^{2k+1+\alpha}$  where  $\alpha$  represents the total number of carbons of A and B.

**Centroidal Alkanes of Carbon Content 11** The third term  $(6 - 2z)y^2x^{11}$  appearing in eq. 96 indicates more complicated situations for carbon content 11, which are depicted in Fig. 4. A notation “Graph:  $x^{11}y^2$ ; 3D  $x^{11}y^2$ ” below a 3D structure indicates that the 3D structure is characterized by  $x^{11}y^2$  as graph and as 3D structure. Another notation “Graph:  $x^{11}y^2$ ; 3D  $zx^{11}y^2$ ” below a 3D structure indicates that the 3D structure is characterized by  $x^{11}y^2$  as graph and by  $x^{11}y^2z$  as 3D structure. The term  $(6 - 2z)y^2x^{11}$  is divided into two parts, i.e.,  $4x^{11}y^2 + (2 - 2z)y^2x^{11}$ .

Among the compounds listed in Fig. 4, there exist four sets of three stereoisomers, i.e., [**12**, **13/13**], [**14**, **15/15**], [**16**, **17/17**], [**18**, **19/19**], where each set contains one achiral stereoisomer (*meso*-compound) and a pair of two enantiomers. As a result, each set is characterized by the term  $x^{11}y^2$  ( $= 4x^{11}y^2 - 3x^{11}y^2$ ), just as the set of [**5**, **6/6**] depicted in the middle row of Fig. 2 is characterized by the term  $x^9y^2$ . Thus, these four sets correspond to the divided term  $4x^{11}y^2$ .

Table 6 of Part 1 of this series lists three enantiomeric pairs of alkyl ligands of carbon content 5 and one enantiomeric pair of alkyl ligands of carbon content 4, where they have one asymmetric carbon. As a result, the formula  $P-\textcircled{C}(A_2)-\overline{P}$  of a *meso*-compound teaches us that the ligand P in this case is selected from the three pairs of enantiomeric ligands of carbon content 5 (when A = H for the top three rows of Table 4) or from a pair of enantiomeric ligands of carbon content 4 (when A = CH<sub>3</sub> for the fourth row of Table 4). This conclusion is in agreement with the results of Table 4.

On the other hand, there exists a set of four stereoisomers, i.e., **20** (an achiral compound), **21** (an achiral compound), and **22/22**, where the two achiral compounds (**20** and **21**) have a pseudoasymmetric carbon. In a similar way to the case shown in Fig. 3, the set is characterized by the term  $(2 - 2z)y^2x^{11}$ , which is in agreement with the divided part  $(2 - 2z)y^2x^{11}$  of the term  $(6 - 2z)y^2x^{11}$ . Thus, we obtain  $4 \times x^{11}y^2 + (2 - 2z)y^2x^{11} = (6 - 2z)y^2x^{11}$ .

**Centroidal Alkanes of Carbon Content 12** The fourth term  $(12 - 12z)y^2x^{12}$  appearing in eq. 96 indicates the presence of pseudoasymmetric cases and related structures, which are depicted in Fig. 5. Each of the rows of Fig. 5 represents a set of four stereoisomers (two achiral compounds and a pair of enantiomers), which are reduced into a single graph. The two achiral compounds exhibit pseudoasymmetry. In a similar way to the case shown in Fig. 3, each set is characterized by the term  $(2 - 2z)y^2x^{12}$ . Totally, we obtain  $6 \times (2 - 2z)y^2x^{12} = (12 - 12z)y^2x^{12}$  in agreement with the six rows of Fig. 5 which correspond to six constitutional

isomers (graphs).

**Centroidal Alkanes of Carbon Content 13** The term  $(28 - 16z)y^2x^{13}$  appearing in eq. 96 is divided into  $12x^{13}y^2$  and  $(16 - 16z)y^2x^{13}$ , each of which can be interpreted on the same line as described above. The former term  $12x^{13}y^2$  stems from 12 *meso*-compounds, which are represented by the formula  $P-\textcircled{C}(A_2)-\bar{P}$ . The ligand P in each of these cases is selected from eight pairs of enantiomeric ligands of carbon content 6 (cf. Table 6 of Part 1 of this series, when  $A = H$ ), from three pairs of enantiomeric ligands of carbon content 5 (cf. Table 6 of Part 1 of this series, when  $A = CH_3$ ), or from a pair of enantiomeric ligands of carbon content 4 (cf. Table 6 of Part 1 of this series, when  $A = CH_2CH_3$ ). Hence, there emerges 12 ( $= 8 + 3 + 1$ ) sets of three stereoisomers so as to satisfy the term  $12x^{13}y^2$ .

