

Detailed Categorization and Enumeration of Primary, Secondary, and Tertiary Monosubstituted Alkanes by Considering Internal Branching

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Abstract

Primary, secondary, and tertiary monosubstituted alkanes are counted as three-dimensional (3D) structures, where branching indicators (q for quaternary carbons, t for tertiary carbons, s for secondary carbons, and p for primary carbons) are introduced to evaluate the effect of internal branching. Each monosubstituted alkane of carbon content k , which is composed of n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons ($k = n_q + n_t + n_s + n_p$), is characterized by the product of branching indicators (named a *branching monomial*), $q^{n_q} t^{n_t} s^{n_s} p^{n_p} x^k$. The number of primary, secondary, or tertiary monosubstituted alkanes as 3D structures is calculated as the coefficient of the term $q^{n_q} t^{n_t} s^{n_s} p^{n_p} x^k$ in a generating function, which is obtained by starting from functional equations involving branching indicators. Three kinds of sphericity indices, i.e., a_d for homospheric cycles, c_d for enantiospheric cycles, and b_d for hemispheric cycles, which have been developed by Fujita's USCI (unit-subduced-cycle-index) approach (S. Fujita, *Symmetry and Combinatorial Enumeration in Chemistry*, Springer-Verlag, 1991) and modified by Fujita's proligand method (S. Fujita, *Theor. Chem. Acc.* **2005**, *113*, 73–79, *113*, 80–86; S. Fujita, *Theor. Chem. Acc.* **2006**, *115*, 37–53), are replaced by $a(x^d, q^d, t^d, s^d, p^d)$, $c(x^d, q^d, t^d, s^d, p^d)$, and $b(x^d, q^d, t^d, s^d, p^d)$ so as to produce functional equations for recursive calculation. Respective functional equations for counting primary, secondary, and tertiary monosubstituted alkanes are derived and used to produce such generating functions. The respective results are collected in tabular forms up to carbon content 15, where the numbers of monosubstituted alkanes as 3D structures are further itemized into achiral and

chiral ones. By omitting the sphericity concept, the functional equations for 3D structures are transformed into the counterparts for graphs, which are applied to the enumeration of primary, secondary, and tertiary monosubstituted alkanes as graphs (chemically, constitutional isomers) or as planted trees, more specifically speaking.

1 Introduction

Henze and Blair have calculated the numbers of primary, secondary, and tertiary aliphatic alcohols of given carbon contents [1], where constitutional isomers were counted separately with respect to each constitution (each molecular formula, i.e., carbon content in the case of alcohols). In other words, the numbers obtained by Henze-Blair's method were concerned with graphs (or with planted trees, more specifically speaking) so that they were calculated on the basis of equivalence or inequivalence as graphs. From a mathematical point of view which has later been introduced by Pólya [2, 3], Henze-Blair's method can be recognized as relying implicitly on the symmetry group of degree 3 (S^3). According to these features, Henze-Blair's method lacks the concept of chirality/achirality so as to be incapable of treating pseudoasymmetric cases properly. For example, two achiral isomers of 3,5-dimethylheptan-4-ol (pseudoasymmetric cases) and one enantiomeric pair of chiral isomers are equalized to degenerate into a single graph, which is counted just once by Henze-Blair's method or even by means of a more mathematical method due to Pólya's theorem [2].

On the other hand, we have recently obtained the numbers of primary, secondary, and tertiary aliphatic alcohols of given carbon contents [4], where the numbers were concerned with three-dimensional (3D) structures. Our method was based on Fujita's proligand method [5–7] and employed equivalence or inequivalence as 3D structures under a point group C_{3v} . It follows that pairs of enantiomers (or achiral 3D-objects as self-enantiomeric pairs) are counted separately with respect to each constitution (or each molecular formula, i.e., carbon content in the case of alcohols). Thereby, our method is capable of treating pseudoasymmetric cases properly, where two achiral isomers of 3,5-dimethylheptan-4-ol (pseudoasymmetric cases) and one enantiomeric pair of chiral isomers are counted separately [4].

