Numbers of Asymmetric and Pseudoasymmetric Centers in Enumeration of Achiral and Chiral Alkanes of Given Carbon Contents

Shinsaku Fujita
Shonan Institute of Chemoinformatics and Mathematical Chemistry,
Kaneko 479-7 Ooimachi, Ashigara-Kami-Gun, Kanagawa-Ken, 258-0019 Japan
E-mail: fujitas@chem.kit.ac.jp
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Abstract

Asymmetric and pseudoasymmetric centers in alkanes (as tree-dimensional trees of degree 4) have been specified by means of newly-defined criteria based on three kinds of attributes of RS-stereoisomers (chirality, RS-stereogenicity, and sclerality), where the classification into five RS-stereoisomeric types (Types I to V) according to S. Fujita, J. Org. Chem., 69, 3158–3165 (2004), S. Fujita, MATCH Commun. Math. Comput. Chem., 54, 39–52 (2005), and S. Fujita, MATCH Commun. Math. Comput. Chem., 58, 611–634 (2007) plays an important role. Among three types of RS-stereogenic promolecules (Types I, III, and V), the central atom of each alkane as a promolecule of Types I and III (chiral/RS-stereogenic) is regarded as an asymmetric center, while the central atom of each alkane as a promolecule of Types V (achiral/RS-stereogenic) is regarded as a pseudoasymmetric center. The data of alkyl ligands, which have been recursively calculated by a personal computer and stored as the coefficients of the term $x^k y^\ell z^m$ of generating functions involving carbon content ($k$), the number of asymmetric carbons ($\ell$), as well as the number of pseudoasymmetric carbons ($m$), have been used to count centroidal and bicentroidal alkanes on the basis of a tetrahedral skeleton. Each itemized number has been obtained as the coefficient of the term $x^k y^\ell z^m$ appearing in a respective generating function, which has been derived by following Fujita’s proligand method. The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with Type I, ..., or Type V as well as with achiral stereoisomers and chiral stereoisomers.
1 Introduction

Enumeration of alkanes (or trees) has been one of long-pending problems which have attracted various approaches of chemists (e.g., Henze and Blair [1, 2]) as well as of mathematicians (e.g., Cayley [3, 4], Pólya [5, 6], Otter [7], and Robinson et al. [8]), as summarized in books [9–12] and reviews [13–16]. Although Robinson et al. [8] reported the enumeration of achiral and chiral alkanes by modifying Pólya’s cycle indices (CIs), even their treatment did not fully take account of problems due to inner structures of ligands, e.g., pseudoasymmetry and meso-compounds.

We have recently developed the proligand method, which takes inner structures of ligands into explicit consideration [17–19]. The merit of Fujita’s proligand method for enumerating three-dimensional (3D) objects (e.g., stereoisomers) was discussed in comparison with Pólya’s theorem by using simple examples of meso and pseudoasymmetric compounds [20]. As an application of the proligand method, we have enumerated monosubstituted alkanes (or alkyl ligands, or mathematically speaking, planted 3D-trees or rooted 3D-trees at the same time) [21–23] so as to provide fundamental data for enumerating alkanes. Thereby, we have been able to investigate the enumeration of achiral and chiral alkanes (mathematically speaking, 3D-trees of degree 4) as further applications of Fujita’s proligand method, which have been conducted:

1. by using the dichotomy of centroidal and bicentroidal alkanes [24],
2. by using another dichotomy of balanced alkanes and unbalanced alkanes, where dual recognition as uninuclear and binuclear promolecules is emphasized so as to get rid of abnormal categorization into achiral and chiral alkanes [25],
3. by using the dichotomy of balanced alkanes and unbalanced alkanes, where an alternative method of compensating the abnormal categorization into achiral and chiral alkanes is discussed along with an implementation with the Maple programming language [26],
4. by the combination of the two dichotomies [27], and
5. by combining Fujita’s proligand method with Fujita’s PCI (partial-cycle-index) method in order to obtain numbers of alkanes subdivided with respect to their point-group symmetries [28].

In these enumerations, we took asymmetric atoms and pseudoasymmetric ones into consideration, but without distinguishing them, because we had no reliable criterion for such distinction. It follows that the resulting values did not concerned with the numbers of asymmetric carbon atoms and those of pseudoasymmetric carbon atoms. For practical purposes of depicting compounds enumerated, it is desirable to enumerate achiral and chiral alkanes with given carbon numbers, where the numbers of asymmetric and pseudoasymmetric atoms were taken into explicit consideration.

As another project of ours, on the other hand, we have investigated the classification of promolecules by means of three kinds of attributes of RS-stereoisomers (chirality, RS-stereogenicity, and sclerality), where any promolecules have been concluded to belong to one of five RS-stereoisomeric types (Types I to V) [29, 30]. This approach has been applied to the enumeration of promolecules, the calculated number of which have been itemized into the five RS-stereoisomeric types (Types I to V) [31].

In the present paper, we first discuss rigorous distinction between asymmetric atoms and pseudoasymmetric ones after we briefly discuss conventional terminologies on them. Thus,
the five $RS$-stereoisomeric types based on chirality, $RS$-stereogenicity, and sclerality [29, 30] are applied to produce a criterion for such rigorous discrimination. According to the newly developed criterion, we next enumerate achiral and chiral alkanes with given carbon numbers by taking numbers of asymmetric and pseudoasymmetric centers into consideration.

2 Asymmetric and Pseudoasymmetric Centers

2.1 The Conventional Terminology

In his famous book [32, page 11], van’t Hoff has claimed that the number of stereoisomers of the formula $C(R_1R_2R_3)C(R_4R_5)C(R_1R_2R_3)$ (1) was equal to three (a pair of enantiomers and an achiral compound) on the same line as there exist three stereoisomers (a pair of enantiomers and an achiral so-called meso-compound) for the formula $C(R_1R_2R_3)C(R_1R_2R_3)$ (2). If our speculation was right, he apparently recognized that the central carbon atom of (1) was not “asymmetric” and the number of asymmetric carbon atoms in (1) was equal to two (then $2(2/2-1) \times (1 + 22/2) = 3$ according to eq. 2 of [32, page 12]), because the two terminals (i.e., $C(R_1R_2R_3)$) were seemingly equivalent. The erroneous conclusion of van’t Hoff on (1) seemed to provide Fischer with some difficulties in his famous work on sugars [33–35]. After he had developed Fischer’s projection as a new device for representing configuration [34], Fischer decided the configuration of pentoses through their relation to trihydroxyglutaric acids (as a special case of (1)), as found in his autobiography [35, page 134]. The case of (1) has been now recognized as a pseudoasymmetric case, where there exist four stereoisomers (a pair of enantiomers and two achiral compounds).

Interests on such pseudoasymmetric cases [36] have been revived in connection with the CIP (Cahn-Ingold-Prelog) system for $RS$-nomenclature [37], because the revised version of the CIP system [37] resulted in a significant change of the connotation of the term “pseudoasymmetry”, as pointed out by Mislow [38]. According to the revised CIP system [37], tetrahedral atoms are recognized as stereogenic units (more specifically as chirality centers or asymmetric centers) or pseudoasymmetric stereogenic units (more specifically as pseudoasymmetric centers), where the algebraic sign (or corresponding descriptor) of a pseudoasymmetric unit is reflection-invariant in contrast to the algebraic sign of a chirality element (a stereogenic unit). As a result, two achiral compounds corresponding to $C(AB\bar{p}p)$ ($A = R_4$, $B = R_5$, $p = R-C(R_1R_2R_3)$ and $\bar{p} = S-C(R_1R_2R_3)$, where $A$ and $B$ are achiral ligands) and four chiral compounds (two pairs of enantiomers) corresponding to $C(Appq)$ or $C(App\bar{p})$ ($A = R_4$, $q$ = a chiral ligand, $p = R-C(R_1R_2R_3$ and $\bar{p} = S-C(R_1R_2R_3$) have been claimed to be both pseudoasymmetric. Note that only the former compound ($C(AB\bar{p}p)$) is in agreement of the original definition of pseudoasymmetry (cf. [36]). Although this change has given some convenience to the descriptive stereochemistry such as the $RS$-nomenclature, it causes essential difficulties from the viewpoints of geometry and combinatorial enumeration. From the geometrical point of view, the central carbon atom of the pseudoasymmetric case of $C(AB\bar{p}p)$ is locally achiral (achirotopic according to [39, 40]), while the central carbon atom of the “pseudoasymmetric” case of $C(Appq)$ (or $C(App\bar{p})$) is locally chiral (chirotopic according to [39, 40]). The concept “reflection-invariant” implies that the non-existence of an enantiomeric pair for the former achiral case is equalized to the existence of an enantiomeric pair $C(Appq)$ and $C(App\bar{p})$ for the latter case. This point results in a drawback from the viewpoint of combinatorial enumeration such that the “pseudoasymmetric” case of $C(Appq)$ or $C(App\bar{p})$ gives the same number (4) of stereoisomers as the “asymmetric”
case of C(ABXp) or C(ABXp) does, whereas the pseudoasymmetric case of C(ABp) gives 2 as the number of achiral compounds.

2.2 New Terminology Based on RS-Stereoisomeric Types

As clarified in the preceding subsection, a more rigorous standpoint is necessary to obtain a reliable criterion for distinguishing between asymmetric atoms and pseudoasymmetric ones. Recently, our analysis of the conventional concepts “chirality” and “stereogenicity” [41–44] has led to the formulation of more specifiable concepts, i.e., chirality, RS-stereogenicity, and sclerality [29, 45, 46]. We adopt these concepts to derive such a reliable criterion.

According to this formulation [29, 45, 46], a quadruplet of promolecules contained in a stereoisogram are called RS-stereoisomers, which are characterized by three relationships, i.e., enantiomeric, RS-diastereomeric, and holantimeric. These relationships correspond to the attributes of the quadruplet (and those of each RS-stereoisomer of the quadruplet at the same time), i.e., chirality, RS-stereogenicity, and sclerality. By combining the three attributes, the quadruplet of promolecules (RS-stereoisomers) is characterized as either one of five RS-stereoisomeric types, i.e., Type I (chiral/RS-stereogenic/ascleral), Type II (chiral/RS-astereogenic/ scleral), Type III (chiral/RS-stereogenic/scleral), Type IV (achiral/RS-astereogenic/ascleral), and Type V (achiral/RS-stereogenic/scleral). The existence of only five types has been proven on a more mathematical basis [47, 30]. Pseudoasymmetry [45] and prochirality [48] have been discussed by using stereoisograms.

By considering Types I–V, we are able to derive a reliable criterion for distinguishing between asymmetric atoms and pseudoasymmetric ones. Suppose that a quadruplet of entities (e.g., promolecules, planted promolecules, etc.) contained in a stereoisogram is characterized as being RS-stereogenic. Then, the center of each entity is characterized as follows:

Criterion 1 (Asymmetric and pseudoasymmetric centers)

1. If the quadruplet of entities contained in a stereoisogram is RS-stereogenic/ -chiral (i.e., Type I or III), the center of each entity is referred to as being asymmetric.
2. If the quadruplet of entities contained in a stereoisogram is RS-stereogenic/ -achiral (i.e., Type V), the center of each entity is referred to as being pseudoasymmetric.

This criterion means that an asymmetric center is capable of generating enantiomers along with RS-diastereomers because of the RS-stereogenic/chiral nature. In contrast, a pseudoasymmetric center is capable of generating RS-diastereomers, but incapable of generating enantiomers (i.e., achiral) because of the RS-stereogenic/achiral nature. This point has been already discussed by using several illustrative examples [45, 49]. It should be emphasized that RS-diastereomers of Type I are superposed upon enantiomers.

2.3 Centroidal Alkanes

2.3.1 Centroids as Asymmetric or Pseudoasymmetric Centers

In the present paper, we start from the dichotomy of centroidal/bicentroidal 3D-trees, which we once applied to the enumeration of alkanes as stereoisomers [24, 50]. We shall first show how to apply Criterion 1 to centroidal alkanes by using representative examples shown in Fig. 1 [51].
<table>
<thead>
<tr>
<th>RS-stereoisomeric type</th>
<th>promolecular representation</th>
<th>centroidal representation</th>
<th>carbon-skeletal representation</th>
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<tbody>
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<tr>
<td><strong>Type III</strong> chiral/RSS-stereogenic/scleral</td>
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<td><img src="image" alt="Type III diagram" /></td>
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</tr>
<tr>
<td><strong>Type IV</strong> achiral/RSS-astereogenic/asceral</td>
<td><img src="image" alt="Type IV diagram" /></td>
<td><img src="image" alt="Type IV diagram" /></td>
<td><img src="image" alt="Type IV diagram" /></td>
</tr>
<tr>
<td><strong>Type V</strong> achiral/RSS-stereogenic/scleral</td>
<td><img src="image" alt="Type V diagram" /></td>
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<td><img src="image" alt="Type V diagram" /></td>
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Figure 1: Examples of five RS-stereoisomeric types for alkanes as 3D-trees. The letters A, B, X, and Y denote achiral proligands, while p/q and q/q represent pairs of enantiomeric proligands. The symbol ⚫ indicates the centroid of each alkane. Each centroid with an asterisk (*) is asymmetric under Criterion 1, while each centroid with a dagger (†) is pseudoasymmetric under Criterion 1.
In Fig. 1, an alkane to be examined is represented in three ways [51]. A promolecular representation (e.g., 3) shows general features of the RS-stereoisomeric type of the alkane, where the letters A, B, X, and Y denote achiral proligands. On the other hand, a centroidal representation (e.g., 4) emphasizes the centroid of the alkane (denoted by the symbol $c$) and relevant ligands. Finally, a carbon-skeletal representation (e.g., 5) corresponds to a common structural formula having wedges and broken bold lines, without showing hydrogen atoms except being necessary to indicate configuration.

The promolecule of Type I (e.g., 3) is chiral, RS-stereogenic, and ascleral so that a quadruplet of a Type-I stereoisogram consists of one pair of enantiomers (corresponding to the chiral nature), which can be alternatively regarded as one pair of RS-diastereomers (corresponding to RS-stereogenic). The superposition of the enantiomeric relationship onto the RS-diastereomeric one is ascribed to the ascleral nature of Type I. The application of Criterion 1 to 2-methylhexane (as an entity) shows that its centroid ($c$) is asymmetric, as indicated by the centroidal representation (4) and by the carbon-skeletal representation (5). The asymmetric nature is denoted by an asterisk ($c^*$). It should be noted that the term asymmetric is linked with the RS-stereogenic nature but not directly with the chirality [52].

