

Systematic Comparison Between Three-Dimensional Structures and Graphs (Part 1). The Fate of Asymmetry and Pseudoasymmetry in the Enumeration of Monosubstituted Alkanes

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Abstract

The present paper is devoted to clarify how asymmetric and pseudoasymmetric centers in monosubstituted alkanes participate in processes during which their three-dimensional (3D) structures are reduced into graphs. After categorized into five types (S. Fujita, *J. Org. Chem.*, **2004**, *69*, 3158–3165), monosubstituted alkanes have been enumerated recursively by considering the numbers of asymmetric and pseudoasymmetric carbons as well as carbon content, where the recursive process adopted in the original program of Fujita's method (S. Fujita, *Bull. Chem. Soc. Jpn.*, **2008**, *81*, 193–219); S. Fujita, *MATCH Commun. Math. Comput. Chem.*, **2008**, *59*, 509–554) has been improved so as to rely on a more simplified structure of recursiveness. To compare between 3D structures and graphs, a graph-reduction condition has been employed. Thereby, the non-recursive functional equations have been reduced into such equations as relevant to graphs. The functional equations for 3D structures have been discussed from the present viewpoint of "3D structures with asymmetries and pseudoasymmetries", which has been compared with the viewpoint of "graphs with asymmetries". In particular, Pólya's special questions described in Section 60 of his

famous article (G. Pólya, *Acta Math.*, **1937**, *68*, 145–254) have been revisited and discussed critically by comparing the two viewpoints. A stereochemical convention that the number of stereoisomers with ℓ asymmetric carbons is equal to 2^ℓ has been examined also by comparing the two viewpoints.

1 Introduction

From the beginning of the graph theory on the 1870s [1, 2], combinatorial enumerations of alkanes (or mathematically trees) and related objects have been representative interdisciplinary problems, which have attracted interests of chemists as well as of mathematicians, as summarized in books [3–7] and reviews [8–11]. In particular, recursive calculations of monosubstituted alkanes or equivalently alkyl ligands, which are main subjects of the present paper, have been conducted under various titles containing such chemical terms as “aliphatic alcohols” (e.g., [12, 13]) or such mathematical terms as “rooted trees” (e.g., [1]) and “planted trees” (e.g., [14]).

The 1870s should be remembered also as the beginning of stereochemistry founded by van’t Hoff [15] and LeBel [16], when the concept of “asymmetric carbons” was emphasized as sources of stereoisomers so that an important rule was established: the presence of ℓ asymmetric carbons generates 2^ℓ stereoisomers. Almost at the same age, exceptional cases against the rule such as *meso*-compounds [15] and “pseudoasymmetric carbons” [17, 18] have been already found so as to modify the rule into an expression “ 2^ℓ stereoisomers maximum”. The modified expression implies complicated situations due to the difference between graphs (constitutional or structural isomers) and three-dimensional (3D) objects (stereoisomers).

During 1930s, Pólya has developed a systematic method for enumerating graphs and applied it to the enumeration of monosubstituted alkanes [14]. The importance of Pólya’s accomplishment has been proven by the fact that an English translation of his article [14] has appeared as a book [7] after 70 years from the original publication. Although Pólya has referred to “asymmetric carbons” [14], his enumeration of monosubstituted alkanes was restricted to graphs or to 3D structures (steric isomers) without differentiating chiral and achiral objects. It follows that the term “asymmetric carbons” seems to be different from the same term used in stereochemistry. Later, Robinson et al. have reported the enumeration of chiral and achiral alkanes and monosubstituted alkanes in their pioneering work [19], where Pólya’s method was modified to treat stereoisomers. Even their treatment, however, did not fully take account of pseudoasymmetric cases.

Recently, we have developed a versatile method for enumerating 3D structures (referred to here as Fujita’s proligand method) [20–22], where the concepts of *sphericities* and *sphericity indices* originally developed to characterize equivalence classes (orbits) [23–27] were modified to the counterparts for characterizing cycles, which were further combined with the concepts of *proligands* and *promolecules* [28]. The importance of the concepts of *sphericities* and *sphericity indices* has been discussed in detail [29]. Fujita’s proligand method has been applied to enumerations of monosubstituted alkanes (as planted 3D trees) [30] and of alkanes (as 3D trees) [31]. Further, we have studied the effect of asymmetric and pseudoasymmetric centers on the enumerations of monosubstituted alkanes [32] and alkanes [33].

During these studies, we have become aware that there exist subtle but critical differences between the term “asymmetric” coined originally by van’t Hoff [15], the same term used conventionally and now referred to as an out-dated term in stereochemistry [34], and the same term used by Pólya [14, 7]. Moreover, they are different from the term “asymmetric” used in recent

papers of ours [32, 33], where the term “pseudoasymmetric” along with the term “asymmetric” was defined by means of a newly defined categorization which was based on stereoisograms [35–37].

The different connotations of the term “asymmetric” together with the presence/absence of the concept of pseudoasymmetry are closely related to a question: how different are graphs from 3D structures? 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 monosubstituted alkanes as a 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 Cycle Indices With and Without Chirality Fittingness

2.1 Cycle Indices With Chirality Fittingness for Types I–V

We have already reported the effects of asymmetric and pseudoasymmetric centers in the enumerations of monosubstituted alkanes (planted 3D trees) [32] and alkanes (3D trees) [33]. Further, we have preliminarily treated the reduction of 3D structures into graphs in the enumeration of monosubstituted alkanes (planted 3D trees) [32]. Several essential items among these results should be briefly referred to for the purpose of discussing the reduction of 3D structures into graphs in the enumeration of alkanes (3D trees).

The crux of the previous enumerations [32, 33] stems from the categorization of monosubstituted alkanes into five *RS*-stereoisomeric types (Types I–V) by means of stereoisograms [35,36, 38–39] based on *RS*-stereoisomeric groups [37, 40]. Thus, Types I–V are characterized by three attributes (chirality, *RS*-stereogenicity, and sclerality): Type I is chiral, *RS*-stereogenic, and ascleral; Type II is chiral, *RS*-astereogenic, and scleral; Type III is chiral, *RS*-stereogenic, and scleral; Type IV is achiral, *RS*-astereogenic, and ascleral; and Type V is achiral, *RS*-stereogenic, and scleral.

This categorization has been combined with the concept of *sphericities* which was proposed in Fujita’s USCI (unit-subduced-cycle-index) approach [23–27] and in Fujita’s proligand method [20–22]. Thereby, orbits or cycles have been characterized by *sphericity indices*, i.e., a_d for homospheric orbits (or homospheric cycles), b_d for hemispheric orbits (or hemispheric cycles), and c_d for enantiospheric orbits (or enantiospheric cycles). Then such sphericity indices have been applied in the form of cycle indices with chirality fittingness (CI-CFs), which have characterized monosubstituted alkanes of Types I–V as follows:

$$\text{CI-CF}^{(\text{I})}(\mathbf{C}_{3f}, a_d) = \frac{1}{3}(a_1^3 + 2a_3) - a_1a_2 \quad (1)$$

$$\text{CI-CF}^{(\text{II})}(\mathbf{C}_{3\bar{v}}, a_d, b_d) = b_1b_2 - a_1a_2 \quad (2)$$

$$\begin{aligned} \text{CI-CF}^{(\text{III})}(\mathbf{C}_3, a_d, b_d, c_d) &= \frac{1}{3}(b_1^3 + 2b_3) - \frac{1}{3}(a_1^3 + 2a_3) \\ &\quad - (b_1b_2 - a_1a_2) - (a_1c_2 - a_1a_2) \end{aligned} \quad (3)$$

$$\text{CI-CF}^{(\text{IV})}(\mathbf{C}_{3v}, a_d) = a_1a_2 \quad (4)$$

$$\text{CI-CF}^{(\text{V})}(\mathbf{C}_{3v}, a_d, c_d) = a_1c_2 - a_1a_2, \quad (5)$$

which are noted in the previous papers: eq. 28 of [32] (eq. 9 of [33]) for eq. 1, eq. 23 of [32] (eq. 10 of [33]) for eq. 2, eq. 30 of [32] (eq. 12 of [33]) for eq. 3, eq. 18 of [32] (eq. 8 of [33]) for

eq. 4, eq. 20 of [32] (eq. 11 of [33]) for eq. 5. The groups represented by C_{3f} , $C_{3\bar{v}}$, C_3 , and C_{3v} have been selected tentatively [33] but can be replaced by C_3 as the net effect of the summation of eqs. 1–5 [32]. According to the categorization by stereoisograms [35–39], Types I, II, and III are chiral while Type IV and V are achiral; Types I, III, and V are *RS*-stereogenic while Type II and IV are *RS*-astereogenic; as well as Types II, III, and V are scleral while Type I and IV are ascleral.

Let us consider the subgroup C_{3v} of the *RS*-stereoisomeric group:

$$C_{3v} \sim \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); \overline{(1)(2\ 3)}, \overline{(2)(1\ 3)}, \overline{(1\ 2)(3)}\}, \quad (6)$$

where the right-hand side represents the coset representation $C_{3v}/(C_s)$ and each number with an overbar represents the alternation of a ligand configuration. Because two chiral monosubstituted alkanes of each enantiomeric pair are counted separately, equations for Types I to III are divided by two and summed up together with those of Types IV and V in order to take the point group C_{3v} into consideration. Thereby we obtain the total number of achiral and chiral monosubstituted alkanes as follows:

$$\begin{aligned} & \text{CI-CF}(C_{3v}, a_d, b_d, c_d) \\ &= \frac{1}{2} \{ \text{CI-CF}^{(I)}(C_{3f}, a_d) + \text{CI-CF}^{(II)}(C_{3\bar{v}}, a_d, b_d) + \text{CI-CF}^{(III)}(C_3, a_d, b_d, c_d) \} \\ & \quad + \text{CI-CF}^{(IV)}(C_{3v}, a_d) + \text{CI-CF}^{(V)}(C_{3v}, a_d, c_d) \\ &= \frac{1}{6} (b_1^3 + 2b_3 + 3a_1c_2), \end{aligned} \quad (7)$$

where each pair of enantiomers is counted once just as each achiral monosubstituted alkane is counted once. Note that Types I, II, and III (divided by 2 in eq. 7) is characterized to be chiral, while Types IV and V (not divided in eq. 7) is characterized to be achiral.

We use an appropriate set of proligands stored in the following warehouse:

$$\mathbf{L} = \{A, B, X; p, \bar{p}; q, \bar{q}; r, \bar{r}\}, \quad (8)$$

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

$$a_d = A^d + B^d + X^d \quad (9)$$

$$b_d = A^d + B^d + X^d + p^d + \bar{p}^d + q^d + \bar{q}^d + r^d + \bar{r}^d \quad (10)$$

$$c_d = A^d + B^d + X^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} + 2r^{d/2}\bar{r}^{d/2}. \quad (11)$$

By introducing the ligand inventories into eq. 7, we are able to obtain the total number of achiral and chiral objects on the basis of the warehouse represented by eq. 8. In the present context, each proligand contained in \mathbf{L} is selected from monosubstituted alkanes (or alkyl ligands).

Let us next consider another subgroup $C_{3\bar{v}}$ of the *RS*-stereoisomeric group:

$$C_{3\bar{v}} \sim \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); (1)(2\ 3), (2)(1\ 3), (1\ 2)(3)\}, \quad (12)$$

which can be equalized to the symmetric group of degree 3, i.e., S^3 . Note that the group $C_{3\bar{v}}$ is correlated to but different from the C_{3v} group in the alteration or preservation of ligand configurations. Suppose that each *RS*-astereogenic monosubstituted alkane of Type II is counted once

under $C_{3\bar{v}}$ (eq. 12) just as each *RS*-astereogenic monosubstituted alkanes of Type IV is counted once under $C_{3\bar{v}}$. Note that this situation is akin to the one in which each achiral monosubstituted alkane of Type V is counted once under C_{3v} (eq. 6) just as each achiral monosubstituted alkanes of Type IV is counted once under C_{3v} .

Two chiral monosubstituted alkanes of each enantiomeric pair of Type I are counted separately under $C_{3\bar{v}}$, because they are also *RS*-stereogenic. Two *RS*-stereogenic monosubstituted alkanes of each *RS*-diastereomeric pair of Type III are counted separately under $C_{3\bar{v}}$. On the same line, two achiral monosubstituted alkanes of Type V which are in an *RS*-diastereomeric relationship are counted separately under $C_{3\bar{v}}$. Thereby we obtain the total number of monosubstituted alkanes under $C_{3\bar{v}}$ as follows:

$$\begin{aligned} & \text{CI-CF}(C_{3\bar{v}}, b_d) \\ &= \frac{1}{2} \{ \text{CI-CF}^{(I)}(C_{3\bar{f}}, a_d) + \text{CI-CF}^{(III)}(C_3, a_d, b_d, c_d) + \text{CI-CF}^{(V)}(C_{3v}, a_d, c_d) \} \\ & \quad + \text{CI-CF}^{(II)}(C_{3\bar{v}}, a_d, b_d) + \text{CI-CF}^{(IV)}(C_{3v}, a_d) \\ &= \frac{1}{6} (b_1^3 + 2b_3 + 3b_1b_2), \end{aligned} \quad (13)$$

where Types I, III, and V (divided by 2 in eq. 13) is characterized to be *RS*-stereogenic, while Types II and IV (not divided in eq. 13) is characterized to be *RS*-astereogenic.

Let us further consider a subgroup $C_{3\hat{f}}$ of the *RS*-stereoisomeric group:

$$C_{3\hat{f}} \sim \{ (1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); \overline{(1)(2)(3)}, \overline{(1\ 2\ 3)}, \overline{(1\ 3\ 2)} \}, \quad (14)$$

Suppose that each enantiomeric pair of chiral monosubstituted alkanes of Type I is counted once under $C_{3\hat{f}}$ (eq. 14) just as each achiral monosubstituted alkanes of Type IV is counted once under $C_{3\hat{f}}$. On a similar line as described above for the other subgroups, we obtain the total number of monosubstituted alkanes under $C_{3\hat{f}}$ as follows:

$$\begin{aligned} & \text{CI-CF}(C_{3\hat{f}}, a_d, b_d) \\ &= \frac{1}{2} \{ \text{CI-CF}^{(II)}(C_{3\bar{v}}, a_d, b_d) + \text{CI-CF}^{(III)}(C_3, a_d, b_d, c_d) + \text{CI-CF}^{(V)}(C_{3v}, a_d, c_d) \} \\ & \quad + \text{CI-CF}^{(I)}(C_{3\hat{f}}, a_d) + \text{CI-CF}^{(IV)}(C_{3v}, a_d) \\ &= \frac{1}{6} (b_1^3 + 2b_3 + a_1^3 + 2a_3), \end{aligned} \quad (15)$$

where Types II, III, and V (divided by 2 in eq. 15) is characterized to be scleral, while Types I and IV (not divided in eq. 15) is characterized to be ascleral.

By summing up equations for Types I to V, on the other hand, we are able to obtain the total number of steric isomers:

$$\begin{aligned} & \text{CI-CF}(C_3, a_d, b_d) \\ &= \text{CI-CF}^{(I)}(C_{3\hat{f}}, a_d) + \text{CI-CF}^{(II)}(C_{3\bar{v}}, a_d, b_d) + \text{CI-CF}^{(III)}(C_3, a_d, b_d, c_d) \\ & \quad + \text{CI-CF}^{(IV)}(C_{3v}, a_d) + \text{CI-CF}^{(V)}(C_{3v}, a_d, c_d) \\ &= \frac{1}{3} (b_1^3 + 2b_3), \end{aligned} \quad (16)$$

where two enantiomers of each pair are counted separately, while each achiral monosubstituted alkane is counted once. Because C_3 is a subgroup common to C_{3v} , $C_{3\bar{v}}$, and $C_{3\hat{f}}$, we can say

that two *RS*-diastereomers of each pair (or two holantimers of each pair) are counted separately under C_3 . It should be noted that the term a_1c_2 of eq. 7 (with omitting the coefficient) stems from the summation of Type IV (eq. 4) and V (eq. 5), that the term b_1b_2 of eq. 13 (with omitting the coefficient) stems from the summation of Type II (eq. 2) and IV (eq. 4), and that the terms $a_1^3 + 2a_3$ of eq. 15 (with omitting the coefficient) stems from the summation of Type I (eq. 1) and IV (eq. 4).

