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Numbers of Achiral and Chiral Monosubstituted Alkanes Having a Given Carbon Content and Given Numbers of Asymmetric and Pseudoasymmetric Centers

Shinsaku Fujita

Shonan Institute of Chemoinformatics and Mathematical Chemistry,
Kaneko 479-7 Ooimachi, Ashigara-Kami-gun, Kanagawa 258-0019

Received May 9, 2007; E-mail: fujitas@chem.kit.ac.jp

Monosubstituted alkanes as stereoisomers have been counted combinatorially by regarding them as nested planted promolecules, where the resulting numbers have been itemized with respect to carbon content (k), to the number of asymmetric carbons (ℓ), as well as to the number of pseudoasymmetric carbons (m). To accomplish such itemization, the definitions of *RS*-stereogenic centers, asymmetric centers, and pseudoasymmetric centers have been discussed in detail. 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 (S. Fujita, *Theor. Chem. Acc.* **2005**, *113*, 73; **2005**, *113*, 80; S. Fujita, *Theor. Chem. Acc.* **2006**, *115*, 37). The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with achiral stereoisomers, chiral stereoisomers, and constitutional isomers (graphs).

Asymmetric carbon atoms have been emphasized as sources of stereoisomerism by van't Hoff[1] at the beginning of stereochemistry, when the number of stereoisomers having ℓ asymmetric carbons was demonstrated to be equal to 2^ℓ except such special cases as *meso*-compounds (e.g., tartaric acids). This value was obtained on an implicit condition that the stereoisomers at issue were derived from a given skeleton and so their carbon contents (or generally their constitutions) were fixed. In other words, a relationship between the carbon content k and the number of asymmetric carbons ℓ was considered to be given as a prerequisite. Such a relationship, however, is not always obvious in general cases, so that it remains as a challenging problem to obtain the number of stereoisomers of carbon content k which have ℓ asymmetric carbons.

Because of the lack of suitable methodology, the problem has not been fully solved even in such simple cases as alkanes and monosubstituted alkanes, as found in reviews[2–5] and books.[6–10] Thus, most previous enumerations of alkanes and monosubstituted alkanes of given carbon contents did not take into account the numbers of asymmetric carbons, as discussed in several articles reported by Cayley,[11,12] Henze and Blair,[13] Pólya[14,15] (in most parts except Section 42), and Otter.[16] Moreover, the enumerated compounds were regarded as graphs (chemically speaking, as constitutional isomers), not as stereoisomers. Although Robinson et al.[17] enumerated alkanes and monosubstituted alkanes of given carbon contents as stereoisomers, their enumeration results did not properly take account of *meso*-compounds and pseudoasymmetric cases and, moreover, the results were not concerned with the numbers of asymmetric carbons. More recent papers on the enumeration of alkanes and related compounds, which were conducted by Quintas and Yarmish,[18] by Balasubramanian,[19–22] by Bytautas and Klein,[23] as well as by Nemba and Emadak,[24] took account of gross chiralities/achiralities of compounds. However, their results have not yet been concerned with the numbers of asymmetric carbons nor with the numbers of pseudoasymmetric carbons. In other words, the concept of sphericities,[25] which controls such inner structures as chiral or achiral ligands (not only the gross chiralities/achiralities of compounds[26,27]) through sphericity indices (i.e., a_d, c_d, and b_d), has not been fully taken into consideration. For the state of the art in this field, recent extensive reviews by Trinajstić et al.[28,29] should be consulted.

To the best of our knowledge, an exception was Section 42 of Pólya's article,[14,15] which took account of asymmetric carbon centers in the enumeration of monosubstituted alkanes. However, Pólya's theorem used therein overlooked the problems of *meso*-compounds and pseudoasymmetry, because its application was inevitably restricted to graphs or, chemically speaking, to constitutional isomers, as we have pointed out in our recent article entitled "Sphericities of Cycles. What Pólya's Theorem is Deficient In for Stereoisomer Enumeration."[30]

We have recently developed the proligand method for enumerating stereoisomers,[31–33] where we integrated the concepts of proligands and promolecules[34–36] and the concept of spher-

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icities[25] so as to enumerate stereoisomers with inner structures in general. The merit of Fujita's proligand method in comparison with Pólya's theorem has been briefly discussed in an article of ours.[30] Fujita's proligand method has been applied to enumerate monosubstituted alkanes[37–39] and alkanes,[40–42] where *meso*-cases and pseudoasymmetric cases were treated properly. In particular, the idea of promolecules having proligands has been applied recursively so as to provide us with the proper evaluation of nonrigidity due to the internal rotation of each methyl group in alkanes and monosubstituted alkanes. Although the concept of wreath products (i.e., Pólya's corona[14,15]) has been applied to evaluate such nonrigidity, its applications have been limited to graphs. Because the recursive application of such promolecules having proligands is concerned with stereoisomers having inner structures, on the other hand, it has a merit over the application of the concept of wreath products. Since the enumeration results of the proligand method were concerned with carbon contents, a remaining problem is to take account of the numbers of asymmetric and pseudoasymmetric centers.

In the present paper, we first make a clear distinction between asymmetric and pseudoasymmetric centers by applying a classification scheme developed for *RS*-stereoisomers.[43] Thereby, we enumerate achiral and chiral monosubstituted alkanes of carbon content k which have ℓ asymmetric carbons and m pseudoasymmetric carbons by using Fujita's proligand method. In particular, we take pseudoasymmetric cases into proper consideration so as to ensure stereoisomer enumeration in terms of Fujita's proligand method and to go further beyond the graph enumeration by Pólya's theorem.

Monosubstituted Alkanes as Stereoisomers

Asymmetric and Pseudoasymmetric Centers. To accomplish such itemized enumeration, the conventional terms "asymmetric," "pseudoasymmetric," and "stereogenic" should be defined distinctively, where we shall introduce the term *RS*-stereogenic as a more distinguishable term than the conventional term "stereogenic."

Because the original usage of the term "asymmetric atom (center)"[1] was transmuted so as to have an inappropriate connotation represented as "asymmetric center $\supset$ pseudoasymmetric center," it has been referred to as an out-dated term that usually should be replaced by "stereogenic center (unit)" or "chirality center."[44] This attitude toward the term "asymmetric atom (center)" was based on a convincing discussion by Mislow and Siegel[45] and came directly from the revision of the CIP system for naming stereoisomers,[46] where the terms "stereogenic center (unit)" and "pseudoasymmetric stereogenic center (unit)" were used in place of the terms "asymmetric atom" and "pseudoasymmetric atom." Note that the term "asymmetric" having the transmuted connotation has been replaced by the term "stereogenic."

Although the transmuted connotation of the term "asymmetric atom (center)" should be replaced by the term "stereogenic center (unit)," the term "asymmetric atom (center)" as its original usage is still effective to mention the difference from the term "pseudoasymmetric atom (center)." In other words, the inappropriate connotation represented by "asymmetric atom $\supset$ pseudoasymmetric atom" can be avoided by adopting the classification represented by "stereogenic center = (asymmetric) stereogenic center + pseudoasymmetric stereogenic center" or simply by the following conceptual scheme:

$$\begin{aligned}&\text{stereogenic center} =\\ &\quad \text{asymmetric center} + \text{pseudoasymmetric center}. \qquad (1)\end{aligned}$$

Even when we adopt the classification shown by Eq. 1, however, there still remains an ambiguity between "asymmetric" and "pseudoasymmetric" according to stereochemical convention, because reflection invariant descriptors r and s have been extended in the revised CIP system so as to be applied to chiral compounds as well as achiral compounds.[46] Note that the original usage of "pseudoasymmetric" and that of the descriptors r and s are concerned with achiral compounds only.[47] To take account of asymmetric and pseudoasymmetric centers in our task of enumerating monosubstituted alkanes, we shall develop succinct and unmistakable definitions of them.

We have recently developed the concept of *RS*-stereoisomers (i.e., enantiomers, *RS*-diastereomers, and holantimers) by using stereoisograms newly defined for restructuring stereochemistry.[43] Moreover, we have coined a set of terms to specify stereochemical features of compounds, i.e., *RS*-stereogenicity (for characterizing *RS*-diastereomers) and sclerality (for characterizing holantimers) in addition to chirality (for characterizing enantiomers). By combining the three terms of the set, we have clarified that tetrahedral compounds are categorized into five 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). This categorization has proven to be suitable for specifying pseudoasymmetric centers, which are ascribed to the carbon centers of Type V compounds.[48]

When we adopt the categorization (Types I–V),[48] the term *RS*-stereogenic center is used to specify the carbon center of an *RS*-stereogenic compound (Type I, III, or V); the term asymmetric center is used to specify a carbon center of Type I or III; and the term pseudoasymmetric center is used to specify a carbon center of Type V. Thereby, we obtain the following conceptual scheme:

$$\begin{aligned}&\underbrace{\textit{RS}\text{-stereogenic center}}_{\text{Types I, III, and V}} =\\ &\quad \underbrace{\text{asymmetric center}}_{\text{Types I and III}} + \underbrace{\text{pseudoasymmetric center}}_{\text{Type V}}. \qquad (2)\end{aligned}$$

This equation indicates that the term asymmetric center is used to specify chiral compounds (i.e., Type I and III) among *RS*-stereogenic compounds, while the term pseudoasymmetric center is used to specify achiral compounds (i.e., Type V) among *RS*-stereogenic compounds. As a result, the asymmetric center defined by Eq. 2 is in agreement with the tetrahedral "asymmetric atom" of van't Hoff.[1]

To show five *RS*-stereoisomeric types for modelling monosubstituted alkanes, Figure 1 collects planted promolecules derived from a methyl skeleton of C_{3v}-symmetry, where a solid circle (●) represents a root; each intersection of four bonds represents a carbon center (a principal vertex, mathematically

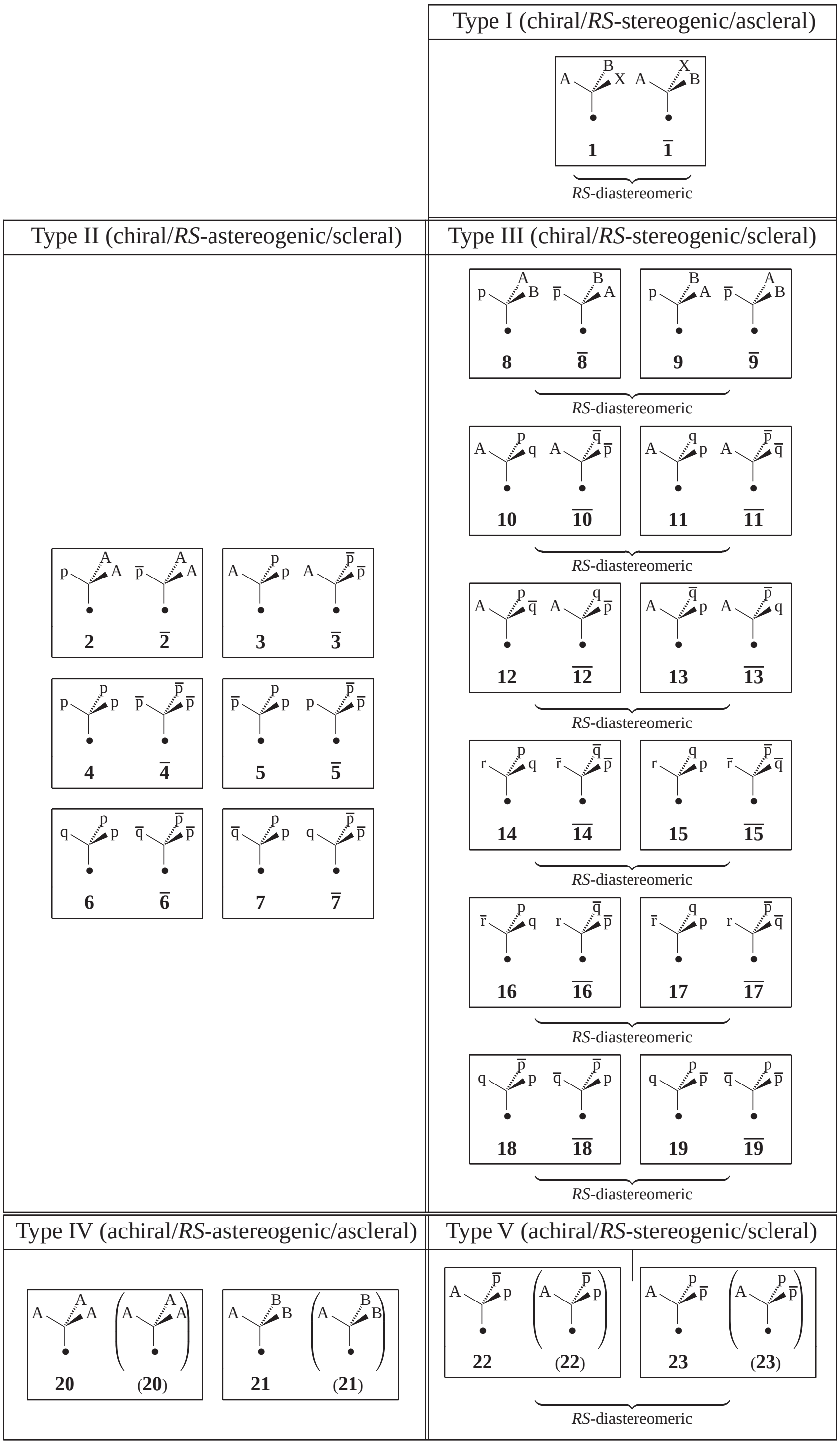

Fig. 1. Five *RS*-stereoisomeric types of planted promolecules based on the C_{3v}-skeleton of a methyl type. The symbols A, B, and X represent achiral proligands, while the pairs, $\mathrm{p}/\overline{\mathrm{p}}$, $\mathrm{q}/\overline{\mathrm{q}}$, and $\mathrm{r}/\overline{\mathrm{r}}$, denote enantiomeric pairs of chiral proligands. Two planted promolecules surrounded by each box are enantiomeric or the same as degenerated into an achiral promolecule. The four enantiomeric pairs **14**–**17** should be accompanied by the other four enantiomeric pairs, which are omitted for the sake of page saving.

speaking); the symbols A, B, and X represent achiral proligands; and the pairs ($\mathrm{p}/\overline{\mathrm{p}}$, $\mathrm{q}/\overline{\mathrm{q}}$, and $\mathrm{r}/\overline{\mathrm{r}}$) denote enantiomeric pairs of chiral proligands. Two enantiomers of an enantiomeric pair are located in a box. For an achiral compound, its formal mirror image, which is identical with the original achiral compound, is shown in a pair of large parentheses. For Type III, a pair of two boxes tied with an underbrace (e.g., $\mathbf{8}/\overline{\mathbf{8}}$ and $\mathbf{9}/\overline{\mathbf{9}}$) exhibits an *RS*-diastereomeric relationship, which indicates that the total of four compounds appear in a single stereoisogram. An *RS*-diastereomeric pair (e.g., $\mathbf{10}/\overline{\mathbf{10}}$ and $\mathbf{11}/\overline{\mathbf{11}}$) and another *RS*-diastereomeric pair (e.g., $\mathbf{12}/\overline{\mathbf{12}}$ and $\mathbf{13}/\overline{\mathbf{13}}$) can construct a set of diastereomers.

To avoid ambiguity in the distinction between asymmetric and pseudoasymmetric centers, we adopt the following criterion.

Criterion 1: An asymmetric center or a pseudoasymmetric center is referred to as an attribute of the principal vertex of a planted promolecule at issue. Chemically speaking, the substitution position of a monosubstituted alkane (or of an alkyl ligand) is regarded as such a principal vertex.

This criterion is necessary because a planted promolecule is contained in another planted promolecule in a nested fashion. In general, an achiral planted promolecule with pseudoasymmetry can be contained in a chiral planted promolecule so that the original pseudoasymmetry is changed into asymmetry. Even in this case, the original pseudoasymmetric center remains to be counted once.

It should be added from the present point of view that the reflection invariant descriptors *r* and *s* in the revised CIP system[46] are concerned with a pair of $\mathbf{18}/\overline{\mathbf{18}}$ or another pair of $\mathbf{19}/\overline{\mathbf{19}}$ for Type III. This means that the invariance of each descriptor (*r* or *s*) is accompanied by the alternation of chirality between **18** and $\overline{\mathbf{18}}$ or between **19** and $\overline{\mathbf{19}}$. On the other hand, the reflection invariant descriptors *r* and *s* are concerned with an achiral compound **22** itself or another achiral compound **23** itself, where no alternation of chirality occurs for Type V.

Enumeration of Planted Promolecules. Planted Promolecules Based on a Methane Skeleton: We recently reported the enumeration of monosubstituted alkanes[37–39] after having developed the proligand method as a general methodology for enumerating stereoisomers.[31–33] We shall briefly discuss the previous results[37] to pursue the present target. For the purpose of enumerating monosubstituted alkanes as planted promolecules on the basis of a methane skeleton of C_{3v}-symmetry, we can use Eq. 2 of Ref. 37:

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

which gives the total numbers of achiral and chiral promolecules (i.e., Types I–V shown in Fig. 1). Because we use the C_{3v}-point group to control transitivity for the methyl skeleton, an achiral promolecule or a pair of enantiomeric promolecules is counted just once. Note that the symbols a_d, c_d, and b_d represent sphericity indices (SIs), where the SI a_d characterizes a homospheric d-cycle, the SI c_d characterizes an enantiospheric d-cycle, and the SI b_d characterizes a hemispheric d-cycle.