The promolecule of Type II (e.g., 6) is chiral, RS-astereogenic, and scleral so that a quadruplet of a Type-II stereoisogram consists of one pair of enantiomers but exhibits RS-astereogenic nature. The application of Criterion 1 to (3R,5R)-3,4,5-trimethylheptane (as an entity) shows that its centroid ($c$) is not asymmetric nor pseudoasymmetric, as indicated by the centroidal representation (7) and by the carbon-skeletal representation (8). The centroidal carbon in 7 (or 8) and the centroidal carbon in its enantiomer 7 (or 8) is in an enantiomeric relationship, so that each of the centroids is locally chiral. It follows that the centroid of being not asymmetric nor pseudoasymmetric is not linked with the chirality, but with the RS-astereogenic nature.

The promolecule of Type III (e.g., 9) is chiral, RS-stereogenic, and scleral, so that a quadruplet of a Type-III stereoisogram consists of two pairs of enantiomers, which can be alternatively regarded as two pairs of RS-diastereomers. The application of Criterion 1 to (3R,4r,5S)-3,5-dimethyl-4-[(2S)-butan-2-yl]octane (as an entity) shows that its centroid ($c^*$) is asymmetric, as indicated by the centroidal representation (10) and by the carbon-skeletal representation (11). It should be noted that the term asymmetric is linked with the RS-stereogenic nature but not with the chirality [52]. According to the CIP-nomenclature, on the other hand, the centroid ($c^*$) is recognized to be reflection-invariant (i.e., “pseudoasymmetric” due to the revised CIP system) so that the descriptor 4r is adopted in the IUPAC name.

Because of the achiral, RS-astereogenic, and ascleral nature of Type IV (e.g., 12), a quadruplet of a Type-IV stereoisogram consists of one promolecule of being self-enantiomeric and of being self-RS-diastereomeric. The application of Criterion 1 to 3,3-dimethylhexane (as an entity) shows that its centroid ($c$) is not asymmetric nor pseudoasymmetric, as indicated by the centroidal representation (13) and by the carbon-skeletal representation (14).

The promolecule of Type V (e.g., 15) is achiral, RS-stereogenic, and scleral, so that a quadruplet of a Type-V stereoisogram consists of one pair of RS-diastereomers, which can be alternatively regarded as two self-enantiomeric pairs (i.e., two achiral promolecules). The application of Criterion 1 to (3R,4r,5S)-3,4,5-trimethylheptane (as an entity) shows that its centroid ($c^+$) is pseudoasymmetric, as indicated by the centroidal representation (16) and by the carbon-skeletal representation (17).
2.3.2 Asymmetric or Pseudoasymmetric Centers Other Than Centroids

The next task is to determine by Criterion 1 whether each carbon center other than the centroid in an alkane is asymmetric, pseudoasymmetric, or not either. To do this task, it is important to select an appropriate entity to which we apply Criterion 1, where the selection should be well-defined so as to give a definite result.

Once a given alkane is determined to be centroidal, its centroid is uniquely fixed. Thereby, the alkane can be regarded as a directed graph (digraph) [9]. In other words, it can be regarded as a kind of rooted tree, in which its centroid is a root. In the present context, a new matter is that the centroidal alkane is regarded as a rooted three-dimensional (3D) tree [24]. This idea is applied to select entities for Criterion 1, as depicted in Fig. 2.

Figure 2: Selection of recursive alkyl ligands by means of directed-tree representations of centroidal alkanes. Each of the alkanes is divided into recursive alkyl ligands (as planted 3D-trees). The symbol \( \oplus \) indicates the principal node of each alkyl ligand, while the symbol \( \bullet \) indicates the root which is occupied commonly by the resulting alkyl ligands.

To discuss distinction between asymmetric centers and pseudoasymmetric ones, let us regard centroidal alkanes of Type III and V as directed 3D-trees, where incident bonds to each centroid are marked with arrows aiming at the centroid. Thereby, we obtain directed-tree representations of the centroidal alkanes, \( 11' \) (Type III) and \( 18 \) (Type V), where the methyl ligand in \( 17 \) is replaced by a pentyl ligand in \( 18 \) for convenience of explanation. Then, suppose that each centroid is replaced by a root (\( \bullet \)) and each neighboring node is regarded as a principal vertex (\( \oplus \)). As a result, we obtain such alkyl ligands as contained in \( 11'' \) or \( 18' \), where they share a single root. Each alkyl ligand in isolation can be regarded as a planted 3D-tree, so that it is categorized into any one of Types I to V (Fig. 3).

As found easily by Fig. 3, RS-stereoisomeric types for alkyl ligands (planted 3D-trees) are discussed in a parallel way to those for centroidal alkanes (Fig. 1), because principal nodes (\( \oplus \)) for Fig. 3 and centroids (\( \circ \)) for Fig. 3 play a common role in determining Types I–V. This means that such alkyl ligands (planted 3D-trees) can be used as entities for Criterion 1, where their principal nodes are used as centers to be examined and their roots are regarded as null proligands (or hypothetical achiral proligands). According to Criterion 1, the principal node of...
Figure 3: Examples of five RS-stereoisomeric types for alkyl ligands as planted 3D-trees. The letters A, B, X, and Y denote achiral proligands, while p/p and q/q represent pairs of enantiomeric proligands. The symbol \( \text{P} \) indicates the principal node of each alkyl ligand, while the symbol \( \ast \) indicates the root. The bond between the principal node and the root is called a stem. Each principal node with an asterisk (*) is asymmetric under Criterion 1, while each principal node with a dagger (†) is pseudoasymmetric under Criterion 1.
a Type-I (or Type-III) alkyl ligand is determined to be asymmetric as marked by an asterisk (*); the principal node of a Type-V alkyl ligand is determined to be pseudoasymmetric as marked by a dagger (†); and the principal node of a Type-II (or Type-IV) is unmarked to be neither asymmetric nor pseudoasymmetric.

Each alkyl ligand is further considered to be a directed 3D-tree in a similar way to Fig. 2 so that the procedure for generating such a directed 3D-tree is found to be recursive, as reported in [21, 22, 23]. Hence, we call such an alkyl ligand a recursive alkyl ligand if necessary.

**Criterion 2 (Selection of Entities for Criterion 1)**

1. A centroidal alkane serves as an entity for Criterion 1, where its centroid plays as a center to be examined.
2. A recursive alkyl ligand serves as an entity for Criterion 1, where its principal node plays as a center to be examined.

### 2.4 Bicentroidal Alkanes

Bicentroidal alkanes have a bicentroid, each terminal of which accommodates a recursive alkyl ligand. Hence, it is sufficient that two recursive alkyl ligands selected from a bicentroidal alkane by Criterion 2 are examined by Criterion 1.

For example, a bicentroidal alkane of meso-type is represented by a directed-tree representation (34), as shown in Fig. 4. Each terminal is dually considered to be a principal vertex (P⃝) of one alkyl ligand and to be a root (●) of the other alkyl ligand. As a result, we obtain such alkyl ligands as contained in 35. Each alkyl ligand in isolation can be regarded as a planted 3D-tree, so that it is categorized into any one of Types I to V (Fig. 3). Hence, each alkyl ligand in isolation can be regarded as a recursive alkyl ligand defined by Criterion 2 so as to be selected as an entity for Criterion 1, where its principal node (P⃝) is regarded as a center to be examined.

![Figure 4](image)

**Figure 4**: Selection of recursive alkyl ligands by means of directed-tree representations of a bicentroidal alkane. The alkane is divided into two recursive alkyl ligands (as planted 3D-trees) at the bicentroid. The symbol P⃝ indicates the principal node of each alkyl ligand, while the symbol ● indicates the root which is occupied commonly by the resulting alkyl ligands.

### 2.5 The Present Methodology vs. the Conventional One

It is worthwhile to compare the present methodology with the conventional one by referring to examples which we encounter in the enumeration of alkanes as 3D-trees.

The centroid of a centroidal alkane of carbon content 29 (36) is determined to be asymmetric in terms of Criterion 1, because the corresponding promolecule (37) belongs to Type III.
Figure 5: Examples of centroidal alkanes, where the determination of asymmetry or pseudoasymmetry (for the center $C_P$) by the present methodology is different from the determination by the revised CIP-system.

(chiral/RS-stereogenic/ascleral). The proligands around the centroid of 36 (or 37) are a heptyl ligand (Type IV: A, achiral), a 5-methylhexyl ligand (Type IV: B, achiral) and a 4-(butan-2-yl)-3,5-dimethyloctan-4-yl ligand (named L1, Type III: p, chiral) and a hydrogen (X, achiral) so as to be represented by C(ABXp) (i.e., Type III). The centroid marked by the symbol $\ast$ in 36 is determined to be asymmetric (stereogenic) and to have $R$-configuration even when we rely on the revised CIP-system.

The centroid of another centroidal alkane of carbon content 29 (38) is determined to be asymmetric in terms of Criterion 1, because the corresponding promolecule (39) belongs to Type I (chiral/RS-stereogenic/ascleral). The proligands around the centroid of 38 (or 39) are found to be a heptyl ligand (Type IV: A, achiral), a 5-methylhexyl ligand (Type IV: B, achiral) and a 4-(butan-2-yl)-3-methylnonan-4-yl ligand (named L2, Type V: Y, achiral) and a hydrogen (X, achiral) so as to be represented by C(ABXY) (i.e., Type I). The centroid marked by the symbol $\ast$ is determined to be asymmetric (stereogenic) and to have $R$-configuration even when we rely on the revised CIP-system.

As long as we focus our attention on the centroids of 36 and 38, they seem to behave similarly under the present methodology and under the revised CIP-system. However, their inner structures behave differently due to the change of viewpoints.

According to Criterion 2 applied to 36, the heptyl ligand (Type IV), the 5-methylhexyl ligand (Type IV) and the 4-(butan-2-yl)-3,5-dimethyloctan-4-yl ligand (named L1, Type III) are selected as entities for Criterion 1. Because Ligand L1 in isolation belongs to Type III (corresponding to the proligand C(ppq), cf. Fig. 3), the principal node represented by the symbol $C_P$ is determined to be asymmetric, as marked by an asterisk. If we alternatively consider the principal node ($C_P$) to be the center of another tetrahedral molecule (the same compound as 36) regardless of Criterion 2, the tetrahedral molecule belongs to Type III (corresponding to the
promolecule C(ppqr), cf. Fig. 1). Hence, the principal node (C_P) as such a tentative center in 36 is also concluded to be asymmetric.

According to Criterion 2 applied to 38, the heptyl ligand (Type IV), the 5-methylhexyl ligand (Type IV) and the 4-(butan-2-yl)-3-methylnonan-4-yl ligand (named L2, Type V) are selected as next entities for Criterion 1. Because Ligand L2 in isolation belongs to Type V (corresponding to the proligand C(Xpp), cf. Fig. 3), the principal node represented by the symbol C_P is determined to be pseudoasymmetric, as marked by a dagger. If we consider the principal node (C_P) to be the tentative center of a tetrahedral molecule, the principal node (C_P) is changed to be asymmetric, because the tetrahedral molecule belongs to Type III (corresponding to the promolecule C(ppqX); cf. Fig. 1).

According to the revised CIP-system, on the other hand, the configuration at the node denoted by C_P in 36 is reflection-invariant so that the node (C_P) is determined to be pseudoasymmetric. On the same line, the configuration at the node denoted by C_P in 38 is reflection-invariant so that the node (C_P) is determined to be pseudoasymmetric. It follows that the S-configurations at C_P in 36 and 38 are designated by a lowercase letter s according to the revised CIP-system. Thus, the viewpoint of the revised CIP-system, which takes no thought of centroids, is in sharp contrast with the present one, where Ligand L1 (p, chiral) around the centroid of 37 and Ligand L2 (Y, achiral) around the centroid of 39 are selected as entities to be examined in agreement with Criterion 2.

3 Enumeration

3.1 Enumeration of Alkyl Ligands

In order to take account of asymmetric and pseudoasymmetric centers, we shall enumerate planted promolecules of Type I and III (for asymmetric centers) and planted promolecules of Type V (for pseudoasymmetric centers). The obtained cycle indices with chirality fittingness (CI-CFs) are then converted into functional equations for counting alkyl ligands.

3.1.1 Cycle Indices with Chirality Fittingness

First, we consider the action of the C_{3v}-point group

\[ C_{3v} \sim \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); (1\ 2\ 3), (1\ 3\ 2), (1\ 2\ 3)\}, \]  

which is represented by its right coset representation \((\mathcal{C}_3 \setminus C_{3v})\) according to the three substitution positions of a methyl skeleton. Note that each overbar indicates the alternation of ligand chirality. We have recently reported the enumeration of monosubstituted alkanes [21–23] after we developed the proligand method as a general methodology for enumerating stereoisomers [17–19]. Although the previous results have taken no account of Types I–V [21], a new view added to explain them in the present paper serves us with one of important parts to evaluate planted promolecules (alkyl ligands) of Types I–V distinctly.

We are able to use Theorem 3 of Ref. 19 and the derived eq. 3 of Ref. 21:

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

to count steric isomers also in the present context without any modification, where the symbol \(b_d\) represents a sphericity index (SI) which characterizes a hemispheric \(d\)-cycle. Note that the
term *steric isomers* is used to denote Types I—V achiral planted promolecules and chiral planted promolecules, where two enantiomers of each pair are counted separately.

To count achiral planted promolecules of Types IV and V only, the elements corresponding to reflections in eq. 1 are used according to eq. 4 of Ref. 21, which has been derived from the first proposition of Theorem 4 of Ref. 19. Thereby we obtain the following CI-CF:

\[
\text{CI-CF}^{(IV/V)}(C_{3\nu}; a_d, c_d) = a_1 c_2.
\]  
(3)

Note that the symbols \(a_d\) and \(c_d\) are used to represent sphericity indices (SIs) other than \(b_d\), where the SI \(a_d\) characterizes a homospheric \(d\)-cycle and the SI \(c_d\) characterizes an enantiospheric \(d\)-cycle.