The latter term  $(16 - 16z)y^2x^{13}$  is interpreted by the existence of eight pseudoasymmetric cases represented by the formula  $P-\textcircled{C}(AB)-\bar{P}$ . The ligand P in each of these cases is selected from three pairs of enantiomeric ligands of carbon content 5 (cf. Table 6 of Part 1 of this series, when  $A = CH_2CH_3$  and  $B = H$ ) or from one pair of enantiomeric ligands of carbon content 4 (cf. Table 6 of Part 1 of this series, when  $A = CH_2CH_2CH_3$  and  $B = CH_3$ ;  $A =$  isopropyl and  $B = CH_3$ ;  $A =$  butyl and  $B = H$ ;  $A = CH_2CH(CH_3)_2$ ,  $B = H$ , or  $A = t$ -butyl and  $B = H$ ). Hence, there emerge eight ( $= 3 + 1 \times 5$ ) sets of four stereoisomers, where each set corresponds to the term  $(2 - 2z)y^2x^{13}$  so as to give the term  $8 \times (2 - 2z)y^2x^{13} = (16 - 16z)y^2x^{13}$ .

The term  $4x^{13}y^3$  appearing in eq. 96 corresponds to the existence of four stereoisomers shown in Fig. 6. Because of the presence of three asymmetric carbon atoms (\*), the stereochemical convention described above (the viewpoint of “graphs with asymmetries”) claims the presence of eight stereoisomers maximum ( $2^3 = 8$ ). But there exist the four 3D structures shown in Fig. 6, i.e., **41/41** and **42/42** as a result of the compensation of asymmetries. Hence, the term  $4x^{13}y^3 (= 8x^{13}y^3 - 4x^{13}y^3)$  appears in eq. 96.

The compensation of asymmetries in Fig. 6 is more clearly demonstrated by representing ligands around the centroid © by appropriate symbols. Suppose that the symbol P represents an *S*-1-methylpropyl ligand in isolation and the symbol  $\bar{P}$  represents an *R*-1-methylpropyl ligand in isolation, where a priority sequence is tentatively considered as “valence bond > ethyl > methyl > hydrogen”. Then, the four stereoisomers are schematically represented as follows: **41** (PPP), **41** ( $\bar{P}\bar{P}\bar{P}$ ), **42** (PP $\bar{P}$ ), and **42** ( $\bar{P}\bar{P}P$ ). It is easy to show that there are no combinations other than these four combinations.

The term  $6x^{13}y^4$  appearing in eq. 96 corresponds to cases in which two ligands selected from two enantiomeric pairs of 1,2-dimethylbutyl ligands ( $P_1/\bar{P}_1$  and  $P_2/\bar{P}_2$  with two asymmetric carbons) are attached to a centroid, as depicted in Fig. 7, where each centroid accommodates two hydrogens in addition. Hence, there exist 10 stereoisomers corresponding to the term  $x^{13}y^4$ . Note that  $P_1-\textcircled{C}-\bar{P}_1$  and  $P_2-\textcircled{C}-\bar{P}_2$  are *meso*-compounds. Because of the presence of four asymmetric carbons, the stereochemical convention described above (the viewpoint of “graphs with asymmetries”) claims the presence of 16 stereoisomers maximum ( $2^4 = 16$ ). Hence, the term  $6x^{13}y^4 (= 16x^{13}y^4 - 10x^{13}y^4)$  appears in eq. 96.

The term  $6x^{13}y^4$  appearing in eq. 96 (centroidal alkanes) is the difference between the value listed in Table 4 and that of Table 2, i.e.,  $5x^{13}(2y)^4 - 74x^{13}y^4 = 6x^{13}y^4$ . The cancelled value, i.e.,  $4x^{13}(2y)^4 - 64x^{13}y^4 = 0$ , corresponds to four graphs, as shown in Fig. 8. Each of the four graphs gives 16 ( $= 2^4$ ) stereoisomers according to the stereochemical convention (the viewpoint of graphs with asymmetries”) because of the presence of four asymmetries.