In order to count steric isomers (i.e., achiral planted promolecules and chiral planted promolecules where two enantiomers of each pair are counted separately), Eq. 3 of Ref. 37 has been derived by using Theorem 3 of Ref. 33 as follows:

$$\text{CI-CF}(C_3; b_d) = \frac{1}{3}(b_1^3 + 2b_3). \tag{4}$$

On the condition that we use the C_3-point group to control transitivity for the methyl skeleton, each achiral promolecule and two enantiomers of each enantiomeric pair are counted separately.

In the present paper, the term "steric isomer" is used when three-dimensional compounds are considered without perception of enantiomeric relationships and of achirality (e.g., under C_3); and the term "stereoisomer" is used when we take account of enantiomeric relationships and achirality in treating three-dimensional compounds (e.g., under C_{3v}).

To count achiral planted promolecules only (i.e., Types IV and V), Eq. 4 of Ref. 37 has been derived from the first proposition of Theorem 4 of Ref. 33 as follows:

$$\text{CI-CF}_A(C_{3v}; a_d, c_d) = a_1c_2. \tag{5}$$

To count chiral planted promolecules only (i.e., Types I, II, and III), Eq. 5 of Ref. 37 has been derived by using the second proposition of Theorem 4 of Ref. 33 as follows:

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

Another elegant approach for enumerating chiral isomers has been reported,[49,50] although the concept of sphericities (which is represented by the sphericity indices, i.e., a_d, c_d, and b_d) has not been taken into consideration. A further approach for enumerating chiral isomers has been reported under the name of the characteristic-monomial (CM) method.[51–53] The CM method has been extended so as to take the concept of sphericities into consideration.[54] More detailed enumerations have been reported under the name of the USCI (unit-subduced-cycle-index) approach, where enumerated data are subdivided into each of chiral and achiral point groups.[55] Its extended version has been developed by taking account of the concept of sphericities.[56] As one of the methods of the USCI approach, the PCI (partial-cycle-index) method has been developed,[25,57,58] where the partial cycle index with chirality fittingness (PCI-CF) for each chiral or achiral point group has been generated in general. Obviously, the summation of the PCI-CFs for the chiral point groups gives a total CI-CF which is equivalent to such a CI-CF as Eq. 6. Thus, an additional approach for enumerating chiral isomers has been reported by the generalization of PCIs, where the concept of sphericities has been taken into consideration.[59] We have recently reported the concept of sphericities of double cosets, which has been linked to the concept of sphericities of cycles.[60] Thereby, we have developed an alternative formulation of Fujita's proligand method, which has provided us with a further approach for enumerating chiral isomers by using such a CI-CF as Eq. 6 (cf. Eq. 137 and Theorem 6[60]). It should be noted that the enumeration by means of Eq. 6 has no recursive nature so that Eq. 6 is not used in recursive calculations.

Suppose that a set of proligands selected from the following proligand warehouse:

$$\mathbf{X} = \{\mathrm{A}, \mathrm{B}, \mathrm{X}; \mathrm{p}, \overline{\mathrm{p}}; \mathrm{q}, \overline{\mathrm{q}}; \mathrm{r}, \overline{\mathrm{r}}\}, \tag{7}$$

where the symbols A, B, and X represent achiral proligands, while the pairs, $\mathrm{p}/\overline{\mathrm{p}}$, $\mathrm{q}/\overline{\mathrm{q}}$, and $\mathrm{r}/\overline{\mathrm{r}}$, denote enantiomeric pairs of chiral proligands. Then, the following ligand inventories are calculated:

$$a_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d, \tag{8}$$

$$c_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + 2\mathrm{p}^{d/2}\overline{\mathrm{p}}^{d/2} + 2\mathrm{q}^{d/2}\overline{\mathrm{q}}^{d/2} + 2\mathrm{r}^{d/2}\overline{\mathrm{r}}^{d/2}, \tag{9}$$

$$b_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{p}^d + \overline{\mathrm{p}}^d + \mathrm{q}^d + \overline{\mathrm{q}}^d + \mathrm{r}^d + \overline{\mathrm{r}}^d. \tag{10}$$

By introducing these ligand inventories into Eqs. 4–6, we are able to obtain generating functions for counting the respective numbers of objects. The resulting generating functions are essentially equivalent to those described in Ref. 33, i.e., Eq. 40 of Example 2, Eq. 45 of Example 3, Eq. 52 of Example 4, and Eq. 53 of Example 4.

In a previous paper,[37] we proposed the concept of diploid, which is effective to evaluate an enantiospheric transitivity of a cycle represented by an SI c_d. Thus, Eq. 10 of Ref. 37 has been derived to count diploids of Types I–V as follows:

$$\text{CI-CF}_D(C_3; c_d) = \frac{1}{3}(c_2^3 + 2c_6). \tag{11}$$

According to the concept of diploid, a pair of enantiomers is regarded as two ordered sets. For example, the enantiomeric pair of **1** and $\overline{\mathbf{1}}$ is ascribed to two ordered sets, i.e., $\{\mathbf{1}, \overline{\mathbf{1}}\}$ and $\{\overline{\mathbf{1}}, \mathbf{1}\}$, which are characterized by the term $2\mathrm{A}^2\mathrm{B}^2\mathrm{X}^2$. Obviously, two enantiomers of a pair correspond to two ordered pairs so that each box of Fig. 1 is regarded as representing two enantiomers (e.g., **1** and $\overline{\mathbf{1}}$) or as representing two ordered sets (e.g., $\{\mathbf{1}, \overline{\mathbf{1}}\}$ and $\{\overline{\mathbf{1}}, \mathbf{1}\}$).

Monosubstituted Alkanes without Itemization Due to Asymmetric Centers: Suppose that generating functions for counting achiral planted promolecules ($a(x)$), planted promolecules as diploids ($c(x^2)$), and planted promolecules as steric isomers ($b(x)$) are represented by the following equations:

$$a(x^d) = \sum_{k=0}^{\infty} \alpha_k x^{dk} \tag{12}$$

$$c(x^d) = \sum_{k=0}^{\infty} \gamma_k x^{dk} \tag{13}$$

$$b(x^d) = \sum_{k=0}^{\infty} \beta_k x^{dk} \tag{14}$$

according to Subsection 4.3 of Ref. 37, where the power d represents the size of a relevant cycle. Note that the coefficient γ_k is slightly modified in comparison with the original definition of Ref. 37.

The SIs a_d and c_d in Eqs. 5 and 11 are replaced by $a(x^d)$ and $c(x^d)$ and the SIs b_d in Eq. 4 are replaced by $b(x^d)$ so that the following functional equations are obtained:

$$a(x) = 1 + xa(x)c(x^2) \tag{15}$$

$$c(x^2) = 1 + \frac{1}{3}c(x^2)^3 + \frac{2}{3}c(x^6) \tag{16}$$

$$b(x) = 1 + \frac{1}{3}b(x)^3 + \frac{2}{3}b(x^3). \tag{17}$$

These functional equations have been already noted in Ref. 37, where their recursive nature has been used to enumerate monosubstituted alkanes as planted promolecules without itemization of asymmetric and pseudoasymmetric centers.

Enumeration of Planted Promolecules of Types I–V. Categorization into Types I–V: In order to take account of asymmetric and pseudoasymmetric centers, we shall enumerate planted promolecules of Types I and III (for asymmetric centers) and promolecules of Type V (for pseudoasymmetric centers).

To begin with, we consider promolecules of Type IV (i.e., achiral and *RS*-astereogenic promolecules). Let us examine Eq. 5 for counting planted promolecules of Types IV and V (achiral planted promolecules), where the SI c_2 permits the accommodation of two achiral proligands of the same kind (e.g., A^2 in Type IV: **20** or **21**) or the accommodation of an enantiomeric pair of chiral proligands (e.g., p and $\overline{\mathrm{p}}$ in Type V: **22** or **23**). As a result, we can select planted promolecules of Type IV by adopting an SI a_2 in place of the SI c_2. Thereby, we construct the corresponding CI-CF as follows:

$$\text{CI-CF}^{(\mathrm{IV})}(C_3; a_d) = a_1 a_2, \tag{18}$$

which counts planted promolecules of Type IV (achiral and *RS*-astereogenic). It should be noted that the SI a_d in Eq. 18 is used under the action of C_3; that is to say, two enantiomeric planted promolecules are counted separately. Even in this condition, an achiral planted promolecule is counted in the same way if we select C_3 in place of C_{3v}.

By introducing Eq. 8 into Eq. 18, we obtain the following generating function:

$$f^{(\mathrm{IV})} = [\mathrm{A}^3 + \ldots] + [\mathrm{AB}^2 + \ldots]. \tag{19}$$

Obviously, the term A^3 corresponds to **20** and the term AB^2 corresponds to **21**. For the sake of simplicity, an appropriate term is given in a pair of brackets as a representative selected from a set of terms showing the same type of constitution. For example, the term A^3 in Eq. 19 is a representative selected from a set of terms A^3, B^3, and X^3.

By subtracting Eq. 18 from Eq. 5, we obtain the following CI-CF for counting planting promolecules of Type V (achiral and *RS*-stereogenic):

$$\begin{aligned} \text{CI-CF}^{(\mathrm{V})}(C_3; a_d, c_d) &= \text{CI-CF}_A(C_{3v}; a_d, c_d) - \text{CI-CF}^{(\mathrm{IV})}(C_3; a_d) \\ &= a_1 c_2 - a_1 a_2. \end{aligned} \tag{20}$$

It should be noted that an achiral planted promolecule (Types IV and V) is counted just once in the same way if we select C_{3v} or C_3.

By introducing Eqs. 8 and 9 into Eq. 20, we obtain the following generating function:

$$f^{(\mathrm{V})} = 2[\mathrm{Ap}\overline{\mathrm{p}} + \ldots], \tag{21}$$

where the term $2\mathrm{Ap}\overline{\mathrm{p}}$ corresponds to **22** and **23**.

To enumerate planted promolecules of Types II and IV (*RS*-astereogenic), we use the following CI-CF:

$$\text{CI-CF}^{(\mathrm{II/IV})}(C_3; b_d) = b_1 b_2, \tag{22}$$

because two proligands of the same kind (A^2 etc., p^2 etc., or $\overline{\mathrm{p}}^2$ etc.) can be accommodated in accord with the SI b_2 and any proligand selected from **X** is suitable for the SI b_1.

By subtracting Eq. 18 from Eq. 22, we obtain the following CI-CF for counting planting promolecules of Type II (chiral and *RS*-astereogenic):

$$\begin{aligned} \text{CI-CF}^{(\mathrm{II})}(C_3; a_d, b_d) &= \text{CI-CF}^{(\mathrm{II/IV})}(C_3; b_d) - \text{CI-CF}^{(\mathrm{IV})}(C_3; a_d) \\ &= b_1 b_2 - a_1 a_2. \end{aligned} \tag{23}$$

By introducing Eqs. 8 and 10 into Eq. 23, we obtain the following generating function:

$$\begin{aligned} f^{(\mathrm{II})} = {} & [(\mathrm{A}^2\mathrm{p} + \mathrm{A}^2\overline{\mathrm{p}}) + \ldots] + [(\mathrm{Ap}^2 + \mathrm{A}\overline{\mathrm{p}}^2) + \ldots] \\ & + [(\mathrm{p}^3 + \overline{\mathrm{p}}^3) + \ldots] \\ & + [(\mathrm{p}^2\overline{\mathrm{p}} + \mathrm{p}\overline{\mathrm{p}}^2) + \ldots] \\ & + [(\mathrm{p}^2\mathrm{q} + \overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \ldots] + [(\mathrm{p}^2\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}) + \ldots]. \end{aligned} \tag{24}$$

Each term appearing in Eq. 24 exhibits the following correspondence: $(\mathrm{A}^2\mathrm{p} + \mathrm{A}^2\overline{\mathrm{p}})$ to **2** and $\overline{\mathbf{2}}$; $(\mathrm{Ap}^2 + \mathrm{A}\overline{\mathrm{p}}^2)$ to **3** and $\overline{\mathbf{3}}$;

$(\mathrm{p}^3 + \overline{\mathrm{p}}^3)$ to **4** and $\overline{\mathbf{4}}$; $(\mathrm{p}^2\overline{\mathrm{p}} + \mathrm{p}\overline{\mathrm{p}}^2)$ to **5** and $\overline{\mathbf{5}}$; $(\mathrm{p}^2\mathrm{q} + \overline{\mathrm{p}}^2\overline{\mathrm{q}})$ to **6** and $\overline{\mathbf{6}}$; as well as $(\mathrm{p}^2\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q})$ to **7** and $\overline{\mathbf{7}}$.

Because the set of steric isomers enumerated by Eq. 4 consists of planted promolecules of Types I–V, the subtraction of Eq. 22 (Types II and IV) and Eq. 20 (Type V) from Eq. 4 leaves promolecules of Types I and III (chiral and *RS*-stereogenic) as follows:

$$\begin{aligned}&\text{CI-CF}^{(\text{I/III})}(C_3; a_d, c_d)\\ &\quad= \text{CI-CF}(C_3, b_d) - \text{CI-CF}^{(\text{II/IV})}(C_3; b_d)\\ &\qquad- \text{CI-CF}^{(\text{V})}(C_3; a_d, c_d)\\ &\quad= \frac{1}{3}(b_1^3 + 2b_3) - b_1b_2 - (a_1c_2 - a_1a_2).\end{aligned} \tag{25}$$

By introducing the ligand inventories (Eqs. 8 to 10) into Eq. 25, we obtain the following generating function:

$$\begin{aligned}f^{(\text{I/III})} &= 2[\mathrm{ABX} + \ldots] + 2[(\mathrm{ABp} + \mathrm{AB}\overline{\mathrm{p}}) + \ldots]\\ &\quad+ 2[(\mathrm{Apq} + \mathrm{A}\overline{\mathrm{pq}}) + \ldots] + 2[(\mathrm{Ap}\overline{\mathrm{q}} + \mathrm{A}\overline{\mathrm{p}}\mathrm{q}) + \ldots]\\ &\quad+ 2[(\mathrm{pqr} + \overline{\mathrm{pqr}}) + \ldots] + 2[(\mathrm{pq}\overline{\mathrm{r}} + \overline{\mathrm{pq}}\mathrm{r}) + \ldots]\\ &\quad+ 2[(\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{qr}}) + \ldots] + 2[(\mathrm{p}\overline{\mathrm{q}}\mathrm{r} + \overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{r}}) + \ldots]\\ &\quad+ 2[(\mathrm{p}\overline{\mathrm{p}}\mathrm{q} + \mathrm{p}\overline{\mathrm{pq}}) + \ldots].\end{aligned} \tag{26}$$

Each term appearing in Eq. 26 exhibits the following correspondence: 2ABX to **1** and $\overline{\mathbf{1}}$; $2(\mathrm{ABp} + \mathrm{AB}\overline{\mathrm{p}})$ to **8**/**9** and $\overline{\mathbf{8}}/\overline{\mathbf{9}}$; $2(\mathrm{Apq} + \mathrm{A}\overline{\mathrm{pq}})$ to **10**/**11** and $\overline{\mathbf{10}}/\overline{\mathbf{11}}$; $2(\mathrm{Ap}\overline{\mathrm{q}} + \mathrm{A}\overline{\mathrm{p}}\mathrm{q})$ to **12**/**13** and $\overline{\mathbf{12}}/\overline{\mathbf{13}}$; $2(\mathrm{pqr} + \overline{\mathrm{pqr}})$ to **14**/**15** and $\overline{\mathbf{14}}/\overline{\mathbf{15}}$; $2(\mathrm{pq}\overline{\mathrm{r}} + \overline{\mathrm{pq}}\mathrm{r})$ to **16**/**17** and $\overline{\mathbf{16}}/\overline{\mathbf{17}}$; as well as $2(\mathrm{p}\overline{\mathrm{p}}\mathrm{q} + \mathrm{p}\overline{\mathrm{pq}})$ to **18**/**19** and $\overline{\mathbf{18}}/\overline{\mathbf{19}}$. The correspondence for the terms $2(\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{qr}})$ and $2(\mathrm{p}\overline{\mathrm{q}}\mathrm{r} + \overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{r}})$ is omitted.

Suppose that proligands for Eq. 4 are restricted to be achiral (A, B, and X). This means that we consider Types I and IV, where the SIs b_1 and b_3 are replaced by the SIs a_1 and a_3. Thereby, we can obtain the following CI-CF:

$$\text{CI-CF}^{(\text{I/IV})}(C_3; a_d) = \frac{1}{3}(a_1^3 + 2a_3), \tag{27}$$

which counts planted promolecules of Types I and IV.

Subtraction of Eq. 18 from Eq. 27 leaves the following CI-CF for counting planting promolecules of Type I (chiral, *RS*-stereogenic, and ascleral):

$$\begin{aligned}\text{CI-CF}^{(\text{I})}(C_3; a_d) &= \text{CI-CF}^{(\text{I/IV})}(C_3; a_d) - \text{CI-CF}^{(\text{IV})}(C_3; a_d)\\ &= \frac{1}{3}(a_1^3 + 2a_3) - a_1a_2.\end{aligned} \tag{28}$$

This equation is alternatively obtained by placing $b_d = c_d = a_d$ in Eq. 25. By introducing Eq. 8 into Eq. 28, we obtain the following generating function:

$$f^{(\text{I})} = 2\mathrm{ABX}. \tag{29}$$

The sole term 2ABX appearing in Eq. 29 corresponds to **1** and $\overline{\mathbf{1}}$, which are counted separately so as to give the coefficient 2 of the term 2ABX.