It is to be noted, however, that our method has focused on the number of stereoisomers *per constitution* (for carbon content), where numerical behaviors of homologs were studied when the constitution (i.e., carbon content) varies [4]. For example, the number of secondary alcohols of carbon content 9 was obtained to be 139 (5 achiral alcohols and 134 pairs of enantiomers) by our method (cf. Table 2 of Ref. [4]), where the two achiral isomers of 3,5-dimethylheptan-4-ol (pseudoasymmetric cases) contribute to the 5 achiral alcohols by two (cf. Fig. 4 of Ref. [4]), while the enantiomeric pair of chiral isomers contributes to the 134 pairs by one.

As found in the discussions described above, the Henze-Blair's enumeration [1] and our enumeration [4] have relied on a common criterion for counting, i.e., *per constitution*, although the two enumerations have been different in their viewpoints, i.e., graphs vs. 3D structures. Although such 3D structures have been categorized by the criterion of chirality/achirality, this criterion is not effective in the categorization of graphs. For the purpose of detailed discussions, it is desirable to develop a new criterion which is common to graphs and 3D structures and more specific than "per constitution".

The lack of such a common criterion remains untouched in related enumerations. The above-mentioned numbers of aliphatic alcohols can be regarded as those of monosubstituted alkanes. There have appeared related articles which dealt with various enumerations of mono-

substituted alkanes [8–10], where they also adopted the criterion “per constitution”. At the same time, the numbers of aliphatic alcohols are considered to be the numbers of alkyl ligands, which have been used as a basic data for counting alkanes, as found in articles appearing in this journal [11–14] and other journals [15, 16]. These articles have also relied on the criterion “per constitution”.

On the other hand, the conventional stereochemistry frequently refers to the number of stereoisomers *per graph* (with respect to one two-dimensional structure), where such a graph is presumed to be specified to have a fixed constitution. In the conventional stereochemistry [17, 18], the number of stereoisomers per graph has been calculated to be 2^ℓ if the graph has ℓ asymmetric carbons, except *meso* or pseudoasymmetric cases. Because such a graph as presumed for 3,5-dimethylheptan-4-ol has two asymmetric centers and may have one pseudoasymmetric center, for example, the corresponding stereoisomers are enumerated manually in the conventional stereochemistry. The adoption of the criterion “per graph” in the conventional stereochemistry means that it abandons the development of a common criterion applicable to graphs and 3D structures. In order to obtain a deeper insight to quantitative aspects of stereochemistry, it is desirable to develop a new criterion as a mathematical tool for bridging the conceptual gap between “per constitution” and “per graph”.

To bridge the gap between “per constitution” and “per graph”, we here propose an intermediate concept “per divergence”, which is characterized by a set of degrees of internal branching. To emphasize the proposal, we develop branching indicators for indicating primary (*p*), secondary (*s*), tertiary (*t*), and quaternary carbons (*q*). Thereby, we obtain the number of stereoisomers *per divergence*, which enables us to develop a detailed categorization of monosubstituted alkanes (e.g., aliphatic alcohols) or of planted 3D trees, mathematical speaking. The detailed categorization is shown to be also applicable even if such 3D objects are regarded as graphs.

2 Preformed Alkyl Moieties (PAMs)

2.1 Monosubstituted Alkanes and Preformed Alkyl Moieties (PAMs)

In previous papers, Fujita’s proligand method [5–7] has been applied to the enumeration of monosubstituted alkanes [4, 8, 9]. In order to extend the previous methodology to enumeration problems with considering internal branching, we should take account of the fact that the degree of branching in a monosubstituted alkane (as an inner alkyl ligand) is altered during a recursive process, as exemplified in Fig. 1.