Let us next consider the action of the permutation group represented by

\[
C_3 \sim \{(1)(2)(3), (1\ 3\ 2); (1)(2\ 3), (1\ 3)(2), (1\ 2)(3)\},
\]  
(4)

which does not involve the alternation of ligand chirality. On the same line as eq. 1 is concerned with chirality/achirality, eq. 4 is concerned with RS-stereogenicity/RS-astereogenicity. This means that the three elements other than those of \(C_3\) can be used to evaluate the number of Types II and IV (RS-astereogenic). In parallel to the derivation of eq. 3, the number of planted promolecules of Type II and IV (RS-astereogenic) can be evaluated by using the following CI-CF:

\[
\text{CI-CF}^{(II/IV)}(C_{3\nu}; b_d) = b_1 b_2.
\]  
(5)

Let us further consider the action of the ligand-inversion group represented by

\[
C_3 \hat{I} \sim \{(1)(2)(3), (1\ 2\ 3), (1\ 3\ 2); (1)(2\ 3), (1\ 3)(2), (1\ 2)(3)\,
\]  
(6)

which is concerned with sclerality/asclerality. The discussions described for deriving eqs. 3 and 5 are effective to the \(C_3\hat{I}\)-group. It follows that the enumeration of planted promolecules of Type I and IV (ascleral) can be conducted by using the following CI-CF:

\[
\text{CI-CF}^{(II/IV)}(C_{3\hat{I}}; a_d, c_d) = \frac{1}{3}(a_1^3 + 2a_3),
\]  
(7)

where the three elements other than those of \(C_3\) in eq. 6 are used to evaluate the added number of Types I and IV (ascleral).

The numbers evaluated by eqs. 3, 5, and 7 commonly contain the number of Type-IV alkyl ligands (i.e., planted promolecules of Type IV). Hence, the next task is to evaluate the number of such Type-IV alkyl ligands. Achiral and RS-astereogenic planted promolecules (Type IV) have constitutions such as \(A_3\) and \(A_2B\), where \(A\) and \(B\) represent achiral ligands (nested planted promolecules). As a result, such planted promolecules of Type IV are represented by the corresponding CI-CF as follows:

\[
\text{CI-CF}^{(IV)}(C_{3\nu}; a_d) = a_1 a_2.
\]  
(8)

Compare eq. 8 with eq. 3, where the product \(a_1 c_2\) demonstrates the participation of Ap\(\bar{p}\) (Type V) along with \(A_3\) and \(A_2B\) (Type IV).

We then subtract eq. 8 from eq. 7 for counting planted promolecules of Type I (chiral, RS-stereogenic, and ascleral); from eq. 5 for counting those of Type II (chiral and RS-astereogenic);
or from eq. 3 for counting those of Type V (achiral and \( RS \)-stereogenic). Thereby, we obtain the following CI-CFs:

\[
\text{CI-CF(I)}(C_3^\hat{I} ; a_d) = 1 \left( \frac{1}{3}a_1^3 + 2a_3 \right) - a_1a_2 \quad (9)
\]

\[
\text{CI-CF(II)}(C_3^\tilde{I}v ; a_d, b_d) = b_1b_2 - a_1a_2 \quad (10)
\]

\[
\text{CI-CF(V)}(C_3^v ; a_d, c_d) = a_1c_2 - a_1a_2 \quad (11)
\]

Finally, by subtracting eqs. 8–11 from eq. 2, we obtain the following CI-CF for counting planted promolecules of Type III (chiral and \( RS \)-stereogenic) as follows:

\[
\text{CI-CF(III)}(C_3 ; a_d, b_d, c_d) = \frac{1}{3}(b_3^3 + 2b_3) - \frac{1}{3}(a_1^3 + 2a_3) - (b_1b_2 - a_1a_2) - (a_1c_2 - a_1a_2), \quad (12)
\]

where the two planted promolecules of each enantiomeric pair are counted separately (i.e., under the action of \( C_3 \)).

3.1.2 Functional Equations for Recursive Calculations

According to previous enumerations of monosubstituted alkanes [21–23], let \( \alpha_k \) be the number of achiral monosubstituted alkanes (alkyl ligands as planted promolecules) of carbon content \( k \); let \( \gamma_k \) be the number of monosubstituted alkanes (diploid as planted promolecules) of carbon content \( k \); and let \( \beta_k \) be the number of monosubstituted alkanes (alkyl ligands as steric isomers) of carbon content \( k \). The present target is to subdivide these numbers (\( \alpha_k, \gamma_k, \text{and} \beta_k \)) with referring to the numbers of asymmetric and pseudoasymmetric centers, which are determined by means of Criteria 1 and 2.

Let \( \alpha_{k\ell m}, \gamma_{k\ell m} \) and \( \beta_{k\ell m} \) be respective subdivided numbers with respect to \( \ell \) asymmetric centers and \( m \) pseudoasymmetric centers, where they are represented by the following summations:

\[
\alpha_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \alpha_{k\ell m} \quad (13)
\]

\[
\gamma_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \gamma_{k\ell m} \quad (14)
\]

\[
\beta_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \beta_{k\ell m} \quad (15)
\]

We regard these numbers (\( \alpha_{k\ell m}, \gamma_{k\ell m}, \text{and} \beta_{k\ell m} \)) as the coefficients of the following generating functions:

\[
a(x^d,y^d,z^d) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \alpha_{k\ell m}z^m \right) y^{d\ell} \right) x^{dk} \quad (16)
\]

\[
c(x^d,y^d,z^d) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \gamma_{k\ell m}z^m \right) y^{d\ell} \right) x^{dk} \quad (17)
\]

\[
b(x^d,y^d,z^d) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \beta_{k\ell m}z^m \right) y^{d\ell} \right) x^{dk}, \quad (18)
\]
where the valuable \( x \) is concerned with carbon content, the valuable \( y \) is concerned with the number of asymmetric centers, and the valuable \( z \) is concerned with the number of pseudoasymmetric centers. We put \( \alpha_{000} = 1, \gamma_{000} = 1, \) and \( \beta_{000} = 1 \) for treating the respective initial (trivial) cases.

We regard these generating functions as functional equations when we take account of the lowest powers, i.e., \( a(x, y, z) (d = 1 \text{ in eq. 16}), c(x^2, y^2, z^2) (d = 2 \text{ in eq. 17 because } d \text{ should be even}), \) and \( b(x, y, z) (d = 1 \text{ in eq. 18}). \)

Suppose that the functional equation \( a(x, y, z) \) has been obtained up to carbon content \( k \) for inner (nested) planted promolecules. Then, the terms of the \( a(x, y, z) \) up to \( k \) can be recursively used to enumerate alkyl ligands (planted promolecules) of carbon content \( k + 1 \), where the numbers of asymmetric and pseudoasymmetric centers satisfies \( \ell < k \) and \( m < k \). Because the resulting functional equation \( a(x, y, z) \) is concerned with achiral planted promolecules (Types IV and V) of carbon content \( k + 1 \), the Type-V planted promolecules (eq. 11) causes an increase of pseudoasymmetric centers by one, while Type-IV planted promolecules (eq. 8) has no effects except the increase of carbon content. As a result, the SIs \( a_1, a_2, \) and \( c_2 \) in eq. 8 (multiplied by \( x \)) and eq. 11 (multiplied by \( xz \)) are replaced by \( a(x, y, z), a(x^2, y^2, z^2), \) and \( c(x^2, y^2, z^2) \) so as to give the following functional equation:

\[
a(x, y, z) = 1 + xa(x, y, z)a(x^2, y^2, z^2) + xz \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\},
\]

where the initial value 1 is added to treat a trivial case of hydrogen substitution.

In a similar way, the functional equation \( b(x, y, z) \), which is concerned with all types of planted promolecules (Types I–V) of carbon content \( k + 1 \), can be constructed by the data obtained up to carbon content \( k \). For this purpose, we take account of eq. 5 (multiplied by \( x \) for Types II and IV because of increasing carbon content \( 1 \)), eq. 11 (multiplied by \( xz \) for Type V because of increasing carbon content 1 and one pseudoasymmetric center) and eqs. 9 and 12 (multiplied by \( xy \) for Types I and III because of increasing carbon content 1 and one asymmetric centers). After the SIs \( a_d, c_d, \) and \( b_d \) in these equations are replaced by \( a(x^d, y^d, z^d), c(x^d, y^d, z^d), \) and \( b(x^d, y^d, z^d) \), they are summed up to give the following functional equation:

\[
b(x, y, z) = 1 + xb(x, y, z)b(x^2, y^2, z^2) + xz \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\}
+ \frac{xy}{3} \{b(x, y, z)^3 + 2b(x^3, y^3, z^3)\} - xyb(x, y, z)b(x^2, y^2, z^2)
- xy \{a(x, y, z)c(x^2, y^2, z^2) - a(x, y, z)a(x^2, y^2, z^2)\},
\]

where the initial value 1 is added to treat a trivial case of hydrogen substitution.

For the purpose of evaluating \( c(x^2, y^2, z^2) \), we have to take account of diploids [21]. Although we omit the details of the derivation, we should replace the terms in eqs. 5, 11, and 9 (and eq. 12), i.e., \( b(x^d, y^d, z^d) \) by \( c(x^2d, y^2d, z^2d) \), \( a(x^d, y^d, z^d) \) by \( a(x^2d, y^2d, z^2d) \), and \( c(x^d, y^d, z^d) \) by \( c(x^2d, y^2d, z^2d) \). After the replacement, it is necessary for the equation of Types II and IV (increasing carbon content 2) to be multiplied by \( x^2z^2 \); for the equation of Type V (increasing carbon content 2 and two pseudoasymmetric centers) to be multiplied by \( x^2z^2 \); as well as for the equation of Types I and III (increasing carbon content 2 and two asymmetric centers) to be multiplied by \( x^2y^2z^2 \). By summing up these equations, we obtain the following functional equation:

\[
c(x^2, y^2, z^2) = 1 + x^2c(x^2, y^2, z^2)c(x^4, y^4, z^4)
+ x^2z^2 \{a(x^2, y^2, z^2)c(x^4, y^4, z^4) - a(x^2, y^2, z^2)a(x^4, y^4, z^4)\}
+ \frac{x^2y^2}{3} \{c(x^2, y^2, z^2)^3 + 2c(x^6, y^6, z^6)\} - x^2y^2c(x^2, y^2, z^2)c(x^4, y^4, z^4)
\]
where the initial value 1 is added to treat a trivial case of hydrogen substitution.

The functional equations, \(a(x, y, z)\) (eq. 19), \(c(x^2, y^2, z^2)\) (eq. 21), and \(b(x, y, z)\) (eq. 20), have recursive nature so that they can be used to evaluate the numbers of relevant planted promolecules recursively as the carbon content \(k\) is increased successively by one. The resulting generating functions have the forms shown in eqs. 16–18.

### 3.2 Enumeration of Centroidal Alkanes

In the previous subsection, we have formulated a recursive method of calculating eqs. 16–18 by using \(a(x, y, z)\) (eq. 19), \(c(x^2, y^2, z^2)\) (eq. 21), and \(b(x, y, z)\) (eq. 20). In the present subsection, the results of the recursive calculation are applied to enumerate alkanes (promolecules) of Types I–V on the basis of a tetrahedral skeleton.

#### 3.2.1 Cycle Indices with Chirality Fittingness

Although the previous results concerned with enumeration of promolecules and its application to centroidal alkanes \([24, 27]\) have not involved subdivision into five types, the methodology can be applied to evaluate promolecules of Types I–V distinctly. Thus, we consider the action of the \(T_d\)-point group:

\[
\]

\[
(1)(2 3)(4), (1 2 4 3), (1 3 4 2), (1 4)(2 3), (1)(2 3 4), (1 2)(3 4), (1 2)(3)(4),
\]

\[
(1 3 2 4), (1 4 2 3), (1)(2 3)(4), (1 2 3 4), (1 3)(2 4), (1 4 3 2)\}
\]

which is represented by its right coset representation \((C_3v\backslash T_d)\) according to the four substitution positions of a tetrahedral skeleton. For the purpose of counting promolecules as steric isomers (i.e., Types I–V), we have reported eq. 2 of Ref. 24 derived by Theorem 3 of Ref. 19:

\[
\text{CI-CF}^{(I-V)}(T; b_d) = \frac{1}{12} (b_1^2 + 3b_2^2 + 8b_1b_3).
\]

where two enantiomers of each pair and each achiral promolecules are counted separately.

To count achiral promolecules only (i.e., Types IV and V), we have reported eq. 3 of Ref. 24 as follows:

\[
\text{CI-CF}^{(IV/V)}(T_d; s_d) = \frac{1}{2} (a_1^2c_2 + c_4),
\]

where the elements corresponding to reflections in eq. 22 are used according to the first proposition of Theorem 4 of Ref. 19.

Let us next consider the permutation group represented as follows:

\[
T_{\bar{d}} = \{(1)(2)(3)(4), (1 2)(3 4), (1 3)(2 4), (1 4)(2 3), (1)(2 3 4), (1 2 3)(4),
\]

\[
(1 3 4)(2), (1 4 2)(3), (1)(2 3 4), (1 2 4)(3), (1 3 2)(4), (1 4 3)(2);
\]

\[
(1)(2 3)(4), (1 2 4 3), (1 3 4 2), (1 4)(2 3), (1)(2 3 4), (1 2)(3 4), (1 2)(3)(4),
\]

\[
(1 3 2 4), (1 4 2 3), (1)(2 3)(4), (1 2 3 4), (1 3)(2 4), (1 4 3 2)\}
\]

Thus, we consider the action of the \(T_{\bar{d}}\)-point group:
which is obtained by omitting the alternation of ligand chirality in $T_d$ (eq. 22). Note that the action of $T_\sigma$ (eq. 25) is concerned with RS-stereogenicity/RS-astereogenicity.

On the same line as the derivation of eq. 24 for $T_d$ (eq. 22), the counterpart CI-CF for $T_\sigma$ (eq. 25) corresponds to RS-astereogenic promolecules (i.e., Types II and IV):

$$
\text{CI-CF}^{(\text{II/IV})}(T_\sigma; b_d) = \frac{1}{2}(b_1^2b_2 + b_4),
$$

where the elements other than those of $T$ in eq. 25 are taken into consideration.

Let us finally consider the ligand-inversion group represented as follows:

$$
(1 3 4)(2), (1 4 2)(3), (1 2 4)(3), (1 3 2)(4), (1 4 3)(2)\},
$$

where the latter half (the twelve elements after a semicolon) is obtained by altering the ligand chirality for the former half of elements (i.e., those of $T$). Note that the action of $T_f$ (eq. 27) is concerned with sclerality/asclerality.