By subtracting Eq. 29 from Eq. 25, we obtain the following CI-CF for counting planting promolecules of Type III (chiral and *RS*-stereogenic) as follows:

$$\begin{aligned}&\text{CI-CF}^{(\text{III})}(C_3; a_d, b_d, c_d)\\ &\quad= \text{CI-CF}^{(\text{I/III})}(C_3; a_d, c_d) - \text{CI-CF}^{(\text{I})}(C_3; a_d)\\ &\quad= \frac{1}{3}(b_1^3 + 2b_3) - \frac{1}{3}(a_1^3 + 2a_3) - (b_1b_2 - a_1a_2)\\ &\qquad- (a_1c_2 - a_1a_2),\end{aligned} \tag{30}$$

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

By introducing the ligand inventories (Eqs. 8 to 10) into Eq. 30, we obtain the following generating function:

$$\begin{aligned}f^{(\text{III})} &= 2[(\mathrm{ABp} + \mathrm{AB}\overline{\mathrm{p}}) + \ldots]\\ &\quad+ 2[(\mathrm{Apq} + \mathrm{A}\overline{\mathrm{pq}}) + \ldots] + 2[(\mathrm{Ap}\overline{\mathrm{q}} + \mathrm{A}\overline{\mathrm{p}}\mathrm{q}) + \ldots]\\ &\quad+ 2[(\mathrm{pqr} + \overline{\mathrm{pqr}}) + \ldots] + 2[(\mathrm{pq}\overline{\mathrm{r}} + \overline{\mathrm{pq}}\mathrm{r}) + \ldots]\\ &\quad+ 2[(\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{qr}}) + \ldots] + 2[(\mathrm{p}\overline{\mathrm{q}}\mathrm{r} + \overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{r}}) + \ldots]\\ &\quad+ 2[(\mathrm{p}\overline{\mathrm{p}}\mathrm{q} + \mathrm{p}\overline{\mathrm{pq}}) + \ldots].\end{aligned} \tag{31}$$

Each term appearing in Eq. 31 exhibits the correspondence described for Eq. 25 except for the term 2ABX corresponding to Type I (**1** and $\overline{\mathbf{1}}$).

Enumeration of Planted Promolecules as Diploids: On the same line as Eq. 5, planted promolecules of Types IV and V (achiral) are counted by the following CI-CF:

$$\text{CI-CF}_D^{(\text{IV/V})}(C_3; a_d, c_d) = a_2c_4. \tag{32}$$

Such an ordered set as {**22**, (**22**)} is characterized by Eq. 32, where the SI c_4 permutes $\mathrm{p}^2\overline{\mathrm{p}}^2$ and the SI a_2 permutes A^2 in agreement with the sphericities of the relevant cycles. Because the relevant promolecules are achiral, the action of C_{3v} gives the same number of isomers as the action of C_3.

On the other hand, planted promolecules of Type IV as diploids can be counted on the same line as Eq. 18 so as to give the following CI-CF:

$$\text{CI-CF}_D^{(\text{IV})}(C_3; a_d) = a_2a_4. \tag{33}$$

Subtraction of Eq. 33 from Eq. 32 leaves the following CI-CF for counting planting promolecules of Type V (achiral and *RS*-astereogenic) as diploids:

$$\begin{aligned}&\text{CI-CF}_D^{(\text{V})}(C_3; a_d, c_d)\\ &\quad= \text{CI-CF}_D^{(\text{IV/V})}(C_3; a_d, c_d) - \text{CI-CF}_D^{(\text{IV})}(C_3, a_d)\\ &\quad= a_2c_4 - a_2a_4.\end{aligned} \tag{34}$$

By introducing the ligand inventories (Eqs. 8 and 10) into Eq. 29, we obtain the following generating function:

$$f_D^{(\text{V})} = 2[\mathrm{A}^2\mathrm{p}^2\overline{\mathrm{p}}^2 + \ldots]. \tag{35}$$

The coefficient 2 of the term $2\mathrm{A}^2\mathrm{p}^2\overline{\mathrm{p}}^2$ indicates the presence of two ordered sets {**22**, (**22**)} and {**23**, (**23**)}, which represent achiral planted promolecules of Type V (so-called pseudoasymmetric ones). Compare Eq. 35 with Eq. 21.

On the same line as Eq. 22, planted promolecules of Types II and IV as diploids can be counted by substituting c_d for the b_d of Eq. 22 to give the following CI-CF:

$$\text{CI-CF}_D^{(\text{II/IV})}(C_3; c_d) = c_2c_4. \tag{36}$$

For example, such an ordered set as {**2**, $\overline{\mathbf{2}}$} (or {$\overline{\mathbf{2}}$, **2**}) is characterized by Eq. 36, where the SI c_4 permutes A^4 and the SI c_2 permutes $\mathrm{p}\overline{\mathrm{p}}$ in agreement with the enantiosphericity of the relevant cycles. The mode of transitivity is more clearly shown by such an ordered set as {**6**, $\overline{\mathbf{6}}$} (or {$\overline{\mathbf{6}}$, **6**}), where the SI c_4

permutes $\mathrm{p}^2\overline{\mathrm{p}}^2$ and the SI c_2 permutes $\mathrm{q}\overline{\mathrm{q}}$ in an enantiospheric fashion. The introduction of the ligand inventory (Eq. 10) into Eq. 36 provides the following generating function:

$$\begin{aligned} f_D^{(\mathrm{II/IV})} &= 2[\mathrm{A}^4\mathrm{p}\overline{\mathrm{p}} + \ldots] + 2[\mathrm{A}^2\mathrm{p}^2\overline{\mathrm{p}}^2 + \ldots] \\ &\quad + 4[\mathrm{p}^3\overline{\mathrm{p}}^3 + \ldots] + 4[\mathrm{p}^2\overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}} + \ldots] \\ &\quad + [\mathrm{A}^6 + \ldots] + [\mathrm{A}^2\mathrm{B}^4 + \ldots]. \end{aligned} \tag{37}$$

By subtracting Eq. 33 from Eq. 36, we obtain the following CI-CF for counting planted promolecules of Type II as diploids:

$$\begin{aligned} &\text{CI-CF}_D^{(\mathrm{II})}(C_3; a_d, c_d) \\ &\quad = \text{CI-CF}_D^{(\mathrm{II/IV})}(C_3; c_d) - \text{CI-CF}_D^{(\mathrm{IV})}(C_3; a_d) \\ &\quad = c_2c_4 - a_2a_4. \end{aligned} \tag{38}$$

The introduction of the ligand inventories (Eqs. 8 and 10) into Eq. 38 produces the following generating function:

$$\begin{aligned} f_D^{(\mathrm{II})} &= 2[\mathrm{A}^4\mathrm{p}\overline{\mathrm{p}} + \ldots] + 2[\mathrm{A}^2\mathrm{p}^2\overline{\mathrm{p}}^2 + \ldots] \\ &\quad + 4[\mathrm{p}^3\overline{\mathrm{p}}^3 + \ldots] + 4[\mathrm{p}^2\overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}} + \ldots]. \end{aligned} \tag{39}$$

Obviously, the coefficient 2 of the term $2\mathrm{A}^4\mathrm{p}\overline{\mathrm{p}}$ corresponds to two ordered sets, i.e., $\{\mathbf{6}, \overline{\mathbf{6}}\}$ and $\{\overline{\mathbf{6}}, \mathbf{6}\}$, and so on. Compare Eq. 39 with Eq. 24. Then note that Eq. 24 contains the term $(\mathrm{A}^2\mathrm{p} + \mathrm{A}^2\overline{\mathrm{p}})$, which counts **6** and $\overline{\mathbf{6}}$ separately.

By referring to Eqs. 11, 34, and 36, we obtain the following CI-CF for counting planted promolecules of Types I and III as diploids:

$$\begin{aligned} &\text{CI-CF}_D^{(\mathrm{I/III})}(C_3; c_d) \\ &\quad = \text{CI-CF}_D(C_3, c_d) - \text{CI-CF}_D^{(\mathrm{II/IV})}(C_3; c_d) \\ &\qquad - \text{CI-CF}_D^{(\mathrm{V})}(C_3; a_d, c_d) \\ &\quad = \frac{1}{3}(c_2^3 + 2c_6) - c_2c_4 - (a_2c_4 - a_2a_4). \end{aligned} \tag{40}$$

By introducing the ligand inventories (Eqs. 8 and 10) into Eq. 40, we obtain the following generating function:

$$\begin{aligned} f_D^{(\mathrm{I/III})} &= 2\mathrm{A}^2\mathrm{B}^2\mathrm{X}^2 + 4[\mathrm{A}^2\mathrm{B}^2\mathrm{p}\overline{\mathrm{p}} + \ldots] + 8[\mathrm{A}^2\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}} + \ldots] \\ &\quad + 16\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}}\mathrm{r}\overline{\mathrm{r}} + 4[\mathrm{p}^2\overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}} + \ldots]. \end{aligned} \tag{41}$$

On the same line as Eq. 27, we can obtain the following CI-CF for counting planted promolecules of Types I and IV as follows:

$$\text{CI-CF}_D^{\mathrm{I/IV}}(C_3; a_d) = \frac{1}{3}(a_2^3 + 2a_6), \tag{42}$$

which counts planted promolecules of Types I and IV.

The subtraction of Eq. 33 from Eq. 42 leaves the following CI-CF for counting planting promolecules of Type I (chiral, *RS*-stereogenic, and ascleral):

$$\begin{aligned} \text{CI-CF}_D^{(\mathrm{I})}(C_3; a_d) &= \text{CI-CF}_D^{(\mathrm{I/IV})}(C_3; a_d) - \text{CI-CF}_D^{(\mathrm{IV})}(C_3; a_d) \\ &= \frac{1}{3}(a_2^3 + 2a_6) - a_2a_4, \end{aligned} \tag{43}$$

which corresponds to Eq. 28. Then the ligand inventory (Eq. 8) is introduced into Eq. 43 to give the following generating function:

$$f_D^{(\mathrm{I})} = 2\mathrm{A}^2\mathrm{B}^2\mathrm{X}^2. \tag{44}$$

The sole term $2\mathrm{A}^2\mathrm{B}^2\mathrm{X}^2$ appearing in Eq. 44 corresponds to two ordered sets, i.e., $\{\mathbf{1}, \overline{\mathbf{1}}\}$ and $\{\overline{\mathbf{1}}, \mathbf{1}\}$.

By subtracting Eq. 43 from Eq. 40, we obtain the following CI-CF for counting planted promolecules of Type III (chiral and *RS*-stereogenic) as diploids:

$$\begin{aligned} &\text{CI-CF}_D^{(\mathrm{III})}(C_3; a_d, b_d, c_d) \\ &\quad = \text{CI-CF}_D^{(\mathrm{I/III})}(C_3; a_d, c_d) - \text{CI-CF}_D^{(\mathrm{I})}(C_3; a_d) \\ &\quad = \frac{1}{3}(c_2^3 + 2c_6) - \frac{1}{3}(a_2^3 + 2a_6) \\ &\qquad - (c_2c_4 - a_2a_4) - (a_2c_4 - a_2a_4), \end{aligned} \tag{45}$$

which corresponds to Eq. 30.

By introducing the ligand inventories (Eq. 8 to 10) into Eq. 45, we obtain the following generating function:

$$\begin{aligned} f_D^{(\mathrm{III})} &= 4[\mathrm{A}^2\mathrm{B}^2\mathrm{p}\overline{\mathrm{p}} + \ldots] + 8[\mathrm{A}^2\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}} + \ldots] \\ &\quad + 16\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}}\mathrm{r}\overline{\mathrm{r}} + 4[\mathrm{p}^2\overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}} + \ldots]. \end{aligned} \tag{46}$$

Compare this equation with Eq. 31. Thereby, we are able to obtain an insight on the difference between the enumeration of diploids and the usual enumeration of compounds. For example, the term $4\mathrm{A}^2\mathrm{B}^2\mathrm{p}\overline{\mathrm{p}}$ appearing in Eq. 46 corresponds to four ordered sets, i.e., $\{\mathbf{8}, \overline{\mathbf{8}}\}$, $\{\overline{\mathbf{8}}, \mathbf{8}\}$; $\{\mathbf{9}, \overline{\mathbf{9}}\}$, and $\{\overline{\mathbf{9}}, \mathbf{9}\}$. In contrast, the term $2(\mathrm{ABp} + \mathrm{AB}\overline{\mathrm{p}})$ appearing in Eq. 31 clarifies the existence of totally four chiral objects, i.e., **8** (ABp), $\overline{\mathbf{8}}$ ($\mathrm{AB}\overline{\mathrm{p}}$), **9** (ABp), and $\overline{\mathbf{9}}$ ($\mathrm{AB}\overline{\mathrm{p}}$). Hence, we can say that the coefficient 4 of the term $4\mathrm{A}^2\mathrm{B}^2\mathrm{p}\overline{\mathrm{p}}$ (Eq. 46) and the summed value 4 (=2 + 2) of the term $2(\mathrm{ABp} + \mathrm{AB}\overline{\mathrm{p}})$ (Eq. 31) count the same things in different ways.

Enumeration of Monosubstituted Alkanes. A monosubstituted alkane is considered to be a methyl derivative (a planted promolecule) substituted by a set of proligands. Each of the proligands can be again considered to be a methyl derivative (a planted promolecule) substituted by a set of proligands. This recursive process can be continued to give a methyl derivative of carbon content 1. At any step of the recursive process, the relevant methyl derivative (the relevant planted promolecule) is regarded as a rigid entity, which is suitable for combinatorial enumeration of three-dimensional entities. Moreover, the recursive process assures the proper evaluation of nonrigidity due to the internal rotation of each methyl group in monosubstituted alkanes. This subsection is devoted to the application of the recursive process to enumeration of monosubstituted alkanes.

Itemization Due to Asymmetric and Pseudoasymmetric Centers: Let $\alpha_{k\ell m}$ be the number of monosubstituted alkanes (as planted promolecules) of carbon content k which have ℓ asymmetric centers and m pseudoasymmetric centers; let $\gamma_{k\ell m}$ be the number of monosubstituted alkanes (as planted promolecules) of carbon content k as diploids, which have ℓ asymmetric centers and m pseudoasymmetric centers; and let $\beta_{k\ell m}$ be the number of monosubstituted alkanes (as planted promolecules) of carbon content k as steric isomers, which have ℓ asymmetric centers and m pseudoasymmetric centers. Thereby, Eqs. 12–14 are represented by the following summations:

$$\alpha_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\alpha_{k\ell m}, \tag{47}$$

$$\gamma_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\gamma_{k\ell m}, \tag{48}$$

$$\beta_k = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty}\beta_{k\ell m}. \tag{49}$$

Suppose that these numbers ($\alpha_{k\ell m}$, $\gamma_{k\ell m}$, and $\beta_{k\ell m}$) are the coefficients of the following generating functions:

$$a(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\alpha_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk}, \tag{50}$$

$$c(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\gamma_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk}, \tag{51}$$

$$b(x^d,y^d,z^d) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}\beta_{k\ell m}z^{dm}\right)y^{d\ell}\right)x^{dk}, \tag{52}$$

where the variable x is concerned with the carbon content, the variable y is concerned with the number of asymmetric centers, and the variable z is concerned with the number of pseudoasymmetric centers and where we put $\alpha_{000} = 1$, $\gamma_{000} = 1$, and $\beta_{000} = 1$ for treating the respective initial (trivial) cases. These generating functions can be regarded as functional equations when we take account of the lowest powers, i.e., $a(x,y,z)$ ($d = 1$ in Eq. 50), $c(x^2,y^2,z^2)$ ($d = 2$ in Eq. 51 because d should be even), and $b(x,y,z)$ ($d = 1$ in Eq. 52). Obviously, we obtain $a(x,1,1) = a(x)$, $c(x^2,1,1) = c(x^2)$, and $b(x,1,1) = b(x)$, where $a(x)$, $c(x^2)$, and $b(x)$ have been evaluated by means of the functional equations described above (Eqs. 15–17).

Suppose that the functional equations of the lowest powers, i.e., $a(x,y,z)$, $c(x^2,y^2,z^2)$, and $b(x,y,z)$, have been obtained up to carbon content k and that the planted promolecules counted up to carbon content k are used to enumerate planted promolecules with carbon content $k+1$. Then, the numbers of asymmetric and pseudoasymmetric centers satisfies $\ell < k$ and $m < k$.