The comparison between eq. 7 (under C_{3v}) and eq. 13 (under $C_{3\bar{v}}$ or $S^{[3]}$) provides us with a hint to grasp the concepts of sphericities and sphericity indices. The CI-CFs (eqs. 7 and 13) commonly contain the terms appearing in eq. 16 because C_{3v} and $C_{3\bar{v}}$ have the same subgroup (C_3). The same values that we enumerate 3D objects under C_3 , i.e., the numbers of steric isomers of given carbon contents where two enantiomers of each pair (or two *RS*-diastereomers of each pair) are counted separately, are interpreted differently if we rely on C_{3v} or $C_{3\bar{v}}$ ($S^{[3]}$). If we rely on C_{3v} , we use the term “steric isomers under the point group C_{3v} ” to refer to the values at issue. On the other hand, if we rely on $C_{3\bar{v}}$ (or $S^{[3]}$), we use the term “steric isomers under the symmetric group $S^{[3]}$ ” to refer to the same values. The difference between them emerges critically, when we consider pseudoasymmetric cases. Fig. 1 shows examples of pseudoasymmetric cases and related ones, where each solid circle represents a root and each intersection of four bonds represents a principal node (or a central carbon atom). Even if we restrict our discussion to the three permutations of C_3 among eq. 6, we should take account of concealed actions of reflection operations, such as $(1)(2\ 3) \times (1)(2\ 3) = (1)(2)(3)$, because each of the operations in the left-hand side is contained in the set $C_{3v} - C_3$, while the resulting $(1)(2)(3)$ is contained in C_3 . Let us consider the successive actions of $(1)(2\ 3)$ on **1**, as shown in the first row of Fig. 1, where there is only one participant, **1**. Similar actions shown in the second and third rows of Fig. 1 indicate that the four steric isomers (**1**, **2**, **3**, and $\bar{\mathbf{3}}$) are categorized into three classes, i.e., **1**; **2**; and $\mathbf{3}/\bar{\mathbf{3}}$. Note that the last class corresponds to a pair of enantiomers.

On the other hand, we should take account of concealed actions of permutation operations such as $(1)(2\ 3) \times (1)(2\ 3) = (1)(2)(3)$, even if we restrict our discussion to the three permutations of C_3 (isomorphic to $\mathcal{A}^{[3]}$) among eq. 12. The successive actions of $(1)(2\ 3)$ shown in the fourth to sixth rows of Fig. 1 indicate that the four steric isomers (**1**, **2**, **3**, and $\bar{\mathbf{3}}$) are categorized into three classes, i.e., **1/2**, **3**, $\bar{\mathbf{3}}$. Note that the first class corresponds to a pair of diastereomers, not a pair of enantiomers.

The discussion described in the preceding section indicates that the C_3 -group of C_{3v} is different from the C_3 -group of $C_{3\bar{v}}$ ($S^{[3]}$) in its implication (Fig. 1). However, the numbers of steric isomers (i.e., **1**, **2**, **3**, and $\bar{\mathbf{3}}$) are calculated to be equal, because they are counted separately under C_3 .

2.2 Cycle Indices Without Chirality Fittingness for Types I–V

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

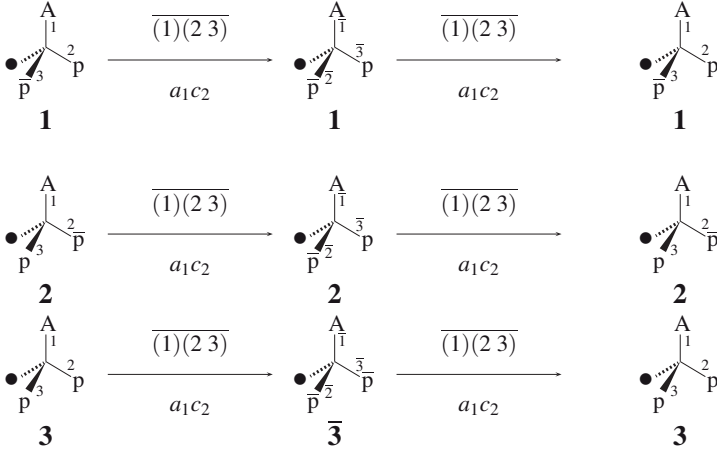
$$a_d = b_d = c_d = r_d. \quad (17)$$

The graph-reduction condition (eq. 17) is introduced into eqs. 1–5 so as to give the following CIs:

$$CI^{(I)}(S^{[3]}, r_d) = \frac{1}{3}(r_1^3 + 2r_3) - r_1r_2 \quad (18)$$

$$CI^{(II)}(S^{[3]}, r_d) = 0 \quad (19)$$

“steric isomers as 3D structures under the point group C_{3v} ”: **1, 2, $3\bar{3}$**



“steric isomers as 3D structures under the symmetric group $S^{[3]} (\sim C_{3v})$ ”: **$1/2, 3, \bar{3}$**

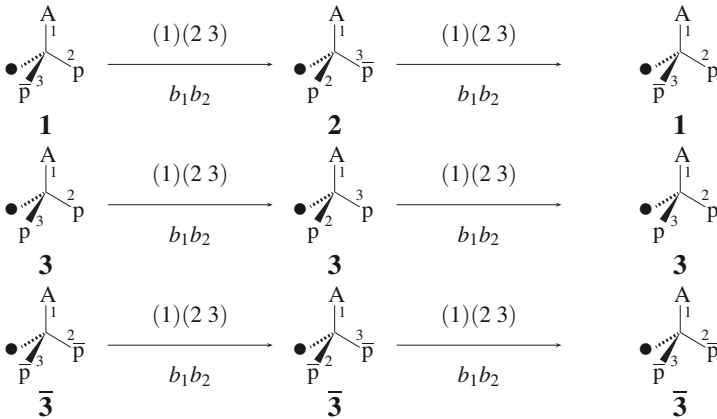


Figure 1: Steric isomers as 3D structures under the point group C_{3v} and under the symmetric group $S^{[3]} (\sim C_{3v})$. The identity operation $(1)(2\ 3)$ is interpreted variously as shown in respective rows.

$$\text{CI}^{(\text{III})}(\mathcal{A}^{[3]}, r_d) = 0 \quad (20)$$

$$\text{CI}^{(\text{IV})}(\mathcal{S}^{[3]}, r_d) = r_1 r_2 \quad (21)$$

$$\text{CI}^{(\text{V})}(\mathcal{S}^{[3]}, r_d) = 0, \quad (22)$$

where the symmetric group of degree 3 ($\mathcal{S}^{[3]}$) and its alternating group ($\mathcal{A}^{[3]}$) are selected tentatively.

On a similar line to the derivation of eq. 7, equations for Types I to III are divided by two and summed up together with those for Types IV and V so as to provide the total number of monosubstituted alkanes as graphs:

$$\begin{aligned} \text{CI}(\mathcal{S}^{[3]}, r_d) &= \frac{1}{2} \left\{ \text{CI}^{(\text{I})}(\mathcal{S}^{[3]}, r_d) + \text{CI}^{(\text{II})}(\mathcal{S}^{[3]}, r_d) + \text{CI}^{(\text{III})}(\mathcal{A}^{[3]}, r_d) \right\} \\ &\quad + \text{CI}^{(\text{IV})}(\mathcal{S}^{[3]}, r_d) + \text{CI}^{(\text{V})}(\mathcal{S}^{[3]}, r_d) \\ &= \frac{1}{2} \text{CI}^{(\text{I})}(\mathcal{S}^{[3]}, r_d) + \text{CI}^{(\text{IV})}(\mathcal{S}^{[3]}, r_d) \\ &= \frac{1}{6} (r_1^3 + 2r_3 + 3r_1 r_2). \end{aligned} \quad (23)$$

This treatment is based on the fact that the subgroup $\mathbf{C}_{3\bar{v}}$ (eq. 12) of the *RS*-stereoisomeric group (which is correlated to the \mathbf{C}_{3v} group) is isomorphic to the symmetric group $\mathcal{S}^{[3]}$.

On a similar line to the derivation of eq. 16, the summing-up of the equations for Types I to V gives the total number of steric isomers as graphs:

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

This equation (eq. 24) can be alternatively obtained by introducing the graph-reduction condition (eq. 17) into eq. 16. It should be noted that eq. 24 is concerned with graphs although it is the same form as eq. 16. Because of the graph-reduction condition (eq. 17), eq. 24 is essentially different from eq. 16 which is concerned with 3D structures (cf. Fig. 1). To clarify the difference, we should examine the graph-reduction condition (eq. 17) in more detail.

According to the graph-reduction condition, the equation $b_2 = c_2$ is converted into the following equation:

$$b_2 - c_2 = (p - \bar{p})^2 + (q - \bar{q})^2 + (r - \bar{r})^2 = 0, \quad (25)$$

by starting from eqs. 10 and 11. Thereby, two enantiomeric ligands can be equalized so that we put $p = \bar{p} = p_g$, $q = \bar{q} = q_g$, and $r = \bar{r} = r_g$. As a result, the warehouse represented by eq. 8 is reduced into the following warehouse:

$$\mathbf{L}' = \{ \mathbf{A}, \mathbf{B}, \mathbf{X}; p_g, q_g, r_g \}. \quad (26)$$

Then, the three ligand inventories (eqs. 9–11) are reduced into the following single inventory:

$$r_d = \mathbf{A}^d + \mathbf{B}^d + \mathbf{X}^d + p_g^d + q_g^d + r_g^d. \quad (27)$$

By introducing this ligand inventory into eq. 23, we are able to obtain the total number of graphs on the basis of the warehouse represented by eq. 26, where each proligand (graph) contained

in \mathbf{L}' is selected from monosubstituted alkanes (or alkyl ligands). Note that the replacement of a_1 (eq. 7) by r_1 (eq. 23) forces eq. 9 to change into eq. 27, which permits the substitution of a chiral ligand (after reduced into a graph) in addition of an achiral ligand.

The comparison between eq. 16 (for 3D structures) and eq. 24 (for graphs) provides us with a hint to grasp the importance of the graph-reduction condition (eq. 17).

1. The former equation for 3D structures (eq. 16) takes implicitly account of Type V (pseudoasymmetric cases), although the effect of Type V vanishes during the derivation of eq. 16. Moreover, eq. 10 is used among the three ligand inventories (eqs. 9–11).
2. On the other hand, the latter equation for graphs (eq. 24) does not take account of Type V (pseudoasymmetric cases), because eqs. 18–22 are used after employing the graph-reduction condition (eq. 17). Moreover, eq. 27 is used in contrast to the usage of eq. 10.
3. The point group \mathbf{C}_3 as a subgroup of the point group \mathbf{C}_{3v} (eq. 6 serving as the basis of eq. 16 via eq. 7) is different from the alternating group $\mathcal{A}^{[3]}$ as a subgroup of the symmetric group $\mathcal{S}^{[3]}$ (eq. 12 serving as the basis of eq. 24 via eq. 23). The difference stems from whether the concept of sphericities is considered or not. It should be noted that the ligand inventory eq. 10 introduced into eq. 16 (for 3D structures) is accompanied by the remaining ligand inventories (eqs. 9 and 11) according to the concept of sphericities. In contrast, the ligand inventory eq. 27 introduced into eq. 24 (for graphs) is a sole inventory without the concept of sphericities.
4. The term “steric isomers under the point group \mathbf{C}_{3v} ” is used in Fig. 1 to emphasize the presence of sphericities in eq. 16. Because the subgroup \mathbf{C}_3 is adopted to derive eq. 16, the term “steric isomers under the symmetric group $\mathcal{S}^{[3]}$ ($\sim \mathbf{C}_{3v}$)” used in Fig. 1 results in the usage of the sphericity indices b_1 and b_3 in eq. 16. In other words, both the two terms presume the usage of eq. 10 as a ligand inventory, although the correspondence of eq. 16 to eq. 7 for the former is different from that of eq. 16 to eq. 13 for the latter. It follows that both the two terms are concerned with 3D structures, even although the latter term is regarded as relying on $\mathcal{S}^{[3]}$ -group ($\sim \mathbf{C}_{3v}$). Note that the $\mathcal{S}^{[3]}$ -group acting on graphs is differentiated from the $\mathcal{S}^{[3]}$ -group ($\sim \mathbf{C}_{3v}$) acting on 3D structures, as found by comparing eq. 24 (for graphs) with eq. 16 (for 3D structures).
5. Note that the sphericity index b_2 (or c_2) in eq. 25 does not appear in eq. 16 and relevantly the term r_2 does not appear in eq. 24. This means that eq. 24 is independent to eq. 27. In contrast, eq. 24 presumes eq. 27 as a ligand inventory. This means that isomers relevant to eq. 24 are regarded as graphs, whereas the $\mathcal{S}^{[3]}$ -group is employed.

3 Monosubstituted Alkanes of Types I–V as 3D Structures

3.1 Functional Equations for Counting Types I–V

To evaluate monosubstituted alkanes as 3D structures, the sphericity indices a_d , b_d , and c_d in CI-CFs are replaced by $a(x^d, y^d, z^d)$, $b(x^d, y^d, z^d)$, and $c(x^d, y^d, z^d)$, which are used to derive functional equations for recursive calculation as follows:

$$a(x, y, z) = 1 + xa(x, y, z)a(x^2, y^2, z^2)$$

$$c(x^2, y^2, z^2) = 1 + xz \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \}, \quad (28)$$

$$\begin{aligned} & + x^2 c(x^2, y^2, z^2)c(x^4, y^4, z^4) \\ & + x^2 z^2 \{ a(x^2, y^2, z^2)c(x^4, y^4, z^4) - a(x^2, y^2, z^2)a(x^4, y^4, z^4) \} \\ & + \frac{x^2 y^2}{3} \{ c(x^2, y^2, z^2)^3 + 2c(x^6, y^6, z^6) \} - x^2 y^2 c(x^2, y^2, z^2)c(x^4, y^4, z^4) \\ & - x^2 y^2 \{ a(x^2, y^2, z^2)c(x^4, y^4, z^4) - a(x^2, y^2, z^2)a(x^4, y^4, z^4) \}, \quad (29) \end{aligned}$$

$$\begin{aligned} b(x, y, z) & = 1 + xb(x, y, z)b(x^2, y^2, z^2) + xz \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \} \\ & + \frac{xy}{3} \{ b(x, y, z)^3 + 2b(x^3, y^3, z^3) \} - xyb(x, y, z)b(x^2, y^2, z^2) \\ & - xy \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \}, \quad (30) \end{aligned}$$

where each principal node is categorized into an asymmetric carbon (y), a pseudoasymmetric carbon (z), or others (no specification). These equations have been noted in previous papers (eqs. 53–55 of Ref. [32] and eqs. 19–21 of Ref. [33]). Each of these functional equations (eqs. 28–30) exhibits a recursive nature.

The sphericity indices a_d , b_d , and c_d in CI-CFs (eqs. 1–5) are replaced by $a(x^d, y^d, z^d)$, $b(x^d, y^d, z^d)$, and $c(x^d, y^d, z^d)$, and the resulting functions are multiplied by x for a principal node, where further multiplications of y or z are added if necessary. Thereby, we obtain functional equations $L^{(I)}(x, y, z) - L^{(V)}(x, y, z)$ for evaluating Types I–V:

$$L^{(I)}(x, y, z) = \frac{xy}{3} \{ a(x, y, z)^3 + 2a(x^3, y^3, z^3) \} - xy a(x, y, z)a(x^2, y^2, z^2) \quad (31)$$

$$L^{(II)}(x, y, z) = x \{ b(x, y, z)b(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \} \quad (32)$$

$$\begin{aligned} L^{(III)}(x, y, z) & = \frac{xy}{3} \{ b(x, y, z)^3 + 2b(x^3, y^3, z^3) \} - \frac{xy}{3} \{ a(x, y, z)^3 + 2a(x^3, y^3, z^3) \} \\ & - xy \{ b(x, y, z)b(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \} \\ & - xy \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \} \quad (33) \end{aligned}$$

$$L^{(IV)}(x, y, z) = xa(x, y, z)a(x^2, y^2, z^2) \quad (34)$$

$$L^{(V)}(x, y, z) = xz \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \}. \quad (35)$$

These equations can be evaluated by introducing generating functions, which are obtained by the recursive calculations of eqs. 28–30. Let the symbol $L_{k\ell m}^{(T)}$ represent the number of mono-substituted alkanes of Type T (T = I, II, ..., V), which contain k carbons among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. The corresponding generating functions are represented as follows:

$$L^{(T)}(x, y, z) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(T)} z^m \right) y^{\ell} \right) x^k, \quad (36)$$

where two enantiomers of each pair (Types I, II, and III) are counted separately and each achiral isomer (Types IV and V) is counted once according to eqs. 31–35.