On the same line as the derivation of eq. 24 for $T_d$ (eq. 22), the counterpart CI-CF for $T_f$ (eq. 27) can be derived so as to count ascleral promolecules (i.e., Types I and IV):

$$
\text{CI-CF}^{(\text{II/IV})}(T_f; S_d) = \frac{1}{12}(a_1^4 + 3c_2^2 + 8a_1a_3),
$$

where the twelve elements other than those of $T$ in eq. 27 are taken into consideration.

The numbers evaluated by eqs. 24, 26, and 28 commonly contain the number of promolecules of Type IV. Hence, the next task is to evaluate the number of such promolecules of Type IV. For this purpose, let us examine the terms appearing in eq. 24. The first term ($a_1^2c_2$) in eq. 24 is related to a pseudoasymmetric promolecule $XYp$ (e.g., 15) along with Type-IV promolecules of $\text{ABX}_2$ (e.g., 12) and $\text{A}_2\text{X}_2$ (+ $\text{X}_2\overline{p}$). The Type-IV promolecules correspond to the terms $a_1^2a_2$ and $a_2c_2$, which contain a duplicated component represented by $a_2^2$. This means that the first term ($a_1^2c_2$) in eq. 24 should be replaced by $a_1^2a_2 + a_2c_2 - a_2^2$ so as to exclude contamination by pseudoasymmetry. The second term ($c_4$) in eq. 24 is not related to pseudoasymmetry. Hence, eq. 24 is converted into the following form:

$$
\text{CI-CF}^{(\text{IV})}(T_d; S_d) = \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4)
$$

for counting Type-IV promolecules.

The combination of the equations derived above gives the following CI-CFs for counting respective RS-stereoisomeric types:

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

$$
\text{CI-CF}^{(\text{II})}(T_\sigma; S_d, b_d) = \frac{1}{2}(b_1^2b_2 + b_4) - \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4)
$$

$$
\text{CI-CF}^{(\text{III})}(T; S_d, b_d) = \frac{1}{12}(b_1^4 + 3b_2^2 + 8b_1b_3) - \frac{1}{12}(a_4^4 + 3c_2^2 + 8a_1a_3) - \frac{1}{2}(b_1^2b_2 + b_4)
- \frac{1}{2}(a_1^2c_2 + c_4) + (a_1^2a_2 + a_2c_2 - a_2^2 + c_4)
$$

$$
\text{CI-CF}^{(\text{IV})}(T_d; S_d) = \frac{1}{2}(a_1^2c_2 - a_2^2a_2) - \frac{1}{2}(a_2c_2 - a_2^2).
$$
Note that the derivations are schematically shown as follows: Type I (eq. 28 minus eq. 29); Type II (eq. 26 minus eq. 29); Type V (eq. 24 minus eq. 29); and Type III (eq. 23 minus eqs. 30, 31, and 24).

### 3.2.2 Functional Equations for Counting Centroidal Alkanes

The CI-CFs for counting centroidal promolecules (eqs. 29–33) should be converted into the corresponding functional equations for counting centroidal alkanes, where each SI is modified so as to accommodate a respective functional equation for counting alkyl ligands (one of eqs. 19–21).

Let $B^{(\tau)}_{k\ell m}$ (\(\tau = I, II, \ldots, V\) or their combinations) be the number of alkanes (promolecules) of Type \(\tau\), which have \(k\) carbons, \(\ell\) asymmetric centers and \(m\) pseudoasymmetric centers. Let the symbol $B^{(\tau)}_k$ be the summation for each type (\(\tau\)) represented as follows:

$$B^{(\tau)}_k = \sum_{\ell=0}^\infty \sum_{m=0}^\infty B^{(\tau)}_{k\ell m},$$

Then, we regard these numbers $B^{(\tau)}_{k\ell m}$ as the coefficients of the following generating functions:

$$B^{(\tau)}(x^d, y^d, z^d) = \sum_{k=0}^\infty \left( \sum_{\ell=0}^\infty \left( \sum_{m=0}^\infty B^{(\tau)}_{k\ell m} x^{dm} \right) y^{\ell m} \right) x^{dk}$$

where the valuable \(x\) is concerned with carbon content, the valuable \(y\) is concerned with the number of asymmetric centers, and the valuable \(z\) is concerned with the number of pseudoasymmetric centers. We put $B^{(\tau)}_{000} = 0$ for treating the respective initial (trivial) cases.

To evaluate the generating functions (eq. 35: \(\tau = I, II, \ldots, V\) and \(d = 1\)), we derive the corresponding functional equations by starting from the CI-CFs (eqs. 29–33). Thus, the SIs $a_d$, $c_d$, and $b_d$ in these equations are replaced by $a(x^d, y^d, z^d)$, $c(x^d, y^d, z^d)$, and $b(x^d, y^d, z^d)$ to give the following functional equations:

$$B^{(I)}(x, y, z) = \frac{xy}{12} \bigg\{ a(x, y, z)^4 + 3c(x, y, z)^2 + 8a(x, y, z)a(x^3, y^3, z^3) \bigg\}$$

$$- \frac{xy}{2} \bigg\{ a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2)$$

$$- a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4) \bigg\}$$

$$B^{(II)}(x, y, z) = \frac{x}{2} \bigg\{ b(x, y, z)^2b(x^2, y^2, z^2) + b(x^2, y^2, z^2) \bigg\}$$

$$- \frac{x}{2} \bigg\{ a(x, y, z)^2a(x^2, y^2, z^2) + a(x^2, y^2, z^2)c(x^2, y^2, z^2)$$

$$- a(x^2, y^2, z^2)^2 + c(x^4, y^4, z^4) \bigg\}$$

$$B^{(III)}(x, y, z) = \frac{xy}{12} \bigg\{ b(x, y, z)^4 + 3b(x^2, y^2, z^2)^2 + 8b(x, y, z)b(x^3, y^3, z^3) \bigg\}$$

$$- \frac{xy}{12} \bigg\{ a(x, y, z)^4 + 3c(x, y, z)^2 + 8a(x, y, z)a(x^3, y^3, z^3) \bigg\}$$

$$- \frac{xy}{2} \bigg\{ b(x, y, z)^2b(x^2, y^2, z^2) + b(x^2, y^2, z^2) \bigg\}$$
where, to treat the effect of the central carbon atom (i.e., the centroid here), we should consider the multiplication of $xy$ for Types I and III in accord with the increase of carbon content and an asymmetric center; that of $x$ for Types II and IV in accord with the increase of carbon content; and that of $xz$ for Type V in accord with the increase of carbon content and a pseudoasymmetric center.

Suppose that we have obtained $a(x, y, z) = \sum_{k=0}^{\mu} \alpha_k x^k, c(x^2, y^2, z^2) = \sum_{k=0}^{\mu} \gamma_k x^k$, and $b(x, y, z) = \sum_{k=0}^{\mu} \beta_k x^k$, where $\mu$ is tentatively fixed. On a similar line to the treatment described in Ref. [27], eqs. 36–40 are evaluated as follows. They are introduced into eqs. 36–40 to give $B^{(\tau)}(x, y, z)$ ($\tau = I, II, \ldots, V$). Let the symbol coeff $(B^{(\tau)(\mu)}(x, y, z), x^{2\mu+1})$ etc. represent the coefficient of the term $x^{2\mu+1}$ appearing in the equation $B^{(\tau)(\mu)}(x, y, z)$ etc. after expansion. Note that the coefficient is a polynomial containing $y^\ell z^m$. Then, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} B_{(2\mu+1)}^{(\tau)}(x, y, z) x^{2\mu+1} \right) y^{\ell} = \text{coeff}(B^{(\tau)(\mu)}(x, y, z), x^{2\mu+1})$$

(41)

for odd carbon contents as well as the following coefficients:

$$\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} B_{(2\mu+2)}^{(\tau)}(x, y, z) x^{2\mu+2} \right) y^{\ell} = \text{coeff}(B^{(\tau)(\mu)}(x, y, z), x^{2\mu+2})$$

(42)

for even carbon contents, where $\tau$ represents I, II, \ldots, or V. Note that the powers of $y$ and $z$ are equal to or less than $2\mu + 2$. These requirements should be considered in the following programming.

Let $A(x, y, z)$, $C(x, y, z)$, and $B(x, y, z)$ be functional equations for calculating the numbers of achiral, chiral, and total (achiral plus chiral) alkanes, where each pair of two enantiomers and each achiral alkane are respectively counted just once. Because the symbols concerning chiral alkanes, i.e., $B^{(I)}(x, y, z)$ (Type I: chiral/RS-stereogenic/ascleral), $B^{(II)}(x, y, z)$ (Type II: chiral/RS-astereogenic/scleral), and $B^{(III)}(x, y, z)$ (Type III: chiral/RS-stereogenic/scleral), represent the separate counting of two enantiomers of each pair, the functional equations $A(x, y, z)$, $C(x, y, z)$, and $B(x, y, z)$ are calculated as follows:

$$A(x, y, z) = B^{(IV)}(x, y, z) + B^{(V)}(x, y, z)$$

(43)

$$C(x, y, z) = \frac{1}{2} \left\{ B^{(I)}(x, y, z) + B^{(II)}(x, y, z) + B^{(III)}(x, y, z) \right\}$$

(44)

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

(45)
On the same line as above, we obtain the following coefficients:

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} A_{(2\mu+1)\ell m} x^m \right) y^\ell = \text{coeff}(A(x,y,z)^{\mu}, x^{2\mu+1})
\]  \hspace{1cm} (46)

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} C_{(2\mu+1)\ell m} x^m \right) y^\ell = \text{coeff}(C(x,y,z)^{\mu}, x^{2\mu+1})
\]  \hspace{1cm} (47)

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} B_{(2\mu+1)\ell m} x^m \right) y^\ell = \text{coeff}(B(x,y,z)^{\mu}, x^{2\mu+1})
\]  \hspace{1cm} (48)

for odd carbon contents as well as the following coefficients:

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} A_{(2\mu+2)\ell m} x^m \right) y^\ell = \text{coeff}(A(x,y,z)^{\mu}, x^{2\mu+2})
\]  \hspace{1cm} (49)

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} C_{(2\mu+2)\ell m} x^m \right) y^\ell = \text{coeff}(C(x,y,z)^{\mu}, x^{2\mu+2})
\]  \hspace{1cm} (50)

\[
\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} B_{(2\mu+2)\ell m} x^m \right) y^\ell = \text{coeff}(B(x,y,z)^{\mu}, x^{2\mu+2})
\]  \hspace{1cm} (51)

for even carbon contents.

### 3.2.3 Programming and Implementation

The functional equations \(a(x^d, y^d, z^d), c(x^d, y^d, z^d), \) and \(b(x^d, y^d, z^d)\) contained in the right-hand sides of eqs. 36–40 have been evaluated respectively by eq. 19, eq. 21, and eq. 20 for alkyl ligands as planted 3D-trees. For the purpose of programming and implementation, the requirements represented by eqs. 41 and 42 as well as eqs. 46–51 should be considered in processes of recursive calculation.

Concretely speaking, suppose that the functional equation \(a(x,y,z)\) (eq. 19), \(c(x^2, y^2, z^2)\) (eq. 21), and \(b(x,y,z)\) (eq. 19) have been recursively calculated up to carbon content \(k\). They are introduced into eqs. 36–40 to count centroidal alkanes. Among the terms appearing in the expanded functional equations, the terms corresponding to \(x^{2k+1}\) and \(x^{2k+2}\) are adopted as new entries according to the definition of centroidal alkanes (cf. eqs. 41 and 42 as well as eqs. 46–51).

The procedure described in the preceding paragraph is implemented by mean of the Maple programming language and stored with the name “Alkane1-30b.mpl”. Although the upper limit of the carbon content \(k\) is tentatively fixed to be 30, it can be freely selected as far as the capacity of a computer permits.

```maple
#Alkane1-30b.mpl
xyz := 1 + x*a111+a222 + x*z*(a111+c222 - a111*a222); cxyz := 1 + x^2+c222*c444 + x^2*z^2*(a222+c444-a222+a444) + (1/3)*x^2*y^2+c222 3 + (2/3)*x^2*y^2*c666 - x^2*y^2*c222*c444 - x^2*y^2*(a222+c444-a222+a444); bxyz := 1 + x*b111+b222 + x*z*(a111+c222 - a111*a222) + (1/3)*x*y*b111^3 + (2/3)*x*y*b333 - x*y*b111*b222 - x*y*(a111+c222 - a111*a222); "Alkanes as Centroidal 3D-Trees";
type1 := (x*y/12)*(a111^4 + 3+c222^2 + 8*a111*a333) - (x*y/2)*(a111^2*a222 + a222*c222 - a222^2 + c444);
```

- 527 -
typeII := (x/2)*(b111^2*b222 + b444) - (x/2)*(a111^2*a222 + a222*c222 - a222^2 + c444);
typeIII:= (x*y/12)*(b111^4 + 3*b222^2 + 8*b111*b333) - (x*y/12)*(a111^4 + 3*c222^2 + 8*a111*a333) + + (x*y/2)*(a111^2*c222 + c444) - (x*y/2)*(b111^2*b222 + b444) + (x*z/2)*(a111^2*c222 - a222*c222 - a222^2 + c444);
typeIV := (x/2)*(a111^2*a222 + a222*c222 - a222^2 + c444);
typeV := (x*z/2)*(a111^2*c222 - a111*a222) - (x*z/2)*(a111^2*c222 - a222^2 - a222^2);

Ah := typeIV + typeV;
Ckh := (1/2)*(typeI + typeII + typeIII);

*Initial Values*;

a111 := 1; a222 := 1; a333 := 1; a444 := 1;
c222 := 1; c444 := 1; c666 := 1;
b111 := 1; b222 := 1; b333 := 1; b444 := 1;
asum := 1; csun := 1; bsum := 1;

Ah := x; Ch := 0;
BtypeI := 0; BtypeII := 0; BtypeIII := 0; BtypeIV := 0; BtypeV := 0;

*Recursive Calculation*;

for k from 1 to 30 by 1 do
Cbxyz:= expand(coeff(bxyz,x^k));
Caxyz:= expand(coeff(axyz,x^k));
Ccxyz:= expand(coeff(cxyz,x^k+2));
blyz := expand(coeff(y*Cbxyz,y));
b2yz := blyz; b3yz := blyz; b4yz := blyz; subbsum := blyz;
alyz := expand(coeff(y*Caxyz,y));
a2yz := alyz; alyz := alyz; alyz := alyz; subasum := alyz;
clyz := expand(coeff(y*Ccxyz,y));
c2yz := clyz; c3yz := clyz; subcsun := clyz;

for m from 1 to degree(Cccxyz,y) by 1 do
CCCxyz:= coeff(Cccxyz,x^z); ccyz := cclyz := cslyz := subcsun := cccxyz;