The resulting set of achiral promolecules of carbon content $k+1$ consists of Type-IV planted promolecules (Eq. 18) and Type-V planted promolecules (Eq. 20), where the latter (Type V) has caused an increase of pseudoasymmetric centers by one. As for Type-IV planted promolecules, the SIs a_1 and a_2 in Eq. 18 are replaced by $a(x,y,z)$ and $a(x^2,y^2,z^2)$, where the resulting function is multiplied by x in accord with the increase of carbon content. As for Type-V planted promolecules, the SIs a_1, a_2, and c_2 in Eq. 20 are replaced by $a(x,y,z)$, $a(x^2,y^2,z^2)$, and $c(x^2,y^2,z^2)$, where the resulting function is multiplied by xz in accord with the increase of carbon content and one pseudoasymmetric center. Thereby, we obtain the following functional equation for counting achiral planted promolecules (Types IV and V):

$$\begin{aligned} a(x,y,z) = 1 &+ xa(x,y,z)a(x^2,y^2,z^2) \\ &+ xz\{a(x,y,z)c(x^2,y^2,z^2) \\ &- a(x,y,z)a(x^2,y^2,z^2)\}, \end{aligned} \tag{53}$$

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

To evaluate $c(x^2,y^2,z^2)$, we should take account of Eq. 36 (Types II and IV increasing carbon content 2, i.e., by x^2), Eq. 34 (Type V increasing carbon content 2 and two pseudoasymmetric centers, i.e., by x^2z^2) and Eq. 40 (Types I and III increasing carbon content 2 and two asymmetric centers, i.e., by x^2y^2). Hence, the SIs a_d and c_d in these equations are replaced by $a(x^d,y^d,z^d)$ and $c(x^d,y^d,z^d)$. After the resulting equations are multiplied by x^2, x^2z^2, and x^2y^2 respectively, they are summed up to give the following functional equation:

$$\begin{aligned} c(x^2,y^2,z^2) = 1 &+ x^2c(x^2,y^2,z^2)c(x^4,y^4,z^4) \\ &+ x^2z^2\{a(x^2,y^2,z^2)c(x^4,y^4,z^4) \\ &- a(x^2,y^2,z^2)a(x^4,y^4,z^4)\} \\ &+ \frac{x^2y^2}{3}\{c(x^2,y^2,z^2)^3 + 2c(x^6,y^6,z^6)\} \\ &- x^2y^2c(x^2,y^2,z^2)c(x^4,y^4,z^4) \\ &- x^2y^2\{a(x^2,y^2,z^2)c(x^4,y^4,z^4) \\ &- a(x^2,y^2,z^2)a(x^4,y^4,z^4)\}, \end{aligned} \tag{54}$$

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

On the same line, we can evaluate $b(x,y,z)$, where we take account of Eq. 22 (Types II and IV increasing carbon content 1), Eq. 20 (Type V increasing carbon content 1 and one pseudoasymmetric center) and Eq. 25 (Types I and III increasing carbon content 1 and one asymmetric centers). Hence, 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 $b(x^d,y^d,z^d)$. After the resulting equations are multiplied by x, xz, and xy respectively, they are summed up to give the following functional equation:

$$\begin{aligned} b(x,y,z) = 1 &+ xb(x,y,z)b(x^2,y^2,z^2) + xz\{a(x,y,z)c(x^2,y^2,z^2) \\ &- a(x,y,z)a(x^2,y^2,z^2)\} \\ &+ \frac{xy}{3}\{b(x,y,z)^3 + 2b(x^3,y^3,z^3)\} \\ &- xyb(x,y,z)b(x^2,y^2,z^2) - xy\{a(x,y,z)c(x^2,y^2,z^2) \\ &- a(x,y,z)a(x^2,y^2,z^2)\}, \end{aligned} \tag{55}$$

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

Let $B(x,y,z)$ be a generating function for enumerating achiral plus chiral planted promolecules, where each enantiomeric pair of chiral planted promolecules is counted just once. Let $C(x,y,z)$ be a generating function for enumerating chiral planted promolecules, where each enantiomeric pair of chiral planted promolecules is counted just once. Then, we find the following generating functions:

$$B(x,y,z) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}B_{k\ell m}z^{m}\right)y^{\ell}\right)x^{k}, \tag{56}$$

$$C(x,y,z) = \sum_{k=0}^{\infty}\left(\sum_{\ell=0}^{\infty}\left(\sum_{m=0}^{\infty}C_{k\ell m}z^{m}\right)y^{\ell}\right)x^{k}, \tag{57}$$

where we place $B_{000} = 1$ and $C_{000} = 1$ for the trivial cases and $B_{k\ell m}$ and $C_{k\ell m}$ represent the numbers of planted promolecules at issue, which have the molecular formula x^k have ℓ asymmetric centers and m pseudoasymmetric centers.

$$B(x,y,z) = \frac{1}{2}\{a(x,y,z) + b(x,y,z)\} \tag{58}$$

$$\begin{aligned}
&= 1 + \frac{x}{2}\left\{b(x,y,z)b(x^2,y^2,z^2) + a(x,y,z)a(x^2,y^2,z^2)\right\} \\
&\quad + xz\left\{a(x,y,z)c(x^2,y^2,z^2) - a(x,y,z)a(x^2,y^2,z^2)\right\} \\
&\quad + \frac{xy}{6}\left\{b(x,y,z)^3 + 2b(x^3,y^3,z^3)\right. \\
&\quad \left. + 3a(x,y,z)c(x^2,y^2,z^2)\right\} \\
&\quad - \frac{xy}{2}\left\{b(x,y,z)b(x^2,y^2,z^2) + a(x,y,z)a(x^2,y^2,z^2)\right\} \\
&\quad - xy\left\{a(x,y,z)c(x^2,y^2,z^2)\right. \\
&\quad \left. - a(x,y,z)a(x^2,y^2,z^2)\right\}. \qquad (59)
\end{aligned}$$

$$\begin{aligned}
C(x,y,z) &= \frac{1}{2}\left\{b(x,y,z) - a(x,y,z)\right\} \qquad (60) \\
&= \frac{x}{2}\left\{b(x,y,z)b(x^2,y^2,z^2) - a(x,y,z)a(x^2,y^2,z^2)\right\} \\
&\quad + \frac{xy}{6}\left\{b(x,y,z)^3 + 2b(x^3,y^3,z^3)\right. \\
&\quad \left. - 3a(x,y,z)c(x^2,y^2,z^2)\right\} \\
&\quad - \frac{xy}{2}\left\{b(x,y,z)b(x^2,y^2,z^2)\right. \\
&\quad \left. - a(x,y,z)a(x^2,y^2,z^2)\right\}. \qquad (61)
\end{aligned}$$

Computer Implementation and Results: The functional equations represented by $a(x,y,z)$ (Eq. 53), $c(x^2,y^2,z^2)$ (Eq. 54), and $b(x,y,z)$ (Eq. 53) have recursive nature so that they are implemented by mean of the Maple programming language as follows. The upper limit of the carbon content (k) is tentatively fixed to be 30, but it can be freely selected as far as the capacity of a computer permits.

```
#Alkyl1-30zfinal9.mpl
axyz := 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);

‘‘Initial Values’’;
a111 := 1; a222 := 1; a444 :=1;
c222 := 1; c444 := 1; c666 := 1;
b111 := 1; b222 := 1; b333 := 1;
asum := 1; csum := 1; bsum := 1;

‘‘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)));

b1yz := expand(coeff(y*Cbxyz,y)):
b2yz := b1yz:
b3yz := b1yz:
subbsum := b1yz:
a1yz := expand(coeff(y*Caxyz,y)):
a2yz := a1yz:
a4yz := a1yz:
subasum := a1yz:
c1yz := expand(coeff(y*Ccxyz,y)):
c2yz := c1yz:
c3yz := c1yz:
subcsum := c1yz:

for l from 1 to degree(Cbxyz,y) by 1 do
CCbxyz:= coeff(Cbxyz, y^l):
bb1yz:= expand(coeff(z*CCbxyz,z)):
bb2yz:= bb1yz:
bb3yz:= bb1yz:
subbsum := subbsum + bb1yz:

CCcxyz:= coeff(Ccxyz, y^(2*l)):
cc1yz:= expand(coeff(z*CCcxyz,z)):
cc2yz:= cc1yz:
cc3yz:= cc1yz:
subcsum := subcsum + cc1yz:

CCaxyz:= coeff(Caxyz, y^l):
aa1yz := expand(coeff(z*CCaxyz,z)):
aa2yz := aa1yz:
aa4yz := aa1yz:
subasum := subasum + aa1yz:

for m from 1 to degree(CCcxyz,z) by 1 do
CCCcxyz:= coeff(CCcxyz, z^(2*m)):
cc1yz:= cc1yz + CCCcxyz*z^(2*m):
cc2yz:= cc2yz + CCCcxyz*z^(4*m):
cc3yz:= cc3yz + CCCcxyz*z^(6*m):
subcsum := subcsum + CCCcxyz:
end do:

for n from 1 to degree(CCaxyz,z) by 1 do
CCCaxyz:= coeff(CCaxyz, z^n):
aa1yz:= aa1yz + CCCaxyz*z^n:
aa2yz:= aa2yz + CCCaxyz*z^(2*n):
aa4yz:= aa4yz + CCCaxyz*z^(4*n):
subasum := subasum + CCCaxyz:
end do:

for p from 1 to degree(CCbxyz,z) by 1 do
CCCbxyz:= coeff(CCbxyz, z^p):
bb1yz:= bb1yz + CCCbxyz*z^p:
bb2yz:= bb2yz + CCCbxyz*z^(2*p):
bb3yz:= bb3yz + CCCbxyz*z^(3*p):
subbsum := subbsum + CCCbxyz:
end do:

c1yz:= c1yz + cc1yz*y^(2*l):
c2yz:= c2yz + cc2yz*y^(4*l):
c3yz:= c3yz + cc3yz*y^(6*l):

a1yz:= a1yz + aa1yz*y^l:
a2yz:= a2yz + aa2yz*y^(2*l):
a4yz:= a4yz + aa4yz*y^(4*l):
```

```
b1yz:= b1yz + bb1yz*y^l:
b2yz:= b2yz + bb2yz*y^(2*l):
b3yz:= b3yz + bb3yz*y^(3*l):
end do:

bsum := bsum + subbsum*x^k:
asum := asum + subasum*x^k:
csum := csum + subcsum*x^(2*k):
b111 := b111 + b1yz*x^k:
b222 := b222 + b2yz*x^(2*k):
b333 := b333 + b3yz*x^(3*k):
a111 := a111 + a1yz*x^k:
a222 := a222 + a2yz*x^(k*2):
a444 := a444 + a4yz*x^(k*4):
c222 := c222 + c1yz*x^(k*2):
c444 := c444 + c2yz*x^(k*4):
c666 := c666 + c3yz*x^(k*6):
end do:

‘‘Total and Chiral Stereoisomers’’;

BBxyz := (1/2)*(a111 + b111):
CCxyz := (1/2)*(b111 − a111):

EBBxyz := expand(BBxyz):
ECCxyz := expand(CCxyz):

Total := (1/2)*(asum + bsum):
Chiral := (1/2)*(bsum − asum):

‘‘Print Out of b111 (Steric)’’;
for k from 1 to 30 by 1 do
carbon_kontent:= k:
Ns := collect(expand(coeff(b111,x^k)),y):
end do;

‘‘Print Out of a111 (Achiral)’’;
for k from 1 to 30 by 1 do
carbon_kontent:= k:
Na := collect(expand(coeff(a111,x^k)),y):
end do;

‘‘Print Out of ECCxyz (Chiral)’’;
for k from 1 to 30 by 1 do
carbon_kontent:= k:
Nc := collect(expand(coeff(ECCxyz,x^k)),y):
end do;

‘‘Print Out of EBBxyz (Total)’’;
for k from 1 to 30 by 1 do
carbon_kontent:= k:
Nt := collect(expand(coeff(EBBxyz,x^k)),y):
end do;

‘‘Validity Test’’;

z:=1;
y:=1;

‘‘b111-bsum’’;
b111-bsum;

‘‘a111-asum’’;
a111-asum;

‘‘c222-csum’’;
c222-csum;
```

This code is stored in a file named “Alkyl1-30zfinal9.mpl” tentatively. In this code, the abbreviated symbols for functional equations are used as follows: `a111` for $a(x, y, z)$ etc.; `c222` for $c(x^2, y^2, z^2)$ etc.; `b111` for $b(x, y, z)$ etc. The symbols `asum`, `csum`, and `bsum` are used to store the series for $a(x)$ (Eq. 12), $c(x)$ (Eq. 12), and $b(x)$ (Eq. 12).

The first part of this code declares three functional equations (Eqs. 53, 54, and 55). In the paragraph “Initial Values,” the initial values $a(x, y, z) = 1$, $c(x^2, y^2, z^2) = 1$, and $b(x, y, z) = 1$ are set by encoding `a111 := 1; c222 := 1;` ... `b333 := 1;`, which means that we put $\alpha_{000} = 1$, $\gamma_{000} = 1$, and $\beta_{000} = 1$ for the initial (trivial) planted promolecule. The paragraph “Recursive Calculation” of the code shows a `do` loop for carbon content k, in which a nested `do` loop for the number of asymmetric centers (l) and three `do` loops further nested for pseudoasymmetric centers (m: `m`, `n`, and `p`) are used. In each `do` loop, the next coefficients are calculated by using a Maple command `coeff` and added to the end of respective functional equations so as to generate intermediate generating functions. After escaping from the outer `do` loop for k, the paragraph “Total and Chiral Stereoisomers” declares the calculation of $B(x, y, z)$ (Eq. 58) and $C(x, y, z)$ (Eq. 60). The paragraphs “Print Out of $\cdots$” of the code show the print-out of the calculation results.

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

```
> read‘‘Alkyl1 − 30zfinal9.mpl″;
```

The above described code gives calculation results according to its print-out sections as follows: `Ns` for steric isomers ($\beta_{k\ell m}$), `Na` for achiral stereoisomers ($\alpha_{k\ell m}$), `Nc` for chiral stereoisomers ($C_{k\ell m}$), and `Nt` for total stereoisomers ($B_{k\ell m}$), where k is successively increased. For example, we obtain the following result:

```
carbon_content := 9

Ns := 39 + 204y + (250 + 2z)y^2 + 56y^3
```

for the coefficient of the term x^9, i.e.,

$$x^9\{39 + 204y + (250 + 2z)y^2 + 56y^3\}, \tag{62}$$

which shows the number of steric isomers ($b(x, y, z)$).

The results printed out by the “Print Out of a111 (Achiral)” section are sorted out in a tabular form (Table 1), where the coefficient ($\alpha_{k\ell m}$) of each term $x^k y^\ell z^m$ is listed up to carbon content $k = 30$. The values beyond the upper limit of ℓ are omitted because they are zero. For example, the values for $k = 9$ appearing in the ($k = 9$, $m = 0$)-row and the ($k = 9$, $m = 1$)-row of Table 1 correspond to the term $x^9(39 + 2y^2 z)$. The total values (α_k) are calculated as the coefficients of a generating function, as shown in the above-mentioned code (`asum`). The generating function stored as `asum` is identical with the generating function $a(x, y, z)$ on the condition of

$y = z = 1$. Because $a(x, y, z)$ is stored as `a111`, the test function `a111-asum` (when $y = 1$ and $z = 1$) shown in the "Validity test" vanishes to zero. The `asum` has been alternatively calculated in a previous paper and reported in a tabular form up to carbon content 100 (Table 1 of Ref. 38).

The results printed out by the "Print Out of ECCxyz (Chiral)" section are shown in a tabular form (Table 2), where the coefficient ($C_{k\ell m}$) of each term $x^k y^\ell z^m$ is listed up to carbon content $k = 30$. The total values ($C_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} C_{k\ell m}$) have been alternatively calculated in a previous paper and reported in a tabular form up to carbon content 100 (Table 1 of Ref. 38).

The results printed out by the "Print Out of EBBxyz (Total)" are shown in a tabular form (Table 3), where the coefficient ($B_{k\ell m}$) of each term $x^k y^\ell z^m$ is listed up to carbon content $k = 30$. The total values ($B_k = \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} B_{k\ell m}$) have been alternatively calculated in a previous paper and reported in a tabular form up to carbon content 100 (Table 1 of Ref. 38).

The results printed out by the "Print Out of b111 (Steric)" are shown in a tabular form (Table 4), where the coefficient ($\beta_{k\ell m}$) of each term $x^k y^\ell z^m$ is listed up to carbon content $k = 30$. The total values (β_k) are calculated as the coefficients of a generating function, as shown in the above-mentioned code (`bsum`). The generating function stored as `bsum` is identical with the generating function $b(x, y, z)$ on the condition of $y = z = 1$. Because $b(x, y, z)$ is stored as `b111`, the test function `b111-bsum` (when $y = 1$ and $z = 1$) shown in the "Validity test" vanishes to zero. The `bsum` has been alternatively calculated in a previous paper and reported in a tabular form up to carbon content 100 (Table 2 of Ref. 38).

By starting from $B(x, y, z)$ (Eq. 58) and $C(x, y, z)$ (Eq. 60), we obtain the following relationships:

$$B(x, y, z) = a(x, y, z) + C(x, y, z), \tag{63}$$

$$b(x, y, z) = a(x, y, z) + 2C(x, y, z) = B(x, y, z) + C(x, y, z). \tag{64}$$

This means that the coefficients of these generating functions satisfy the following relationships:

$$B_{k\ell m} = \alpha_{k\ell m} + C_{k\ell m}, \tag{65}$$

$$\beta_{k\ell m} = \alpha_{k\ell m} + 2C_{k\ell m} = B_{k\ell m} + C_{k\ell m}. \tag{66}$$

These relationships can be confirmed by referring to Table 1 ($\alpha_{k\ell m}$), Table 2 ($C_{k\ell m}$), Table 3 ($B_{k\ell m}$), and Table 4 ($\beta_{k\ell m}$). Hence, we obtain the relationships between the tables: Table 1 + Table 2 = Table 3 and Table 2 + Table 3 = Table 4.

Monosubstituted Alkanes as Constitutional Isomers

In the present enumeration, monosubstituted alkanes are regarded as planted promolecules having nested planted promolecules.[37–39] Mathematically speaking, such planted promolecules as modelling monosubstituted alkanes are regarded as planted three-dimensional trees (or rooted three-dimensional trees from a slightly different viewpoint).[31–33] The three-dimensional point of view has long been overlooked in the conventional combinatorial enumeration so that monosubstituted alkanes have long been enumerated as trees (or more generally graphs, or chemically speaking constitutional isomers), as found in Pólya's article.[14,15] From the viewpoint of the present article, the result described in Section 42 of Pólya's article[14,15] can be regarded as a special case of the present functional equation (Eq. 59). Let $R_{k\ell}$ be the number of monosubstituted alkanes of carbon content k (as graphs or constitutional isomers) which have ℓ asymmetric centers. The $R_{k\ell}$ is the coefficient of the term $x^k y^\ell$ appearing in the generating function:

$$\phi(x, y) = \sum_{k=0}^{\infty} \left(\sum_{\ell=0}^{\infty} R_{k\ell} y^\ell \right) x^k. \tag{67}$$

Note that monosubstituted alkanes as graphs or as constitutional isomers are regarded as having no pseudoasymmetric centers. This means that the concept of sphericity is not taken into consideration. As a result, the component functions appearing in the right-hand side of Eq. 59 are replaced as follows: $\phi(x, y) = a(x, y, z) = b(x, y, z)$ and $\phi(x^2, y^2) = c(x^2, y^2, z^2)$. Because pseudoasymmetric centers vanish during this replacement, we can presume that $\phi(x, y)$ does not contain the variable z. This replacement provides recursivity so that we can place $B(x, y, z) = \phi(x, y)$ in the left-hand side of Eq. 59. Thereby, we obtain the following functional equation:

$$\begin{aligned}\phi(x, y) = {} & 1 + x\phi(x, y)\phi(x^2, y^2) \\ & + \frac{xy}{6}\left\{\phi(x, y)^3 + 2\phi(x^3, y^3) - 3\phi(x, y)\phi(x^2, y^2)\right\}.\end{aligned} \tag{68}$$

This equation was first noted by Pólya[14,15] in terms of an alternative formulation.