In a similar way to the derivation of eq. 7, we use eqs. 31–35 to derive the following functional equation:

$$L^{(B)}(x, y, z) = \frac{1}{2} \{ L^{(I)}(x, y, z) + L^{(II)}(x, y, z) + L^{(III)}(x, y, z) \} + L^{(IV)}(x, y, z) + L^{(V)}(x, y, z)$$

$$\begin{aligned}
 &= \frac{xy}{6} \{b(x, y, z)^3 + 2b(x^3, y^3, z^3) - 3b(x, y, z)b(x^2, y^2, z^2)\} \\
 &\quad - \frac{xy}{2} \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\} \\
 &\quad + \frac{x}{2} \{b(x, y, z)b(x^2, y^2, z^2) + a(x, y, z)a(x^2, y^2, z^2)\} \\
 &\quad + xz \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\}, \tag{37}
 \end{aligned}$$

which gives the number of achiral and chiral monosubstituted alkanes, where a pair of enantiomers is counted just once. This equation can be evaluated by introducing generating functions ($a(x, y, z)$, $b(x, y, z)$, and $c(x^2, y^2, z^2)$), which are obtained by the recursive calculations of eqs. 28–30. Let the symbol $L_{k\ell m}^{(B)}$ represent the number of chiral plus achiral monosubstituted alkanes, which contain k carbons among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. The corresponding generating functions are represented as follows:

$$L^{(B)}(x, y, z) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(B)} z^m \right) y^{\ell} \right) x^k, \tag{38}$$

where each pair of enantiomers counted once and each achiral isomer is counted once.

The equation (eq. 37) can be alternatively obtained by putting as follows:

$$L^{(B)}(x, y, z) = \frac{1}{2} \{[a(x, y, z) - 1] + [b(x, y, z) - 1]\}, \tag{39}$$

because of eqs. 28 and 30. The resulting equation (eq. 37) is essentially equivalent to eq. 59 of Ref. [32], which was derived by putting $(1/2)\{a(x, y, z) + b(x, y, z)\}$ (except the initial value 1). The numbers of achiral and chiral monosubstituted alkanes have been evaluated in this way and reported in a tabular form (Table 3 of Ref. [32]).

In a similar way to the derivation of eq. 16, we use eqs. 31–35 to derive the following functional equation:

$$\begin{aligned}
 L^{(S)}(x, y, z) &= L^{(I)}(x, y, z) + L^{(II)}(x, y, z) + L^{(III)}(x, y, z) + L^{(IV)}(x, y, z) + L^{(V)}(x, y, z) \\
 &= \frac{xy}{3} \{b(x, y, z)^3 + 2b(x^3, y^3, z^3)\} - xyb(x, y, z)b(x^2, y^2, z^2) \\
 &\quad - xy \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\} \\
 &\quad + xb(x, y, z)b(x^2, y^2, z^2) \\
 &\quad + xz \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\}, \tag{40}
 \end{aligned}$$

which gives the number of steric isomers of monosubstituted alkanes, where two enantiomers of each pair are counted separately. This equation can be evaluated by introducing generating functions ($a(x, y, z)$, $b(x, y, z)$, and $c(x^2, y^2, z^2)$), which are obtained by the recursive calculations of eqs. 28–30. Let the symbol $L_{k\ell m}^{(S)}$ represent the number of steric isomers of monosubstituted alkanes, which contain k carbons among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. The corresponding generating functions are represented as follows:

$$L^{(S)}(x, y, z) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(S)} z^m \right) y^{\ell} \right) x^k, \tag{41}$$

where two enantiomers of each pair counted separately and each achiral isomer is counted once.

As found easily by comparing eq. 40 with eq. 30, we obtain

$$L^{(S)}(x,y,z) = b(x,y,z) - 1. \quad (42)$$

The number of steric isomers of monosubstituted alkanes have been evaluated in this way and reported in a tabular form (Table 4 of Ref. [32]).

3.2 Implementation and Results for 3D Structures

The enumeration of monosubstituted alkanes as 3D structures has been conducted in detail by considering the numbers of asymmetric and pseudoasymmetric carbons [32]. Although the categorization of Types I–V was used to evaluate the numbers of asymmetric and pseudoasymmetric carbons, subdivided numbers of monosubstituted alkanes of Types I–V have not concretely been calculated. Because data of such subdivided numbers are necessary for the purpose of discussing the conceptual reduction of from 3D structures to graphs, the previous calculations have been improved to give the following program (3DAlky101.mpl), where the multiple recursive processes of the previous programs (Alky11-30zfinal9.mpl of [32]) have been simplified into a single do loop by using the Maple command `subs`. Thereby, the subdivided numbers of monosubstituted alkanes are obtained as data of 3D structures.

```
#3DAlky101.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);

"Categorization of Alkyl Ligands as Planted 3D Trees";
TypeI := (x*y/3)*(a1^3 + 2*a3) - (x*y)*a1*a2;
TypeII := x*(b1*b2 - a1*a2);
TypeIII := (x*y/3)*(b1^3 + 2*b3) - (x*y/3)*(a1^3 + 2*a3)
- x*y*(b1*b2 - a1*a2) - x*y*(a1*c2 - a1*a2);
TypeIV := x*a1*a2;
TypeV := x*z*(a1*c2 - a1*a2);
Lxh := (1/2)*(TypeI + TypeII + TypeIII) + TypeIV + TypeV;
Lxs := TypeI + TypeII + TypeIII + TypeIV + TypeV;
#Lxt := (1/2)*(TypeI + TypeIII + TypeV) + TypeII + TypeIV;

"Initial Values";
a1 := 1; a2 := 1; a3 := 1; a4 := 1;
c2 := 1; c4 := 1; c6 := 1;
b1 := 1; b2 := 1; b3 := 1; b4 := 1;
Lh := 0;
#Lt := 0;
Ls := 0;
TypeIh := 0; TypeIIh := 0; TypeIIIh := 0; TypeIVh := 0; TypeVh := 0;

"Recursive Calculation";
kmax := 20;
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);
Lh := Lh + coeff(expand(Lxh),x^k)*x^k;
Ls := Ls + coeff(expand(Lxs),x^k)*x^k;
#Lt := Lt + coeff(expand(Lxt),x^k)*x^k;
TypeIh := TypeIh + coeff(expand(TypeI),x^k)*x^k;
TypeIIh := TypeIIh + coeff(expand(TypeII),x^k)*x^k;
TypeIIIh := TypeIIIh + coeff(expand(TypeIII),x^k)*x^k;
TypeIVh := TypeIVh + coeff(expand(TypeIV),x^k)*x^k;
TypeVh := TypeVh + coeff(expand(TypeV),x^k)*x^k;
end do;

Test0:= expand((b1-1) - Ls);
Test1:= expand((1/2)*(a1-1)+(b1-1)) - Lh);

"Print Out: Total Alkyl (Achiral+Chiral)";
for k from 1 to kmax by 1 do
BLh := sort(collect(expand(coeff(Lh,x^k)),y),
[z,y],ascending)*x^k;
TLh := subs({y=1,z=1},expand(coeff(Lh,x^k)));
end do;

"Print Out: Total Alkyl (Steric)";
for k from 1 to kmax by 1 do
BLs := sort(collect(expand(coeff(Ls,x^k)),y),
[z,y],ascending)*x^k;
TLs := subs({y=1,z=1},expand(coeff(Ls,x^k)));
end do;

"Print Out: Type I Alkyl";
for k from 1 to kmax by 1 do
LTypeI := sort(collect(expand(coeff(TypeIh,x^k)),y),
[z,y],ascending)*x^k;
TTypeI := subs({y=1,z=1},expand(coeff(TypeIh,x^k)));
end do;

(omitted)

```

The part “Alkyl Ligands as Planted 3D-Trees” in the program named “3DAlkyl01.mpl” declares three recursive functional equations, i.e., eqs. 28–30, by the symbols $axyz$, $cxyz$, and $bxyz$, where the symbols $a1$, $c2$, $b1$, etc. are used to designate $a(x,y,z)$, $c(x^2,y^2,z^2)$, $b(x,y,z)$, etc. in the right-hand sides. The part “Categorization of Alkyl Ligands as Planted 3D Trees” declares the functional equations represented by $L^{(I)}(x,y,z)$ (eq. 31)– $L^{(V)}(x,y,z)$ (eq. 35) by using the symbols $TypeI$ – $TypeV$. The resulting series corresponding to eq. 36 are stored in $TypeIh$ to $TypeVh$. The symbol Lxh declares the functional equation $L^{(B)}(x,y,z)$ (eq. 37), where the resulting series corresponding to eq. 38 is stored in Lh . The symbol Lxs declares the functional equation $L^{(S)}(x,y,z)$ (eq. 40), where the resulting series corresponding to eq. 41 is stored in Ls . The part “Initial Values” sets the initial values for the series for storing generating functions.

The `do` loop of the part “Recursive Calculation” calculates recursively the three functional equations `axyz`, `cxyz`, and `bxyz`, where the data stored in `a1`, `c2`, and `b1` for carbon content $k-1$ are used to calculate the data of next step of carbon content k by using the Maple command `coeff`. The resulting coefficients are stored in `a1`, `c2`, and `b1` recursively. They are used to calculate the other non-recursive functional equations, which are stored stepwise in the series `Lh`, `Ls`, and `TypeIh-TypeVh`.

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, which are represented in the form of generating functions concerning $x^k y^\ell z^m$. By putting $y = 1$ and $z = 1$, we are able to obtain the total numbers of monosubstituted alkanes (as 3D structures) of carbon content k .

The term `Test0` is calculated for a test for eq. 42, which is calculated to be equal to zero. The term `Test1` is calculated for a test for eq. 39, which is calculated to be equal to zero.

Each term of the generating function stored in `TypeIh` (corresponding to eq. 31 and eq. 36) is shown in Table 1. Each row of Table 1 shows a polynomial concerning $x^k y^\ell z^m$, where the coefficient of each term $x^k y^\ell z^m$ represents the number of Type-I monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Note that Type-I monosubstituted alkanes are chiral, *RS*-stereogenic, and ascleral, where two enantiomers of each pair are counted separately. The “Total” column of Table 1 is the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(I)} \right)$ for each carbon content k , where the value is obtained by putting $x = y = z = 1$.

Table 2 lists polynomials of $x^k y^\ell z^m$ appearing in the generating function stored in `TypeIIh` (corresponding to eq. 32 and eq. 36), where the coefficient of each term $x^k y^\ell z^m$ represents the number of Type-II monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Because Type-II monosubstituted alkanes are chiral, *RS*-astereogenic, and scleral, two enantiomers of each pair are counted separately. The “Total” column of Table 2 collects the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(II)} \right)$ for each carbon content k .

Table 3 lists the data of Type-III monosubstituted alkanes, which are stored in `TypeIIIh` (corresponding to eq. 33 and eq. 36). The coefficient of each term $x^k y^\ell z^m$ represents the number of Type-III monosubstituted alkanes of carbon content k (as 3D structures), which contain ℓ asymmetric and m pseudoasymmetric carbons. Because Type-III monosubstituted alkanes are chiral, *RS*-stereogenic, and scleral, two enantiomers of each pair are counted separately. The “Total” column of Table 3 lists the sum of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(III)} \right)$ for each carbon content k .

It should be noted here that Tables 1–Table 3 contain terms concerning z for pseudoasymmetric carbons. Because the determination of pseudoasymmetry is conducted at each recursive step, an alkyl ligand at such step may be achiral as a substituent so that it may exhibit pseudoasymmetry. Once the pseudoasymmetry of the internal alkyl ligand is detected by a variable z , the variable z remains effective, even when the internal alkyl ligand is finally incorporated in a chiral monosubstituted alkane.

The data of Type-IV monosubstituted alkanes, which are achiral, *RS*-astereogenic, and ascleral, are listed in Table 4, each row of which contains a polynomial of carbon content k appearing in the series `TypeIVh` (corresponding to eq. 34 and eq. 36). The coefficient of each term $x^k y^\ell z^m$ represents the number of Type-IV monosubstituted alkanes of carbon content k (as 3D structures), which contain ℓ asymmetric and m pseudoasymmetric carbons. The “Total” col-

Table 1: Numbers of Type-I Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(I)}\right) y^{\ell}\right) x^k$ (cf. eqs. 31 and 36)	Total
$2yx^4$	2
$4yx^5$	4
$10yx^6$	10
$22yx^7$	22
$46yx^8$	46
$94yx^9$	94
$190yx^{10}$	190
$(370y + 4zy^3)x^{11}$	374
$(718y + 12zy^3)x^{12}$	730
$(1376y + 44zy^3)x^{13}$	1420
$(2606y + 116zy^3)x^{14}$	2722
$(4898y + 312zy^3 + 8zy^5)x^{15}$	5218
$(9150y + 740zy^3 + 24zy^5)x^{16}$	9914
$(16970y + 1752zy^3 + 104zy^5)x^{17}$	18826
$(31320y + 3900zy^3 + 280zy^5)x^{18}$	35500
$(57526y + 8596zy^3 + (840z + 2z^2)y^5 + 16zy^7)x^{19}$	66980
$(105198y + 18300zy^3 + (2064z + 26z^2)y^5 + 48zy^7)x^{20}$	125636
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-I monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Two enantiomers of each pair are counted separately.

umn of Table 4 lists the sum of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(IV)}\right)$ for each carbon content k .

Table 5 collects the data of Type-V monosubstituted alkanes, which are achiral, *RS*-stereogenic, and scleral. Each of these monosubstituted alkanes exhibits pseudoasymmetry at its principal vertex (the carbon which is attached by a substituent). Each row of which contains a polynomial of carbon content k appearing in the series `TypeVh` (corresponding to eq. 35 and eq. 36). The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-V monosubstituted alkanes of carbon content k (as 3D structures), which contain ℓ asymmetric and m pseudoasymmetric carbons. The ‘‘Total’’ column of Table 5 lists the sum of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(V)}\right)$ for each carbon content k .

Table 6 lists polynomials of $x^k y^{\ell} z^m$ appearing in the generating function stored in `Lh` (corresponding to eq. 37 and eq. 38), where the coefficient of each term $x^k y^{\ell} z^m$ represents the number of monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Note that each pair of enantiomers is counted once, just as each achiral monosubstituted alkane is counted once. The ‘‘Total’’ column of Table 6 collects the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(B)}\right)$ for each

Table 2: Numbers of Type-II Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{\ell m}^{(II)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 51)	Total
$2yx^5$	2
$6yx^6$	6
$(18y + 4y^2)x^7$	22
$(46y + 20y^2)x^8$	66
$(110y + 82y^2 + 8y^3)x^9$	200
$(250y + 272y^2 + 56y^3)x^{10}$	578
$(552y + 820y^2 + 304y^3 + 16y^4)x^{11}$	1692
$(1178y + 2280y^2 + (1284 + 4z)y^3 + 160y^4)x^{12}$	4906
$(2466y + 6020y^2 + (4756 + 16z)y^3 + 1076y^4 + 32y^5)x^{13}$	14366
$(5066y + 15188y^2 + (15872 + 64z)y^3 + (5520 + 8z)y^4 + 424y^5)x^{14}$	42142
$(10250y + 37046y^2 + (49256 + 196z)y^3 + (24188 + 56z)y^4 + 3504y^5 + 64y^6)x^{15}$	124560
$(20470y + 87748y^2 + (144080 + 572z)y^3 + (94176 + 288z)y^4 + (21480 + 24z)y^5 + 1104y^6)x^{16}$	369942
$(40440y + 202926y^2 + (402344 + 1508z)y^3 + (336064 + 1168z)y^4 + (109856 + 208z)y^5 + 10888y^6 + 128y^7)x^{17}$	1105530
$(79104y + 459564y^2 + (1080688 + 3836z)y^3 + (1118568 + 4180z)y^4 + (491800 + 1312z)y^5 + (78168 + 48z)y^6 + 2768y^7)x^{18}$	3320036
$(153444y + 1022372y^2 + (2810148 + 9260z)y^3 + (3520374 + 13508z)y^4 + (1992772 + 6376z)y^5 + (459344 + 624z)y^6 + 32320y^7 + 256y^8)x^{19}$	10020798
$(295402y + 2238724y^2 + (7106336 + 21756z)y^3 + (10574128 + 40704z)y^4 + (7459156 + 26944z + 2z^2)y^5 + (2333728 + 4896z)y^6 + (268504 + 112z)y^7 + 6816y^8)x^{20}$	30377208
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-II monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Two enantiomers of each pair are counted separately.

carbon content k . As found easily, the data of Table 6 can be obtained by following the scheme: $(1/2)\{\text{Table 1} + \text{Table 2} + \text{Table 3}\} + \text{Table 4} + \text{Table 5}$.