CCaxyz := coeff(Ccaxyz, y^l); aa1yz := expand(coeff(x*CCaxyz,y));
aa2yz := a1yz; a1yz := a1yz; a1yz := a1yz; subasum := subasum + a1yz;

for n from 1 to degree(Ccxyz,y) by 1 do
CCcxyz := coeff(Cccxyz, z^m); cclyz := cclyz := cclyz := subcsun := cccxyz;

for p from 1 to degree(Ccxyz,z) by 1 do
CCcxyz := coeff(Ccxyz, z^n); aayz := a1yz + CCCxyz*z; aa2yz := aa1yz + CCCxyz*z^2; a3yz := aa1yz + CCCxyz*z^3; aa4yz := aa1yz + CCCxyz*z^4; subasum := subasum + CCCxyz;

end do:

for n from 1 to degree(Cccxyz,y) by 1 do
CCcxyz := coeff(Cccxyz, y^z); aa1yz := a1yz + CCCxyz*y; aa2yz := aa1yz + CCCxyz*y^2; aa3yz := aa1yz + CCCxyz*y^3; aa4yz := aa1yz + CCCxyz*y^4; subasum := subasum + CCCxyz;

end do:

for p from 1 to degree(Cccxyz,y) by 1 do
CCcxyz := coeff(Cccxyz, z^p); bblyz := bblyz + CCCbxyz*y^z; bb2yz := bblyz + CCCbxyz*y^z; bb3yz := bblyz + CCCbxyz*y^z; subbsun := subbsun + CCCbxyz;

end do:

end do:

Bh := Ah + Ch;

BtypeI := BtypeI + coeff(typeI,x*q)*x*q + coeff(typeI,x*(q+1))*x*(q+1);
BtypeII := BtypeII + coeff(typeII,x*q)*x*q + coeff(typeII,x*(q+1))*x*(q+1);
BtypeIII := BtypeIII + coeff(typeIII,x*q)*x*q + coeff(typeIII,x*(q+1))*x*(q+1);
BtypeIV := BtypeIV + coeff(typeIV,x*q)*x*q + coeff(typeIV,x*(q+1))*x*(q+1);
BtypeV := BtypeV + coeff(typeV,x*q)*x*q + coeff(typeV,x*(q+1))*x*(q+1);

Ah := Ah + coeff(Ah,x*q)*x*q + coeff(Ah,x*(q+1))*x*(q+1);
Ch := Ch + coeff(Ch,x*q)*x*q + coeff(Ch,x*(q+1))*x*(q+1);

end do:

Bh := Ah + Ch;
In this code named “Alkane1-30b.mpl”, the abbreviated symbols for functional equations (as generating functions) are used as follows: \texttt{all1} for \(a(x,y,z)\) etc.; \texttt{c222} for \(c(x^2,y^2,z^2)\) etc.; \texttt{b111} for \(b(x,y,z)\) etc. so that they store calculated values in the form of counting series of generating functions. The symbols \texttt{asum}, \texttt{csum}, and \texttt{bsum} are used to store the series for \(a(x,1,1)\), and \(c(x^2,1,1)\), and \(b(x,1,1)\).

The first part of this code declares three functional equations for alkyl ligands, i.e., \texttt{axyz} for \(a(x,y,z)\) (eq. 19), \texttt{cxyz} for \(c(x^2,y^2,z^2)\) (eq. 21), and \texttt{bxyz} for \(b(x,y,z)\) (eq. 20), as well as five functional equations for alkanes, i.e., \texttt{typeI} for \(B^{(I)}(x,y,z)\) (eq. 36), \texttt{typeII} for \(B^{(II)}(x,y,z)\) (eq. 37), \texttt{typeIII} for \(B^{(III)}(x,y,z)\) (eq. 38), \texttt{typeIV} for \(B^{(IV)}(x,y,z)\) (eq. 39), \texttt{typeV} for \(B^{(V)}(x,y,z)\) (eq. 40). In addition, \texttt{Ah} for \(A(x,y,z)\) (eq. 43) and \texttt{Ch} for \(C(x,y,z)\) (eq. 44) are involved.

In the paragraph “Initial Values”, the initial values for the initial (trivial) alkyl ligands as well as the initial centroidal alkanes. Note that the setting of \texttt{Ah} := \texttt{x} and \texttt{BtypeIV} := \texttt{x} represents their initial values, each of which consists of the first value \(x (= 1 \cdot x^1)\) for \(q = 1\) (i.e., \(q = 2k + 1, k = 0\)) and the second value \(0 (= 0 \cdot x^3)\) for \(q + 1 = 2\), because there are no centroidal alkanes of carbon content 2 and we start from \(k = 1 (q = 3)\) in a do loop for carbon content \(k\).

The paragraph “Recursive Calculation” of the code shows the do loop for carbon content \(k\), in which a nested do loop for the number of asymmetric centers \(l\) and three do loops nested further for pseudoasymmetric centers \((m, n, \text{and } p\) are used). In each do loop, the next coefficients are calculated by using a Maple command \texttt{coeff} and added to the end of respective functional equations so as to generate intermediate generating functions. In the last part of the do loop for carbon content \(k\), resulting coefficients are stored in counting series represented by \texttt{BtypeI} etc. After escaping from the outer do loop for \(k\), the code \texttt{Bh} := \texttt{Ah} + \texttt{Ch} calculates \(B(x,y,z)\) (eq. 45). The paragraph “Print Out of Type I (Chiral/RS-Stereogenic/Ascleral)” and omitted paragraphs of the code show the print-out of the calculation results. Strictly speaking, \(k\) represents the carbon content of an alkyl ligand, while \(q\) represents the carbon content of an alkane. In the print-out sections, however, \(k\) is used in place of \(q\) for the sake of convenience.

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

\[
> \text{read} \ "\text{Alkane1-30b.mpl}";
\]

The above described code gives calculation results according to the indication of its print-out sections. For example, we obtain the following result:

\[
k = 19;
\]
for the coefficient of the term $x^{19}$ of $B^{(t)}(x,y,z)$, which is stored as the counting series $B_{\text{typeI}}$. The output of $NtI$ means the term:

$$x^{19} \left( 19104 y + 380 y^3 z + 6 y^5 \right),$$

which shows the numbers of Type-I alkanes of of carbon content 19. The last two lines of the output are intended to construct rows of a table with respect to $k = 19; m = 0, 1$; and $\ell = 0$ to $5 \times (x^k y^\ell z^m)$ (cf. Table 1 shown below). As found by the code, when the carbon content of alkyl ligands runs from 1 to 30, the carbon content of alkanes runs from 3 to 62. For the sake of page saving, however, calculated values are shown up to 30.

### 3.2.4 Results and Illustrative Examples

#### Centroidal Alkanes of Type I

Table 1 lists the coefficient $B_{k\ell}^{(t)}$ of the term $x^k y^\ell z^m$ calculated by means of $B^{(t)}(x,y,z)$ (eq. 36), where each coefficient is stored in the series obtained as $B_{\text{typeI}}$ of the code “Alkane1-30b.mpl”.

In order to grasp the gist of the data collected in Table 1, it is worthwhile to examine several lower cases of carbon content. For example, the value 380 at the intersection between the $(k = 19, m = 1)$-row and the $(\ell = 3)$-column corresponds to the term $380 x^{19} y^3 z$ (cf. eq. 52). Hence, there exist 380 chiral centroidal alkanes of Type I which have three asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. Because the centroid of each of the 380 alkanes is asymmetric, the one pseudoasymmetric center is involved in an achiral alkyl ligand which belongs to Type V (e.g., 31). It follows that each of the 380 alkanes is represented by the formula 40 or 41, where the symbols A, B, and X represent a hydrogen atom or alkyl ligands. The alkyl ligands should be selected from achiral alkyl ligands of carbon content 1–8 so as to keep the central atom being a centroid.

![Figure 6: Chiral centroidal alkanes of Type I corresponding to the term 380$x^{19}y^3z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbols A, B, and X represent a hydrogen atom or alkyl ligands, which are selected from achiral alkyl ligands of carbon content 1–8 to keep the central atom being a centroid. An appropriate enantiomer of a pair is depicted as a representative.](image)

The value 380 of the term $380 x^{19} y^3 z$ can be verified by using the data of $a(x,y,z)$ (for achiral alkyl ligands) up to $x^8$ appearing in the following generating function:

$$a(x,y,z) = x + x^2 + 2x^3 + 3x^4 + 5x^5 + 8x^6 + 14x^7 + 23x^8 + (39 + 2y^2z)x^9 + \cdots,$$

(53)
Table 1: Centroidal Alkanes of Type I (Chiral/RS-Stereogenic/Ascleral)

<table>
<thead>
<tr>
<th>Carbon Content (k)</th>
<th>No. of Pseudoasym. Centers (ℓ = 0)</th>
<th>1 2 3 4 5 6 7 8 9 10 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>k = 1</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 2</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 3</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 4</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 5</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 6</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 7</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 8</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 9</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 10</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 11</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 12</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 13</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 14</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 15</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 16</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 17</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 18</td>
<td>m = 0</td>
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</tr>
<tr>
<td>k = 19</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 20</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 21</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 22</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 23</td>
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</tr>
<tr>
<td>k = 24</td>
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</tr>
<tr>
<td>k = 25</td>
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<td>0</td>
</tr>
<tr>
<td>k = 26</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 27</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 28</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 29</td>
<td>m = 0</td>
<td>0</td>
</tr>
<tr>
<td>k = 30</td>
<td>m = 0</td>
<td>0</td>
</tr>
</tbody>
</table>

Two chiral alkanes of each enantiomeric pair are counted separately.

which is stored in all the six partitions during the recursive calculation by the code “Alkan1-30b.mpl”. Let the partition \([k_1, k_2, k_3] \) represent the carbon contents of A, B, and X under the condition of \(A \neq B, A \neq X, B \neq X\) and \(k_1 + k_2 + k_3 = 9\). Then, the number of enantiomeric pairs is calculated by using the coefficients appearing in the right-side of eq. 53 as follows:

\[
\begin{align*}
[8,1,0] & \quad 23 \times 1 \times 1 = 23; & [7,2,0] & \quad 14 \times 1 \times 1 = 14 \\
[6,3,0] & \quad 8 \times 2 \times 1 = 16; & [6,2,1] & \quad 8 \times 1 \times 1 = 8 \\
[5,4,0] & \quad 5 \times 3 \times 1 = 15; & [5,3,1] & \quad 5 \times 2 \times 1 = 10 \\
[4,4,1] & \quad (2+1) \times 1 = 3; & [4,3,2] & \quad 3 \times 2 \times 1 = 6 \\
\end{align*}
\]

\[
\text{total: 95}
\]

It should be noted that the three pairs of butyl ligands (A and B) for the partition [4,4,1] can
Figure 7: Chiral centroidal alkanes of Type I corresponding to the term $6x^{19}y^5$. Each pair of enantiomers ($42/42$, $43/43$, or $44/44$) is RS-diastereomeric at the same time.

be selected from three achiral butyl ligands (cf. $3x^4$ in eq. 53) under the condition of $A \neq B$: i.e., $n$-butyl—iso-butyl, $n$-butyl—$t$-butyl, and iso-butyl—$t$-butyl. Because there exist two enantiomers for each of 95 enantiomeric pairs on the basis of $40$ or $41$, we obtain the number of alkanes at issue to be $95 \times 2 \times 2 = 380$, which is equal to the coefficient of the term $380x^{19}y^5z$.

Because we can manually depict the achiral isomers of alkanes of carbon content 1–8, we are able to depict the 380 stereoisomers based on $40$ and $41$ if we would go to such trouble.

We should here emphasize the importance of Criterion 2. The pseudoasymmetric center of $40$ (or $41$) is determined at the step of the alkyl ligand of carbon content 9 under Criterion 2. If the same carbon center is examined at the step of the constructed alkane ($40$ or $41$), it is determined to be asymmetric, because the corresponding promolecule belongs to Type III. The latter determination is not permitted if we start from Criterion 2. Compare the present case with 11, which has been determined to be Type III.

The value 6 at the intersection between the ($k = 19$, $m = 0$)-row and the ($\ell = 5$)-column corresponds to the term $6x^{19}y^5$ (cf. eq. 52). This means that there exist six chiral centroidal Type-I alkanes which have five asymmetric centers and no pseudoasymmetric centers according to Criteria 1 and 2. Because there exist one enantiomeric pair of carbon content 4 ($p/p$) and three enantiomeric pairs of carbon content 5 ($q/q$, $r/r$ and $s/s$), we are able to generate six of alkanes depicted in Fig. 7 ($42$–$44$ and their enantiomers). It should be noted that the centroid of $42$ (or $43$ or $44$) is asymmetric because of Type I (chiral/RS-stereogenic/ascleral) under Criterion 1. The chiral, RS-stereogenic, and ascleral nature of Type I causes the superposition of an enantiomeric relationship onto an RS-diastereomeric relationship, as found in each pair of enantiomers ($42/42$, $43/43$, or $44/44$).

From the viewpoint of the revised CIP-system, on the other hand, a reflection operation
converts each $RS$-descriptor for 42–44 into the opposite one for the corresponding enantiomers (42–44). This means that the centers (©) are reflection-variant so as not to be pseudoasymmetric, but to be asymmetric. In spite of the presence of an enantiomeric pair p/保罗, alkanes of Type I (e.g., Fig. 7) are chiral and not pseudoasymmetric (according to the CIP system). According to the CIP system, the effect of the pair p/保罗 upon pseudoasymmetry is different between Type I and Types III/V, so that alkanes of Type III (e.g., 11 in Fig. 1) are chiral and pseudoasymmetric and so that alkanes of Type V (e.g., 17 in Fig. 1) are achiral and pseudoasymmetric. This difference implies that the effect of such reflection-invariance as adopted by the revised CIP-system should be re-examined in more detail.

**Centroidal Alkanes of Type II** The coefficient $B^{(II)}_{klm}$ of the term $x^k y^l z^m$ is calculated by means of $B^{(II)}(x, y, z)$ (eq. 37), where each coefficient is stored in the series obtained as $B_{typeII}$ of the code “Alkanel-30b.mpl”. The results of calculation are listed in Table 2.