The functional equation represented by $\phi(x, y)$ (Eq. 68) is implemented by mean of the Maple programming language. The recursive calculation is executed to give the concrete form of Eq. 67, where $R_{k\ell}$ appears as the coefficient of the term $x^k y^\ell$. The resulting coefficients are listed up to carbon content 30 in Table 5. The total values ($R_k = \sum_{\ell=0}^{\infty} R_{k\ell}$) have been alternatively calculated in a previous paper and reported in a tabular form up to carbon content 100 (Table 2 of Ref. 38).

Discussion

Asymmetric Centers. To exemplify the effect of itemization with respect to asymmetric centers, Figure 2 shows monosubstituted alkanes of carbon content 6. As found at the intersection between the ($k = 6$, $m = 0$)-row and the ($\ell = 0$)-column in Table 1, there exist 8 achiral compounds (**24**–**31** corresponding to the term $8x^6$), where each one is depicted in a square box to show its achirality in Fig. 2. Throughout the present article, the symbol Z (or X) is used to denote a substituent such as an atom (e.g., Cl) or a monovalent ligand (e.g., OH). Because of achirality, the same value 8 appears at the intersection between the ($k = 6$, $m = 0$)-row and the ($\ell = 0$)-column in Table 4 as well as at the intersection between the ($k = 6$)-row and the ($\ell = 0$)-column in Table 5.

The value 8 appearing at the intersection between the ($k = 6$, $m = 0$)-row and the ($\ell = 1$)-column in Table 2 indicates the existence of 8 enantiomeric pairs of chiral compounds (**32**–**39** corresponding to the term $8x^6y$), where the two enantiomers of each pair (e.g., **32**/$\overline{\mathbf{32}}$) are depicted in a box to show their enantiomeric relationship in Fig. 2. Note that each pair of enantiomers is counted just once in the present enumeration for giving Table 2. The two enantiomers of each pair are counted separately in the enumeration as steric isomers, so that the value 16 (=8 × 2) appears at the intersection

Table 1. Achiral Monosubstituted Alkanes (Achiral Planted Trees)[a)]

Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)												
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12
$k = 1$:	$m = 0$:	1												
$k = 2$:	$m = 0$:	1												
$k = 3$:	$m = 0$:	2												
$k = 4$:	$m = 0$:	3												
$k = 5$:	$m = 0$:	5												
$k = 6$:	$m = 0$:	8												
$k = 7$:	$m = 0$:	14												
$k = 8$:	$m = 0$:	23												
$k = 9$:	$m = 0$:	39												
	$m = 1$:	0	0	2										
$k = 10$:	$m = 0$:	65												
	$m = 1$:	0	0	4										
$k = 11$:	$m = 0$:	110												
	$m = 1$:	0	0	12										
$k = 12$:	$m = 0$:	184												
	$m = 1$:	0	0	24										
$k = 13$:	$m = 0$:	310												
	$m = 1$:	0	0	56	0	4								
$k = 14$:	$m = 0$:	520												
	$m = 1$:	0	0	108	0	8								
$k = 15$:	$m = 0$:	876												
	$m = 1$:	0	0	226	0	32								
$k = 16$:	$m = 0$:	1471												
	$m = 1$:	0	0	428	0	64								
$k = 17$:	$m = 0$:	2475												
	$m = 1$:	0	0	842	0	180	0	8						
$k = 18$:	$m = 0$:	4159												
	$m = 1$:	0	0	1568	0	352	0	16						
	$m = 2$:	0	0	0	0	4								
$k = 19$:	$m = 0$:	6996												
	$m = 1$:	0	0	2976	0	842	0	80						
	$m = 2$:	0	0	0	0	14								
$k = 20$:	$m = 0$:	11759												
	$m = 1$:	0	0	5468	0	1620	0	160						
	$m = 2$:	0	0	0	0	52								
$k = 21$:	$m = 0$:	19775												
	$m = 1$:	0	0	10138	0	3514	0	552	0	16				
	$m = 2$:	0	0	0	0	134								

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Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)												
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12
$k = 22$:	$m = 0$:	33244												
	$m = 1$:	0	0	18424	0	6660	0	1088	0	32				
	$m = 2$:	0	0	0	0	372	0	16						
$k = 23$:	$m = 0$:	55902												
	$m = 1$:	0	0	33606	0	13594	0	3020	0	208				
	$m = 2$:	0	0	0	0	874	0	48						
	$m = 3$:	0	0	0	0	0	0	4						
$k = 24$:	$m = 0$:	93984												
	$m = 1$:	0	0	60528	0	25424	0	5880	0	416				
	$m = 2$:	0	0	0	0	2112	0	224						
	$m = 3$:	0	0	0	0	0	0	8						
$k = 25$:	$m = 0$:	158030												
	$m = 1$:	0	0	109120	0	49796	0	14356	0	1712	0	32		
	$m = 2$:	0	0	0	0	4656	0	592						
	$m = 3$:	0	0	0	0	0	0	28						
$k = 26$:	$m = 0$:	265696												
	$m = 1$:	0	0	195084	0	92060	0	27592	0	3392	0	64		
	$m = 2$:	0	0	0	0	10388	0	1872	0	48				
	$m = 3$:	0	0	0	0	0	0	56						
$k = 27$:	$m = 0$:	446746												
	$m = 1$:	0	0	348628	0	175166	0	61812	0	10860	0	520		
	$m = 2$:	0	0	0	0	21942	0	4544	0	148				
	$m = 3$:	0	0	0	0	0	0	160	0	8				
$k = 28$:	$m = 0$:	751128												
	$m = 1$:	0	0	619452	0	320596	0	117392	0	21304	0	1040		
	$m = 2$:	0	0	0	0	46452	0	12056	0	776				
	$m = 3$:	0	0	0	0	0	0	336	0	16				
$k = 29$:	$m = 0$:	1262940												
	$m = 1$:	0	0	1099494	0	597270	0	247716	0	58432	0	5096	0	64
	$m = 2$:	0	0	0	0	94962	0	27576	0	2084				
	$m = 3$:	0	0	0	0	0	0	856	0	80				
$k = 30$:	$m = 0$:	2123444												
	$m = 1$:	0	0	1943564	0	1083664	0	465264	0	113408	0	10128	0	128
	$m = 2$:	0	0	0	0	193788	0	66024	0	7336	0	128		
	$m = 3$:	0	0	0	0	0	0	1872	0	160				

a) Each value at the intersection between a (k, m)-row and an ℓ-column is the coefficient of the term $x^k y^\ell z^m$ of the corresponding generating function, which represents the number of achiral monosubstituted alkanes (or achiral planted trees) of carbon content k having ℓ asymmetric centers, and m pseudoasymmetric centers.

Table 2. Chiral Monosubstituted Alkanes (Chiral Planted Trees)[a)]

Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 1$:	$m = 0$:	0														
$k = 2$:	$m = 0$:	0														
$k = 3$:	$m = 0$:	0														
$k = 4$:	$m = 0$:	0	1													
$k = 5$:	$m = 0$:	0	3													
$k = 6$:	$m = 0$:	0	8	2												
$k = 7$:	$m = 0$:	0	20	10												
$k = 8$:	$m = 0$:	0	46	38	4											
$k = 9$:	$m = 0$:	0	102	125	28											
$k = 10$:	$m = 0$:	0	220	366	148	8										
$k = 11$:	$m = 0$:	0	461	1000	614	80										
	$m = 1$:	0	0	0	2											
$k = 12$:	$m = 0$:	0	948	2588	2224	528	16									
	$m = 1$:	0	0	0	8											
$k = 13$:	$m = 0$:	0	1921	6430	7288	2678	212									
	$m = 1$:	0	0	0	30	4										
$k = 14$:	$m = 0$:	0	3836	15442	22226	11542	1736	32								
	$m = 1$:	0	0	0	90	28										
$k = 15$:	$m = 0$:	0	7574	36099	64024	44296	10528	552								
	$m = 1$:	0	0	0	254	140	12									
$k = 16$:	$m = 0$:	0	14810	82440	176258	155804	53164	5408	64							
	$m = 1$:	0	0	0	656	556	104									
$k = 17$:	$m = 0$:	0	28705	184621	467348	511772	235092	38528	1384							
	$m = 1$:	0	0	0	1630	1944	644	24								
$k = 18$:	$m = 0$:	0	55212	406418	1200794	1590560	941082	224176	16096	128						
	$m = 1$:	0	0	0	3868	6166	3084	312								
$k = 19$:	$m = 0$:	0	105485	881444	3003264	4722211	3481998	1127548	132868	3408						
	$m = 1$:	0	0	0	8928	18242	12812	2424	56							
	$m = 2$:	0	0	0	0	0	1									
$k = 20$:	$m = 0$:	0	200300	1886502	7338342	13488470	12087376	5078308	881084	46240	256					
	$m = 1$:	0	0	0	20028	51044	47544	14188	912							
	$m = 2$:	0	0	0	0	0	14									
$k = 21$:	$m = 0$:	0	378262	3990383	17568320	37274597	39792736	20957372	4989428	437224	8208					
	$m = 1$:	0	0	0	44026	136646	162618	69604	8600	112						
	$m = 2$:	0	0	0	0	0	71	10								
$k = 22$:	$m = 0$:	0	710795	8351598	41306770	100090370	125256596	80543360	25059532	3271600	128896	512				
	$m = 1$:	0	0	0	94896	352580	520388	300284	59504	2480						
	$m = 2$:	0	0	0	0	0	286	96								
$k = 23$:	$m = 0$:	0	1329603	17313245	95569188	262079935	379374736	291709476	114424760	20682904	1382992	19488				
	$m = 1$:	0	0	0	201410	882134	1579116	1175808	338512	28256	240					
	$m = 2$:	0	0	0	0	0	969	572	48							
$k = 24$:	$m = 0$:	0	2476817	35580590	217938684	671102784	1111200994	1004636584	483372116	114973656	11586048	350400	1024			
	$m = 1$:	0	0	0	421330	2149552	4582190	4263028	1669032	229488	6560					
	$m = 2$:	0	0	0	0	0	3006	2658	548							

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Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 25$:	$m = 0$:	0	4596297	72544848	490539158	1684609112	3160355482	3313212250	1913443172	576975336	81194320	4232120	45600			
	$m = 1$:	0	0	0	870782	5119776	12806106	14518996	7384788	1498336	88704	480				
	$m = 2$:	0	0	0	0	0	8606	10604	3760	192						
	$m = 3$:	0	0	0	0	0	0	0	4							
$k = 26$:	$m = 0$:	0	8499396	146838658	1091072398	4153720622	8756831268	10521901730	7167249928	2662854952	496411152	39419992	932096	2048		
	$m = 1$:	0	0	0	1779648	11953052	34648042	46936356	29975448	8363560	832272	16736				
	$m = 2$:	0	0	0	0	0	23386	37916	20176	2488						
	$m = 3$:	0	0	0	0	0	0	0	16							
$k = 27$:	$m = 0$:	0	15665681	295234350	2400601600	10077336701	23704462360	32322699636	25597167948	11457640774	2722286132	304375676	12585768	105536		
	$m = 1$:	0	0	0	3601960	27418554	91146360	145177284	113418548	41436576	6170160	266368	992			
	$m = 2$:	0	0	0	0	0	60615	124930	91876	20008	654					
	$m = 3$:	0	0	0	0	0	0	0	64	8						
$k = 28$:	$m = 0$:	0	28786696	589935412	5229519678	24091300100	62834709062	96406282724	87693394778	46442174708	13655333760	2035586312	129578880	2433408	4096	
	$m = 1$:	0	0	0	7225288	61913932	233916522	432299644	404675668	186750664	38623072	2864112	41792			
	$m = 2$:	0	0	0	0	0	151740	385970	372732	123410	10108					
	$m = 3$:	0	0	0	0	0	0	0	204	56						
$k = 29$:	$m = 0$:	0	52747907	1172058697	11288046304	56823815029	163424779716	280049588272	289611339358	178783431380	63562862420	12138815436	1096595328	36512848	241728	
	$m = 1$:	0	0	0	14378442	137851954	587327436	1245399496	1373689864	779024760	212551796	23916256	773736	1984		
	$m = 2$:	0	0	0	0	0	368029	1132038	1382752	640482	94026	2044				
	$m = 3$:	0	0	0	0	0	0	0	656	292	24					
$k = 30$:	$m = 0$:	0	96398485	2316192378	24159668348	132383741136	417758600542	794388675966	925766439062	657897809376	277591784504	65882588392	7984323808	413361888	6248960	8192
	$m = 1$:	0	0	0	28403928	303051650	1446125922	3484984988	4467008244	3046262712	1055942912	166680864	9442656	102080		
	$m = 2$:	0	0	0	0	0	870384	3180112	4780684	2930222	661828	37232				
	$m = 3$:	0	0	0	0	0	0	0	1964	1276	208					

a) Each value at the intersection between a (k, m)-row and an ℓ-column is the coefficient of the term $x^k y^\ell z^m$ of the corresponding generating function, which represents the number of chiral monosubstituted alkanes (or chiral planted trees) of carbon content k having ℓ asymmetric centers, and m pseudoasymmetric centers. A pair of enantiomeric monosubstituted alkanes is counted just once.

Table 3. Achiral and Chiral Monosubstituted Alkanes (Achiral and Chiral Planted Trees)[a)]

Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 1$:	$m = 0$:	1														
$k = 2$:	$m = 0$:	1														
$k = 3$:	$m = 0$:	2														
$k = 4$:	$m = 0$:	3	1													
$k = 5$:	$m = 0$:	5	3													
$k = 6$:	$m = 0$:	8	8	2												
$k = 7$:	$m = 0$:	14	20	10												
$k = 8$:	$m = 0$:	23	46	38	4											
$k = 9$:	$m = 0$:	39	102	125	28											
	$m = 1$:	0	0	2												
$k = 10$:	$m = 0$:	65	220	366	148	8										
	$m = 1$:	0	0	4												
$k = 11$:	$m = 0$:	110	461	1000	614	80										
	$m = 1$:	0	0	12	2											
$k = 12$:	$m = 0$:	184	948	2588	2224	528	16									
	$m = 1$:	0	0	24	8											
$k = 13$:	$m = 0$:	310	1921	6430	7288	2678	212									
	$m = 1$:	0	0	56	30	8										
$k = 14$:	$m = 0$:	520	3836	15442	22226	11542	1736	32								
	$m = 1$:	0	0	108	90	36										
$k = 15$:	$m = 0$:	876	7574	36099	64024	44296	10528	552								
	$m = 1$:	0	0	226	254	172	12									
$k = 16$:	$m = 0$:	1471	14810	82440	176258	155804	53164	5408	64							
	$m = 1$:	0	0	428	656	620	104									
$k = 17$:	$m = 0$:	2475	28705	184621	467348	511772	235092	38528	1384							
	$m = 1$:	0	0	842	1630	2124	644	32								
$k = 18$:	$m = 0$:	4159	55212	406418	1200794	1590560	941082	224176	16096	128						
	$m = 1$:	0	0	1568	3868	6518	3084	328								
	$m = 2$:	0	0	0	0	4										
$k = 19$:	$m = 0$:	6996	105485	881444	3003264	4722211	3481998	1127548	132868	3408						
	$m = 1$:	0	0	2976	8928	19084	12812	2504	56							
	$m = 2$:	0	0	0	0	14	1									
$k = 20$:	$m = 0$:	11759	200300	1886502	7338342	13488470	12087376	5078308	881084	46240	256					
	$m = 1$:	0	0	5468	20028	52664	47544	14348	912							
	$m = 2$:	0	0	0	0	52	14									
$k = 21$:	$m = 0$:	19775	378262	3990383	17568320	37274597	39792736	20957372	4989428	437224	8208					
	$m = 1$:	0	0	10138	44026	140160	162618	70156	8600	128						
	$m = 2$:	0	0	0	0	134	71	10								
$k = 22$:	$m = 0$:	33244	710795	8351598	41306770	100090370	125256596	80543360	25059532	3271600	128896	512				
	$m = 1$:	0	0	18424	94896	359240	520388	301372	59504	2512						
	$m = 2$:	0	0	0	0	372	286	112								
$k = 23$:	$m = 0$:	55902	1329603	17313245	95569188	262079935	379374736	291709476	114424760	20682904	1382992	19488				
	$m = 1$:	0	0	33606	201410	895728	1579116	1178828	338512	28464	240					
	$m = 2$:	0	0	0	0	874	969	620	48							
	$m = 3$:	0	0	0	0	0	0	4								