Let us examine the generation of a tertiary monosubstituted alkane (**4**) by starting from lower monosubstituted alkanes (**1–3**), where we pay attention to the degree of the principal carbon attached by a Z-substituent in each of the participants at issue. The primary carbon (1°) of **1**, the secondary carbon (2°) of **3**, and the tertiary carbon (3°) of **2** are promoted respectively into a secondary, a tertiary, and a quaternary one after incorporated into the resulting monosubstituted alkane (**4**). This means that the conversion of lower monosubstituted alkanes (e.g., **1–3**) into a higher one (e.g., **4**) is not recursive with respect to the degree of branching at each principal carbon, although recursive nature has been found if we have taken account of carbon content only [4].

To assure recursive nature with respect to degrees of branching as well as to carbon content, preformed alkyl moieties (PAMs) **1’–3’** are considered in place of **1–3**, where the branching degree of each principal carbon is promoted by one (methyl to primary, primary to secondary,

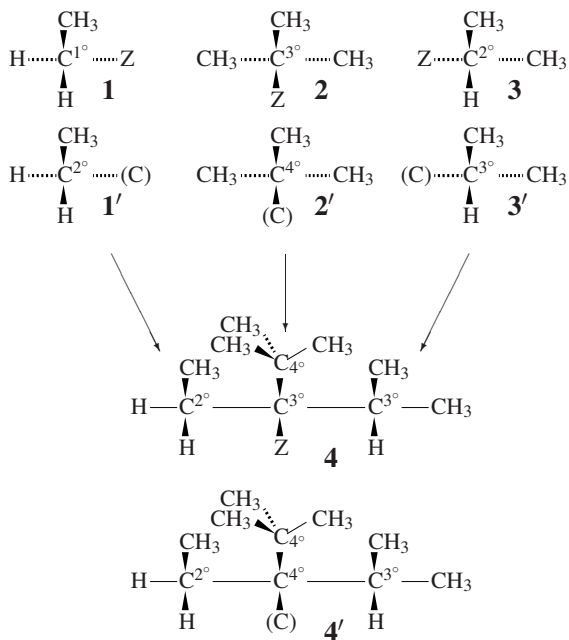


Figure 1: Degrees of branching (1°–4°) in monosubstituted alkanes (1–4) and preformed alkyl moieties (PAMs, 1'–4') during recursive processes of substitution. Configurations are shown by wedged bonds and/or hashed dash bonds.

secondary to tertiary, and tertiary to quaternary) in advance under the precondition that a further substitution shall occur on a carbon of the next step (as found in **4**). Moreover, the tertiary carbon (3°) attached by Z in **4** is changed into a quaternary carbon (4°) in a PAM (**4'**), which participates in a further substitution. By considering these PAMs, the process represented by $1' + 2' + 3' \rightarrow 4'$ accompanies no change of branching degrees so as to exhibit recursive nature.

2.2 Branching Indicators for Preformed Alkyl Moieties (PAMs)

To develop the concept “per divergence” as an intermediate concept between “per constitution” and “per graph”, let us now introduce *branching indicators* for indicating such divergence (i.e., degrees of branching). They are dummy variables defined as follows: q for n_q quaternary carbons, t for n_t tertiary carbons, s for n_s secondary carbons, and p for n_p primary carbons, where a set of these carbons is contained in a compound of carbon content k ($= n_q + n_t + n_s + n_p$). Thereby, the compound is characterized by a monomial expression, $q^{n_q} t^{n_t} s^{n_s} p^{n_p} x^k$, which is here called a *branching monomial* (BM). For example, the monosubstituted alkane (**4**) corresponds to a BM $qt^2sp^6x^{10}$, while the corresponding PAM (**4'**) is characterized by a BM $q^2tsp^6x^{10}$. Note that all of the six terminal methyl ligands consist of primary carbons. It should be commented here that an extreme case (e.g., methanol) is represented by a BM x , while the corresponding PAM (i.e., methyl—(C)) is regarded as being primary and represented by a