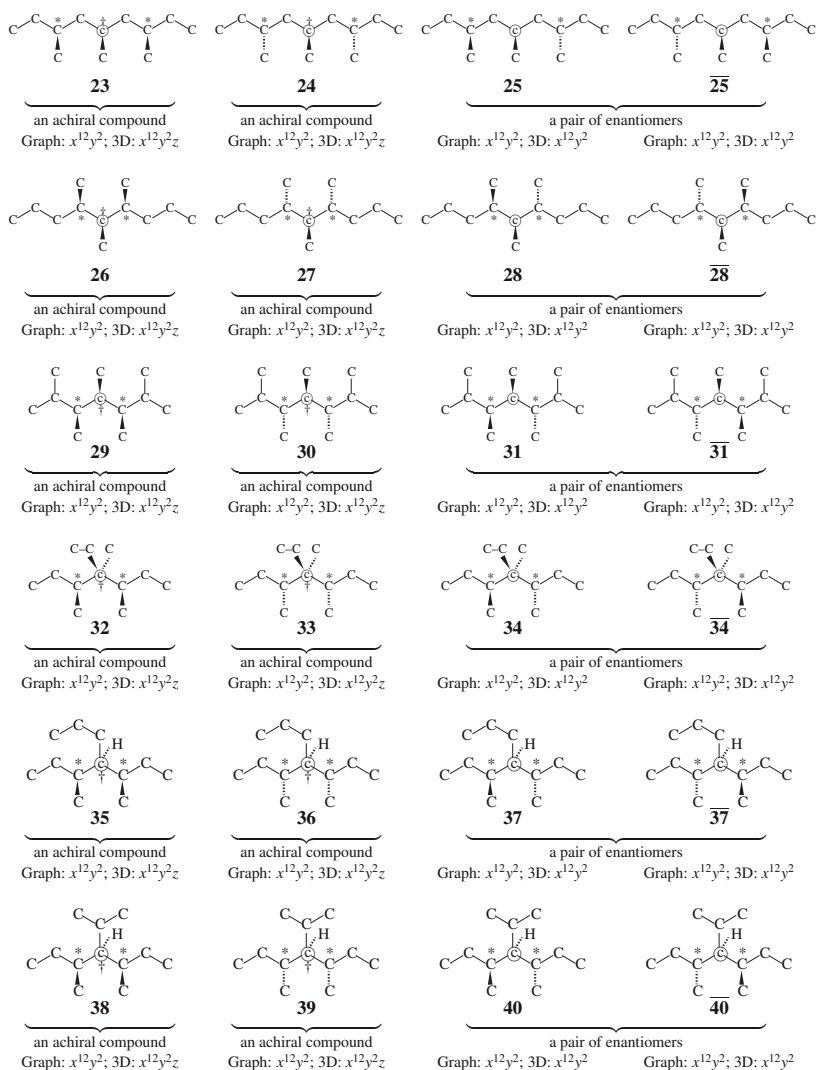


Figure 5: Centroidal alkanes corresponding to the term  $(12 - 12z)y^2x^{12}$  appearing in eq. 96 where each row represents a single graph. The symbol \* represents an asymmetric carbon and the symbol † represents a pseudoasymmetric carbon. The symbol © represents a centroid.

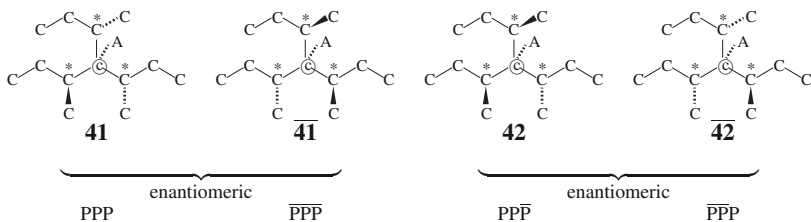


Figure 6: Centroidal alkanes ( $A = H$ ) corresponding to the term  $4x^{13}y^3$  appearing in eq. 96. Three asymmetric carbon atoms (\*) generate four 3D structures in spite of the general expression  $2^3 = 8$ . The four 3D structures coalesce to give a single graph (structure).

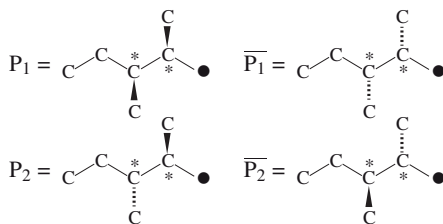
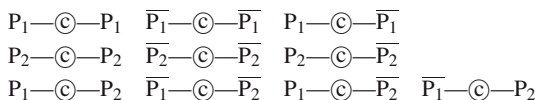


Figure 7: Ten centroidal steric alkanes of carbon content 13, each of which has four asymmetric carbons, where there occurs compensation of asymmetries.

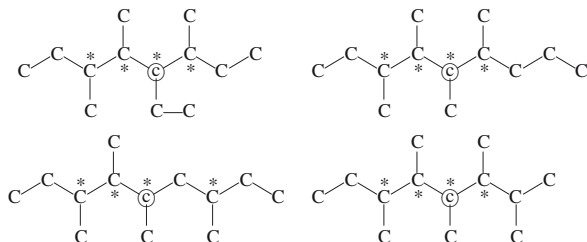


Figure 8: Four centroidal graphs of carbon content 13, each of which has four asymmetric carbons. The presence of four asymmetric carbons gives 16 ( $= 2^4$ ) stereoisomers for each graph without compensation of asymmetries.