Although apparent modes of presentation (a polynomial form vs. a tabular form) are different, the data of Table 6 are identical to those reported in a previous paper (Table 3 of Ref. [32]), which was alternatively calculated by using eq. 39 without an explicit categorization of five types. The equivalency of the two alternative calculations is confirmed in the program “3DAalkyl01.mpl” described above, where `Test1` is calculated to be equal to zero. The values collected in the “Total” column of Table 6 are identical to those reported in a previous paper (Table 2 of Ref. [30], the “ B_n ” column), which was calculated in an alternative way without considering the numbers of asymmetric and pseudoasymmetric carbons.

Table 7 lists polynomials of $x^k y^{\ell} z^m$ appearing in the generating function stored in `LS` (corresponding to eq. 40 and eq. 41), where the coefficient of each term $x^k y^{\ell} z^m$ represents the number of steric isomers of monosubstituted alkanes of carbon content k (as 3D structures)

Table 3: Numbers of Type-III Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(III)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 52)	Total
$4y^2x^6$	4
$16y^2x^7$	16
$(56y^2 + 8y^3)x^8$	64
$(168y^2 + 48y^3)x^9$	216
$(460y^2 + 240y^3 + 16y^4)x^{10}$	716
$(1180y^2 + 924y^3 + 144y^4)x^{11}$	2248
$(2896y^2 + 3164y^3 + 896y^4 + 32y^5)x^{12}$	6988
$(6840y^2 + 9820y^3 + (4280 + 8z)y^4 + 392y^5)x^{13}$	21340
$(15696y^2 + 28580y^3 + (17564 + 48z)y^4 + 3048y^5 + 64y^6)x^{14}$	65000
$(35152y^2 + 78792y^3 + (64404 + 224z)y^4 + (17552 + 16z)y^5 + 1040y^6)x^{15}$	197180
$(77132y^2 + 208436y^3 + (217432 + 824z)y^4 + (84848 + 160z)y^5 + 9712y^6 + 128y^7)x^{16}$	598672
$(166316y^2 + 532352y^3 + (687480 + 2720z)y^4 + (360328 + 976z)y^5 + (66168 + 48z)y^6 + 2640y^7)x^{17}$	1819028
$(353272y^2 + 1320900y^3 + (2062552 + 8152z)y^4 + (1390364 + 4576z)y^5 + (370184 + 576z)y^6 + 29424y^7 + 256y^8)x^{18}$	5540256
$(740516y^2 + 3196380y^3 + (5924048 + 22976z)y^4 + (4971224 + 18408z)y^5 + (1795752 + 4224z)y^6 + (233416 + 96z)y^7 + 6560y^8)x^{19}$	16913600
$(1534280y^2 + 7570348y^3 + (16402812 + 61384z)y^4 + (16715596 + 66080z)y^5 + (7822888 + 23480z)y^6 + (1493664 + 1664z)y^7 + 85664y^8 + 512y^9)x^{20}$	51778372
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-III monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Two enantiomers of each pair are counted separately.

among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Note that two enantiomers of each pair are counted separately, while each achiral monosubstituted alkane is counted once. The “Total” column of Table 7 collects the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(S)}\right)$ for each carbon content k . As found easily, the data of Table 7 can be obtained by summing up Tables 1—5.

The data of Table 7 are identical to those reported in a previous paper (Table 4 of Ref. [32]), which was alternatively calculated by using eq. 42 without the categorization of five types. The equivalency of the two alternative calculations is confirmed in the program “3DAlkyl01.mpl” described above, where `Test0` is calculated to be equal to zero. The values collected in the “Total” column of Table 7 are identical to those reported in a previous paper (Table 2 of Ref. [30], the “ β_n ” column), which was calculated in an alternative way without considering the numbers of asymmetric and pseudoasymmetric carbons.

Table 4: Numbers of Type-IV Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{klm}^{(IV)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 53)	Total
x	1
x^2	1
$2x^3$	2
$3x^4$	3
$5x^5$	5
$8x^6$	8
$14x^7$	14
$23x^8$	23
$39x^9$	39
$(65 + 2zy^2)x^{10}$	67
$(110 + 4zy^2)x^{11}$	114
$(184 + 14zy^2)x^{12}$	198
$(310 + 28zy^2)x^{13}$	338
$(520 + 70zy^2 + 4zy^4)x^{14}$	594
$(876 + 136zy^2 + 8zy^4)x^{15}$	1020
$(1471 + 298zy^2 + 36zy^4)x^{16}$	1805
$(2475 + 568zy^2 + 72zy^4)x^{17}$	3115
$(4159 + 1154zy^2 + 216zy^4 + 8zy^6)x^{18}$	5537
$(6996 + 2164zy^2 + (424z + 6z^2)y^4 + 16zy^6)x^{19}$	9606
$(11759 + 4202zy^2 + (1062z + 16z^2)y^4 + 88zy^6)x^{20}$	17127
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-IV monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Each achiral monosubstituted alkane of Type IV is counted just once.

3.3 Linking the Data of Types I–V to Previous Enumerations

By starting from eqs. 31–33, we are able to derive the functional equation for counting chiral monosubstituted alkanes as follows:

$$\begin{aligned}
 L^{(C)}(x, y, z) &= \frac{1}{2} \{L^{(I)}(x, y, z) + L^{(II)}(x, y, z) + L^{(III)}(x, y, z)\} \\
 &= \frac{xy}{6} \{b(x, y, z)^3 + 2b(x^3, y^3, z^3) - 3b(x, y, z)b(x^2, y^2, z^2)\} \\
 &\quad - \frac{xy}{2} \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\} \\
 &\quad + \frac{x}{2} \{b(x, y, z)b(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\} \quad (43)
 \end{aligned}$$

where a pair of enantiomers is counted just once. This equation can be evaluated by introducing generating functions ($a(x, y, z)$, $b(x, y, z)$, and $c(x^2, y^2, z^2)$), which are obtained by the recursive

Table 5: Numbers of Type-V Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(V)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 54)	Total
$2zy^2x^9$	2
$2zy^2x^{10}$	2
$8zy^2x^{11}$	8
$10zy^2x^{12}$	10
$(28zy^2 + 4zy^4)x^{13}$	32
$(38zy^2 + 4zy^4)x^{14}$	42
$(90zy^2 + 24zy^4)x^{15}$	114
$(130zy^2 + 28zy^4)x^{16}$	158
$(274zy^2 + 108zy^4 + 8zy^6)x^{17}$	390
$(414zy^2 + (136z + 4z^2)y^4 + 8zy^6)x^{18}$	562
$(812zy^2 + (418z + 8z^2)y^4 + 64zy^6)x^{19}$	1302
$(1266zy^2 + (558z + 36z^2)y^4 + 72zy^6)x^{20}$	1932
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of Type-V monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Each achiral monosubstituted alkane of Type V is counted just once.

calculations of eqs. 28–30. Let the symbol $L_{k\ell m}^{(C)}$ represent the number of chiral monosubstituted alkanes, which contain k carbons among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. The corresponding generating functions are represented as follows:

$$L^{(C)}(x, y, z) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(C)} z^m \right) y^{\ell} \right) x^k, \quad (44)$$

where each pair of enantiomers counted once and each achiral isomer is counted once.

The equation (eq. 43) can be alternatively obtained by putting as follows:

$$L^{(C)}(x, y, z) = \frac{1}{2} \{ [b(x, y, z) - 1] - [a(x, y, z) - 1] \}, \quad (45)$$

because of eqs. 28 and 30. The resulting equation (eq. 45) is essentially equivalent to eq. 61 of Ref. [32], which was derived by putting $(1/2)\{b(x, y, z) - a(x, y, z)\}$. The numbers of chiral monosubstituted alkanes have been evaluated in this way and reported in a tabular form (Table 2 of Ref. [32]). The same data can be obtained by summing up Tables 1–3 and dividing the sum by 2, i.e., $(1/2)\{\text{Table 1} + \text{Table 2} + \text{Table 3}\}$.

On the other hand, eqs. 34 and 35 are summed up to derive the functional equation for counting achiral monosubstituted alkanes as follows:

$$\begin{aligned} L^{(A)}(x, y, z) &= L^{(IV)}(x, y, z) + L^{(V)}(x, y, z) \\ &= xa(x, y, z)a(x^2, y^2, z^2) \\ &\quad + xz \{ a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2) \}. \end{aligned} \quad (46)$$

Table 6: Numbers of Chiral and Achiral Monosubstituted Alkanes as 3D Structures^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(B)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 37)	Total
x	1
x^2	1
$2x^3$	2
$(3+y)x^4$	4
$(5+3y)x^5$	8
$(8+8y+2y^2)x^6$	18
$(14+20y+10y^2)x^7$	44
$(23+46y+38y^2+4y^3)x^8$	111
$(39+102y+(125+2z)y^2+28y^3)x^9$	296
$(65+220y+(366+4z)y^2+148y^3+8y^4)x^{10}$	811
$(110+461y+(1000+12z)y^2+(614+2z)y^3+80y^4)x^{11}$	2279
$(184+948y+(2588+24z)y^2+(2224+8z)y^3+528y^4+16y^5)x^{12}$	6520
$(310+1921y+(6430+56z)y^2+(7288+30z)y^3+(2678+8z)y^4+212y^5)x^{13}$	18933
$(520+3836y+(15442+108z)y^2+(22226+90z)y^3+(11542+36z)y^4+1736y^5+32y^6)x^{14}$	55568
$(876+7574y+(36099+226z)y^2+(64024+254z)y^3+(44296+172z)y^4+(10528+12z)y^5+552y^6)x^{15}$	164613
$(1471+14810y+(82440+428z)y^2+(176258+656z)y^3+(155804+620z)y^4+(53164+104z)y^5+5408y^6+64y^7)x^{16}$	491227
$(2475+28705y+(184621+842z)y^2+(467348+1630z)y^3+(511772+2124z)y^4+(235092+644z)y^5+(38528+32z)y^6+1384y^7)x^{17}$	1475197
$(4159+55212y+(406418+1568z)y^2+(1200794+3868z)y^3+(1590560+6518z+4z^2)y^4+(941082+3084z)y^5+(224176+328z)y^6+16096y^7+128y^8)x^{18}$	4453995
$(6996+105485y+(881444+2976z)y^2+(3003264+8928z)y^3+(4722211+19084z+14z^2)y^4+(3481998+12812z+z^2)y^5+(1127548+2504z)y^6+(132868+56z)y^7+3408y^8)x^{19}$	13511597
$(11759+200300y+(1886502+5468z)y^2+(7338342+20028z)y^3+(13488470+52664z+52z^2)y^4+(12087376+47544z+14z^2)y^5+(5078308+14348z)y^6+(881084+912z)y^7+46240y^8+256y^9)x^{20}$	41159667
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of chiral and achiral monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Each pair of enantiomers is counted once, just as each achiral monosubstituted alkane is counted once.

Table 7: Numbers of Monosubstituted Alkanes (Steric Isomers) with Considering Asymmetries and Pseudoasymmetries^{a)}

The term $\left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(S)} z^m\right) y^{\ell}\right) x^k$ (cf. eq. 40)	Total
x	1
x^2	1
$2x^3$	2
$(3 + 2y)x^4$	5
$(5 + 6y)x^5$	11
$(8 + 16y + 4y^2)x^6$	28
$(14 + 40y + 20y^2)x^7$	74
$(23 + 92y + 76y^2 + 8y^3)x^8$	199
$(39 + 204y + (250 + 2z)y^2 + 56y^3)x^9$	551
$(65 + 440y + (732 + 4z)y^2 + 296y^3 + 16y^4)x^{10}$	1553
$(110 + 922y + (2000 + 12z)y^2 + (1228 + 4z)y^3 + 160y^4)x^{11}$	4436
$(184 + 1896y + (5176 + 24z)y^2 + (4448 + 16z)y^3 + 1056y^4 + 32y^5)x^{12}$	12832
$(310 + 3842y + (12860 + 56z)y^2 + (14576 + 60z)y^3 + (5356 + 12z)y^4 + 424y^5)x^{13}$	37496
$(520 + 7672y + (30884 + 108z)y^2 + (44452 + 180z)y^3 + (23084 + 64z)y^4 + 3472y^5 + 64y^6)x^{14}$	110500
$(876 + 15148y + (72198 + 226z)y^2 + (128048 + 508z)y^3 + (88592 + 312z)y^4 + (21056 + 24z)y^5 + 1104y^6)x^{15}$	328092
$(1471 + 29620y + (164880 + 428z)y^2 + (352516 + 1312z)y^3 + (311608 + 1176z)y^4 + (106328 + 208z)y^5 + 10816y^6 + 128y^7)x^{16}$	980491
$(2475 + 57410y + (369242 + 842z)y^2 + (934696 + 3260z)y^3 + (1023544 + 4068z)y^4 + (470184 + 1288z)y^5 + (77056 + 56z)y^6 + 2768y^7)x^{17}$	2946889
$(4159 + 110424y + (812836 + 1568z)y^2 + (2401588 + 7736z)y^3 + (3181120 + 12684z + 4z^2)y^4 + (1882164 + 6168z)y^5 + (448352 + 640z)y^6 + 32192y^7 + 256y^8)x^{18}$	8901891
$(6996 + 210970y + (1762888 + 2976z)y^2 + (6006528 + 17856z)y^3 + (9444422 + 37326z + 14z^2)y^4 + (6963996 + 25624z + 2z^2)y^5 + (2255096 + 4928z)y^6 + (265736 + 112z)y^7 + 6816y^8)x^{19}$	27012286
$(11759 + 400600y + (3773004 + 5468z)y^2 + (14676684 + 40056z)y^3 + (26976940 + 103708z + 52z^2)y^4 + (24174752 + 95088z + 28z^2)y^5 + (10156616 + 28536z)y^6 + (1762168 + 1824z)y^7 + 92480y^8 + 512y^9)x^{20}$	82300275
(omitted)	

^{a)}The coefficient of each term $x^k y^{\ell} z^m$ represents the number of monosubstituted alkanes (steric isomers) of carbon content k (as 3D structures) among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. Two enantiomers of each pair are counted separately and each achiral monosubstituted alkane is counted once.

This equation can be evaluated by introducing generating functions ($a(x, y, z)$, $b(x, y, z)$, and $c(x^2, y^2, z^2)$), which are obtained by the recursive calculations of eqs. 28–30. Let the symbol $L_{k\ell m}^{(A)}$ represent the number of achiral monosubstituted alkanes, which contain k carbons among which ℓ carbons are asymmetric and m carbons are pseudoasymmetric. The corresponding generating function is represented as follows:

$$L^{(A)}(x, y, z) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} \left(\sum_{m=0}^{\infty} L_{k\ell m}^{(A)} z^m \right) y^{\ell} \right) x^k, \quad (47)$$

where each achiral isomer is counted once.

The equation (eq. 46) can be alternatively obtained by putting as follows:

$$L^{(A)}(x, y, z) = a(x, y, z) - 1, \quad (48)$$

because of eq. 28. The resulting equation (eq. 46) is essentially equivalent to eq. 53 of Ref. [32], which was equalized to be $a(x, y, z)$. The numbers of achiral monosubstituted alkanes have been evaluated in this way and reported in a tabular form (Table 1 of Ref. [32]). The same data can be obtained by summing up Tables 4 and 5.