Table 1: Products of Sphericity Indices for Monosubstituted Alkanes [4]

	primary	secondary	tertiary
achiral	a_1 (eq. 13 of Ref. [4])	c_2 (eq. 23 of Ref. [4])	$a_1 c_2$ (eq. 33 of Ref. [4])
steric	b_1 (eq. 12 of Ref. [4])	b_1^2 (eq. 22 of Ref. [4])	$\frac{1}{3}(b_1^3 + 2b_3)$ (eq. 32 of Ref. [4])
diploid	c_2	c_2^2	and $\frac{1}{3}(c_2^3 + 2c_6)$

BM px . We also refer to the term $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$ without x^k under the same name *branching monomial* (BM) if we do not put stress on the carbon content k .

2.3 Recursive Enumeration of PAMs as 3D structures

Let the symbol $\alpha_{kn_q n_t n_s n_p}$ be the number of inequivalent achiral PAMs of carbon content k which have a divergence characterized by n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons; the symbol $\beta_{kn_q n_t n_s n_p}$ be the number of inequivalent steric isomers of PAMs of the same carbon content and divergence; and the symbol $\gamma_{kn_q n_t n_s n_p}$ be the number of inequivalent diploids of PAMs of the same carbon content and divergence. For the terms “steric isomers” and “diploids”, see Refs. [5–7]. Following Fujita’s proligand method [5–7], we are able to write down generating functions of these numbers on the basis of the above-described branching indicators, (i.e., $q, t, s,$ and p) as follows:

$$a(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} \alpha_{kn_q n_t n_s n_p} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (1)$$

$$b(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} \beta_{kn_q n_t n_s n_p} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (2)$$

$$c(x^2, q^2, t^2, s^2, p^2) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} \gamma_{kn_q n_t n_s n_p} p^{2n_p} \right) s^{2n_s} \right) t^{2n_t} \right) q^{2n_q} \right) x^{2k}, \quad (3)$$

where the orders of the summations can be exchanged freely. Thus, the number ($\alpha_{kn_q n_t n_s n_p}$, $\beta_{kn_q n_t n_s n_p}$, or $\gamma_{kn_q n_t n_s n_p}$) appears as the coefficient of the term $q^{n_q} t^{n_t} s^{n_s} p^{n_p} x^k$ in eq. 1 or eq. 2 (or $q^{2n_q} t^{2n_t} s^{2n_s} p^{2n_p} x^{2k}$ in eq. 3).

The data of products of sphericity indices (Table 1) have been previously obtained without considering internal branching [4] by following Fujita’s proligand method [5–7]. The data (Table 1) are extended and applied to evaluate how primary, secondary, and tertiary cases contribute to internal branching.

To convert a product of sphericity indices (collected in Table 1) into a functional equation, the component sphericity indices ($a_k, b_k,$ and c_k) are replaced by respective functions, $a(x^k, q^k, t^k, s^k, p^k)$, $b(x^k, q^k, t^k, s^k, p^k)$, and $c(x^k, q^k, t^k, s^k, p^k)$. Thereby, the data at the “achiral” row of Table 1 provide the following functions:

$$\text{primary} \quad xs \{a(x, q, t, s, p) - 1\} \quad (4)$$

$$\text{secondary} \quad xt \{c(x^2, q^2, t^2, s^2, p^2) - 1\} \quad (5)$$

$$\text{tertiary} \quad xq \{a(x, q, t, s, p) - 1\} \{c(x^2, q^2, t^2, s^2, p^2) - 1\}. \quad (6)$$

Note that, if we have obtained $a(x, q, t, s, p)$ for treating achiral objects, the substitution of achiral objects on a central carbon atom is represented by a function $xs \{a(x, q, t, s, p) - 1\}$ as found in eq. 4. The term xs shows that the central carbon results in the appearance of one secondary carbon; and the remaining part $\{a(x, q, t, s, p) - 1\}$ stems from the term a_1 , where the subtraction of 1 is to delete the unit (1) for treating a trivial case (substitution of a hydrogen). Similarly, eqs. 5 and 6 can be derived on the basis of the products of sphericities collected in Table 1.