**Centroidal Alkanes of Carbon Content 14** The term  $(54 - 54z)y^2x^{14}$  appearing in eq. 96 is interpreted by the existence of 27 pseudoasymmetric cases represented by the formula  $P-\textcircled{C}(AB)-\bar{P}$ , where  $P/\bar{P}$  represents a pair of enantiomeric ligands with one asymmetric carbon; and the symbols A and B represent achiral ligands. Table 6 of Part 1 of this series has given the numbers of such ligands P of carbon contents 4 to 6. Hence, the ligand P in each of these cases is selected from eight pairs of enantiomeric ligands of carbon content 6 (Case 1), three pairs of enantiomeric ligands of carbon content 5 (Case 2), or one pair of enantiomeric ligands of carbon content 4 (Case 3). Each case permits the following combinations of A and B: Case 1 (one combination of AB, i.e., A = CH<sub>3</sub>, B = H), Case 2 (three combinations of AB, i.e., A = propyl, B = H; A = isopropyl, B = H; and A = ethyl, B = methyl), or Case 3 (total 10 combinations of AB, i.e., A = five pentyls, B = H; A = three butyls, B = CH<sub>3</sub>; and A = two propyls, B = ethyl). It follows that there appear 27 (= 8 × 1 + 3 × 3 + 1 × 10) combinations for the formula  $P-\textcircled{C}(AB)-\bar{P}$ . Because each combination corresponds to the term  $(2 - 2z)y^2x^{14}$ , we are able to obtain the term  $27 \times (2 - 2z)y^2x^{13} = (54 - 54z)y^2x^{14}$ .

The remaining terms for carbon content 14 are converted into an interpretative form as follows:

$$\begin{aligned} & (16y^3 - 4zy^4 - 8y^5)x^{14} \\ & = 4y^3x^{14} + (12y^3 - 12y^4)x^{14} + (4 - 4z)y^4x^{14} + (8y^4 - 8y^5)x^{14}. \end{aligned} \quad (97)$$

The term  $4y^3x^{14}$  of eq. 97 can be interpreted on the same line as shown in Fig. 6, i.e., **41/41** (A = CH<sub>3</sub>) and **42/42** (A = CH<sub>3</sub>). The coefficient 4 of the term  $4y^3x^{14}$  is calculated by the difference  $2^3 - 4$ , where the power 3 is the number of asymmetric carbons.

The term  $(12y^3 - 12y^4)x^{14}$  of eq. 97 can be explained by using Fig. 9, where the symbols  $Q/\bar{Q}$  represents a pair of enantiomeric ligands of carbon content 5, which is selected from three pairs of enantiomeric ligands with one asymmetric carbon.

When  $Q/\bar{Q}$  is fixed, each of **43/43** and **44/44** shown in the first row of Fig. 9 is characterized by the term  $x^{14}y^3$  as a graph, because each centroid ( $\textcircled{C}$ ) is not regarded as an asymmetric carbon. In contrast, such a centroid as contained in a 3D structure is regarded as an asymmetric carbon so as to be characterized by the term  $x^{14}y^4$ . Note that the four alkanes listed in the first row (**43/43** and **44/44**) are categorized into Type III. It follows that they are characterized by  $4x^{14}y^3$  (as graphs) and  $4x^{14}y^4$  (as 3D structures). On the other hand, the four structures shown in the second row of Fig. 9 (**45/45** and **46/46**) are characterized by  $4x^{14}y^3$  as graphs and as 3D structures, because the relevant centroids are not regarded as asymmetric carbons in graphs nor in 3D structures. Note that they are categorized into Type II. Hence, the difference between graphs and 3D structures is characterized by  $8x^{14}y^3 - (4x^{14}y^3 + 4x^{14}y^4) = (4y^3 - 4y^4)x^{14}$ , when  $Q/\bar{Q}$  is fixed. Because there exist three pairs of enantiomers for  $Q/\bar{Q}$ , we can calculate the contribution of the structures collected in Fig. 9 to be  $3 \times (4y^3 - 4y^4)x^{14} = (12y^3 - 12y^4)x^{14}$ .

It should be noted that the eight 3D structures collected in Fig. 9 are reduced into a single graph, when  $Q/\bar{Q}$  is fixed. This means that they are stereoisomeric to one another.

When  $Q/\bar{Q}$  is fixed, the four structures shown in the first row of Fig. 9 (**43/43** and **44/44**) are *RS*-stereoisomeric so that they are contained in a single stereoisogram of Type III. The two structures **45/45** are *RS*-stereoisomeric so that they are contained in a single stereoisogram of Type II. The two structures **46/46** are *RS*-stereoisomeric so that they are contained in another single stereoisogram of Type II.