4 Monosubstituted Alkanes as Graphs

4.1 Functional Equations for Graphs of Types I–V

On the same line as we have converted CI-CFs (eqs. 1–5) into CIs (eqs. 18–22), the reduction procedure of 3D structures into graphs is applied to the functional equations (eqs. 31–31) for 3D structures of Types I–V. For this purpose, the graph-reduction condition (eq. 17) is modified to be applicable to the functional equations:

$$a(x^d, y^d, z^d) = b(x^d, y^d, z^d) = c(x^d, y^d, z^d) = r(x^d, y^d) \quad (49)$$

The graph-reduction condition (eq. 49) is introduced into the right-hand sides of eqs. 31–35 and we put the left hand-sides as follows: $L_g^{(T)}(x, y) = L^{(T)}(x, y, z)$ ($T = \text{I, II, } \dots \text{ V}$). The function $r(x^d, y^d)$ is used in place of $r(x^d, y^d, z^d)$ because the terms depending on the variable z (Type V) vanishes to zero, as found following results:

$$L_g^{(\text{I})}(x, y) = \frac{xy}{3} \{r(x, y)^3 + 2r(x^3, y^3) - 3r(x, y)r(x^2, y^2)\} \quad (50)$$

$$L_g^{(\text{II})}(x, y) = x \{r(x, y)r(x^2, y^2) - r(x, y)r(x^2, y^2)\} = 0 \quad (51)$$

$$\begin{aligned} L_g^{(\text{III})}(x, y) &= \frac{xy}{3} \{r(x, y)^3 + 2r(x^3, y^3)\} - \frac{xy}{3} \{r(x, y)^3 + 2r(x^3, y^3)\} \\ &\quad - xy \{r(x, y)r(x^2, y^2) - r(x, y)r(x^2, y^2)\} \\ &\quad - xy \{r(x, y)r(x^2, y^2) - r(x, y)r(x^2, y^2)\} = 0 \end{aligned} \quad (52)$$

$$L_g^{(\text{IV})}(x, y) = xr(x, y)r(x^2, y^2) \quad (53)$$

$$L_g^{(\text{V})}(x, y) = xz \{r(x, y)r(x^2, y^2) - r(x, y)r(x^2, y^2)\} = 0. \quad (54)$$

In a parallel way to the derivation of eq. 37, we are able to derive a functional equation for evaluating the total number of graphs:

$$L_g^{(\text{B})}(x, y) = \frac{1}{2} \{L_g^{(\text{I})}(x, y) + L_g^{(\text{II})}(x, y) + L_g^{(\text{III})}(x, y)\} + L_g^{(\text{IV})}(x, y) + L_g^{(\text{V})}(x, y)$$

$$\begin{aligned}
 &= \frac{1}{2}L_g^{(I)}(x,y) + L_g^{(IV)}(x,y) \\
 &= \frac{xy}{6} \{r(x,y)^3 + 2r(x^3,y^3) - 3r(x,y)r(x^2,y^2)\} + xr(x,y)r(x^2,y^2). \quad (55)
 \end{aligned}$$

It should be noted that only the functional equations of Types I and IV remain in the derivation process of eq. 55. The functional equation (eq. 55) can be alternatively derived by the application of the graph-reduction condition (eq. 49) to the right-hand side of eq. 37 and by the replacement of the left-hand side $L^{(B)}(x,y,z)$ by $L_g^{(B)}(x,y)$.

Let the symbol $L_{(g)k\ell}^{(B)}$ represent the number of monosubstituted alkanes as graphs, which contain k carbons among which ℓ carbons are asymmetric. The corresponding generating functions are represented as follows:

$$L_g^{(B)}(x,y) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} L_{(g)k\ell}^{(B)} y^{\ell} \right) x^k, \quad (56)$$

where each pair of enantiomers is counted once and each achiral isomer is counted once.

If we presume a recursiveness on the basis of eq. 55, we are able to obtain a recursive functional equation as follows:

$$r(x,y) = 1 + \frac{xy}{6} \{r(x,y)^3 + 2r(x^3,y^3) - 3r(x,y)r(x^2,y^2)\} + xr(x,y)r(x^2,y^2), \quad (57)$$

where the left-hand side of eq. 55 (i.e., $L_g^{(B)}(x,y)$) is replaced by $r(x,y)$ in order to assure the recursiveness and the addition of 1 in the top of the right-hand side is to take account of the substitution of a hydrogen atom. Obviously, the equation (eq. 56) can be alternatively obtained by putting as follows:

$$L_g^{(B)}(x,y,z) = r(x,y) - 1. \quad (58)$$

The equation (eq. 57) has been already noted in Ref. [32] (eq. 68) although the counterparts of eq. 37 and eq. 55 have been obtained in a different way from the present derivation, i.e., without the explicit derivations of eqs. 31–35 and eqs. 50–54. The recursive calculation on the basis of eq. 57 has been also reported in a tabular form up to carbon content 30 (Table 5 of [32]).

By putting $z = y$, the recursive functional equation $b(x,y,z)$ (eq. 30) is converted into the following equation:

$$s(x,y) = 1 + \frac{xy}{3} \{s(x,y)^3 + 2s(x^3,y^3) - 3s(x,y)s(x^2,y^2)\} + xs(x,y)s(x^2,y^2), \quad (59)$$

where we put $b(x,y,y) = s(x,y)$. This conversion presumes that pseudoasymmetric carbons are regarded as being the same as asymmetric carbons. Note that the functions $a(x,y,z)$ and $c(x,y,z)$ vanish during this conversion. We are able to presume the recursiveness of eq. 59 because of the recursiveness of the original function $b(x,y,z)$.

By putting $z = y$ according to the derivation of eq. 59, eq. 40 is converted into the following functional equation:

$$L^{\overline{(S)}}(x,y) = \frac{xy}{3} \{s(x,y)^3 + 2s(x^3,y^3) - 3s(x,y)s(x^2,y^2)\} + xs(x,y)s(x^2,y^2), \quad (60)$$

where we put $L^{(S)}(x,y,y) = L^{\overline{(S)}}(x,y)$.

Let the symbol $L_{k\ell}^{\overline{(S)}}$ represent the number of monosubstituted alkanes as steric isomers, where pseudoasymmetric carbons are regarded as being the same as asymmetric carbons to

give ℓ asymmetric carbons among totally k carbons. The corresponding generating functions are represented as follows:

$$L^{\overline{(S)}}(x, y) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} L_{k\ell}^{\overline{(S)}} y^{\ell} \right) x^k. \quad (61)$$

Obviously, we obtain

$$L^{\overline{(S)}}(x, y) = s(x, y) - 1 \quad (62)$$

by comparing eq. 60 with eq. 59.

4.2 Implementation and Results for Graphs

The enumeration of monosubstituted alkanes as Graphs has been conducted in detail by considering the numbers of asymmetric carbons [32]. In order to discuss the relationship between the present enumeration and Pólya's one, necessary data among the previous ones are recalculated by means of an improved Maple program named "GraphAlkyl-2.mpl", in which the previous multiple `do` loops have been simplified into a single `do` loop by using the Maple command `subs`. Further, additional data for comparison are newly calculated.

```
#GraphAlkyl-2.mpl
"Functional Equations for Alkyl Ligands as Graphs";
rxy := 1 + (1/6)*x*y*(r1^3 + 2*r3 - 3*r1*r2) + x*r1*r2;

"Monosubstituted Alkanes as Graphs";
Lxyg := (x*y/6)*(r1^3 + 2*r3 - 3*r1*r2) + x*r1*r2;

"Functional Equations for Alkyl Ligands: Steric as 3D structures";
sxy := 1 + (x*y/3)*(s1^3 + 2*s3 - 3*s1*s2) + x*s1*s2;

"Steric Isomers of Monosubstituted Alkanes as 3D structures";
LSxy3D := (x*y/3)*(s1^3 + 2*s3 - 3*s1*s2) + x*s1*s2;

"Initial Values";
r1 := 1: r2 := 1: r3 := 1:
s1 := 1: s2 := 1: s3 := 1:
Lg := 0;
LSD := 0;

"Recursive Calculation";
kmax:= 20;
for k from 1 to kmax by 1 do
Crxy := expand(coeff(rxy,x^k)):
Csxy := expand(coeff(sxy,x^k)):
CLxyg := expand(coeff(Lxyg,x^k)):
CLSxy3D := expand(coeff(LSxy3D,x^k)):
r1 := r1 + Crxy*x^k:
r2 := subs({x=x^2,y=y^2},r1):
r3 := subs({x=x^3,y=y^3},r1):
s1 := s1 + Csxy*x^k:
s2 := subs({x=x^2,y=y^2},s1):
s3 := subs({x=x^3,y=y^3},s1):
Lg := Lg + CLxyg*x^k:
LSD := LSD + CLSxy3D*x^k:
end do:

Test0 := expand((r1-1)-Lg);
Test1 := expand((s1-1)-LSD);
```


Table 8: Numbers of Monosubstituted Alkanes as Graphs^{a)}

The term $\left(\sum_{\ell=0}^{\infty} L_{(g)k\ell}^{(B)} y^{\ell}\right) x^k$ (cf. eq. 55 and eq. 56)	Total
x	1
x^2	1
$2x^3$	2
$(3+y)x^4$	4
$(5+3y)x^5$	8
$(8+8y+y^2)x^6$	17
$(14+20y+5y^2)x^7$	39
$(23+46y+19y^2+y^3)x^8$	89
$(39+102y+63y^2+7y^3)x^9$	211
$(65+220y+184y^2+37y^3+y^4)x^{10}$	507
$(110+461y+503y^2+154y^3+10y^4)x^{11}$	1238
$(184+948y+1300y^2+558y^3+66y^4+y^5)x^{12}$	3057
$(310+1921y+3229y^2+1830y^3+336y^4+13y^5)x^{13}$	7639
$(520+3836y+7748y^2+5581y^3+1447y^4+108y^5+y^6)x^{14}$	19241
$(876+7574y+18106y^2+16077y^3+5558y^4+657y^5+17y^6)x^{15}$	48865
$(1471+14810y+41327y^2+44251y^3+19553y^4+3325y^5+168y^6+y^7)x^{16}$	124906
$(2475+28705y+92521y^2+117308y^3+64246y^4+14721y^5+1201y^6+21y^7)x^{17}$	321198
$(4159+55212y+203601y^2+301330y^3+199683y^4+58983y^5+7001y^6+249y^7+y^8)x^{18}$	830219
$(6996+105485y+441466y^2+753458y^3+592876y^4+218374y^5+35265y^6+2064y^7+26y^8)x^{19}$	2156010
$(11759+200300y+944618y^2+1840568y^3+1693381y^4+758406y^5+158988y^6+13731y^7+357y^8+y^9)x^{20}$	5622109
(omitted)	

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

```
"Print Out: Total Alkyl Ligands as Graphs";
for k from 1 to kmax by 1 do
  BLg := sort(collect(expand(coeff(Lg, x^k)), y),
    [z, y], ascending) * x^k;
  TLg := subs({y=1, z=1}, expand(coeff(Lg, x^k)));
end do;
```

```
"Print Out: Steric Isomers of Monosubstituted Alkanes";
for k from 1 to kmax by 1 do
  BLSD := sort(collect(expand(coeff(LSD, x^k)), y),
    [z, y], ascending) * x^k;
  TLSD := subs({y=1, z=1}, expand(coeff(LSD, x^k)));
end do;
```

Table 9: Numbers of Monosubstituted Alkanes (Steric Isomers) with Considering Asymmetries Only^{a)}

The term $\left(\sum_{\ell=0}^{\infty} L_{k\ell}^{\overline{S}} y^{\ell}\right) x^k$ (cf. eq. 60 and eq. 61)	Total
x	1
x^2	1
$2x^3$	2
$(3 + 2y)x^4$	5
$(5 + 6y)x^5$	11
$(8 + 16y + 4y^2)x^6$	28
$(14 + 40y + 20y^2)x^7$	74
$(23 + 92y + 76y^2 + 8y^3)x^8$	199
$(39 + 204y + 250y^2 + 58y^3)x^9$	551
$(65 + 440y + 732y^2 + 300y^3 + 16y^4)x^{10}$	1553
$(110 + 922y + 2000y^2 + 1240y^3 + 164y^4)x^{11}$	4436
$(184 + 1896y + 5176y^2 + 4472y^3 + 1072y^4 + 32y^5)x^{12}$	12832
$(310 + 3842y + 12860y^2 + 14632y^3 + 5416y^4 + 436y^5)x^{13}$	37496
$(520 + 7672y + 30884y^2 + 44560y^3 + 23264y^4 + 3536y^5 + 64y^6)x^{14}$	110500
$(876 + 15148y + 72198y^2 + 128274y^3 + 89100y^4 + 21368y^5 + 1128y^6)x^{15}$	328092
$(1471 + 29620y + 164880y^2 + 352944y^3 + 312920y^4 + 107504y^5 + 11024y^6 + 128y^7)x^{16}$	980491
$(2475 + 57410y + 369242y^2 + 935538y^3 + 1026804y^4 + 474252y^5 + 78344y^6 + 2824y^7)x^{17}$	2946889
$(4159 + 110424y + 812836y^2 + 2403156y^3 + 3188856y^4 + 1894848y^5 + 454524y^6 + 32832y^7 + 256y^8)x^{18}$	8901891
$(6996 + 210970y + 1762888y^2 + 6009504y^3 + 9462278y^4 + 7001322y^5 + 2280734y^6 + 270666y^7 + 6928y^8)x^{19}$	27012286
$(11759 + 400600y + 3773004y^2 + 14682152y^3 + 27016996y^4 + 24278460y^5 + 10251756y^6 + 1790732y^7 + 94304y^8 + 512y^9)x^{20}$	82300275
(omitted)	

^{a)}The coefficient of each term $y^{\ell}x^k$ represents the number of monosubstituted alkanes of carbon content k (as steric isomers) among which ℓ carbons are asymmetric.

```
Test2 := sort (collect (expand (subs ({y=2*y}, Lg) - LSD), x),
[x, y], ascending);
Test2A:= sort (subs ({y=1}, expand (Test2)), [x], ascending);
Test3 := sort (subs ({y=2}, expand (Lg)), [x], ascending);
Test4 := sort (subs ({y=1}, expand (LSD)), [x], ascending);
Test5 := sort (Test3-Test4, [x], ascending);
```

The symbol `rxy` is used to declare the recursive functional equation represented by eq. 57, where the resulting values are stored in a series `r1` as a generating function. The symbol `Lxyg` declares eq. 55. On the other hand, the symbol `sxy` is used to declare the recursive functional equation represented by eq. 59. The resulting values are stored in a series `s1`. The symbol

LSxy3D declares eq. 60.

The `do` loop of the part “Recursive Calculation” calculates recursively the three functional equations `rxy` and `sxy`, where the data stored in `r1` and `s2` for carbon content $k-1$ are used to calculate the data of next step of carbon content k by using the Maple command `coeff`. The resulting coefficients of x^k are stored in `r1` and `s1` recursively. They are used to calculate the other non-recursive functional equations, which are stored stepwise in the series `Lg` (for $\left(\sum_{\ell=0}^{\infty} L_{(g)k\ell}^{(B)} y^{\ell}\right) x^k$, cf. eq. 56) and `LSD` (for $\left(\sum_{\ell=0}^{\infty} L_{k\ell}^{(S)} y^{\ell}\right) x^k$, cf. eq. 61).

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, which are represented in the form of generating functions concerning $x^k y^{\ell}$. By putting $y = 1$, we are able to obtain the total numbers of monosubstituted alkanes (as graphs or steric isomers) of carbon content k .

The term `Test0` is calculated for a test for eq. 58, which is calculated to be equal to zero. The term `Test1` is calculated for a test for eq. 62, which is calculated to be equal to zero. The remaining testing terms `Test2` etc. will be explained below in relevant subjects.

Table 8 lists polynomials of $x^k y^{\ell}$ appearing in the generating function stored in `Lg` (corresponding to eq. 55 and eq. 56), where the coefficient of each term $x^k y^{\ell}$ represents the number of monosubstituted alkanes of carbon content k (as graphs) among which ℓ carbons are asymmetric. The “Total” column of Table 8 collects the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} L_{(g)k\ell}^{(B)}$ for each carbon content k . Although apparent modes of presentation (a polynomial form vs. a tabular form) are different, the data of Table 8 are identical to those reported in a previous paper (Table 5 of Ref. [32]).

Table 9 lists polynomials of $x^k y^{\ell}$ appearing in the generating function stored in `LSD` (corresponding to eq. 60 and eq. 61), where the coefficient of each term $x^k y^{\ell}$ represents the number of steric isomers of monosubstituted alkanes of carbon content k (as 3D structures) among which ℓ carbons are asymmetric. Note that two enantiomers of each pair are counted separately, while each achiral monosubstituted alkane is counted once. The “Total” column of Table 9 collects the total of the coefficients appearing in each row, i.e., $\sum_{\ell=0}^{\infty} L_{k\ell}^{(S)}$ for each carbon content k .

Because the functional equation $L^{(S)}(x, y)$ (eq. 60) is derived by putting $z = y$ in the functional equation $L^{(S)}(x, y, z)$ (eq. 40), the data of Table 9 can be obtained by putting $z = y$ in the data of Table 7. As a matter of course, each value in the “Total” column of Table 9 is equal to the corresponding value appearing in the “Total” column of Table 7.