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Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 24$:	$m = 0$:	93984	2476817	35580590	217938684	671102784	1111200994	1004636584	483372116	114973656	11586048	350400	1024			
	$m = 1$:	0	0	60528	421330	2174976	4582190	4268908	1669032	229904	6560					
	$m = 2$:	0	0	0	0	2112	3006	2882	548							
	$m = 3$:	0	0	0	0	0	0	8								
$k = 25$:	$m = 0$:	158030	4596297	72544848	490539158	1684609112	3160355482	3313212250	1913443172	576975336	81194320	4232120	45600			
	$m = 1$:	0	0	109120	870782	5169572	12806106	14533352	7384788	1500048	88704	512				
	$m = 2$:	0	0	0	0	4656	8606	11196	3760	192						
	$m = 3$:	0	0	0	0	0	0	28	4							
$k = 26$:	$m = 0$:	265696	8499396	146838658	1091072398	4153720622	8756831268	10521901730	7167249928	2662854952	496411152	39419992	932096	2048		
	$m = 1$:	0	0	195084	1779648	12045112	34648042	46963948	29975448	8366952	832272	16800				
	$m = 2$:	0	0	0	0	10388	23386	39788	20176	2536						
	$m = 3$:	0	0	0	0	0	0	56	16							
$k = 27$:	$m = 0$:	446746	15665681	295234350	2400601600	10077336701	23704462360	32322699636	25597167948	11457640774	2722286132	304375676	12585768	105536		
	$m = 1$:	0	0	348628	3601960	27593720	91146360	145239096	113418548	41447436	6170160	266888	992			
	$m = 2$:	0	0	0	0	21942	60615	129474	91876	20156	654					
	$m = 3$:	0	0	0	0	0	0	160	64	16						
$k = 28$:	$m = 0$:	751128	28786696	589935412	5229519678	24091300100	62834709062	96406282724	87693394778	46442174708	13655333760	2035586312	129578880	2433408	4096	
	$m = 1$:	0	0	619452	7225288	62234528	233916522	432417036	404675668	186771968	38623072	2865152	41792			
	$m = 2$:	0	0	0	0	46452	151740	398026	372732	124186	10108					
	$m = 3$:	0	0	0	0	0	0	336	204	72						
$k = 29$:	$m = 0$:	1262940	52747907	1172058697	11288046304	56823815029	163424779716	280049588272	289611339358	178783431380	63562862420	12138815436	1096595328	36512848	241728	
	$m = 1$:	0	0	1099494	14378442	138449224	587327436	1245647212	1373689864	779083192	212551796	23921352	773736	2048		
	$m = 2$:	0	0	0	0	94962	368029	1159614	1382752	642566	94026	2044				
	$m = 3$:	0	0	0	0	0	0	856	656	372	24					
$k = 30$:	$m = 0$:	2123444	96398485	2316192378	24159668348	132383741136	417758600542	794388675966	925766439062	657897809376	277591784504	65882588392	7984323808	413361888	6248960	8192
	$m = 1$:	0	0	1943564	28403928	304135314	1446125922	3485450252	4467008244	3046376120	1055942912	166690992	9442656	102208		
	$m = 2$:	0	0	0	0	193788	870384	3246136	4780684	2937558	661828	37360				
	$m = 3$:	0	0	0	0	0	0	1872	1964	1436	208					

a) Each value at the intersection between a (k, m)-row and an ℓ-column is the coefficient of the term $x^k y^\ell z^m$ of the corresponding generating function, which represents the number of achiral and chiral monosubstituted alkanes (or achiral and chiral planted trees) of carbon content k having ℓ asymmetric centers, and m pseudoasymmetric centers. A pair of enantiomeric monosubstituted alkanes is counted just once.

Table 4. Monosubstituted Alkanes as Steric Isomers (Planted Trees as Steric Isomers)[a)]

Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 1$:	$m = 0$:	1														
$k = 2$:	$m = 0$:	1														
$k = 3$:	$m = 0$:	2														
$k = 4$:	$m = 0$:	3	2													
$k = 5$:	$m = 0$:	5	6													
$k = 6$:	$m = 0$:	8	16	4												
$k = 7$:	$m = 0$:	14	40	20												
$k = 8$:	$m = 0$:	23	92	76	8											
$k = 9$:	$m = 0$:	39	204	250	56											
	$m = 1$:	0	0	2												
$k = 10$:	$m = 0$:	65	440	732	296	16										
	$m = 1$:	0	0	4												
$k = 11$:	$m = 0$:	110	922	2000	1228	160										
	$m = 1$:	0	0	12	4											
$k = 12$:	$m = 0$:	184	1896	5176	4448	1056	32									
	$m = 1$:	0	0	24	16											
$k = 13$:	$m = 0$:	310	3842	12860	14576	5356	424									
	$m = 1$:	0	0	56	60	12										
$k = 14$:	$m = 0$:	520	7672	30884	44452	23084	3472	64								
	$m = 1$:	0	0	108	180	64										
$k = 15$:	$m = 0$:	876	15148	72198	128048	88592	21056	1104								
	$m = 1$:	0	0	226	508	312	24									
$k = 16$:	$m = 0$:	1471	29620	164880	352516	311608	106328	10816	128							
	$m = 1$:	0	0	428	1312	1176	208									
$k = 17$:	$m = 0$:	2475	57410	369242	934696	1023544	470184	77056	2768							
	$m = 1$:	0	0	842	3260	4068	1288	56								
$k = 18$:	$m = 0$:	4159	110424	812836	2401588	3181120	1882164	448352	32192	256						
	$m = 1$:	0	0	1568	7736	12684	6168	640								
	$m = 2$:	0	0	0	0	4										
$k = 19$:	$m = 0$:	6996	210970	1762888	6006528	9444422	6963996	2255096	265736	6816						
	$m = 1$:	0	0	2976	17856	37326	25624	4928	112							
	$m = 2$:	0	0	0	0	14	2									
$k = 20$:	$m = 0$:	11759	400600	3773004	14676684	26976940	24174752	10156616	1762168	92480	512					
	$m = 1$:	0	0	5468	40056	103708	95088	28536	1824							
	$m = 2$:	0	0	0	0	52	28									
$k = 21$:	$m = 0$:	19775	756524	7980766	35136640	74549194	79585472	41914744	9978856	874448	16416					
	$m = 1$:	0	0	10138	88052	276806	325236	139760	17200	240						
	$m = 2$:	0	0	0	0	134	142	20								
$k = 22$:	$m = 0$:	33244	1421590	16703196	82613540	200180740	250513192	161086720	50119064	6543200	257792	1024				
	$m = 1$:	0	0	18424	189792	711820	1040776	601656	119008	4992						
	$m = 2$:	0	0	0	0	372	572	208								
$k = 23$:	$m = 0$:	55902	2659206	34626490	191138376	524159870	758749472	583418952	228849520	41365808	2765984	38976				
	$m = 1$:	0	0	33606	402820	1777862	3158232	2354636	677024	56720	480					
	$m = 2$:	0	0	0	0	874	1938	1192	96							
	$m = 3$:	0	0	0	0	0	0	4								

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Carbon content (k)	No. of pseudoasym. centers (m)	No. of asymmetric centers (ℓ)														
		$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$k = 24$:	$m = 0$:	93984	4953634	71161180	435877368	1342205568	2222401988	2009273168	966744232	229947312	23172096	700800	2048			
	$m = 1$:	0	0	60528	842660	4324528	9164380	8531936	3338064	459392	13120					
	$m = 2$:	0	0	0	0	2112	6012	5540	1096							
	$m = 3$:	0	0	0	0	0	0	8								
$k = 25$:	$m = 0$:	158030	9192594	145089696	981078316	3369218224	6320710964	6626424500	3826886344	1153950672	162388640	8464240	91200			
	$m = 1$:	0	0	109120	1741564	10289348	25612212	29052348	14769576	2998384	177408	992				
	$m = 2$:	0	0	0	0	4656	17212	21800	7520	384						
	$m = 3$:	0	0	0	0	0	0	28	8							
$k = 26$:	$m = 0$:	265696	16998792	293677316	2182144796	8307441244	17513662536	21043803460	14334499856	5325709904	992822304	78839984	1864192	4096		
	$m = 1$:	0	0	195084	3559296	23998164	69296084	93900304	59950896	16730512	1664544	33536				
	$m = 2$:	0	0	0	0	10388	46772	77704	40352	5024						
	$m = 3$:	0	0	0	0	0	0	56	32							
$k = 27$:	$m = 0$:	446746	31331362	590468700	4801203200	20154673402	47408924720	64645399272	51194335896	22915281548	5444572264	608751352	25171536	211072		
	$m = 1$:	0	0	348628	7203920	55012274	182292720	290416380	226837096	82884012	12340320	533256	1984			
	$m = 2$:	0	0	0	0	21942	121230	254404	183752	40164	1308					
	$m = 3$:	0	0	0	0	0	0	160	128	24						
$k = 28$:	$m = 0$:	751128	57573392	1179870824	10459039356	48182600200	125669418124	192812565448	175386789556	92884349416	27310667520	4071172624	259157760	4866816	8192	
	$m = 1$:	0	0	619452	14450576	124148460	467833044	864716680	809351336	373522632	77246144	5729264	83584			
	$m = 2$:	0	0	0	0	46452	303480	783996	745464	247596	20216					
	$m = 3$:	0	0	0	0	0	0	336	408	128						
$k = 29$:	$m = 0$:	1262940	105495814	2344117394	22576092608	113647630058	326849559432	560099176544	579222678716	357566862760	127125724840	24277630872	2193190656	73025696	483456	
	$m = 1$:	0	0	1099494	28756884	276301178	1174654872	2491046708	2747379728	1558107952	425103592	47837608	1547472	4032		
	$m = 2$:	0	0	0	0	94962	736058	2291652	2765504	1283048	188052	4088				
	$m = 3$:	0	0	0	0	0	0	856	1312	664	48					
$k = 30$:	$m = 0$:	2123444	192796970	4632384756	48319336696	264767482272	835517201084	1588777351932	1851532878124	1315795618752	555183569008	131765176784	15968647616	826723776	12497920	16384
	$m = 1$:	0	0	1943564	56807856	607186964	2892251844	6970435240	8934016488	6092638832	2111885824	333371856	18885312	204288		
	$m = 2$:	0	0	0	0	193788	1740768	6426248	9561368	5867780	1323656	74592				
	$m = 3$:	0	0	0	0	0	0	1872	3928	2712	416					

a) Each value at the intersection between a (k, m)-row and an ℓ-column is the coefficient of the term $x^k y^\ell z^m$ of the corresponding generating function, which represents the number of steric-isomeric monosubstituted alkanes (or planted trees) of carbon content k having ℓ asymmetric centers, and m pseudoasymmetric centers. The term "steric isomers" means that two enantiomeric monosubstituted alkanes of each pair as well as each achiral monosubstituted alkane are counted separately.

Table 5. Monosubstituted Alkanes as Constitutional Isomers (Planted Trees as Graphs)[a)]

Carbon content (k)	No. of asymmetric centers (ℓ)															Total
	$\ell = 0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
$k = 1$:	1															1
$k = 2$:	1															1
$k = 3$:	2															2
$k = 4$:	3	1														4
$k = 5$:	5	3														8
$k = 6$:	8	8	1													17
$k = 7$:	14	20	5													39
$k = 8$:	23	46	19	1												89
$k = 9$:	39	102	63	7												211
$k = 10$:	65	220	184	37	1											507
$k = 11$:	110	461	503	154	10											1238
$k = 12$:	184	948	1300	558	66	1										3057
$k = 13$:	310	1921	3229	1830	336	13										7639
$k = 14$:	520	3836	7748	5581	1447	108	1									19241
$k = 15$:	876	7574	18106	16077	5558	657	17									48865
$k = 16$:	1471	14810	41327	44251	19553	3325	168	1								124906
$k = 17$:	2475	28705	92521	117308	64246	14721	1201	21								321198
$k = 18$:	4159	55212	203601	301330	199683	58983	7001	249	1							830219
$k = 19$:	6996	105485	441466	753458	592876	218374	35265	2064	26							2156010
$k = 20$:	11759	200300	944618	1840568	1693381	758406	158988	13731	357	1						5622109
$k = 21$:	19775	378262	1997726	4405344	4679194	2497521	656673	77896	3391	31						14715813
$k = 22$:	33244	710795	4180405	10355493	12563059	7863097	2525319	391792	25451	496	1					38649152
$k = 23$:	55902	1329603	8665024	23953832	32890944	23818373	9150776	1790854	161234	5348	37					101821927
$k = 24$:	93984	2476817	17805427	54614151	84209834	69768308	31526948	7571690	897673	44979	673	1				269010485
$k = 25$:	158030	4596297	36299704	122903818	211350124	198427258	104003493	29993281	4510393	315956	8170	43				712566567
$k = 26$:	265696	8499396	73468100	273320540	521036453	549788043	330356126	112409211	20837236	1935267	76382	893	1			1891993344
$k = 27$:	446746	15665681	147704332	601273377	1263877089	1488156714	1014979050	401637790	89732628	10627949	591302	12120	50			5034704828
$k = 28$:	751128	28786696	295122569	1309641376	3020984153	3944381970	3027555010	1376459204	363973318	53373564	3962350	125303	1164	1		13425117806
$k = 29$:	1262940	52747907	586304222	2826528077	7124425584	10257729294	8795080038	4547075713	1401964120	248685802	23666190	1063372	17553	57		35866550869
$k = 30$:	2123444	96398485	1158582080	6048868456	16595396005	26218501826	24948258845	14538172582	5161527642	1086960570	128614892	7759462	199506	1492	1	95991365288

a) Each value at the intersection between a (k)-row and an ℓ-column is the coefficient of the term $x^k y^\ell$ of the corresponding generating function, which represents the number of constitutional-isomeric monosubstituted alkanes (or planted trees) of carbon content k having ℓ asymmetric centers. The term "constitutional isomers" means that each inequivalent constitutional isomer is counted as a graph.

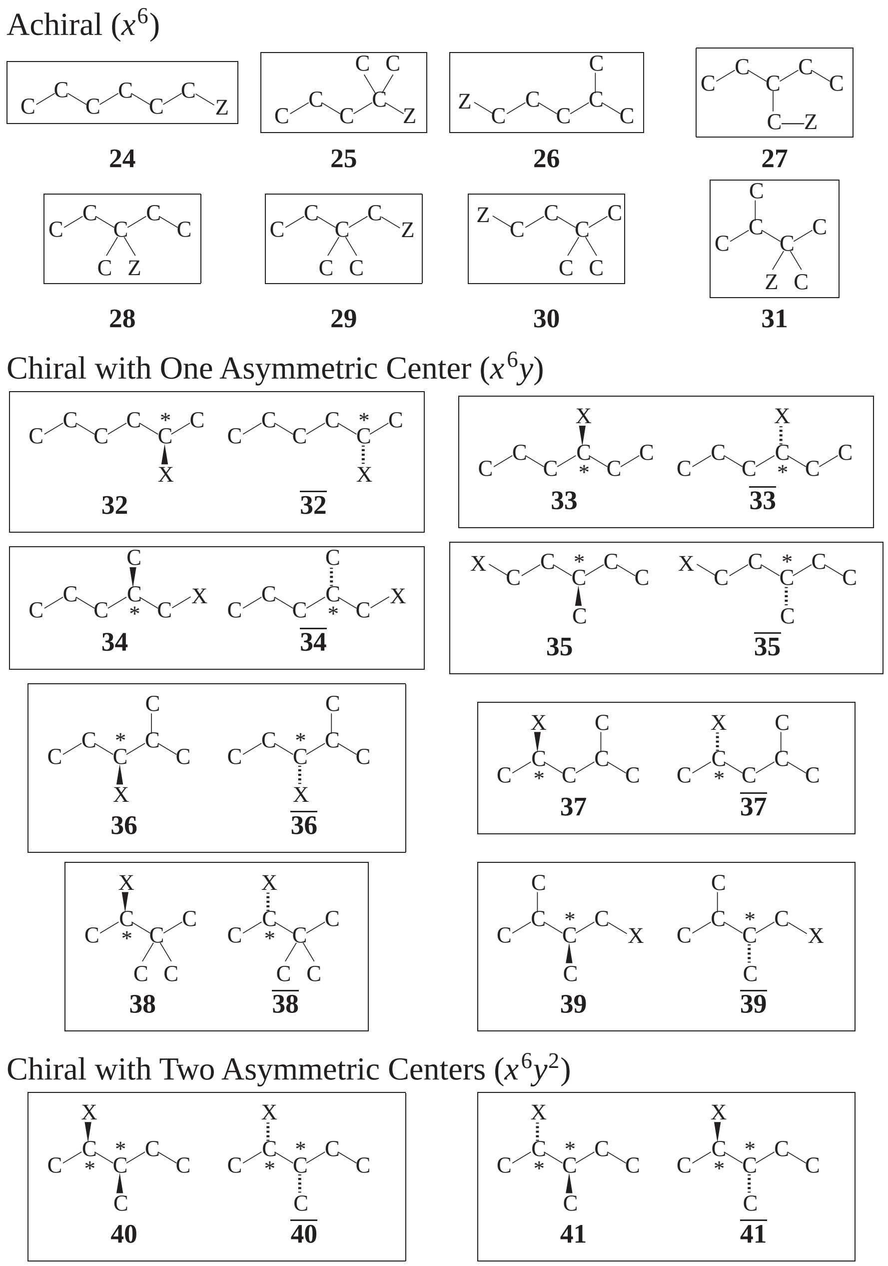

Fig. 2. Monosubstituted alkanes of carbon content 6, which are itemized with respect to the number of asymmetric centers. The symbol Z (or X) denotes an atom (e.g., Cl) or an achiral ligand (e.g., OH) which is regarded as a monovalent substituent. Each asymmetric center is denoted by an asterisk.

between the ($k = 6$, $m = 0$)-row and the ($\ell = 1$)-column in Table 4. On the other hand, the value 8 at the intersection between the ($k = 6$)-row and the ($\ell = 1$)-column in Table 5 indicates the existence of 8 constitutional isomers in agreement with the fact that the number of constitutional isomers is equal to that of enantiomeric pairs with a single asymmetric center.