**Table 2: Centroidal Alkanes of Type II (Chiral/RS-Astereogenic/Scleral)$^a$**

<table>
<thead>
<tr>
<th>Carbon (k)</th>
<th>No. of</th>
<th>Cont. (k)</th>
<th>P. C. (m)</th>
<th>No. of Asymmetric Centers (ℓ)</th>
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</thead>
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<td>29</td>
<td>29</td>
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</tbody>
</table>

$^a$Two chiral alkanes of each enantiomeric pair are counted separately.

The value 500 at the intersection between the ($k = 19$, $m = 1$)-row and the ($ℓ = 3$)-column corresponds to the term 500$x^{19}y^3z$. Hence, there exist 500 chiral centroidal alkanes of Type II which have three asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. On a similar line to the formula 40 or 41 in Fig. 6, each of the 500 alkanes is represented by the formula 45 or 46, where the symbol A represents a hydrogen atom, a methyl ligand, or...
Figure 8: Chiral centroidal alkanes of Type II corresponding to the term $500x^{19}y^3z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbol A represents a hydrogen atom, a methyl ligand, or an ethyl ligand, while the symbol p is a chiral ligand with one asymmetric center. The ligands A and p are selected to keep the central atom being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

The value 500 of the term $500x^{19}y^3z$ can be verified as follows. By using the data of $a(x,y,z)$ (eq. 53) and the data of $b(x,y,z)$ up to $x^9$, we obtain the following generating function for counting chiral alkyl ligands:

$$\frac{1}{2}\{b(x,y,z) - a(x,y,z)\} = yx^4 + 3yx^5 + (8y + 2y^2)x^6 + (20y + 10y^2)x^7 + (46y + 38y^2 + 4y^3)x^8 + (102y + 125y^2 + 28y^3)x^9 + \cdots,$$

(eq. 54)

where the data are stored by $a_{111}$ and $b_{111}$ during the recursive calculation by the code “Alkane1-30b.mpl”. Note that eq. 54 counts each pair of enantiomers just once. Let the partition $[k_1,k_2,k_2]$ represent the carbon contents of p and A under the condition of $k_1 + 2k_2 = 9$. Then, the number of enantiomeric pairs is calculated by using the coefficients of the terms containing $y$, which appear in the right-side of eq. 54. Thereby we obtain the following numbers for respective partitions:

- $[9,0,0]$: $102 \times 1 \times 1 = 102$
- $[7,1,1]$: $20 \times 1 \times 1 = 20$
- $[5,2,2]$: $3 \times 1 \times 1 = 3$

total: 125

Because there exist two enantiomers for each of 125 enantiomeric pairs on the basis of 45 or 46, we obtain the number of alkanes at issue to be $125 \times 2 \times 2 = 500$, which is equal to the coefficient of the term $500x^{19}y^3z$.

Centroidal Alkanes of Type III Table 3 collects the coefficient $B_{k\ell m}^{III}$ of each term $x^ky^\ell z^m$, which is calculated by means of $B_{k\ell m}^{III}(x,y,z)$ (eq. 38). Each of the coefficients is stored in the series obtained as $B_{typeIII}$ of the code “Alkane1-30b.mpl”.

The value 920 at the intersection between the $(k = 19, m = 1)$-row and the $(\ell = 4)$-column corresponds to the term $920x^{19}y^4z$. On the analogy of the formula 40 or 41 in Fig. 6, we can adopt the same alkyl ligand having one pseudoasymmetric center as 40 (or 41), so that each of the 920 alkanes is represented by one of the formulas 47—50. The symbols A and B represent
obtain the number of alkanes at issue to be 115. 

Note that because there exist two enantiomers for each of 115 pairs on the basis of one of the coefficients appearing in the right-side of eq. 53 (for $k_2$ and $k_3$) and in the one of eq. 54 (for $k_1$). The following partitions are effective to maintain the Type-III nature of centroidal alkanes:

![Table 3: Centroidal Alkanes of Type III (Chiral/RS-Stereogenic/Scleral)](image)

Two chiral alkanes of each enantiomeric pair are counted separately.

a hydrogen atom or an achiral ligand, while the symbol p is a chiral ligand with one asymmetric center. The ligands A, B, and p are so selected as to keep the central atom $\mathbb{C}$ being a centroid. Note that 47 and 48 are RS-diastereomeric and 49 and 50 are RS-diastereomeric in accord with the Type-III nature of these alkanes.

Let the partition $|k_1, k_2, k_3|$ represent the carbon contents of p, A and B under the condition of $A \neq B$ and $k_1 + k_2 + k_3 = 9$. Then, the number of enantiomeric pairs is calculated by using the coefficients appearing in the right-side of eq. 53 (for $k_2$ and $k_3$) and in the one of eq. 54 (for $k_1$). The following partitions are effective to maintain the Type-III nature of centroidal alkanes:

\[
\begin{align*}
|8,1,0| & \quad 46 \times 1 \times 1 = 46; \\
|7,2,0| & \quad 20 \times 1 \times 1 = 20 \\
|6,3,0| & \quad 8 \times 2 \times 1 = 16; \\
|6,2,1| & \quad 8 \times 1 \times 1 = 8 \\
|5,4,0| & \quad 3 \times 3 \times 1 = 9; \\
|5,3,1| & \quad 3 \times 2 \times 1 = 6 \\
|4,5,0| & \quad 5 \times 1 \times 1 = 5; \\
|4,4,1| & \quad 1 \times 3 \times 1 = 3 \\
|4,3,2| & \quad 1 \times 2 \times 1 = 2; \\
\end{align*}
\]

total: 115

Because there exist two enantiomers for each of 115 pairs on the basis of one of 47—50, we obtain the number of alkanes at issue to be 115 $\times$ 2 $\times$ 4 = 920, which is equal to the coefficient of the term $920x^{19}y^4z^2$. 

- 535 -
Figure 9: Chiral centroidal alkanes of Type III corresponding to the term $920x^{19}y^4z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbols A and B represent a hydrogen atom or achiral alkyl ligands, while p represents a chiral alkyl ligand with one asymmetric center. The alkyl ligands are selected from alkyl ligands of carbon content 1–8 to keep the central atom $\circ$ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

**Centroidal Alkanes of Type IV** The coefficient $B_{k\ell m}^{(IV)}$ of the term $x^k y^\ell z^m$ is calculated by means of $B_{k\ell m}^{(IV)}(x,y,z)$ (eq. 39), where each coefficient is stored in the series named $B_{\text{typeIV}}$ in the code “Alkane1-30b.mpl”. The results of calculation are listed in Table 4.

Figure 10: Achiral centroidal alkanes of Type IV corresponding to the term $130x^{19}y^2z$, where one substituent is an achiral alkyl ligand having a pseudoasymmetric center. The symbol A and B represents a hydrogen atom or an alkyl ligand, where A may be equal to B. The ligands A and B are selected to keep the central atom $\circ$ being a centroid. An appropriate enantiomer of a pair is depicted as a representative.

To illustrate the generation of alkanes by substituting alkyl ligands, let us examine the value 130 at the intersection between the $(k = 19, m = 1)$-row and the $(\ell = 2)$-column in Table 4, which corresponds to the term $130x^{19}y^2z$. This means that there exist 130 achiral centroidal alkanes of Type IV which have two asymmetric centers and one pseudoasymmetric center according to Criteria 1 and 2. On a similar line to the formula 40 or 41 in Fig. 6, each of the 130 alkanes is represented by the formula 51 or 52 (Fig. 10), where the symbols A and B represents a hydrogen atom or an alkyl ligand. The ligands A and B are selected to keep the central atom $\circ$ being a centroid.

Let the partition $[k_1, k_1, k_2]$ represent the carbon contents of A, A and B under the condition that A may be equal to B and we put $2k_1 + k_3 = 9$. Then, the number of constitutional isomers is calculated by using the coefficients appearing in the right-side of eq. 53 (for $k_1$ and $k_2$). The following partitions are effective to maintain the Type-IV nature of centroidal alkanes:
Because the 65 constitutional isomers are achiral and have the formula $51$ or $52$, the number of alkanes at issue is calculated to be $65 \times 2 = 130$, which is equal to the coefficient of the term $130x^{19}y^{2}z$.

Centroidal Alkanes of Type V Table 5 lists the coefficient $B_{k\ell m}^{(V)}$ of the term $x^{k}y^{\ell}z^{m}$, which is calculated by means of $B_{k\ell}^{(V)}(x,y,z)$ (eq. 40). Each of the coefficients is stored in the series obtained as $B_{\text{type V}}$ of the code “Alkane1-30b.mpl”.

The examination of the value 12 at the intersection between the $(k = 12, m = 1)$-row and the
Table 5: Centroidal Alkanes of Type V (Achiral/RS-Stereogenic/Scleral)

<table>
<thead>
<tr>
<th>Carbon (k)</th>
<th>No. of P. C. (m)</th>
<th>No. of Asymmetric Centers (ℓ)</th>
</tr>
</thead>
<tbody>
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<td>k = 1:</td>
<td>m = 0: 0</td>
<td>ℓ = 0 1 2 3 4 5 6 7 8 9 10 11 12</td>
</tr>
<tr>
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<td>k = 2: m = 0: 0</td>
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</tr>
<tr>
<td></td>
<td>k = 3: m = 0: 0</td>
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<td>k = 4: m = 0: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>k = 5: m = 0: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>k = 6: m = 0: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>k = 7: m = 0: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>k = 8: m = 0: 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>k = 9: m = 0: 0</td>
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</tr>
<tr>
<td></td>
<td>k = 10: m = 0: 0</td>
<td></td>
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<td>k = 30: m = 0: 0</td>
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</tbody>
</table>

- 538 -
Figure 11: Achiral centroidal alkanes of Type V corresponding to the term $12x^{12}y^{2}z$. They are typical examples of pseudoasymmetric molecules.

$(\ell = 2)$-column of Table 5 (corresponding to the term $12x^{12}y^{2}z$) is illustrative to understand typical pseudoasymmetric cases. The 12 achiral centroidal alkanes of Type V have two asymmetric centers and one pseudoasymmetric center under Criteria 1 and 2. The total carbon content 12 restricts the carbon contents of involved chiral ligands, so that a pair involved in each of the centroidal alkanes should be selected from one pair of enantiomeric butan-2-yl ligands (carbon content 4) or from three pairs of enantiomeric ligands of carbon content 5 (cf. eq. 54). For the list of these enantiomeric ligands, see the bottom part of Fig. 7. As a result, the 12 achiral centroidal alkanes of Type V have structures shown in Fig. 11.

### 3.2.5 Comparison with Previous Results

**Achiral Centroidal Alkanes**

The total numbers of achiral centroidal alkanes can be obtained as the coefficients $A_{k\ell m}$ of the term $x^{k}y^{\ell}z^{m}$ appearing in $A(x, y, z)$ (eq. 43), which is stored in the series obtained as $A_{h}$ of the code “Alkane1-30b.mpl”. The results of calculation are listed in Table 6. Because we can put

$$A_{k\ell m} = B_{k\ell m}^{(IV)} + B_{k\ell m}^{(V)},$$

each value of Table 6 can be obtained by summing up corresponding values appearing in Table 4 and Table 5.

The total number of achiral centroidal alkanes of carbon content $k$ is calculated by using eq. 34 as follows:

$$\hat{A}_{k} = B_{k}^{(IV)} + B_{k}^{(V)} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} A_{k\ell m},$$

(56)
Table 6: Achiral Centroidal Alkanes (Type IV and Type V)

<table>
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<tr>
<th>Carbon No.</th>
<th>Cont. ($k$)</th>
<th>P. C. ($m$)</th>
<th>No. of Asymmetric Centers ($\ell$)</th>
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<td>$k = 30$:</td>
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The total numbers $\hat{A}_k$ ($k = 1$ to $20$) have been directly obtained as a generating function and collected in Table 2 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning $k = 20$ (Table 6) are summed up to give the following result:

$$
\begin{array}{cccccc}
 k = 20: & m = 0: & 3767 & 3767 & & & \\
 & m = 1: & 0 & 0 & 2474 & 0 & 810 & 0 & 80 & 3364 & & \\
 & m = 2: & 0 & 0 & 0 & 0 & 18 & & & & 18 & \\
\end{array}
$$

The total number $7149$ is equal to the value reported previously in Table 2 of Ref. [24].

Moreover, the functional equation for calculating the total numbers (eq. 38 of Ref. [24]) can be derived by starting from eq. 43. When we put $y = z = 1$ in eq. 43, we obtain the following equation:

$$
A(x, 1, 1) = B^{(IV)}(x, 1, 1) + B^{(V)}(x, 1, 1)
\frac{x}{2} \left\{ a(x, 1, 1)^2 c(x^2, 1, 1) + c(x^4, 1, 1) \right\}.
$$

The latter equation (eq. 58) can be directly obtained from eq. 24, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. Note that the coefficient of the term $x^k$ in $B^{(\tau)}(x, 1, 1)$ ($\tau = I, II, \ldots, V$) is equal to the value of $B_k^{(\tau)}$ (eq. 34). By putting $A(x, 1, 1) = \hat{A}(x), a(x, 1, 1) = a(x),$ and $c(x^2, 1, 1) = c(x^2),$ eq. 58 is converted into the following functional equation:

$$
\hat{A}(x) = \frac{x}{2} \left( a(x)^2 c(x^2) + c(x^4) \right),
$$

which is identical with eq. 38 of Ref. [24].

**Chiral Centroidal Alkanes** The total numbers of chiral centroidal alkanes can be obtained as the coefficients $C_{k\ell m}$ of the term $x^k y^\ell z^m$ appearing in $C(x, y, z)$ (eq. 44), which is stored in the series obtained as Ch of the code “Alkane1-30b.mpl”. The results of calculation are listed in Table 7. Because we can put

$$
C_{k\ell m} = \frac{1}{2} \left\{ B_{k\ell m}^{(I)} + B_{k\ell m}^{(II)} + B_{k\ell m}^{(III)} \right\},
$$

each value of Table 7 can be obtained by the half of the sum of corresponding values appearing in Tables 1, 2, and 3.

The total number of chiral centroidal alkanes of carbon content $k$ is calculated by using eq. 34 as follows:

$$
\hat{C}_k = \frac{1}{2} \left\{ B_k^{(I)} + B_k^{(II)} + B_k^{(III)} \right\} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} C_{k\ell m}.
$$

The total numbers $\hat{C}_k$ ($k = 1$ to $20$) have been directly obtained as a generating function and collected in Table 2 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning $k = 20$ (Table 7) are summed up to give the following result:

$$
\begin{array}{cccccc}
 k = 20: & m = 0: & 0 & 25540 & 135307 & 318682 & 365211 & 196180 & 44580 & 3180 & 1088680 \\
 & m = 1: & 0 & 0 & 0 & 482 & 1268 & 3932 & 144 & & 2826 \\
 & m = 2: & 0 & 0 & 0 & 0 & 1 & & & & 1 \\
\end{array}
$$
The total number 1091507 is equal to the value reported previously in Table 2 of Ref. [24].