5 Discussions

5.1 Asymmetric and Pseudoasymmetric Carbons

The recursive functional equation equivalent to eq. 57 has been originally noted by Pólya [14, 7] (eq. 2.22 of [14]), where the symmetric group of degree 3 ($\mathcal{S}^{[3]}$) and the corresponding alternating group ($\mathcal{A}^{[3]}$) were directly used in his derivation. Although Pólya’s formulation has taken asymmetric carbons into consideration, it has not involved the concept of pseudoasymmetric carbons throughout his derivation of eq. 57. This point exhibits a sharp contrast to the present formulation, in which both asymmetric (Types I and III) and pseudoasymmetric carbons (Type V) are initially taken into account and the latter carbons are automatically eliminated during the derivation of eq. 57.

During the recursive process based on eq. 57, internal alkyl ligands are regarded as graphs, whether they are achiral or chiral or whether they are *RS*-stereogenic or *RS*-astereogenic. For

example, the alkyl ligands **1**, **2**, **3**, and $\bar{3}$ (Fig. 1) are so equivalent as to be regarded as a single graph, which is counted just once. The pair of $\bar{1/2}$ is *RS*-stereogenic so as to be in an *RS*-diastereomeric relationship, while the pair of $3/\bar{3}$ is chiral so as to be in an enantiomeric relationship. The relationship between the two pairs ($\bar{1/2}$ vs. $3/\bar{3}$) cannot be specified in the present framework of terminology. However this drawback can be avoided if we demand that the internal alkyls (\bar{p} and \bar{p}) are also regarded as a single object in spite of their opposite chiralities in isolation. Thereby, the alkyl ligands **1**, **2**, **3**, and $\bar{3}$ (Fig. 1) are regarded as a single object.

The discussion in the preceding paragraph is based on the pair of chirality/achirality and the pair of *RS*-stereogenicity/*RS*-astereogenicity. However, the re-examination from another viewpoint is necessary to understand the reduction of 3D structures into graphs. Let us re-examine the graph-reduction condition (eq. 49), which has reduced the set of eqs. 31–35 into another set of eqs. 50–54. In this reduction, Types II, III, and V vanish, as found in the latter set (eqs. 51, 52, and 54). Note that Type II is chiral, *RS*-astereogenic, and scleral; Type III is chiral, *RS*-stereogenic, and scleral; and Type V is achiral, *RS*-stereogenic, and scleral, where the sclerality is common to the three types. On the other hand, Type I is chiral, *RS*-stereogenic, and ascleral and Type IV is achiral, *RS*-astereogenic, and ascleral, where the asclerality is common to the two types. As a result, we have reached an important conclusion: *The common nature to the vanishing Types II, III, and V is being scleral. On the other hand, the common nature to the remaining Types I and IV is being ascleral.*

The ascleral nature of Types I and IV inevitably requires the superposition of enantiomeric relationships onto *RS*-diastereomeric relationships. In particular, the superposition in Type I causes the confusion between enantiomeric relationships (due to chirality) and *RS*-diastereomeric relationships (due to *RS*-stereogenicity). As a result, this confusion has resulted in an erroneous proposition that an asymmetric carbon is the source of chirality. It follows that the term “asymmetric” has been referred to as an out-dated term [34].

However, the term “asymmetric” has been revived in the present approach [32, 33] in order to characterize a carbon atom in Types I and III which exhibits *RS*-stereogenicity (and chirality); and the term “pseudosymmetric” is employed to characterize a carbon atom in Type V which also exhibits *RS*-stereogenicity (and achirality). Note that Type III does not exhibit the superposition of enantiomeric relationships onto *RS*-diastereomeric relationships.

5.2 On Pólya’s “Spezielle Fragen”

Section 60 of Pólya’s famous article ([14]: an English translation [7]) has described two special questions on the enumeration of monosubstituted alkanes (or aliphatic alcohols). These questions will be revisited here by means of the present data.

On the Pólya’s First Question: Determination of the Lowest $C_kH_{2k+1}OH$ with a Given Number of Asymmetric C-Atoms Pólya’s conclusion on this question is as follows: *An alcohol $C_kH_{2k+1}OH$ containing ℓ asymmetric C-atoms must have at least $2\ell + 2$ carbon atoms. If the number of C-atoms is $k = 2\ell + 2$, there exist exactly one structure $C_kH_{2k+1}OH$ with ℓ asymmetric C-atoms.* as found in Section 60 of Ref. [14]. This conclusion can be understood more concretely by using the present data.

Let us start monosubstituted alkanes of carbon content 4, one of which (**4**) is the lowest example having one asymmetric carbon ($\ell = 1$), as shown in Fig. 2. The monosubstituted alkane **4** and its enantiomer ($\bar{4}$) construct a single graph (one structure) which satisfies $4 = 2 \times 1 + 2$ as

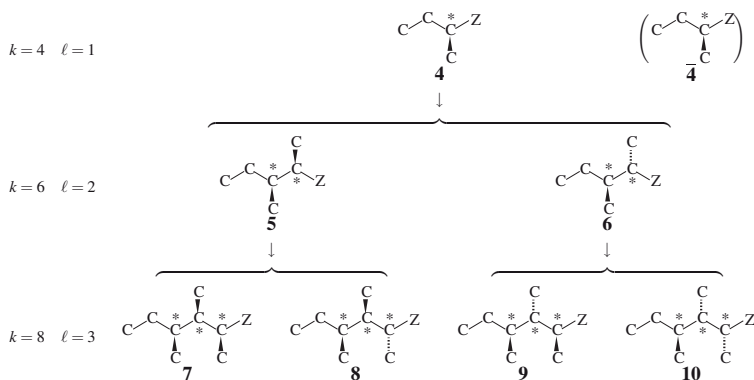


Figure 2: On determination of the lowest $C_k H_{2k+1} - Z$ with a given number of asymmetric C-atoms. When the number ℓ of asymmetric carbons is given, the monosubstituted alkane of the carbon content k (even) satisfies the relationship $k = 2\ell + 2$.

the lowest case of the condition $k = 2\ell + 2$. The monosubstituted alkane **4** (or its enantiomer $\bar{4}$) is regarded as an alkyl ligand (p) so as to be incident to one carbon unit as a next principal node, i.e., $p-CH_2-Z$, where p represents a 1-methylpropyl ligand derived from **4**. This step can be regarded as the insertion of a methylene unit ($-CH_2-$), which causes the increase of carbon content by one but no increase of the number of asymmetric carbons. Thus, this step provides a monosubstituted alkane of carbon content 5 without increase of asymmetric carbons ($\ell = 1$). Hence, the condition $k > 2\ell + 2$ is satisfied (i.e., $5 > 2 \times 1 + 2$).

The monosubstituted alkane **4** as an alkyl ligand (p) and a methyl ligand are incident to one carbon unit (i.e., $p-CH(CH_3)-Z$) so as to generate a monosubstituted alkane of carbon content 6 with increase of one asymmetric carbon (i.e., $\ell = 2$). This step can be regarded as the insertion of a methylmethine unit ($-CH(CH_3)-$), which causes the increase of carbon content by two as well as the increase of the number of asymmetric carbons by one. The resulting monosubstituted alkanes (**5**, **6**, and their enantiomers) correspond to a single graph (one structure) which satisfies $6 = 2 \times 2 + 2$ as the second case of the condition $k = 2\ell + 2$.

Suppose that a monosubstituted alkane $p-Z$ of carbon content k has ℓ asymmetric carbons and satisfies $k = 2\ell + 2$. Then, an induced monosubstituted alkane $p-CH_2-Z$ of carbon content of $k + 1$ exhibits no increase of asymmetric carbons so as to satisfy $k + 1 > 2\ell + 2$. On the other hand, the next induced monosubstituted alkane $p-CH(CH_3)-Z$ of carbon content of $k + 2$ has one additional asymmetric carbon (i.e., totally $\ell + 1$ asymmetric carbons). Because of $k = 2\ell + 2$, we are able to obtain the relationship $k + 2 = 2(\ell + 1) + 2$, which is a relationship to be proven for this mathematical induction. Note that the increase of the unit $-CH(CH_3)-Z$ gives stereoisomers which are regarded as a single graph (structure).

A merit of the present proof based on mathematical induction is to provide chemical meanings more clearly than Pólya's proof (Section 60 of Ref. [14, 7]). The recursiveness of the relationship $k = 2\ell + 2$ can be confirmed by the inspection of Table 8, where each term $x^k y^{(k/2)-1}$ (i.e., $\ell = (k/2) - 1$) in the row of even k has the highest power of y and its coefficient is equal to one.

The above discussion on graphs can be compared with the data of 3D structure. Table 6 is concerned with the numbers of chiral plus achiral monosubstituted alkanes as 3D structures, where each pair of enantiomers is counted once, just as each achiral monosubstituted alkane is counted once. This means that the presence of ℓ asymmetric carbons corresponds to $2^{\ell-1}$ enantiomeric pairs. Hence, each term $x^k y^{(k/2)-1}$ (i.e., $\ell = (k/2) - 1$) in the row of even k has the coefficient $2^{\ell-1}$, e.g., $x^4 y$, $2x^6 y^2$, $4x^8 y^3$, ..., $256x^{20} y^9$, ... as found in Table 6. Note that the $2^{\ell-1}$ pairs of enantiomers are reduced into a single graph (structure), where lower examples are depicted in Fig. 2.

On the other hand, each term $x^k y^{(k/2)-1}$ (i.e., $\ell = (k/2) - 1$) appearing in the k -row of Table 7 (k : even) has the coefficient 2^ℓ , e.g., $2x^4 y$, $4x^6 y^2$, $8x^8 y^3$, ..., $512x^{20} y^9$, ..., because two enantiomers of each pair are counted separately in Table 7. The 2^ℓ stereoisomers are reduced into a single graph (structure).

The results of the term $x^k y^{(k/2)-1}$ of Table 7 (described in the preceding paragraph) are essentially equivalent to those collected in Table 9, where the latter table takes only asymmetric carbons into consideration. Thus, the effect of pseudoasymmetric carbons considered in Table 7 does not emerge in solving this special question of Pólya.

From the present viewpoint, the first case of this series, i.e., **4**, is a Type-I monosubstituted alkane, while the other cases (e.g., **5**, etc.) belong to Type III. Hence, the term $2yx^4$ collected in Table 1 (Type I) shows the existence of two enantiomers (**4** and $\bar{\mathbf{4}}$) of a pair. On the other hand, the term $x^k y^{(k/2)-1}$ of Table 3 (Type III, $k \geq 6$: even) has the coefficient $2^{(k/2)-1}$ so as to show the existence of $2^{(k/2)-1}$ stereoisomers, which are reduced into a single graph.

On the Pólya's 2nd Question: Determination of the Lowest $C_k H_{2k+1} OH$ in Which the Asymmetries Compensate Each Other Pólya's conclusion on this question is that *compensation of asymmetries occurs in monosubstituted alkanes of carbon contents equal to or larger than 13*. Because of the enhanced capacity of computers as well as of the development of versatile software (e.g., the Maple system), Pólya's analytical treatment of this question can be replaced by a more concrete procedure.

The number ℓ of asymmetric carbons generate 2^ℓ stereoisomers except that such asymmetries compensate each other. Hence, we are able to evaluate full entries without considering such exceptional cases by calculating $L_g^{(B)}(x, 2)$, where we put $y = 2$ in the series eq. 56, which has been calculated by eq. 55 and collected in Table 8. In the program "GraphAlkyl-2.mpl", the term `Test3` is used to calculate $L_g^{(B)}(x, 2)$ as follows:

$$\begin{aligned} L_g^{(B)}(x, 2) = & x + x^2 + 2x^3 + 5x^4 + 11x^5 + 28x^6 + 74x^7 + 199x^8 + 551x^9 \\ & + 1553x^{10} + 4436x^{11} + 12832x^{12} + 37500x^{13} + 110504x^{14} \\ & + 328104x^{15} + 980535x^{16} + 2946993x^{17} + 8902203x^{18} \\ & + 27013286x^{19} + 82303167x^{20} + \dots \end{aligned} \quad (63)$$

On the other hand, eq. 61 (calculated by eq. 60) has already taken account of the effect of asymmetric carbons on isomer numbers so that we put $y = 1$ in the series (eq. 61) to evaluate steric isomers. In the program "GraphAlkyl-2.mpl", the term `Test4` is used to calculate $L^{(S)}(x, 1)$ as follows. By putting $y = z = 1$ in eq. 41 (derived from eq. 40), the resulting $L^{(S)}(x, 1, 1)$ give a series identical with $L^{(S)}(x, 1)$.

$$L^{(\overline{S})}(x, 1) = L^{(S)}(x, 1, 1) \quad (64)$$

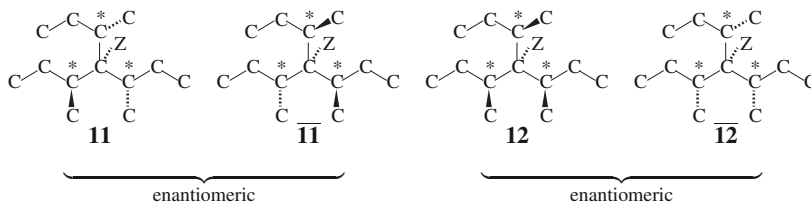


Figure 3: The lowest $C_kH_{2k+1}Z$ ($k = 13$) in which the asymmetries compensate each other, as noted by Pólya [14, 7]. Three asymmetric carbon atoms (*) generate four 3D structures in spite of the general expression $2^3 = 8$. The four 3D structures coalesce to give a single graph (structure).

$$\begin{aligned}
 &= x + x^2 + 2x^3 + 5x^4 + 11x^5 + 28x^6 + 74x^7 + 199x^8 + 551x^9 \\
 &\quad + 1553x^{10} + 4436x^{11} + 12832x^{12} + 37496x^{13} + 110500x^{14} \\
 &\quad + 328092x^{15} + 980491x^{16} + 2946889x^{17} + 8901891x^{18} \\
 &\quad + 27012286x^{19} + 82300275x^{20} + \dots
 \end{aligned} \tag{65}$$

Obviously, the coefficients appearing in eq. 65 have already collected in the “Total” column of Table 9.

The above-mentioned Pólya’s conclusion can be derived by comparing between eq. 63 and eq. 65. The term `Test5` in the program “GraphAlkyl-2.mpl” is used to calculate the difference between them:

$$L_g^{(B)}(x, 2) - L^{(S)}(x, 1) = L_g^{(B)}(x, 2) - L^{(S)}(x, 1, 1) \tag{66}$$

$$\begin{aligned}
 &= 4x^{13} + 4x^{14} + 12x^{15} + 44x^{16} \\
 &\quad + 104x^{17} + 312x^{18} + 1000x^{19} + 2892x^{20} + \dots
 \end{aligned} \tag{67}$$

As a result, if we follow the Pólya’s discussion, we may conclude that the lowest case of the 2nd question corresponds to the term $4x^{13}$. Four structures corresponding to the coefficient 4 have been noted by Pólya [14, 7], as depicted in Fig. 3. Because of the presence of three asymmetric carbon atoms (*), the general formula $2^3 = 8$ would indicate the existence of 8 possibilities. However, there exist only four stereoisomers (3D structures) ($11/\bar{11}$ and $12/\bar{12}$), which coalesce to give a single graph (structure).

5.3 Systematic Comparison Between Graphs and 3D Structures

The above-mentioned discussion on the Pólya’s 2nd question has not taken account of pseudoasymmetries. The present section is devoted to clarify the effect of such pseudoasymmetries which has been disregarded in the above-mentioned discussion. Thereby, we are able to show that the term $4x^{13}$ in eq. 67 implies more complicated situations than those illustrated in Fig. 3.

5.3.1 Two Viewpoints to Characterize Stereoisomerism

The methodology based on the function $L_g^{(B)}(x, 2)$ is essentially equivalent to the discussion described by Pólya (Section 60 of Ref. [14, 7]). We here refer to the methodology as the viewpoint

of “graphs with asymmetries”. This section is devoted to emphasize the present methodology, i.e., the viewpoint of “3D structures with asymmetries and pseudoasymmetries”.