The value 2 appearing at the intersection between the ($k = 6$, $m = 0$)-row and the ($\ell = 2$)-column in Table 2 indicates the existence of two enantiomeric pairs of chiral compounds (**40** and **41** corresponding to the term $8x^6y^2$), where the power 2 of the variable y indicates the presence of two asymmetric centers. They are also depicted in Fig. 2. The value 4 ($=2 \times 2$) which appears at the intersection between the ($k = 6$, $m = 0$)-row and the ($\ell = 1$)-column in Table 4 is in agreement with the result of Table 2, because the two enantiomers of each pair are counted separately. On the other hand, the value 1 at the intersection between the ($k = 6$)-row and the ($\ell = 2$)-column in Table 5 shows that **40**/$\overline{\mathbf{40}}$ and **41**/$\overline{\mathbf{41}}$ degenerate to give a single constitutional isomer (one graph).

Pseudoasymmetric Centers. Pseudoasymmetry for Carbon Content 9: As found in Fig. 1, planted promolecules of Type V (achiral and *RS*-astereogenic) such as **22** and **23** are accompanied by a pair of enantiomers of Type II such as **3**/$\overline{\mathbf{3}}$. By keeping this general result in mind, let us examine the present enumeration of monosubstituted alkanes.

Table 1 shows that there appear the lowest examples of

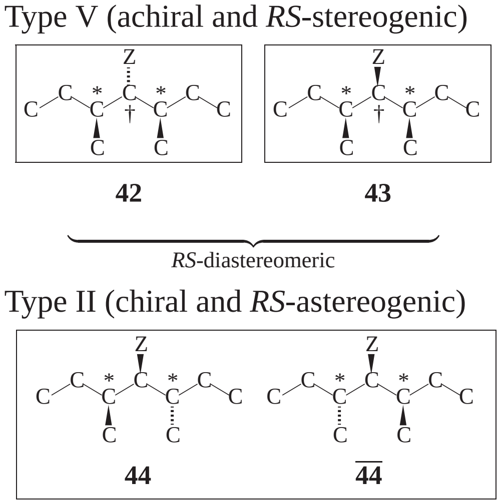

Fig. 3. Achiral monosubstituted alkanes (**42** and **43**) of Type V corresponding to the term $2x^9y^2z$, which exhibit pseudoasymmetry, as well as a related enantiomeric pair of chiral monosubstituted alkanes (**44** and $\overline{\mathbf{44}}$) of Type II, which is contained by one in the coefficient 125 of the term $125x^9y^2$. Each carbon center with an asterisk is an asymmetric center, while each one with a dagger is a pseudoasymmetric center.

pseudoasymmetry at the rows of carbon content $k = 9$, where the relevant values correspond to the term $x^9(39 + 2y^2z)$ in the generating function (Eq. 50). Thus, the integer 2 at the intersection of the ($\ell = 2$)-column and the ($m = 1$)-row in Table 1 corresponds to the term $2x^9y^2z$, which shows the existence of two monosubstituted alkanes, where the variable z (i.e., z^1) shows the presence of a single pseudoasymmetric center in each of them. They belong to Type V, which are depicted in Fig. 3 (**42** and **43**). Two enantiomeric ligands of opposite chiralities (i.e., *sec*-butyl ligands) in each of them (**42** and **43**) compensate their opposite effects so that the carbon center at the 4-position (marked with a dagger) is regarded as a pseudoasymmetric center.

As chiral counterparts of the achiral monosubstituted alkanes (**42** and **43**) of Type V, one pair of enantiomers (**44** and $\overline{\mathbf{44}}$) is also depicted in Fig. 3. Because the values appearing in the ($k = 9$, $m = 0$)-row of Table 2 corresponds to the generating function $x^9(102y + 125y^2 + 28y^3)$ according to Eq. 57, the pair of **44** and $\overline{\mathbf{44}}$ contributes by one to the coefficient 125 of the term $125x^9y^2$. This contribution can be rationalized by referring to Table 5, where the ($k = 9$)-row indicates a generating function $x^9(39 + 102y + 63y^2 + 7y^3)$. Because the enumeration collected in Table 5 ignores pseudoasymmetric centers, the two achiral compounds (**42** and **43**) and the pair of enantiomers (**44** and $\overline{\mathbf{44}}$) are equalized to be regarded as one constitutional isomer (a single graph), which contributes by one to the coefficient 63 of the term $63x^9y^2$. Thereby, we can conclude that the remaining 62 constitutional isomers generate stereoisomers with two asymmetric centers. Because the present enumeration of chiral compounds is based on the criterion that each pair of enantiomers is counted just one, the coefficient 125 of the term $125x^9y^2$ can be calculated as follows:

$$\frac{62 \times 2^2}{2} + 1 = 125. \tag{69}$$

Coefficient 28 of term $28y^3$ appearing in the ($k = 9$, $m = 0$)-row of Table 1 can be correlated to coefficient 7 of term $7y^3$ appearing in the ($k = 9$)-row of Table 5 as follows:

$$\frac{7 \times 2^3}{2} = 28. \tag{70}$$

Coefficient 39 of term $39x^9$ appearing in the ($k = 9$, $m = 0$)-row of Table 1 is identical with coefficient 39 of term $39x^9$ appearing in the ($k = 9$)-row of Table 5, because each achiral compound corresponds to one constitutional isomer in general. Coefficient 102 of term $102x^9y$ appearing in the ($k = 9$, $m = 0$)-row of Table 2 is identical with coefficient 102 of term $102x^9y$ appearing in the ($k = 9$)-row of Table 5 because of $(102 \times 2^1)/2 = 102$ according to the present criterion.

Pseudoasymmetric and Related Asymmetric Centers: As found in Fig. 1, planted promolecules of Type V (achiral and *RS*-stereogenic) such as **22** and **23** are closely related to planted promolecules of Type III (chiral and *RS*-stereogenic) such as **18** and **19**, if A and q ($\overline{\mathrm{q}}$) are constitutionally isomeric to each other. By keeping this general result in mind, let us examine the present enumeration of monosubstituted alkanes of carbon content 14 where the pair $\mathrm{p}/\overline{\mathrm{p}}$ is selected from the pair of *sec*-butyl ligands of opposite configurations (x^4y); the achiral ligand A is selected from five achiral pentyl ligands ($5x^5$); and the pair of chiral ligands $\mathrm{q}/\overline{\mathrm{q}}$ is selected from three pairs of chiral pentyl ligands ($3x^5y$). For the sake of simplicity, they are referred to as $xz(x^4y)^2(x^5)$-type (one of Type V), $x(x^4y)^2(x^5y)$-type (one of Type II), or $xy(x^4y)^2(x^5y)$-type (one of Type III).

The ($k = 14$, $m = 0$)- and ($k = 14$, $m = 1$)-rows of Table 1 correspond to a generating function $x^{14}(520 + 108y^2z + 8y^4z)$ according to Eq. 50. The coefficient 108 of the term $108x^{14}y^2z$ indicates the existence of 108 monosubstituted alkanes of Type V. Manual enumeration shows the existence of ten $xz(x^4y)^2(x^5)$-type compounds among 108 monosubstituted alkanes of Type V as shown in Fig. 4.

The existence of ten $xz(x^4y)^2(x^5)$-type compounds (Fig. 4) is more clearly demonstrated as follows. Achiral monosubstituted alkanes of Type V can be counted by a modification of Eq. 20:

$$\begin{aligned}\text{CI-CF}^{(\mathrm{V})}(C_{3v}; a_d, c_d) &= xz\text{CI-CF}^{(\mathrm{V})}(C_3; a_d, c_d)\\ &= xz(a_1c_2 - a_1a_2),\end{aligned} \tag{71}$$

because the change of C_3 into C_{3v} gives identical results in cases of achiral compounds. In order to enumerate such $xz(x^4y)^2(x^5)$-type compounds, we use the following ligand inventories:

$$a_d = 5x^{5d}, \tag{72}$$

$$\begin{aligned}c_d &= 5x^{5d} + 2 \times 3(x^{5d/2}y^{d/2} \times x^{5d/2}y^{d/2})\\ &\quad + 2(x^{4d/2}y^{d/2} \times x^{4d/2}y^{d/2})\\ &= 5x^{5d} + 6x^{5d}y^d + 2x^{4d}y^d,\end{aligned} \tag{73}$$

$$\begin{aligned}b_d &= 5x^{5d} + (3x^{5d}y^d + 3x^{5d}y^d) + (x^{4d}y^d + x^{4d}y^d)\\ &= 5x^{5d} + 6x^{5d}y^d + 2x^{4d}y^d.\end{aligned} \tag{74}$$

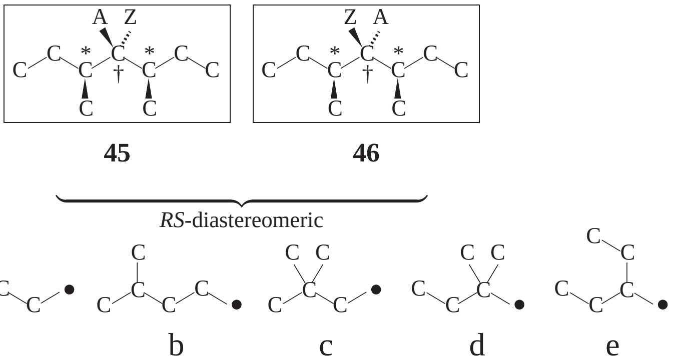

Fig. 4. Achiral monosubstituted alkanes of Type V corresponding to the term $10x^{14}y^2z$, which exhibit pseudoasymmetry. Each carbon center with an asterisk is an asymmetric center, while each one with a dagger is a pseudoasymmetric center. Two achiral monosubstituted alkanes with the same substituent (A) (e.g., **45a** vs. **46a**) are *RS*-diastereomeric.

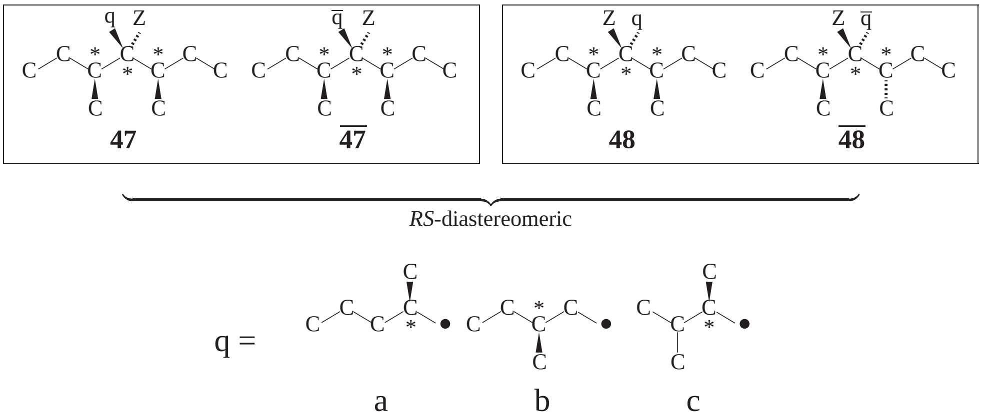

Fig. 5. Chiral monosubstituted alkanes of Type III corresponding to the term $6x^{14}y^4$, which are related to but do not exhibit pseudoasymmetry. Each carbon center with an asterisk is an asymmetric center. Each pair of enantiomers (i.e., **47a**/$\overline{\textbf{47a}}$, **47b**/$\overline{\textbf{47b}}$, **47c**/$\overline{\textbf{47c}}$; **48a**/$\overline{\textbf{48a}}$, **48b**/$\overline{\textbf{48b}}$, or **48c**/$\overline{\textbf{48c}}$) is counted just once. One chiral ligand of carbon content 5 is depicted as q which is a representation of each enantiomeric pair of q and $\overline{\text{q}}$.

It should be noted $2 \times 3(x^{5d/2}y^{d/2} \times x^{5d/2}y^{d/2})$ for c_d and $(3x^{5d}y^d + 3x^{5d}y^d)$ for b_d give the same term $6x^{5d}y^d$. These ligand inventories are introduced into Eq. 71. The resulting equation is expanded to give the following generating function:

$$g^{(\mathrm{V})} = 10x^{14}y^2z + 30x^{16}y^2z, \tag{75}$$

where the coefficient 10 of the first term in the right-hand side shows the existence of ten $xz(x^4y)^2(x^5)$-type compounds (Fig. 4).

To exemplify the relationship between Type V (e.g., **22** and **23**) and Type III (e.g. **18** and **19**), the achiral ligands for A (Fig. 4) are replaced by q (or $\overline{\text{q}}$). Thereby, we obtain six planted promolecules of Type III ($xy(x^4y)^2(x^5y)$-type) as shown in Fig. 5 (i.e., **47a**/$\overline{\textbf{47a}}$, **47b**/$\overline{\textbf{47b}}$, **47c**/$\overline{\textbf{47c}}$; **48a**/$\overline{\textbf{48a}}$, **48b**/$\overline{\textbf{48b}}$, and **48c**/$\overline{\textbf{48c}}$), where each pair of enantiomers surrounded by a box is counted just once. The number 6 for the $xy(x^4y)^2(x^5y)$-type is a part of the value 11542 appearing at the intersection of the ($k = 14$, $m = 0$)-row and the ($\ell = 4$)-column in Table 2 (corresponding to the term $11542x^{14}y^4$).

The existence of six $xy(x^4y)^2(x^5y)$-type compounds (Fig. 5) is more clearly demonstrated by starting from Eq. 30. Because Eq. 30 counts two enantiomers of each pair separately, each pair can be counted just once by calculating the half of Eq. 30 as follows:

$$\begin{aligned}
&\text{CI-CF}^{(\mathrm{III})}(C_{3v}; a_d, b_d, c_d)\\
&\quad = \frac{xy}{2}\,\text{CI-CF}^{(\mathrm{III})}(C_3; a_d, b_d, c_d)\\
&\quad = \frac{xy}{6}(b_1^3 + 2b_3) - \frac{xy}{6}(a_1^3 + 2a_3)\\
&\qquad - \frac{xy}{2}(b_1b_2 - a_1a_2) - \frac{xy}{2}(a_1c_2 - a_1a_2),
\end{aligned} \tag{76}$$

where xy is multiplied because the principal vertex newly introduced is an asymmetric center. The ligand inventories shown in Eqs. 72–74 are introduced into Eq. 76 and the resulting equation is expanded to give the following generating function:

$$\begin{aligned}
g^{(\mathrm{III})} &= 6x^{14}y^4 + x^{15}(20y^2 + 60y^3 + 30y^4)\\
&\quad + x^{16}(60y^2 + 60y^3 + 20y^4).
\end{aligned} \tag{77}$$

The coefficient 6 of the first term $6x^{14}y^4$ ($=6xy(x^4y)^2(x^5y)$) in the right-hand side shows the existence of six $xy(x^4y)^2(x^5y)$-type compounds, which have been already depicted in Fig. 5.

To exemplify a relationship between Type V (e.g., **22** and **23**) and Type II (e.g. **3** and **3**), the pair of chiral ligands (p/$\overline{\text{p}}$) (Fig. 4) is replaced by two p's (or p's). Thereby, we obtain five planted promolecules of Type II ($x(x^4y)^2(x^5)$-type) as shown in

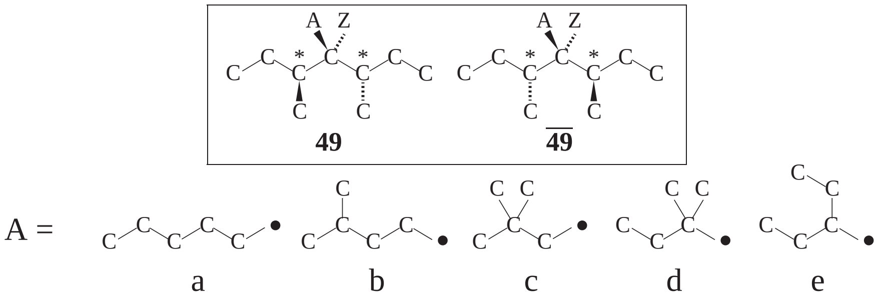

Fig. 6. Chiral monosubstituted alkanes of Type II corresponding to the term $5x^{14}y^2$, which are related to but do not exhibit pseudoasymmetry. Each carbon center with an asterisk is an asymmetric center. Each pair of enantiomers (i.e., **49a**/$\overline{\mathbf{49a}}$, **49b**/$\overline{\mathbf{49b}}$, **49c**/$\overline{\mathbf{49c}}$, **49d**/$\overline{\mathbf{49d}}$, or **49e**/$\overline{\mathbf{49e}}$) is counted just once.

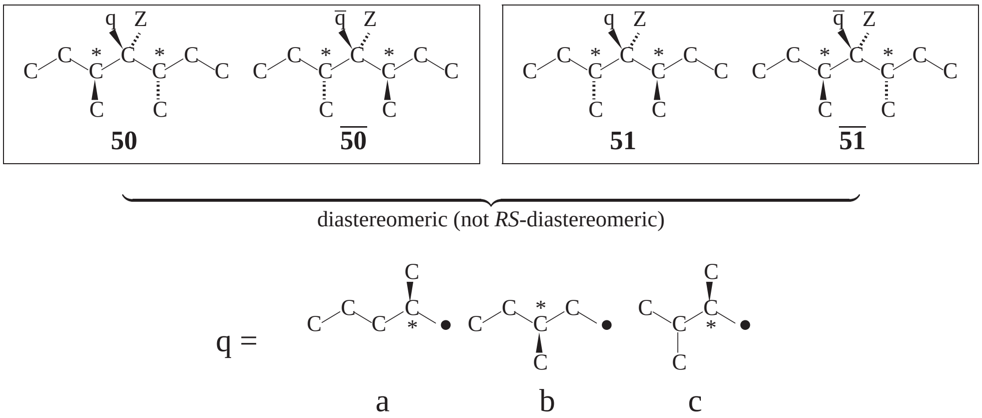

Fig. 7. Chiral monosubstituted alkanes of Type II corresponding to the term $6x^{14}y^3$, which are related to but do not exhibit pseudoasymmetry. Each carbon center with an asterisk is an asymmetric center. Each pair of enantiomers (i.e., **50a**/$\overline{\mathbf{50a}}$, **50b**/$\overline{\mathbf{50b}}$, **50c**/$\overline{\mathbf{50c}}$; **51a**/$\overline{\mathbf{51a}}$, **51b**/$\overline{\mathbf{51b}}$, or **51c**/$\overline{\mathbf{51c}}$) is counted just once. One chiral ligand of carbon content 5 is depicted as q which is a representation of each enantiomeric pair of q and $\overline{\text{q}}$.