The term  $(4 - 4z)y^4x^{14}$  appearing in eq. 97 corresponds to eight stereoisomers listed in Fig. 10, where the first row involves one set of **47/47** (an enantiomeric pair), **48** (an achiral

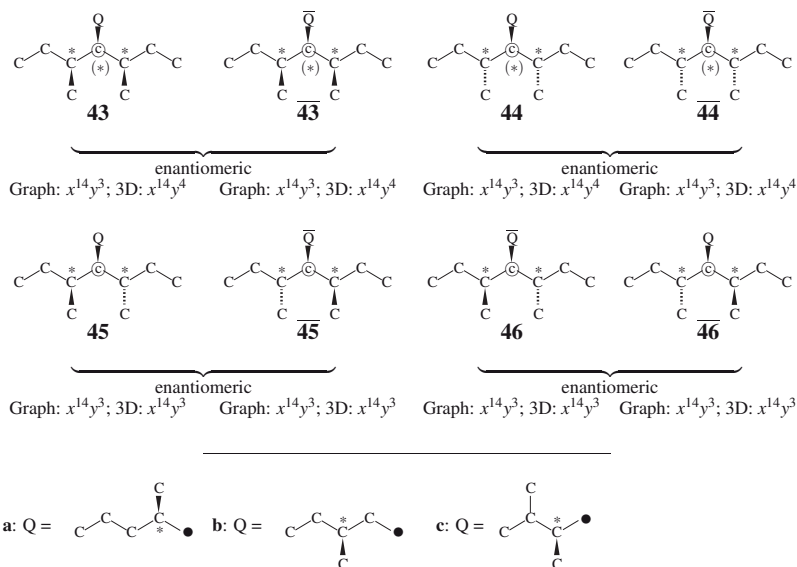


Figure 9: Centroidal alkanes corresponding to the term  $(12y^3 - 12y^4)x^{14}$  appearing in eq. 97. The symbol \* represents an asymmetric carbon. The symbol (\*) represents an asymmetric carbon in a 3D structure. The symbol © represents a centroid.

compound), and **49** (an achiral compound); and the second row involves another set of **50/50** (an enantiomeric pair), **51** (an achiral compound), and **52** (an achiral compound). Note that the two achiral structures of each row are *RS*-stereoisomeric so that they are contained in a single stereoisogram of Type V (a pseudoasymmetric case). As found in the above-mentioned discussions on pseudoasymmetric cases, each row corresponds to the term  $(2 - 2z)y^4x^{14}$ . Hence, we obtain  $2 \times (2 - 2z)y^4x^{14} = (4 - 4z)y^4x^{14}$ , which is identical to the corresponding term in eq. 97.

The term  $(8y^4 - 8y^5)x^{14}$  appearing in eq. 97 clearly shows the difference between graphs and 3D structures. The corresponding 8 stereoisomers are listed in Fig. 11. If two diastereomeric pairs of 1,2-dimethylbutyl ligands of opposite configurations are represented by the symbols  $P/\bar{P}$  and  $Q/\bar{Q}$ , the eight isomers are categorized into two sets of *RS*-stereoisomers. The first row shows a set of four *RS*-stereoisomers, i.e., **53** ( $P-\text{CH}(\text{CH}_3)-Q$ ), **53** ( $\bar{Q}-\text{CH}(\text{CH}_3)-\bar{P}$ ), **54** ( $\bar{P}-\text{CH}(\text{CH}_3)-\bar{Q}$ ), and **54** ( $Q-\text{CH}(\text{CH}_3)-P$ ), which are contained in a stereoisogram of Type III. The second row shows another set of four *RS*-stereoisomers, i.e., **55** ( $\bar{P}-\text{CH}(\text{CH}_3)-Q$ ), **55** ( $\bar{Q}-\text{CH}(\text{CH}_3)-P$ ), **56** ( $P-\text{CH}(\text{CH}_3)-\bar{Q}$ ), and **56** ( $Q-\text{CH}(\text{CH}_3)-\bar{P}$ ), which are contained in another stereoisogram of Type III. Because the alkyl ligands  $P/\bar{P}$  and  $Q/\bar{Q}$  coalesce into a single graph, the central atoms of the 8 stereoisomers (Fig. 11) are characterized not to be asymmetric. This means that they are characterized by the term  $8y^4x^{14}$  from the viewpoint of “graphs with asymmetries”. The same central atoms are characterized to be asymmetric from the viewpoint of 3D structures with “asymmetries and pseudoasymmetries” so that the 8 stereoisomers are characterized by the term  $8y^5x^{14}$ . The difference between these terms is