In place of the function $L_g^{(B)}(x, 2)$ for deriving eq. 63, let us calculate $L_g^{(B)}(x, 2y)$ by the replacement of y by $2y$ in the series eq. 56 (derived from eq. 55). Then, we obtain the coefficient $2^\ell L_{(g)k\ell}^{(B)}$ of the term $y^\ell x^k$ in place of the coefficient $L_{(g)k\ell}^{(B)}$ appearing in the series $L_g^{(B)}(x, y)$ (cf. eq. 56 and eq. 55). The factor 2^ℓ represents the possible maximum number of stereoisomers which stem from ℓ asymmetric carbons. On the other hand, let us consider $L^{(S)}(x, y, z)$ (eq. 38 derived from eq. 37) in place of $L^{(S)}(x, 1, 1)$ ($= L^{(S)}(x, 1)$). Their difference is calculated to give the following equation:

$$\begin{aligned} & L_g^{(B)}(x, 2y) - L^{(S)}(x, y, z) \\ &= (2 - 2z)y^2x^9 + (4 - 4z)y^2x^{10} + ((12 - 12z)y^2 + (4 - 4z)y^3)x^{11} \\ &\quad + ((24 - 24z)y^2 + (16 - 16z)y^3)x^{12} \\ &\quad + ((56 - 56z)y^2 + (64 - 60z)y^3 + (20 - 12z)y^4 - 8y^5)x^{13} \\ &\quad + ((108 - 108z)y^2 + (196 - 180z)y^3 + (68 - 64z)y^4 - 16y^5)x^{14} \\ &\quad + ((226 - 226z)y^2 + (568 - 508z)y^3 + (336 - 312z)y^4 \\ &\quad \quad + (-32 - 24z)y^5 - 16y^6)x^{15} + \dots \end{aligned} \quad (68)$$

Because eq. 68 can be converted into eq. 67 by introducing $y = z = 1$, these two equations (eqs. 67 and 68) differently interpret the same set of monosubstituted alkanes. In contrast to the result that eq. 67 contains the terms of $k \geq 13$, the difference represented by eq. 68 takes account of pseudoasymmetries by means of the variable z , so that it involves the terms of $k \geq 9$. The correspondence between eqs. 67 and 68 are more concretely shown by introducing $z = 1$ into eq. 68. Thereby, we obtain the following result:

$$\begin{aligned} & L_g^{(B)}(x, 2y) - L^{(S)}(x, y, 1) \\ &= (4y^3 + 8y^4 - 8y^5)x^{13} + (16y^3 + 4y^4 - 16y^5)x^{14} \\ &\quad + (60y^3 + 24y^4 - 56y^5 - 16y^6)x^{15} + \dots \end{aligned} \quad (69)$$

where all of the terms of $k < 13$ disappear and the other terms ($k \geq 13$) are left.

Obviously, eq. 67 is alternatively derived by introducing $y = 1$ into eq. 69. Although eq. 69 and eq. 67 commonly retain the terms of $k \geq 13$, they are different in their contents. For example, the difference between $(4y^3 + 8y^4 - 8y^5)x^{13}$ (eq. 69) and $4x^{13}$ (eq. 67) indicates that chemical meanings of the term $(8y^4 - 8y^5)x^{13}$ should be carefully examined because $8y^4$ and $8y^5$ contain different numbers of asymmetric carbons. This and related subjects will be the target of the following subsections.

5.3.2 Pseudoasymmetries During Processes of Converting Graphs into 3D Structures

The term $(2 - 2z)y^2x^9$ left in eq. 68 comes from four monosubstituted alkanes shown in Fig. 4: two enantiomers (**13**/**13**), an achiral compound (**14**), and another achiral compound (**15**), where the latter two achiral compounds (**14** and **15**) exhibit pseudoasymmetries (\dagger). If they are treated according to Pólya by starting from graphs with asymmetries [14, 7], they are characterized by

the term $4x^9y^2$, which does not contain the variable z for evaluating pseudoasymmetries. If they are treated according to the present approach by starting from 3D structures with asymmetries and pseudoasymmetries, the two enantiomers (**13/13**) are characterized by $2x^9y^2$, while **14** and **15** are characterized by $2x^9y^2z$. The difference between such graphs and such 3D structures is calculated to be $4x^9y^2 - (2x^9y^2 + 2x^9y^2z) = (2 - 2z)y^2x^9$, which appears in eq. 68. Note that the term $(2 - 2z)y^2x^9$ vanishes to zero, if we put $z = 1$, which corresponds to the disregard of pseudoasymmetries.

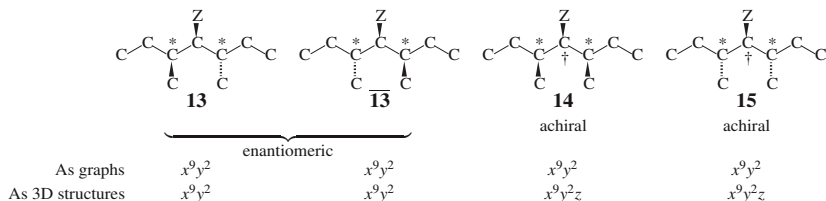


Figure 4: Monosubstituted alkanes of carbon content 9 which are related pseudoasymmetry. They are detected by the term $(2 - 2z)y^2x^9$ appearing in eq. 68. The symbol * represents an asymmetric carbon, while the symbol † represents a pseudoasymmetric carbon.

According to a stereochemical convention, the power 2 of y^2 in the term x^9y^2 implies the maximum number of stereoisomers ($2^2 = 4$), where the convention presumes the appearance of two enantiomeric pairs, each of which contains two stereoisomers of opposite configurations. Pólya's viewpoint of "graphs with asymmetries" for interpreting the four stereoisomers of Fig. 4 seemingly relies on this conventional presumption, because the term x^9y^2 disappears in eq. 67. The disappearance would claim no compensation of asymmetries at carbon content 9 so that the expression "compensation of asymmetries for $k \geq 13$ " in Pólya's conclusion on his 2nd question seemingly holds true on the basis of the conventional presumption. Strictly speaking, however, such compensation of asymmetries occurs even at carbon content 9. We tend to overlook this fact, if we forget essential aspects provided by the viewpoint of "graphs with asymmetries". These aspects will be demonstrated more clearly in the next paragraphs.

Let us consider a graph with two asymmetries (**16**) as a starting species, where its carbon skeleton, a Z-substituent, bonds shown by a straight line, and omitted hydrogen atoms are laid on a plane, as shown in Fig. 5.

1. First, one of the asymmetric carbons ($\textcircled{*}$) in the species **16** is made active so as to be drawn as a wedged bond (β bond) and a broken-lined bond (α bond). This procedure causes the appearance of two species **17** and **18**, which are different from each other.
2. Next, the other asymmetric carbon ($\textcircled{*}$) of the resulting species **17** or **18** is activated so as to be drawn as a wedged bond (β bond) and a broken-lined bond (α bond). Thereby, the species **17** produces **19** and **20**, while the other species **18** produces **20'** and **21**.
3. Note that the species **20** derived from **17** is identical to the species **20'** derived from **18**, although the latter emerges reversely. Thus, there emerge the three species **19**, **20** (= **20'**), and **21**, as shown in the upper part of Fig. 5 bisected by a double horizontal line.
4. In contrast, the discussion based on eq. 67 (in particular, $y = 2$ for $L_g^{(B)}(x, 2)$) seems to postulate four species, where **20** (\leftarrow **17**) is implicitly differentiated from **20'** (\leftarrow **18**).

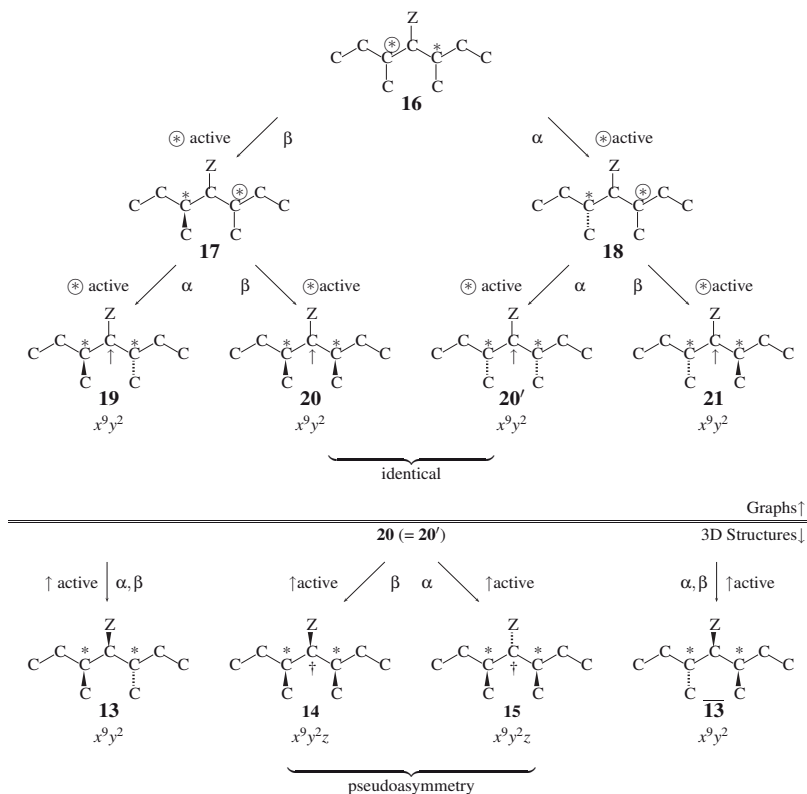


Figure 5: Stepwise conversions of a graph with two asymmetries into 3D structures (stereoisomers).

That is to say, compensation of asymmetries occurs even at carbon content 9, so long as we rely on the viewpoint of “graphs with asymmetries”.

These steps indicate concealed aspects on what happens in the derivation of $L_g^{(B)}(x, 2)$ (eq. 63) or in the derivation of $L_g^{(B)}(x, 2y)$ (cf. eq. 68). We can safely say that the misleading postulation of the four species (19, 20, 20', and 21) in place of the three species (19, 20 (= 20'), and 21) would be hidden in the expression “compensation of asymmetries for $k \geq 13$ ” in Pólya’s conclusion on his 2nd question.

Furthermore, the presence of the four species (19, 20, 20', and 21) is unconsciously confused with the presence of four 3D structure (13, 13-bar, 14, and 15).

1. In order to convert the three species 19, 20 (= 20'), and 21 into the four 3D structure (13, 13-bar, 14, and 15), we should activate each carbon denoted by the symbol (\uparrow), as shown in the bottom part of Fig. 5 bisected by a double horizontal line. Thereby, the species 19 (or 21) generates a single 3D structure 13 (or 13-bar), while the species 20 (= 20') generates

two 3D structures **14** and **15**. Obviously, the last step from graphs to 3D structures is concerned with pseudoasymmetries correlated to the variable z .

2. If we do not take account of pseudoasymmetries, the accidental value 4 due to the set of **19**, **20**, **20'** (differentiated from **20**), and **21** is equalized to the isomer number 4 due to the set of **13**, **13**, **14**, and **15**. This equalization causes the disappearance of the term x^9y^2 (also the terms up to carbon content 12) in eq. 67 so as to provide the conclusion on Pólya's 2nd question, i.e., "compensation of asymmetries for $k \geq 13$ ".
3. If we take account pseudoasymmetries by means of the variable z on the other hand, the last step shown in Fig. 5 can be properly treated. This situation is what happens in the derivation of $L^{(S)}(x, 1)$ (eq. 65) or in the derivation of $L^{(S)}(x, y, z)$ (cf. eq. 68). Thus, the present viewpoint of "3D structures with asymmetries and pseudoasymmetries" lefts the term $(2 - 2z)y^2x^9$ in eq. 68.

Thereby, the effect of pseudoasymmetries has been properly evaluated so that Fig. 4 shows the appearance of two enantiomers (**13**/**13**), an achiral compound (**14**), and another achiral compound (**15**). These four stereoisomers coalesce into a single graph, which is regarded as a constitutional (structural) isomer from a stereochemical point of view. It should be emphasized that the different results (eq. 67 vs. eq. 68) have been obtained depending on whether or not the variable z is taken into consideration.

5.3.3 Further Examples of Carbon Contents 10–12

The term $(4 - 4z)y^2x^{10}$ appearing in eq. 68 can be converted into $2 \times (2 - 2z)y^2x^{10}$, which means the appearance of two cases similar to the term $(2 - 2z)y^2x^9$ described above. Hence, the term $(4 - 4z)y^2x^{10}$ corresponds to two sets of stereoisomers shown in Fig. 6: [**22**/**22**, **23**, **24**] and [**25**/**25**, **26**, **27**], each of which corresponds to a single graph, which is regarded as a constitutional (structural) isomer from a stereochemical point of view.

On a similar line, the term $(12 - 12z)y^2x^{11}$ appearing in eq. 68 can be converted into $6 \times (2 - 2z)y^2x^{10}$. As a result, we find that there appear six cases similar to the term $(2 - 2z)y^2x^9$ described above. On the other hand, the term $(4 - 4z)y^3x^{11}$ appearing in eq. 68 corresponds to the appearance of four pairs of enantiomers shown in Fig. 7, where the eight stereoisomers of the four enantiomeric pairs coalesce into a single graph (structure). They are characterized by the term $8x^{11}y^3$ from the viewpoint of "graphs with asymmetries". In contrast, from the present viewpoint of "3D structures with asymmetries and pseudoasymmetries", **28**/**28** and **29**/**29** are characterized by the term $4x^{11}y^3$, while **30**/**30** and **31**/**31** are characterized by the term $4x^{11}y^3z$. Hence, the difference between the two viewpoints is calculated to be $8x^{11}y^3 - (4x^{11}y^3 + 4x^{11}y^3z) = (4 - 4z)y^3x^{11}$.

As for the cases of carbon content 12, the term $(24 - 24z)y^2x^{12}$ of eq. 68 is factorized into $12 \times (2 - 2y)y^2x^{12}$ so that there exist twelve sets of four stereoisomers, where each of the sets is similar to the case of Fig. 4. The other term $(16 - 16z)y^3x^{12}$ for carbon content 12 in eq. 68 is factorized into $3 \times (4 - 4y)y^3x^{12}$ so that there exist three sets of eight stereoisomers, where each of the sets is akin to the case of Fig. 7.

5.3.4 Scrutinizing Cases of Carbon Contents 13

On the same line, the term $(56 - 56z)y^2x^{13}$ for carbon content 13 in eq. 68 is factorized into $28 \times (2 - 2y)y^2x^{13}$ so that there exist 28 sets of four stereoisomers, where each of the sets is

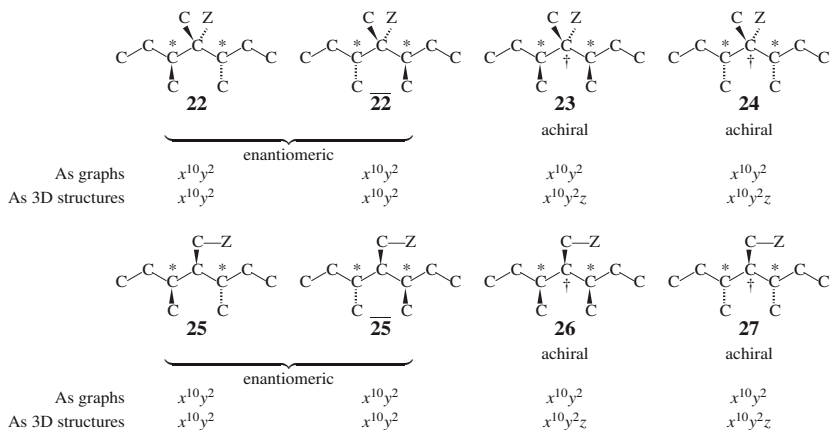


Figure 6: Monosubstituted alkanes of carbon content 10 which are related pseudoasymmetry. They are detected by the term $(4 - 4z)y^2x^{10}$ appearing in eq. 68. The symbol * represents an asymmetric carbon, while the symbol † represents a pseudoasymmetric carbon.

similar to the case of Fig. 4.

On the other hand, the term $(64 - 60z)y^3x^{13}$ of eq. 68 is factorized into two parts, i.e., $(4 + 15 \times (4 - 4z))y^3x^{13}$, where the term $15 \times (4 - 4z)y^3x^{13}$ can be interpreted by considering 15 sets of eight stereoisomers (cf. Fig. 7). The remaining term $4x^{13}y^3$ corresponds to the four stereoisomers shown in Fig. 3, where there appear no terms containing the variable z even from the viewpoint of “3D structures with asymmetries and pseudoasymmetries” (cf. eq. 68). As a matter of course, this case indicates the term $4x^{13}$ in eq. 67 from the viewpoint of “graphs with asymmetries”, because the term is obtained by introducing $y = 1$ into $4x^{13}y^3$.

The stepwise conversion corresponding to the term $4x^{13}y^3$ can be depicted in Fig. 8, which corresponds to the step just above the double horizontal lines of Fig. 5. Among eight possible species shown in Fig. 8, the species **32**, **32'**, and **32''** are identical with one another. Similarly, the species **33**, **33'**, and **33''** are identical with one another. As a result, there exist four species, i.e., **32**, **33**, **34**, and **35**. Thus, compensation of asymmetries occurs so as to give the decrease of 4 ($= 8 - 4$) from the viewpoint of “graphs with asymmetries”.