Fig. 6 (i.e., **49a**/$\overline{\mathbf{49a}}$, **49b**/$\overline{\mathbf{49b}}$, **49c**/$\overline{\mathbf{49c}}$, **49d**/$\overline{\mathbf{49d}}$, and **49e**/$\overline{\mathbf{49e}}$), where each pair of enantiomers surrounded by a box is counted just once. The number 5 for the $x(x^4y)^2(x^5)$-type is part of the value 15442 appearing at the intersection of the ($k = 14$, $m = 0$)-row and the ($\ell = 2$)-column in Table 2 (corresponding to the term $15442x^{14}y^2$).

Another relationship between Type V (e.g., **22** and **23**) and Type II (e.g. **6** and **7**) emerges when the achiral ligand A (Fig. 4) is replaced by a chiral ligand q (or $\overline{\text{q}}$) and the pair of chiral ligands (p/$\overline{\text{p}}$) is replaced by two p's (or p's). Thereby, we obtain six planted promolecules of Type II ($x(x^4y)^2(x^5y)$-type) as shown in Fig. 7 (i.e., **50a**/$\overline{\mathbf{50a}}$, **50b**/$\overline{\mathbf{50b}}$, **50c**/$\overline{\mathbf{50c}}$; **51a**/$\overline{\mathbf{51a}}$, **51b**/$\overline{\mathbf{51b}}$, and **51c**/$\overline{\mathbf{51c}}$) where each pair of enantiomers surrounded by a box is counted just once. The number 6 for the $x(x^4y)^2(x^5y)$-type is part of the value 22226 appearing at the intersection of the ($k = 14$, $m = 0$)-row and the ($\ell = 3$)-column in Table 2 (corresponding to the term $22226x^{14}y^3$).

The number 5 for the $x(x^4y)^2(x^5)$-type (Fig. 6) and the number 6 for the $x(x^4y)^2(x^5y)$-type (Fig. 7) are more clearly demonstrated by starting from Eq. 23. Because Eq. 23 counts two enantiomers of each pair separately, each pair can be counted just once by calculating the half of Eq. 23 as follows:

$$\begin{aligned}\text{CI-CF}^{(\text{II})}(C_{3v}; a_d, b_d) &= \frac{x}{2}\,\text{CI-CF}^{(\text{II})}(C_3; a_d, b_d)\\ &= \frac{x}{2}(b_1b_2 - a_1a_2). \end{aligned} \tag{78}$$

The ligand inventories shown in Eqs. 72–74 are introduced into Eq. 78. The resulting equation is expanded to give the following generating function:

$$\begin{aligned} g^{(\text{II})} &= 2x^{13}y^3 + x^{14}(5y^2 + 6y^3) + x^{15}(5y + 6y^3)\\ &\quad + x^{16}(15y + y^2 + 18y^3). \end{aligned} \tag{79}$$

The coefficient 5 of the term $5x^{14}y^2$ corresponds to the $x(x^4y)^2(x^5)$-type (Fig. 6) and the coefficient 6 of the term $6x^{14}y^3$ corresponds to the number 6 for the $x(x^4y)^2(x^5y)$-type (Fig. 7).

On the same line as above, the number of planted promolecules of Type I is derived from Eq. 28, while the number on planted promolecules of Type IV is derived from Eq. 18:

$$\begin{aligned}\text{CI-CF}^{(\text{I})}(C_{3v}; a_d) &= \frac{xy}{2}\,\text{CI-CF}^{(\text{I})}(C_3; a_d)\\ &= \frac{xy}{6}(a_1^3 + 2a_3 - 3a_1a_2). \end{aligned} \tag{80}$$

$$\begin{aligned}\text{CI-CF}^{(\text{IV})}(C_{3v}; a_d) &= x\text{CI-CF}^{(\text{IV})}(C_3; a_d)\\ &= xa_1a_2. \end{aligned} \tag{81}$$

The ligand inventories shown in Eqs. 72–74 are introduced into Eqs. 80 and 81. The resulting equations are expanded to give the following generating functions:

$$g^{(\text{I})} = 10x^{16}y, \tag{82}$$

$$g^{(\text{IV})} = 25x^{16}. \tag{83}$$

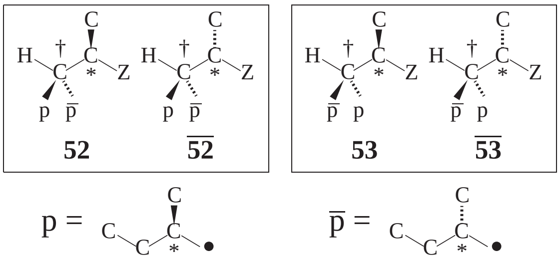

Fig. 8. Two enantiomeric pairs of chiral monosubstituted alkanes of Type I corresponding to the term $x^{11}y^{3}z$. A terminal hydrogen atom is added to show the configuration of each terminal carbon center. The carbon atom with an asterisk is an asymmetric center. Each pseudoasymmetric center with a dagger is restricted into an asymmetric center.

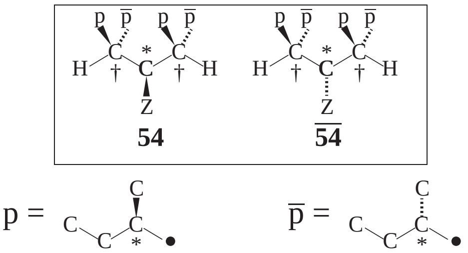

Fig. 9. An enantiomeric pair of chiral monosubstituted alkanes of Type I corresponding to the term $x^{19}y^{5}z^{2}$. Terminal hydrogen atoms are added to show the configurations of the terminal carbon centers. The central carbon atom with an asterisk is an asymmetric center. Each pseudoasymmetric center with a dagger is restricted into an asymmetric center.

Restriction of Pseudoasymmetric Centers into Asymmetric Ones. Pseudoasymmetric Centers in Chiral Monosubstituted Alkanes: It depends upon the global chirality/achirality of a given promolecule whether a carbon with a pair of enantiomeric proligands (e.g., p and $\bar{p}$) in the promolecule is asymmetric or pseudoasymmetric. In other words, pseudoasymmetric centers determined by means of Criterion 1 described above may be restricted into asymmetric centers if they are nested in a chiral promolecule.

The lowest examples of such a restriction are illustrated in Fig. 8. The two enantiomeric pairs (**52**/$\overline{\mathbf{52}}$ and **53**/$\overline{\mathbf{53}}$) correspond to the term $2x^{11}y^{3}z$, which is listed as the value 2 at the intersection of the ($k = 11$, $m = 1$)-row and the ($\ell = 3$)-column in Table 2.

According to Criterion 1, the pseudoasymmetry of an achiral proligand (A = $\mathrm{p\bar{p}CH}$–, i.e., **42**) in **52** ($\overline{\mathbf{52}}$) or that of an achiral proligand of the same constitution (B = $\mathrm{\bar{p}pCH}$–, i.e., **43**) in **53** ($\overline{\mathbf{53}}$) is determined in isolation, i.e., without being incorporated in the promolecule **52** ($\overline{\mathbf{52}}$) or **53** ($\overline{\mathbf{53}}$). These proligands (achiral in isolation) are, however, restricted into chiral ones in **52** ($\overline{\mathbf{52}}$) or **53** ($\overline{\mathbf{53}}$). As a result, the pseudoasymmetric centers (†) are restricted into asymmetric centers.

By using the *RS*-diastereomeric pair of achiral proligands, A (**42**) and B (**43**), another example of Type I (ABHC–Z) is constructed as shown in Fig. 9. This example corresponds to the value 1 appearing at the intersection of the ($k = 19$, $m = 2$)-row and the ($\ell = 5$)-column in Table 2, which shows the existence of a pair of enantiomeric monosubstituted alkanes (**54**/$\overline{\mathbf{54}}$) shown in Fig. 9. The pseudoasymmetric centers (†) of the achiral proligands, i.e., A (**42**) and B (**43**), are restricted into asymmetric centers when incorporated in the enantiomeric monosubstituted alkanes (**54**/$\overline{\mathbf{54}}$).

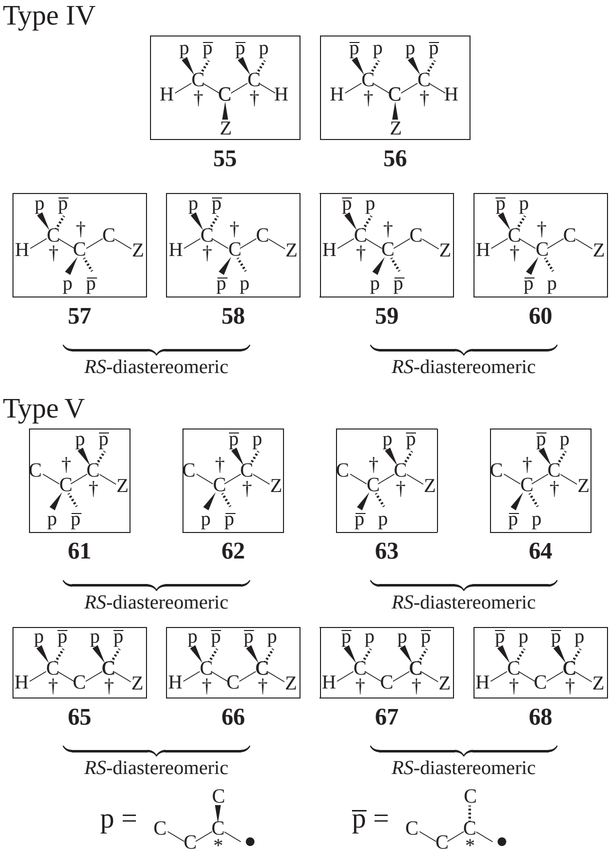

Fig. 10. Achiral monosubstituted alkanes of Types IV and V corresponding to the term $x^{19}y^{4}z^{2}$. A hydrogen atom is added to show configuration if necessary. Each carbon center with a dagger is a pseudoasymmetric center. Each pseudoasymmetric center of **55** or **56** is restricted into an asymmetric center, while each pseudoasymmetric center of the remaining Type IV or of Type V exhibits no restriction.

Pseudoasymmetric Centers in Achiral Monosubstituted Alkanes: Even if they are nested in an achiral promolecule, pseudoasymmetric centers due to Criterion 1 may be restricted into asymmetric centers. Let us examine achiral monosubstituted alkanes which correspond to the value 14 appearing at the intersection of the ($k = 19$, $m = 2$)-row and the ($\ell = 4$)-column in Table 1. Among the 14 compounds, **55** ($\mathrm{B_2HC}$–Z) and **56** ($\mathrm{A_2HC}$–Z) belong to Type IV, where we use A (**42**) and B (**43**) as achiral proligands. There are four compounds of another Type IV (**57**–**60**). The remaining 8 compounds (**61**–**68**) belong to Type V as shown in Fig. 10.

Each pseudoasymmetric center of **55** or **56** is restricted into an asymmetric center, because the two achiral ligands $\mathrm{B_2}$ of **55** ($\mathrm{B_2HC}$–Z) or $\mathrm{A_2}$ of **56** ($\mathrm{A_2HC}$–Z) construct an orbit governed by the coset representation $(C_1\backslash)C_s$. In other words, each B (or A) belongs to the local symmetry C_1 (i.e., chiral and asymmetric). Hence the carbon center (†) of the B (or A) is restricted into an asymmetric center so that **55** and **56** are concluded to be prochiral.

On the other hand, each of the four compounds (**57**–**60**) has a principal vertex of primary carbon center, so that it is classified into a planted promolecule of **21**, where B is hydrogen and A is the remaining ligand. Note that the proligand A belongs to the local symmetry C_s. This means that the carbon centers (†) of A are not restricted and remain to be pseudoasymmetric.

Each pseudoasymmetric center of Type V (**61**–**68**) exhibits no restriction, because it belongs to the local symmetry C_s (achiral). For example, the pseudoasymmetry of the carbon attached to Z in **61** stems from the fact that **61** is ascribed to **22** of Type V because **61** consists of three proligands, A (=$\mathrm{CH_3p\overline{p}C}$–), p, and $\overline{\mathrm{p}}$. The proligand A ($\mathrm{CH_3p\overline{p}C}$–) is governed by the coset representation $(C_s\backslash)C_s$ when incorporated in **61**. The proligand A (=$\mathrm{CH_3p\overline{p}C}$–) in isolation belongs to C_s, which is identical with the local symmetry decided by $(C_s\backslash)C_s$. The proligand A (=$\mathrm{CH_3p\overline{p}C}$–) in isolation is also ascribed to **22** of Type V because the proligand A consists of three proligands, $\mathrm{CH_3}$ (achiral), p, and $\overline{\mathrm{p}}$. It follows that the principal vertex of the proligand A (=$\mathrm{CH_3p\overline{p}C}$–) is concluded to be pseudoasymmetric. Similar rationalization can be applied to the remaining monosubstituted alkanes (**62**–**68**).

Potentialities as Basic Data for Enumerating Alkanes. It is worthwhile to add some comments from a viewpoint of applications of the present enumeration data, i.e., potentialities of the present enumeration data of substituted alkanes as basic data for further enumerations of alkanes and their derivatives. Because enumeration data of substituted alkanes (planted trees) are the same as those of alkyl ligands in general, they have been used to count alkanes (trees). Various approaches to treat alkanes or trees have appeared, e.g., a chemistry-oriented method using recursive formulas,[13] a recursive method using functional equations,[14,17] a generating-function method based on the dissimilarity characteristic equation,[16] an enumeration method of general acyclic hydrocarbons,[61] a tree-pruning algorithm,[22,62] an IUPAC-name-oriented algorithm,[63] and a constructive enumeration.[64] These approaches have capabilities of being combined with the concept of sphericities, which is one of the key concepts of the present enumeration.

In previous papers, we have obtained the enumeration data of substituted alkanes or planted trees as three-dimensional (3D) objects,[37–39] where the data have taken account of the concept of sphericities. They have been applied to treat alkanes or trees as 3D-objects, where the substituted alkanes (or planted trees) are presumed to be recursively restricted as inner (pro)ligands by means of the concept of sphericities. According to this guideline derived from the concept of sphericities, Fujita's proligand method[31–33] has been applied to the enumeration of achiral and chiral alkanes (mathematically speaking, 3D-trees of degree 4), e.g., (1) an enumeration based on the dichotomy of centroidal and bicentroidal alkanes;[40] (2) an enumeration based on 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;[65] (3) an enumeration based on 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;[41] (4) an enumeration based on the combination of the two dichotomies;[42] as well as (5) an enumeration by combining Fujita's proligand method with Fujita's PCI method in order to obtain numbers of alkanes subdivided with respect to their point-group symmetries.[66]

Because these enumerations (1)–(5) have not been itemized with respect to the numbers of asymmetric and pseudoasymmetric carbons, they should be extended to cover such itemization by starting from the present enumeration data. In order to accomplish these extended enumerations, a method of categorizing tetrahedral molecules into *RS*-stereoisomeric types should be developed according to the introduction of the concepts of *RS*-stereoisomeric groups and stereoisograms.[43,48,67–70] The concept of sphericities, which was originally formulated on the basis of point groups in Fujita's USCI approach,[25,71–73] should be extended to retain consistency during the conceptual extension of point groups into *RS*-stereoisomeric groups. Because a prototype of such a categorizing method as assuring the consistency has been developed,[74] the next task will be to develop the extended versions of (1)–(5) as well as those of various approaches described in the first paragraph of the present subsection, where resulting values will be itemized with respect to the numbers of asymmetric and pseudoasymmetric carbons by starting from the data of the present paper.

Conclusion

Planted promolecules derived from a methane skeleton of C_{3v}-symmetry have been counted and categorized into five types (Types I–V) in terms of chirality, *RS*-stereogenicity, and sclerality by the method recently developed.[43] *RS*-Stereogenic planted promolecules (Types I, III, and V) are divided into chiral (Types I and III) and achiral ones (Type V), where the central atom of each planted promolecule of Types I and III is regarded as an asymmetric center, while the central atom of each planted promolecule of Type V is regarded as a pseudoasymmetric center. Monosubstituted alkanes as stereoisomers 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 (ℓ), as well as to the number of pseudoasymmetric carbons (m). Each itemized number has been obtained as the coefficient of the term $x^k y^\ell z^m$ appearing in the respective generating function, which has been derived by following Fujita's proligand method.[31–33] The itemized values up to carbon content 30 have been listed in tabular forms, which are distinctively concerned with achiral stereoisomers, chiral stereoisomers, and steric isomers. Monosubstituted alkanes as constitutional isomers (graphs) have been also counted by omitting pseudoasymmetry. Thereby, Pólya's previous result[14,15] has been formulated as a special case of the present enumeration.

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