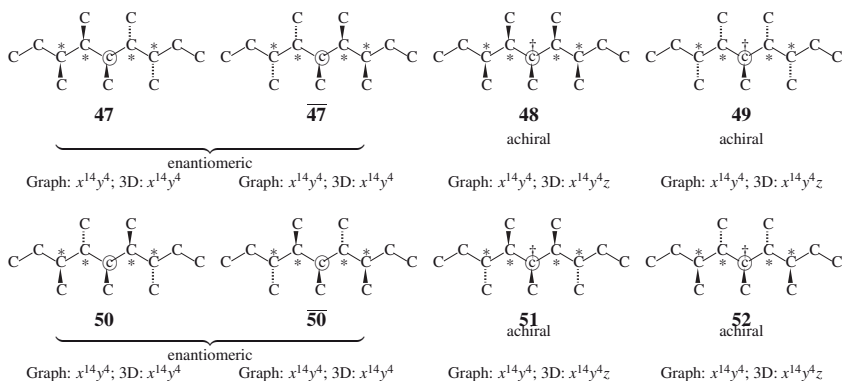


Figure 10: Centroidal alkanes of carbon content 14 corresponding to the term  $(4 - 4z)y^4x^{14}$  of eq. 97, where these stereoisomers coalesce into a single graph.

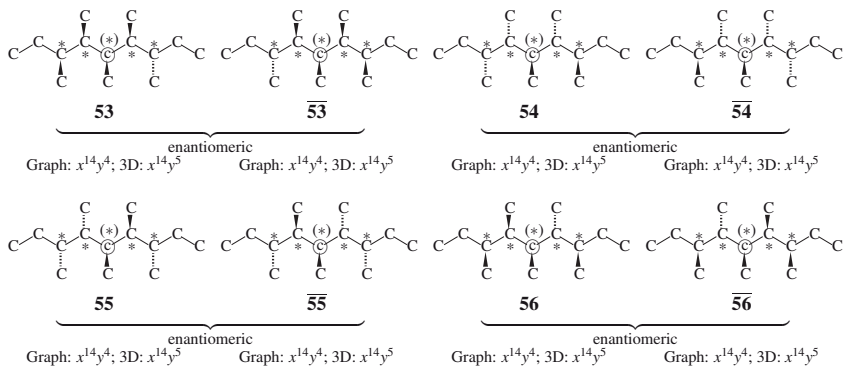


Figure 11: Centroidal alkanes of carbon content 14 corresponding to the term  $(8y^4 - 8y^5)x^{14}$  of eq. 97, where these stereoisomers (in addition to those listed in Fig. 10) coalesce into a single graph. The symbol \* represents an asymmetric carbon except that an asterisk in a pair of parentheses represents an asymmetric carbon as a 3D structure but causes no specification as a graph.

calculated to be  $(8y^4 - 8y^5)x^{14}$ , which is identical to the corresponding term in eq. 97.

As shown in Figs. 10 and 11, there exist totally 16 stereoisomers. This fact is seemingly in agreement with the stereochemical convention that there exist 16 ( $= 2^4$ ) stereoisomers maximum from the viewpoint of “graphs with asymmetries”. It should be noted, however, that we should take account of more complicated situations, as found in the careful examination of the terms  $(4 - 4z)y^4x^{14} + (8y^4 - 8y^5)x^{14}$  (appearing in eq. 97).

### 4.3.3 Bicentroidal Alkanes From Two Viewpoints for Characterizing Stereoisomerism

Because  $\tilde{B}_g(x, 2y)$  (eq. 95) and  $\tilde{S}(x, y, z)$  (eq. 31) are concerned with the same set of bicentroidal alkanes, their difference is useful to detect the difference between the two viewpoints:

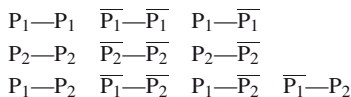
$$\begin{aligned} & \tilde{B}_g(x, 2y) - \tilde{S}(x, y, z) \\ &= y^2x^8 + 3y^2x^{10} + (8y^2 + 6y^4)x^{12} + (20y^2 + 30y^4)x^{14} \\ & \quad + (46y^2 + 114y^4 + 28y^6)x^{16} \\ & \quad + ((180 - 78z)y^2 + (408 - 408z)y^3 + (881 - 500z - 3z^2)y^4 \\ & \quad \quad + (112 - 112z)y^5 + 196y^6)x^{18} \\ & \quad + ((480 - 260z)y^2 + (1760 - 1760z)y^3 + (4042 - 2928z - 10z^2)y^4 \\ & \quad \quad + (1184 - 1184z)y^5 + (1100 - 64z)y^6 + 120y^8)x^{20} + \dots \end{aligned} \quad (98)$$

**Bicentroidal Alkanes of Carbon Contents 8, 10, and 12** The coefficient 1 of the first term  $x^8y^2$  appearing in eq. 98 is interpreted by examining Fig. 1, which contains three stereoisomers, i.e., a *meso*-compound (1) and a pair of enantiomers (2/2̄). Hence, the coefficient is calculated to be  $2^2 - 3 = 1$ , where the power 2 stems from the presence of two asymmetric carbons.