The functional equation for calculating the total numbers (eq. 40 of Ref. [24]) is regarded as a special case of eq. 44, so that it can be derived by starting from this equation. When we put $y = z = 1$ in eq. 44, we obtain the following equation:

$$C(x, 1, 1) = \frac{1}{2} \left\{ B^{(I)}(x, 1, 1) + B^{(II)}(x, 1, 1) + B^{(III)}(x, 1, 1) \right\}$$

$$= \frac{x}{24} \left\{ b(x, 1, 1)^4 + 3b(x^2, 1, 1)^2 + 8b(x, 1, 1)b(x^3, 1, 1) - 6a(x, 1, 1)^2c(x^2, 1, 1) - 6c(x^4, 1, 1) \right\}$$

(62)

By putting $C(x, 1, 1) = \hat{C}(x)$, $a(x, 1, 1) = a(x)$, $c(x^2, 1, 1) = c(x^2)$, and $b(x, 1, 1) = b(x)$, eq. 62 is converted into the following functional equation:

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

(63)

which is identical with eq. 40 of Ref. [24].

### Achiral Centroidal Alkanes and Enantiomeric Pairs of Chiral Ones

Table 8 lists the total numbers of achiral and chiral centroidal alkanes, which are obtained as the coefficients $B_{klm}$ of the term $x^k y^{l} z^m$ appearing in $B(x, y, z)$ (eq. 45). Each of the numbers is stored in the series...
Table 8: Achiral Centroidal Alkanes and Enantiomeric Pairs of Chiral Ones

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>P. C. (m)</th>
<th>No. of Asymmetric Centers (ℓ)</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>1</td>
</tr>
<tr>
<td>k = 0:</td>
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<td>k = 1:</td>
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<td>0</td>
</tr>
<tr>
<td>k = 2:</td>
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</tr>
<tr>
<td>k = 3:</td>
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</tr>
<tr>
<td>k = 4:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 5:</td>
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<td>0</td>
</tr>
<tr>
<td>k = 6:</td>
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<td>0</td>
</tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>k = 10:</td>
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</tr>
<tr>
<td>k = 11:</td>
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</tr>
<tr>
<td>k = 12:</td>
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</tr>
<tr>
<td>k = 13:</td>
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</tr>
<tr>
<td>k = 14:</td>
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<td>0</td>
</tr>
<tr>
<td>k = 15:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 16:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 17:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 18:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 19:</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>k = 20:</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The total number 1098656 is equal to the value reported previously in Table 2 of Ref. [24].
Moreover, the functional equation for calculating the total numbers (eq. 29 of Ref. [24]) can be derived by starting from eq. 45. When we put \( y = z = 1 \) in eq. 45, we obtain the following equation:

\[
B(x, 1, 1) = \frac{1}{2} \left\{ B^{(I)}(x, 1, 1) + B^{(II)}(x, 1, 1) + B^{(III)}(x, 1, 1) \right\} + B^{(IV)}(x, 1, 1) + B^{(V)}(x, 1, 1)
\]

By putting \( B(x, 1, 1) = \tilde{B}(x) \), \( a(x, 1, 1) = a(x) \), \( c(x^2, 1, 1) = c(x^2) \), and \( b(x, 1, 1) = b(x) \), eq. 65 is converted into the following functional equation:

\[
\tilde{B}(x) = \frac{x}{24} \left\{ b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3) + 6a(x)^2c(x^2) + 6c(x^4) \right\},
\]

which is identical with eq. 29 of Ref. [24].

Under the condition of \( y = z = 1 \), we obtain the following equation:

\[
B^{(I-V)}(x, 1, 1) = B^{(I)}(x, 1, 1) + B^{(II)}(x, 1, 1) + B^{(III)}(x, 1, 1) + B^{(IV)}(x, 1, 1) + B^{(V)}(x, 1, 1)(67)
\]

The latter equation (eq. 68) can be directly obtained from eq. 23, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. By putting \( B^{(I-V)}(x, 1, 1) = \tilde{E}(x) \) and \( b(x, 1, 1) = b(x) \), eq. 68 is converted into the following functional equation:

\[
\tilde{E}(x) = \frac{x}{12} \left\{ b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3) \right\},
\]

which is identical with eq. 36 of Ref. [24].

### 3.3 Enumeration of Bicentroidal Alkanes

The categorization into RS-stereoisomeric types is not so effective to treat bicentroidal alkanes, because these belong to either Type II or Type IV [29]. Hence, it is sufficient to discuss achiral and chiral bicentroidal alkanes. By using \( a(x, y, z) \) (eq. 19), \( c(x^2, y^2, z^2) \) (eq. 21), and \( b(x, y, z) \) (eq. 20), we enumerate bicentroidal alkanes on the basis of a dumbbell-like skeleton. Although the skeleton has been previously formulated without regard to RS-stereoisomeric types [24], its theoretical essence can be applied to the present enumeration after slight modification.

#### 3.3.1 Cycle Indices with Chirality Fittingness

Although the previous results concerned with centroidal alkanes [24, 27] have not taken RS-stereoisomeric types, the methodology can be applied to evaluate bicentroidal alkanes. Thus, we consider the action of the K-factor group \( K = D_{\infty h}/C_{oov} \) and its maximum chiral group \( K_2 \) on the dumbbell-like skeleton:

\[
K \sim \{(1)(2), (1\ 2)\; ; (1\ 2)(1\ 2)\}
\]

\[
K_2 \sim \{(1)(2), (1\ 2)\}
\]
Because bicentroidal alkanes are RS-astereogenic, the K-group itself can be regarded as a point subgroup and as a ligand-inversion subgroup. This means that it is sufficient to examine only the chiral/achiral nature of bicentroidal alkanes.

On the same line as the derivation of eq. 23 for T (contained in eq. 22), we collect products of SIs concerning rotoreflections of $K_2$ (eq. 71) in order to obtain a CI-CF for counting achiral plus chiral bicentroidal promolecules (i.e., Types II and IV):

$$\text{CI-CF}^{(II/IV)}(K_2; b_d) = \frac{1}{2}(b_1^2 + b_2),$$

where achiral alkanes and two enantiomers of each pair are counted separately.

On the same line as the derivation of eq. 24 for $T_d$ (eq. 22), we collect products of SIs concerning rotoreflections of $K$ (eq. 70), to obtain a CI-CF for counting achiral bicentroidal alkanes (i.e., Type IV):

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

The subtraction of eq. 74 from eq. 73 leaves the CI-CF for counting chiral bicentroidal alkanes (i.e., Type II):

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

### 3.3.2 Functional Equations for Counting Bicentroidal Alkanes

Let $\tilde{B}_{k\ell m}(\tau)$ ($\tau = II$ or IV or their combinations) be the number of bicentroidal alkanes (promolecules) of Type T, which have $k$ carbons, $\ell$ asymmetric centers and $m$ pseudoasymmetric centers. Let the symbol $\tilde{B}_{k}(\tau)$ be the summation for each type ($\tau$) represented as follows:

$$\tilde{B}_{k}(\tau) = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \tilde{B}_{k\ell m}(\tau).$$

We now regard these numbers $\tilde{B}_{k\ell m}(\tau)$ as the coefficients of the following generating functions:

$$\tilde{B}(\tau)(x^d, y^d, z^d) = \sum_{k=0}^{\infty} \left( \sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{B}_{k\ell m}(\tau) x^{d\ell} y^{dm} \right) y^d \right) x^{dk},$$

where the valuable $x$ is concerned with carbon content, the valuable $y$ is concerned with the number of asymmetric centers, and the valuable $z$ is concerned with the number of pseudoasymmetric centers. We put $\tilde{B}_{000}(\tau) = 0$ for treating the respective initial (trivial) cases.

To evaluate the generating functions (eq. 77, $d = 1$), we derive the corresponding functional equations by starting from the CI-CFs (eqs. 74 and 75). Thus, the SIs $a_d, c_d,$ and $b_d$ in these equations are replaced by $a(x^d, y^d, z^d), c(x^d, y^d, z^d),$ and $b(x^d, y^d, z^d)$ to give the following functional equations:

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

$$\tilde{B}^{(IV)}(x, y, z) = \frac{1}{2} \left\{ a(x, y, z)^2 + c(x^2, y^2, z^2) \right\}.$$
Let $\tilde{A}(x,y,z)$, $\tilde{C}(x,y,z)$, and $\tilde{B}(x,y,z)$ be functional equations for calculating the numbers of achiral, chiral, and total (achiral plus chiral) bicentroidal alkanes, where each pair of two enantiomers and each achiral alkane are respectively counted just once. Because the symbol $\tilde{B}^{(\text{II})}(x,y,z)$ (Type II: chiral/RS-astereogenic/scleral) counts two enantiomers of each pair separately, the numbers are calculated as follows:

$$\tilde{A}(x,y,z) = \tilde{B}^{(\text{IV})}(x,y,z) = \frac{1}{2} \left\{ a(x,y,z)^2 + c(x^2,y^2,z^2) \right\}$$ (80)

$$\tilde{C}(x,y,z) = \frac{1}{2} \tilde{B}^{(\text{II})}(x,y,z) = \frac{1}{4} \left\{ b(x,y,z)^2 + b(x^2,y^2,z^2) - a(x,y,z)^2 - c(x^2,y^2,z^2) \right\}$$ (81)

$$\tilde{B}(x,y,z) = \frac{1}{2} \tilde{B}^{(\text{II})}(x,y,z) + B^{(\text{IV})}(x,y,z) = \frac{1}{4} \left\{ b(x,y,z)^2 + b(x^2,y^2,z^2) + a(x,y,z)^2 + c(x^2,y^2,z^2) \right\}$$ (82)

Suppose that we have obtained $a(x,y,z) = \sum_{\mu=0}^{\mu} \alpha_k x^k$, $c(x^2,y^2,z^2) = \sum_{0}^{\mu} \gamma_k x^{2k}$, and $b(x,y,z) = \sum_{k=0}^{\mu} \beta_k x^k$, where $\mu$ is tentatively fixed. They are introduced into eqs. 80–82 so as to give $\tilde{A}(x,y,z)(\mu)$, $\tilde{C}(x,y,z)(\mu)$, and $\tilde{B}(x,y,z)(\mu)$, where the coefficient of the resulting term $x^{2\mu}$ is effective after expansion. Note that the coefficient is a polynomial containing $y^c z^m$. Thereby, we obtain the following coefficients:

$$\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{A}(2\mu) c^m \right) y^\ell = \text{coeff}(\tilde{A}(x,y,z)(\mu), x^{2\mu})$$ (83)

$$\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{C}(2\mu) c^m \right) y^\ell = \text{coeff}(\tilde{C}(x,y,z)(\mu), x^{2\mu})$$ (84)

$$\sum_{\ell=0}^{\infty} \left( \sum_{m=0}^{\infty} \tilde{B}(2\mu) c^m \right) y^\ell = \text{coeff}(\tilde{B}(x,y,z)(\mu), x^{2\mu})$$ (85)

### 3.3.3 Programming and Implementation

The recursive calculations of $a(x^d, y^d, z^d)$, $c(x^d, y^d, z^d)$, and $b(x^d, y^d, z^d)$ in the right-hand sides of eqs. 80–82 are the same as described in the code “Alkane1-30b.mpl”, although they are omitted. The paragraph “Alkanes as Centroidal 3D-Trees” in the code “Alkane1-30b.mpl” is replaced as follows in the code “BAAlkane1-30b.mpl” for calculating bicentroidal alkanes:

```plaintext
# BAAlkane1-30b.mpl
(collapsed)
"Alkanes as Bicentroidal 3D-Trees":
Bxt := (1/4) * (b111^2 + b222 + a111^2 + c222);
Bxt := (1/2) * (a111^2 + c222);
Cxt := (1/4) * (b111^2 + b222 - a111^2 - c222);
```

in accord with eqs. 80–82. The storage part from the line “q := 2*k + 1;” to the line “end do;” is replaced as follows:

```plaintext
q := 2*k;
Bt := Bt + coeff(Bxt,x^q)*x^q;
At := At + coeff(Axt,x^q)*x^q;
Ct := Ct + coeff(Cxt,x^q)*x^q;
end do;
```

which is in agreement with the bicentroidal nature of alkanes to be counted (cf. eqs. 83–85).
3.3.4 Results and Illustrative Examples

Achiral Bicentroidal Alkanes  Table 9 lists the coefficient \( \tilde{A}_{k\ell m} \) of the term \( x^k y^\ell z^m \) calculated by means of \( \tilde{A}(x,y,z) \) (eq. 80), where each coefficient is stored in the series obtained as \( \texttt{At} \) of the code “\texttt{BAlkane1-30b.mpl}”.

<table>
<thead>
<tr>
<th>Carbon No. of Asymmetric Centers (( \ell ))</th>
<th>No. of Asymmetric Centers (( \ell ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cont. (( k ))</td>
<td>P. C. (( m ))</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>( k = 2 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 4 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 6 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 8 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 10 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 12 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 14 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 16 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( k = 18 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 20 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 22 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 24 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 26 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 28 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
<tr>
<td>( k = 30 )</td>
<td>( m = 0 )</td>
</tr>
<tr>
<td>( m = 1 )</td>
<td>0</td>
</tr>
<tr>
<td>( m = 2 )</td>
<td>0</td>
</tr>
</tbody>
</table>

The value 6 at the intersection between the \((k = 8, m = 0)\)-row and the \((\ell = 0)\)-column in Table 9 corresponds to the term \(6x^8\). Hence, there exist six achiral bicentroidal alkanes (65–70) which have no asymmetric center and no pseudoasymmetric center, as depicted in Fig. 12.

On the other hand, the value 1 at the intersection between the \((k = 8, m = 0)\)-row and the \((\ell = 2)\)-column in Table 9 corresponds to the term \(6x^8y^2\). Hence, there exists one achiral bicentroidal alkane (71) which has two asymmetric center and no pseudoasymmetric center (a meso-case).