The four species (**32**, **33**, **34**, and **35**) are converted respectively into **12**, **12-bar**, **11-bar**, and **11** when the configuration of a Z-substituent is activated. This activation is not concerned with the variable z so that the four species generate the four stereoisomers. Hence, the decrease of 4 is also found from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”.

The remaining terms for carbon content 13, i.e., $((20 - 12z)y^4 - 8y^5)x^{13}$ exhibit a more complicated situation to be examined carefully. By scrutinizing the entangled situation, we find that the terms should be rearranged as follows:

$$\left((20 - 12z)y^4 - 8y^5 \right) x^{13} = (8 - 8z)y^4x^{13} + (4 - 4z)y^4x^{13} + (8y^4 - 8y^5)x^{13}. \quad (70)$$

The resulting term $(8 - 8z)y^4x^{13}$ corresponds to 16 stereoisomers listed in Fig. 9. Let us examine these stereoisomers by paying attention to an *S*-1-methylpropyl ligand and an *R*-1-

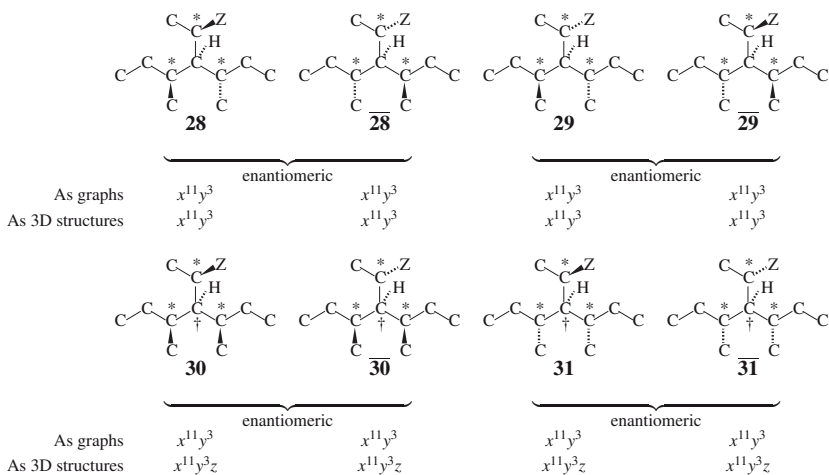


Figure 7: Monosubstituted alkanes of carbon content 11 corresponding to the term $(4-4z)y^3x^{11}$ of eq. 68. Each stereoisomer in the bottom row has an achiral ligand which exhibits inner pseudoasymmetry (\dagger). The symbol * represents an asymmetric carbon.

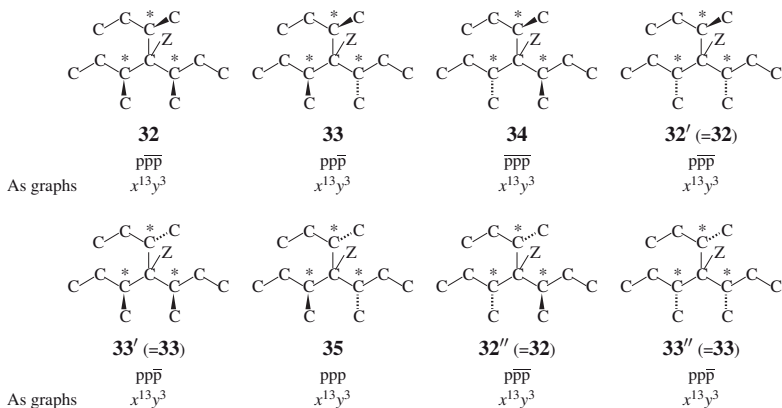


Figure 8: Possible species for monosubstituted alkanes of carbon content 13, which are derived from a graph with three asymmetric carbons (*). Note that the configuration of a Z-substituent is not specified at this step (cf. Fig. 5). The four species (**32**, **33**, **34**, and **35**) are left to be effective.

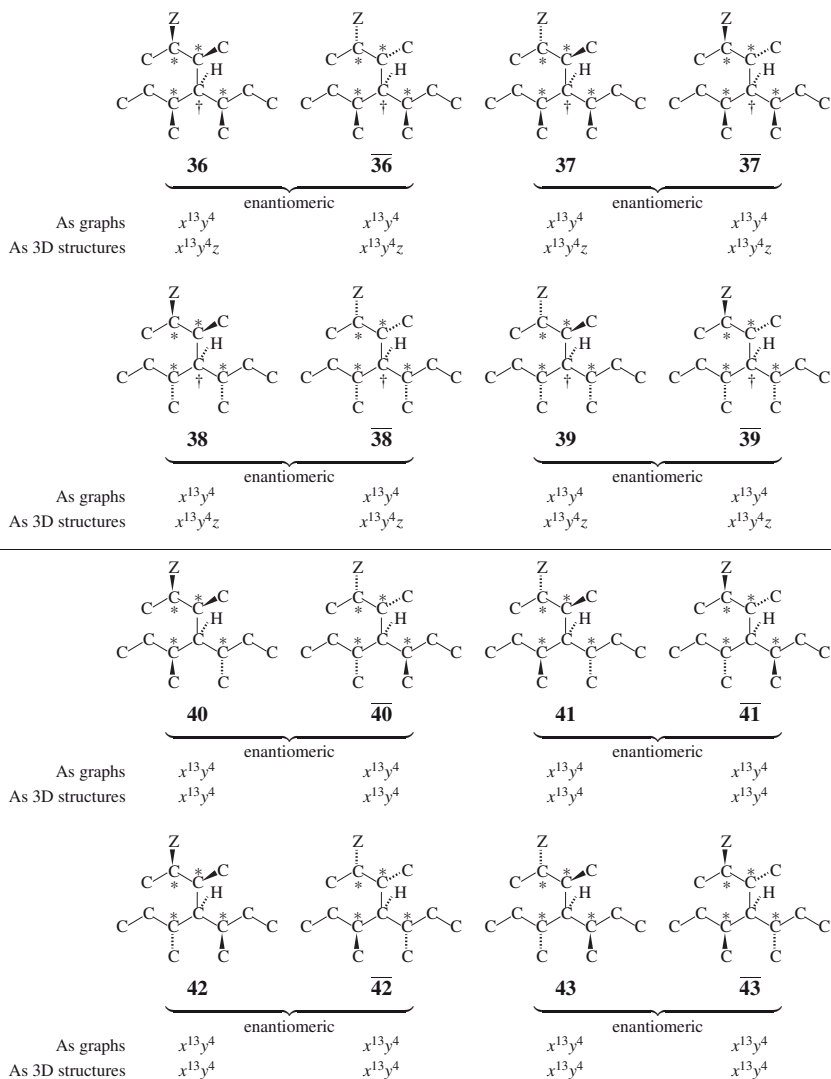


Figure 9: Monosubstituted alkanes of carbon content 13 corresponding to the term $(8 - 8z)y^4x^{13}$ of eq. 68, where these stereoisomers coalesce into a single graph. Each stereoisomer in the first and second rows has an achiral ligand which exhibits inner pseudoasymmetry (†). The symbol * represents an asymmetric carbon.

methylpropyl ligand, which are represented by p and \bar{p} respectively, where we tentatively postulate a priority sequence: a valence bond $> C_2H_5 > CH_3 > H$. Then, the internal alkyl ligand in **36**, **36** **37**, or **37** is represented by the formula $-CHp\bar{p}$, while the internal alkyl ligand in **38**, **38** **39**, or **39** is represented by the formula $-CH\bar{p}p$. Both the alkyl ligands $-CHp\bar{p}$ and $-CH\bar{p}p$ are achiral and contain a pseudoasymmetric carbon (\dagger) at this step of the recursive construction of the relevant monosubstituted alkanes. Hence, the eight molecules **36/36**, **37/37**, **38/38**, and **39/39** are characterized by the monomial $x^{13}y^4$ from the viewpoint of “graphs with asymmetries” and by the monomial $x^{13}y^4z$ from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”.

On the other hand, the internal alkyl ligand in **40**, **41**, **42**, or **43** is represented by the formula $-CHpp$, while the internal alkyl ligand in **40**, **41**, **42**, or **43** is represented by the formula $-CH\bar{p}\bar{p}$. Each central atom of the alkyl ligands $-CHpp$ and $-CH\bar{p}\bar{p}$ is specified not to be an asymmetric carbon nor a pseudoasymmetric carbon at this step of the recursive construction of the relevant monosubstituted alkanes. Hence, the eight molecules **40/40**, **41/41**, **42/42**, and **43/43** are characterized by the monomial $x^{13}y^4$ from the viewpoint of “graphs with asymmetries” as well as from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”.

It follows that 16 stereoisomers in Fig. 9 are characterized by $16x^{13}y^4$ (as graphs) and $8x^{13}y^4z + 8x^{13}y^4$ (as 3D structures) so that the difference between these terms is calculated to be $16x^{13}y^4 - (8x^{13}y^4z + 8x^{13}y^4) = (8 - 8z)y^4x^{13}$, which is identical to the corresponding term in eq. 70.

The term $(4 - 4z)y^4x^{13}$ appearing in eq. 70 corresponds to 8 stereoisomers listed in Fig. 10, where the first row involves one set of **44/44** (an enantiomeric pair), **45** (an achiral compound), and **46** (an achiral compound); and the second row involves another set of **47/47** (an enantiomeric pair), **48** (an achiral compound), and **49** (an achiral compound). 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 represented schematically as follows:

(the first row)

44 ($P-CHZ-P$), **44** ($\bar{P}-CHZ-\bar{P}$), **45** ($P-CHZ-\bar{P}$), and **46** ($\bar{P}-CHZ-P$);

and (the second row)

47 ($Q-CHZ-Q$), **47** ($\bar{Q}-CHZ-\bar{Q}$), **48** ($Q-CHZ-\bar{Q}$), and **49** ($\bar{Q}-CHZ-Q$).

The two achiral compounds contained in each row exhibit pseudoasymmetric nature so as to be characterized by the term $x^{13}y^4z$ from the viewpoint of “3D structures with asymmetries and pseudoasymmetries”. It follows that 8 stereoisomers in Fig. 10 are characterized by $8x^{13}y^4$ (as graphs) and $4x^{13}y^4 + 4x^{13}y^4z$ (as 3D structures). The difference between these terms is calculated to be $8x^{13}y^4 - (4x^{13}y^4 + 4x^{13}y^4z) = (4 - 4z)y^4x^{13}$, which is identical to the corresponding term in eq. 70.

The term $(8y^4 - 8y^5)x^{13}$ appearing in eq. 70 clearly shows the difference between graphs and 3D structures. The corresponding 8 stereoisomers are listed in Fig. 11. By using the symbols P/\bar{P} and Q/\bar{Q} , the eight isomers are represented schematically as follows:

(the first row)

50 ($P-CHZ-Q$), **50** ($\bar{Q}-CHZ-\bar{P}$), **51** ($\bar{P}-CHZ-\bar{Q}$), and **51** ($Q-CHZ-P$);

and (the second row)

52 ($\bar{P}-CHZ-Q$), **52** ($\bar{Q}-CHZ-P$), **53** ($P-CHZ-\bar{Q}$), and **53** ($Q-CHZ-\bar{P}$).

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

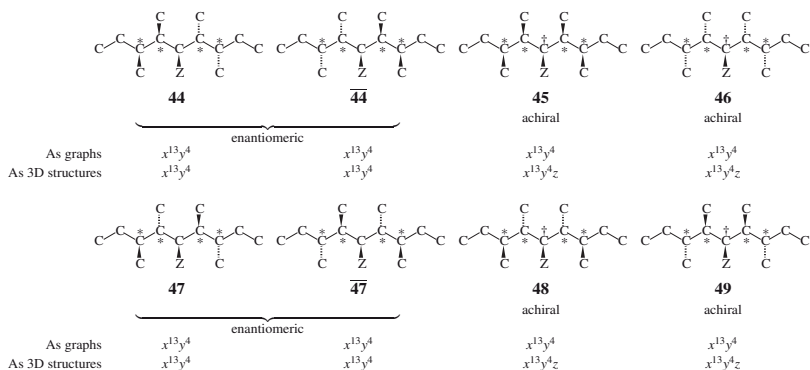


Figure 10: Monosubstituted alkanes of carbon content 13 corresponding to the term $(4 - 4z)y^4x^{13}$ of eq. 68, where these stereoisomers coalesce into a single graph.

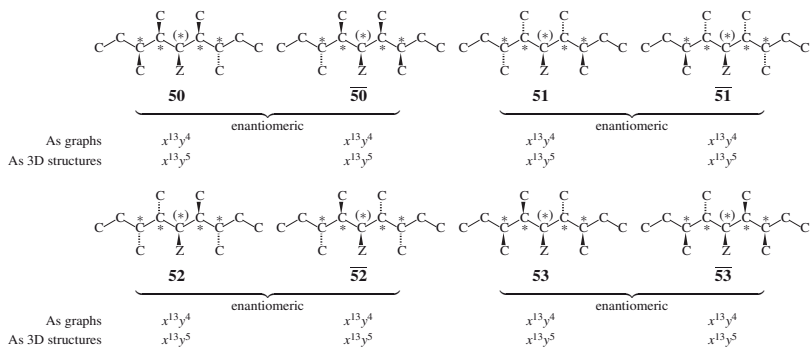


Figure 11: Monosubstituted alkanes of carbon content 13 corresponding to the term $(8y^4 - 8y^5)x^{13}$ of eq. 68, where these stereoisomers (in addition to those listed in Fig. 10) coalesce into a single graph. The symbol * represents an asymmetric carbon except that an asterisk in a pair of parentheses represents an asymmetric carbon as a 3D structure but causes no specification as a graph.

by the term $8x^{13}y^4$ 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 $8x^{13}y^5$. The difference between these terms is calculated to be $(8y^4 - 8y^5)x^{13}$, which is identical to the corresponding term in eq. 70. This term has also appeared in eq. 69.

As a result, there exist totally 16 stereoisomers, as shown in Figs. 10 and 11, where possible terms corresponding to these stereoisomers disappear and only the term $4x^{13}$ (for Figs. 3 and 8) is conserved in eq. 67. Because of four asymmetric carbons, the existence of 16 stereoisomers (Figs. 10 and 11) is seemingly in agreement with the stereochemical convention that ℓ

asymmetric carbons bring about 2^ℓ stereoisomers. It should be noted, however, that we should take account of more complicated situations, as found in the careful examination of the terms $(4 - 4z)y^4x^{13} + (8y^4 - 8y^5)x^{13}$ (appearing in eq. 70). If we put $z = 1$ and if one of five y 's is equal to 1, the terms totally vanish to zero so that we can claim the stereochemical convention that ℓ asymmetric carbons bring about 2^ℓ stereoisomers.

6 Conclusion

Monosubstituted alkanes (or alkyl ligands) are classified into five types by means of stereoisograms [35–39], where Types I, II, and III are chiral while Type IV and V are achiral; Types I, III, and V are *RS*-stereogenic while Type II and IV are *RS*-astereogenic; as well as Types II, III, and V are scleral while Type I and IV are ascleral. They are characterized by cycle indices with chirality fittingness (CI-CFs), which are composed of sphericity indices a_d , b_d , and c_d . The sphericity indices are substituted by the functions $a(x^d, y^d, z^d)$, $b(x^d, y^d, z^d)$, and $c(x^d, y^d, z^d)$, where the variable x is used to show carbon contents, y to show the numbers of asymmetric carbons, and z to show the numbers of pseudoasymmetric carbons. Thereby, functional equations for 3D structures are derived to characterize Types I–V. Such a graph-reduction condition as $a_d = b_d = c_d$ or $a(x^d, y^d, z^d) = b(x^d, y^d, z^d) = c(x^d, y^d, z^d)$ is discussed in order to reduce the functional equations for 3D structures into those for graphs. During the reduction, functional equations of Type II, III, and V are found to vanish. The remaining functional equations of Types I and IV are used to derive the functional equations for graphs. The viewpoint of “3D structures with asymmetries and pseudoasymmetries” based on the functional equations for 3D structures are compared with the viewpoint of “graphs with asymmetries” based on the functional equations for graphs. In particular, Pólya’s special questions described in Section 60 of Pólya’s famous report [14, 7] are discussed critically by comparing the two viewpoints. A stereochemical convention that the number of stereoisomers with ℓ asymmetric carbons is equal to 2^ℓ is also examined by comparing the two viewpoints.

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