The coefficient 3 of the second term  $x^{10}y^2$  appearing in eq. 98 stems from the presence of three pairs of enantiomeric ligands which are characterized by carbon content 5 and one asymmetric atoms (cf. three Q's listed in the bottom row of Fig. 9). The relevant bicentroidal alkanes of carbon content 10 are depicted in Fig. 12, where each row contains a *meso*-compound (e.g., 57) and a pair of enantiomers (e.g., 58/58̄). Hence, the coefficient 3 is calculated to be  $3 \times (2^2 - 3) = 3$ , where the power 2 stems from the presence of two asymmetric carbons.

The term  $8x^{12}y^2$  appearing in eq. 98 stems from eight *meso*-compounds, which are represented by the formula P—P̄. The ligand P in each of these cases is selected from eight pairs of enantiomeric ligands of carbon content 6 (cf. Table 6 of Part I of this series). Hence, there emerge eight sets of three stereoisomers so as to satisfy the term  $8x^{12}y^2$ .

The term  $6x^{12}y^4$  appearing in eq. 98 corresponds to cases in which two ligands selected from two enantiomeric pairs of 1,2-dimethylbutyl ligands (P<sub>1</sub>/P̄<sub>1</sub> and P<sub>2</sub>/P̄<sub>2</sub> with two asymmetric carbons among six carbons) are linked directly to each other:



Hence, there exist 10 stereoisomers corresponding to the term  $x^{12}y^4$  from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”. Note that  $P_1-\overline{P_1}$  and  $P_2-\overline{P_2}$  are *meso*-compounds. Because of the presence of four asymmetric carbons, the stereochemical convention described above (the viewpoint of “graphs with asymmetries”) claims the presence of 16 stereoisomers maximum ( $2^4 = 16$ ). Hence, the term  $6x^{12}y^4 (= 16x^{12}y^4 - 10x^{12}y^4)$  appears in eq. 98.

Obviously, this discussion is parallel to the above-described discussion on the term  $6x^{13}y^4$  appearing in eq. 96 (cf. Fig. 7). Note that a pair of enantiomeric ligands P<sub>1</sub>/P̄<sub>1</sub> and another pair of enantiomeric ligands P<sub>2</sub>/P̄<sub>2</sub> are stereoisomeric so as to be reduced into a single graph,

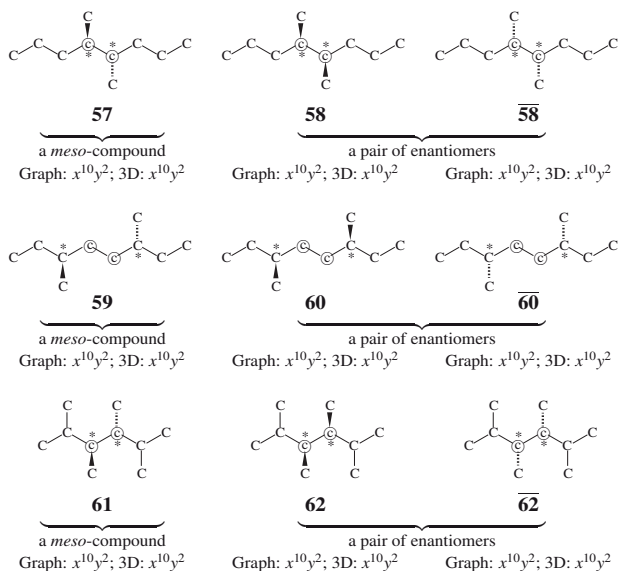


Figure 12: Bicentroidal alkanes corresponding to the term  $3x^{10}y^2$  appearing in eq. 98 where each row represents a single graph. The symbol \* represents an asymmetric carbon. The symbol  $\textcircled{C}-\textcircled{C}$  represents a bicentroid.

where each of the ligands contains two asymmetric carbons. The term  $6x^{12}y^4$  appearing in eq. 98 (bicentroidal alkanes) is the difference between the value listed in Table 5 and that of Table 3, i.e.,  $x^{12}(2y)^4 - 10x^{12}y^4 = 6x^{12}y^4$ . This means that only one graph (cf. the coefficient 1 of the term  $x^{12}y^4$  listed in Table 5) participates in the present case.