The seven alkanes collected in Fig. 12 have been already illustrated in Fig. 6 of Ref. [24], where they are not itemized with respect to the number of asymmetric centers. The present enumeration discriminates such meso-cases as 71 from cases in which two terminal alkyl ligands are alkyl ligands having no asymmetric centers and no pseudoasymmetric centers. As a result, the value \(\tilde{A}_{k00}\) at the intersection between the \((k, m = 0)\)-row and the \((\ell = 0)\)-column can be calculated by using the data \(\alpha_{(k/2)00}\) (cf. eq. 53), i.e., \(\tilde{A}_{k00} = \alpha_{(k/2)00}(\alpha_{(k/2)00} + 1)/2\). For example, we obtain \(39 \times (39 + 1)/2 = 780\), which is equal to the value appearing at the intersection between the \((k = 18, m = 0)\)-row and the \((\ell = 0)\)-column in Table 9.

The total number of achiral bicentroidal alkanes of carbon content \(k\) is calculated by using eq. 76 as follows:

\[
\tilde{A}_k = \tilde{B}_k^{\text{IV}} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \tilde{A}_{k\ell m}.
\]
Figure 12: Six achiral bicentroidal alkanes (65–70) corresponding to the term $6x^8$ as well as one achiral bicentroidal alkane (71) corresponding to the term $x^8y^2$.

The total numbers $\tilde{A}_k$ ($k = 1$ to 20) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning $k = 20$ (Table 9) are summed up to give the following result:

<table>
<thead>
<tr>
<th>$k = 20$:</th>
<th>$m = 0$:</th>
<th>2145</th>
<th>0</th>
<th>220</th>
<th>0</th>
<th>366</th>
<th>0</th>
<th>148</th>
<th>0</th>
<th>8</th>
<th>2887</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m = 1$:</td>
<td>0</td>
<td>0</td>
<td>260</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>260</td>
</tr>
<tr>
<td>$m = 2$:</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

The total number 3157 is equal to the value reported previously in Table 3 of Ref. [24].

The numerical confirmation described above can be traced in general. Thus, the functional equation for calculating the total numbers (eq. 56 of Ref. [24]) can be derived by starting from eq. 80. When we put $y = z = 1$ in eq. 80, we obtain the following equation:

$$
\tilde{A}(x, 1, 1) = \tilde{B}^{(IV)}(x, 1, 1) = x \left\{ a(x, 1, 1)^2 + c(x^2, 1, 1) \right\}
$$

The latter equation (eq. 88) can be directly obtained from eq. 74, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. Note that the coefficient of the term $x^k$ in $\tilde{B}^{(IV)}(x, 1, 1)$ is equal to the value of $\tilde{B}_k^{(IV)}$ (eq. 76). By putting $\tilde{A}(x, 1, 1) = \tilde{A}(x)$, $a(x, 1, 1) = a(x)$, and $c(x^2, 1, 1) = c(x^2)$, eq. 88 is converted into the following functional equation:

$$
\tilde{A}(x) = \frac{1}{2} \left\{ a(x)^2 + c(x^2) \right\},
$$

which is identical with eq. 56 of Ref. [24].

**Chiral Bicentroidal Alkanes** Table 10 lists the coefficient $\tilde{C}_{k\ell m}$ of the term $x^k y^\ell z^m$, which is calculated by means of $\tilde{C}(x, y, z)$ (eq. 81) and stored in the series obtained as $Ct$ of the code “BAlkane1-30b.mpl”.
Table 10: Enantiomeric Pairs of Chiral Bicentroidal Alkanes

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>No. of Cont. (ℓ)</th>
<th>No. of Asymmetric Centers (k)</th>
<th>P. C. (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ℓ = 0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>k = 2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>k = 4</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 4</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>k = 6</td>
<td>0</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 6</td>
<td>0</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>k = 8</td>
<td>0</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 8</td>
<td>0</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>k = 10</td>
<td>0</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 10</td>
<td>0</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>k = 12</td>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 12</td>
<td>0</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>k = 14</td>
<td>0</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 14</td>
<td>0</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td>k = 16</td>
<td>0</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>ℓ = 16</td>
<td>0</td>
<td>30</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 13: Three chiral bicentroidal alkanes (72–74) of corresponding to the term 3x^k y and one chiral bicentroidal alkane (75) of corresponding to the term x^k y^2. An appropriate chiral alkane is depicted as a representative of each pair of enantiomers.

To illustrate the data of Table 10, let us examine the value 3 at the intersection between the (k = 8, m = 0)-row and the (ℓ = 1)-column, where the value corresponds to the term 3x^k y. The value 3 indicates that there exist three pairs of chiral bicentroidal alkanes (72–74) which have one asymmetric center and no pseudoasymmetric center, as depicted in the first row of Fig. 13. This result can be confirmed by the fact that there exist one enantiomeric pair of chiral butan-2-yl ligands (cf. eq. 54) and three achiral ligands of carbon content 4 (cf. eq. 53).

On the other hand, the value 1 at the intersection between the (k = 8, m = 0)-row and the (ℓ = 2)-column in Table 10 corresponds to the term x^k y^2. Hence, there exists one chiral bicentroidal alkane (75) which has two asymmetric centers and no pseudoasymmetric center, as shown in the second row of Fig. 13.

The four alkanes collected in Fig. 13 have been already illustrated in Fig. 6 of Ref. [24], where they are not itemized with respect to the number of asymmetric centers. The present enumeration discriminates the cases having one asymmetric center (72–74) from the case having two asymmetric centers (75).

The total number of chiral bicentroidal alkanes of carbon content k is calculated by using
\[ \tilde{C}_k = \frac{1}{2} \tilde{B}^{(II)}_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \tilde{C}_{k \ell m}. \]  

(90)

The total numbers \( \tilde{C}_k \) (\( k = 1 \) to \( 20 \)) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are numerically confirmed by the present itemized enumeration. For example, the rows concerning \( k = 20 \) (Table 10) are summed up to give the following result:

\[
\begin{array}{cccccccccccc}
  k = 20: & m = 0: & 0 & 14300 & 72190 & 170660 & 199596 & 111856 & 27760 & 2368 & 64 & 598794 \\
  m = 1: & 0 & 0 & 0 & 880 & 1464 & 592 & 32 & 27792 & 2368 & 64 & 601762 \\
  m = 2: & 0 & 0 & 0 & 0 & 10 & 10 & 10 & 10 & 10 & 10 & 10 \\
\end{array}
\]

The total number 601762 is equal to the value reported previously in Table 3 of Ref. [24].

In addition to the numerical confirmation, the functional equation for calculating the total numbers (eq. 58 of Ref. [24]) can be algebraically derived by starting from eq. 81. When we put \( y = z = 1 \) in eq. 81, we obtain the following equation:

\[
\tilde{C}(x, 1, 1) = \frac{1}{4} \left\{ b(x, 1, 1)^2 + b(x^2, 1, 1) - a(x, 1, 1)^2 - c(x^2, 1, 1) \right\}
\]

(91)

The latter equation (eq. 91) can be directly obtained from eq. 75, where we take no account of the numbers of asymmetric and pseudoasymmetric centers. By putting \( \tilde{C}(x, 1, 1) = \tilde{C}(x) \), \( a(x, 1, 1) = a(x) \), and \( c(x^2, 1, 1) = c(x^2) \), eq. 91 is converted into the following functional equation:

\[
\tilde{C}(x) = \frac{1}{4} \left\{ b(x)^2 + b(x^2) - a(x)^2 - c(x^2) \right\},
\]

(92)

which is identical with eq. 58 of Ref. [24].

Achiral Bicentroidal Alkanes and Enantiomeric Pairs of Chiral Ones Table 11 lists the coefficient \( \tilde{B}_{k \ell m} \) of the term \( x^k y^\ell z^m \) calculated by means of \( \tilde{B}(x, y, z) \) (eq. 82), where each coefficient is stored in the series obtained as \( B \) of the code “BAlkane1-30b.mpl”.

The total number of bicentroidal alkanes of carbon content \( k \) is calculated by using eq. 76 as follows:

\[ \tilde{B}_k = \frac{1}{2} \tilde{B}_k^{(II)} + \tilde{B}_k^{(IV)} = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} \tilde{B}_{k \ell m}. \] 

(93)

The total numbers \( \tilde{B}_k \) (\( k = 1 \) to \( 20 \)) have been directly obtained as a generating function and collected in Table 3 of Ref. [24]. They are confirmed by the present itemized enumeration. For example, the rows concerning \( k = 20 \) (Table 11) are summed up to give the following result:

\[
\begin{array}{cccccccccccc}
  k = 20: & m = 0: & 2145 & 14300 & 72410 & 170660 & 199962 & 111856 & 27908 & 2368 & 72 & 601681 \\
  m = 1: & 0 & 0 & 0 & 260 & 880 & 1464 & 592 & 32 & 27940 & 2368 & 64 & 604919 \\
\end{array}
\]

The total number 604919 is equal to the value reported previously in Table 3 of Ref. [24].
Moreover, the functional equation for calculating the total numbers (eq. 52 of Ref. [24]) can be derived by starting from eq. 82. When we put $y = z = 1$ in eq. 82, we obtain the following equation:

$$\hat{B}(x, 1, 1) = \frac{1}{2} \hat{B}^{(II)}(x, 1, 1) + \hat{B}^{(IV)}(x, 1, 1) = \frac{1}{4} \left\{ b(x, 1, 1)^2 + b(x^2, 1, 1) + a(x, 1, 1)^2 + c(x^2, 1, 1) \right\}$$  

(94)

By putting $\hat{B}(x, 1, 1) = \hat{B}(x)$, $a(x, 1, 1) = a(x)$, and $c(x^2, 1, 1) = c(x^2)$, eq. 94 is converted into the following functional equation:

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

(95)

which is identical with eq. 52 of Ref. [24].

4 Conclusions

A criterion for specifying asymmetric and pseudoasymmetric centers in alkanes has been developed on the basis of three kinds of attributes of $RS$-stereoisomers (chirality, $RS$-stereogenicity, and sclerality), which were formulated by a recently-developed method [29]. The three kinds of attributes are capable of defining five $RS$-stereoisomeric types (Types I–V), so that $RS$-stereogenic promolecules (Type I, III, and V) are divided into chiral (Types I and III) and achiral ones (Type V). After another criterion has been formulated to select entities for the application of the first criterion, the central atom of each promolecule of Types I and III is defined as an asymmetric center, while the central atom of each promolecule of Type V is defined as a pseudoasymmetric center. According to the Criteria, alkyl ligands (equivalently, monosubstituted alkanes) have been regarded as nested planted promolecules, where each participating planted promolecule is categorized into an asymmetric (Types I/III), a pseudoasymmetric (Type V), or a
symmetric one (Types II/IV). Thereby, they have been counted combinatorially with itemization with respect to carbon content \((k)\), to the number of asymmetric carbons \((\ell)\), as well as to the number of pseudoasymmetric carbons \((m)\). The data of alkyl ligands stored as generating functions have been used to count centroidal and bicentroidal alkanes on the basis of a tetrahedral skeleton, where the criteria are effective to categorize alkanes into Types I–V. Each itemized number has been obtained as the coefficient of the term \(x^k y^\ell z^m\) appearing in a respective generating function, which has been derived by following Fujita’s proligand method [17–19]. The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with Type I, \ldots, or Type V as well as with achiral stereoisomers and chiral stereoisomers.

References

Such locally chiral nature of a site is characterized by the term “chirotopic”, whether the site is contained in an achiral or chiral 3D-object [39]. We have emphasized an equivalence class (orbit) of sites, which is characterized as being enantiospheric or hemispheric [53–55].

The present argument indicates that a pair of p/\bar{p} for Type V (pseudoasymmetry) is discriminated from pairs of p/\bar{p} for Type I and III (asymmetry) in agreement with the incapability/capability of generating enantiomers. In other words, the present Criterion reinforces the original conclusion of Prelog and Helmchen’s arguments [36]. From this point of view, the “pseudoasymmetry” due to the revised CIP system [37] means that pairs of p/\bar{p} for Types III and V are discriminated from a pair of p/\bar{p} for Type I (cf. Fig. 7 below). On the other hand, the vigorous disputation by Hirschmann and Hanson [56] to the Prelog and Helmchen’s arguments [36] implies that pairs of p/\bar{p} for Types I, III, and V exhibit “pseudoasymmetric” nature all together, although cases of Type I have not been explicitly discussed. If pairs of p/\bar{p} of Types I, III, and V are brought all together, they are not necessary to be discriminated from other proligands in Types I, III, or V. Thus, the Hirschmann and Hanson’s argument [56] implies, despite of their intention, that the term “pseudoasymmetry” is no longer necessary because the term “RS-stereogenic” is sufficient under the condition that p and \bar{p} can be discriminated as 3D-objects in isolation. Rigorously speaking, we should adopt Type I, III, or V for an RS-stereogenic center in place of the term asymmetric or pseudoasymmetric. Even in this case, however, such an appropriate criterion as Criterion 2 is necessary to be defined.

Note that the concept of centroidal/bicentroidal trees was originally formulated as graphs by Jordan [57] and applied to the enumeration of trees (as graphs) by Pólya [5, 6].
In the enumeration of alkanes, we have defined a chemical set of terms promolecule and proligands (planted promolecules) and a mathematical set of terms 3D-trees and planted 3D-trees to abstract essential symmetrical properties of a more concrete set of terms alkanes and monosubstituted alkanes (alkyl ligands). See Ref. [21, 24]. To do well with these sets of terms in the present paper, promolecular representations shown in Fig. 1 are used to demonstrate the chemical set, while carbon-skeletal representations demonstrate the mathematical set. Centroidal representations intermediate between the promolecular representations and carbon-skeletal representations.

The term “asymmetric center” has been referred to as an out-dated term that usually should be replaced by “stereogenic center (unit)” or “chirality center” [58]. From the present viewpoint, however, problematic is the transmuted usage of the term “asymmetric center” so as to cover an erroneous connotation “asymmetric center ⊃ pseudoasymmetric center” in place of a more plausible connotation “stereogenic center ⊃ pseudoasymmetric center”. The plausible connotation implies that the concept of chirality is a subsidiary concept beneath the concept of stereogenicity, i.e., “stereogenic center = chirality center + pseudoasymmetric center”. In contrast, the present methodology is based on the concept of RS-stereogenicity which appears in a stereoisogram, independent of the concept of chirality. Hence, we can recognize that “RS-stereogenic center = asymmetric center + pseudoasymmetric center”, where the term “asymmetric center” is adopted in place of the term “chirality center”.