**Bicentroidal Alkanes with Pseudoasymmetries** As an example of bicentroidal alkanes with pseudoasymmetric carbons, let us examine the term  $(180 - 78z)y^2x^{18}$  appearing in eq. 98. The term is divided into two parts:

$$(180 - 78z)y^2x^{18} = 102x^{18}y^2 + (78 - 78z)y^2x^{18}. \quad (99)$$

The term  $102x^{18}y^2$  appearing in the right-hand side of eq. 99 corresponds to 102 pairs of enantiomeric ligands of carbon content 9 with one asymmetric carbon ( $102x^9y$ , cf. Table 6 in Part 1 of this series). Each of the pairs contributes to the coefficient of the term  $x^{18}y^2$  by one ( $= 2^2 - 3$ ) on the same line as the case of Fig. 1.

The term  $(78 - 78z)y^2x^{18}$  appearing in eq. 99 stems from 39 sets of three stereoisomers shown in Fig. 13, where the symbol  $\textcircled{C}A$  represents an achiral ligand of carbon content 9 in which its principal node is identical with one terminal node of the bicentroid. Note that there exist 39 achiral alkyl ligands of carbon content 9 ( $39x^9$ , cf. Table 6 in Part 1 of this series) and that **63** and **64** are achiral and exhibit pseudoasymmetry. When  $\textcircled{C}A$  is fixed, each set of three stereoisomers corresponds to the term  $(2 - 2z)y^2x^{18}$ . Hence, we obtain  $39 \times (2 - 2z)y^2x^{18} = (78 - 78z)y^2x^{18}$ , which is in agreement with eq. 99.

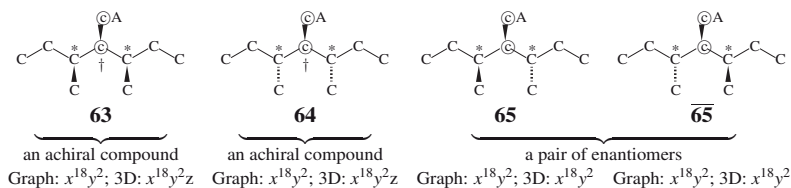


Figure 13: Bicentroidal alkanes corresponding to the term  $(78 - 78z)y^2x^{18}$  appearing in eq. 99. The symbol \* represents an asymmetric carbon. The symbol † represents a pseudoasymmetric carbon. The symbol ⊙—⊙ represents a bicentroid. The symbol ⊙A represents an achiral ligand of carbon content 9 in which its principal node is identical with one terminal node of the bicentroid.

## 5 Conclusion

Three functional equations have been derived to count alkyl ligands, i.e.,  $a(x, y, z)$  for enumerating achiral ligands,  $c(x^2, y^2, z^2)$  for enumerating diploids, and  $b(x, y, z)$  for enumerating achiral and chiral ligands as steric isomers. They are recursively evaluated to give generating functions in which each coefficient of the term  $x^k y^\ell z^m$  represents the number of respective objects with  $k$  carbons,  $\ell$  asymmetric carbons, and  $m$  pseudoasymmetric carbons. After alkanes are categorized into Types I–V by means of stereoisograms, non-recursive functional equations for counting alkanes of Types I–V (as 3D structures) are derived by using  $a(x, y, z)$ ,  $c(x^2, y^2, z^2)$ , and  $b(x, y, z)$ . The resulting generating functions give isomer numbers from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”.

When a graph-reduction condition represented by  $a(x, y, z) = c(x, y, z) = b(x, y, z) = r(x, y)$  is employed, the non-recursive functional equations are reduced into the corresponding ones for counting alkanes as graphs. During this reduction, the non-recursive functional equations for counting Types II, III, and V vanish to zero. In particular, the variable  $z$  for characterizing pseudoasymmetric carbons disappears during the graph-reduction process, while the variable  $y$  for characterizing asymmetric carbons remains. The resulting non-recursive functional equations are identical with the counterparts derived alternatively by starting from Pólya’s theorem. They give isomer numbers from the viewpoint of “graphs with asymmetries”.

The data from the viewpoint of “3D structures with asymmetries and pseudoasymmetries” are systematically compared with the data from the viewpoint of “graphs with asymmetries”, where the fate of asymmetries and pseudoasymmetries are demonstrated. In particular, a stereochemical convention that the number of stereoisomers with  $\ell$  asymmetric carbons is equal to  $2^\ell$  has been examined by comparing the two viewpoints.

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