After eqs. 4–6 for achiral cases are summed up, the term (1) is added to treat a trivial case (a hydrogen atom) as well as the term xp is added to evaluate the contribution of a methyl ligand. Thereby, we obtain the following functional equation:

$$\begin{aligned} a(x, q, t, s, p) = & 1 + xp + xs \{a(x, q, t, s, p) - 1\} + xt \{c(x^2, q^2, t^2, s^2, p^2) - 1\} \\ & + xq \{a(x, q, t, s, p) - 1\} \{c(x^2, q^2, t^2, s^2, p^2) - 1\}. \end{aligned} \quad (7)$$

On the same line, the data at the “steric” and “diploid” rows of Table 1 provide the following functional equations:

$$\begin{aligned} b(x, q, t, s, p) = & 1 + xp + xs \{b(x, q, t, s, p) - 1\} + xt \{b(x, q, t, s, p) - 1\}^2 \\ & + \frac{xq}{3} \{[b(x, q, t, s, p) - 1]^3 + 2[b(x^3, q^3, t^3, s^3, p^3) - 1]\}, \end{aligned} \quad (8)$$

$$\begin{aligned} c(x^2, q^2, t^2, s^2, p^2) = & 1 + x^2 p^2 + x^2 s^2 \{c(x^2, q^2, t^2, s^2, p^2) - 1\} \\ & + x^2 t^2 \{c(x^2, q^2, t^2, s^2, p^2) - 1\}^2 \\ & + \frac{x^2 q^2}{3} \{[c(x^2, q^2, t^2, s^2, p^2) - 1]^3 + 2[c(x^6, q^6, t^6, s^6, p^6) - 1]\}, \end{aligned} \quad (9)$$

where the first term (1) is added to treat a trivial case (a hydrogen atom) and the second term (xp or $x^2 p^2$) is added to evaluate the contribution of a methyl ligand.

The functional equations (eqs. 7–9) have recursive nature. Hence, the generating functions for enumerating PAMs (eqs. 1–3) are obtained stepwise. Thus, we are able to evaluate the data of carbon content $k + 1$ by introducing the data of carbon content k into the right-hand sides of these functional equations. The resulting generation functions (eqs. 1–3) can be used to evaluate the numbers of primary, secondary, and tertiary monosubstituted alkanes, as discussed detailedly from the next subsection on.

3 Enumeration as Three-Dimensional Structures

3.1 Primary Monosubstituted Alkanes

Let the symbol $P_{kn_q n_t n_s n_p}^{(A)}$ be the number of inequivalent achiral monosubstituted alkanes of primary type, where k carbons in each monosubstituted alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons; the symbol $P_{kn_q n_t n_s n_p}^{(C)}$ be the number of inequivalent chiral monosubstituted alkanes of primary type under a similar categorization, where each pair of enantiomers is counted once; and the symbol $P_{kn_q n_t n_s n_p}^{(B)}$ be the total number of inequivalent monosubstituted alkanes of primary type

under a similar categorization, where each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once. Thereby, we are able to write down generating functions of these numbers by using the above-described branching indicators, (i.e., q , t , s , and p) as follows:

$$P^{(A)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_sn_p}^{(A)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (10)$$

$$P^{(C)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_sn_p}^{(C)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (11)$$

$$P^{(B)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_sn_p}^{(B)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (12)$$

The task of the present section is to derive functional equations for producing these generating functions (eqs. 10–12).

Because we deal with primary monosubstituted alkanes, we employ the term xp in place of xs used in the processes for deriving eq. 4 and so on. Hence, the data at the “achiral” column of Table 1 (the “achiral” row and the “steric” row) provide us with the following functional equations:

$$P^{(a)}(x, q, t, s, p) = xp\{a(x, q, t, s, p) - 1\} \quad (13)$$

$$P^{(b)}(x, q, t, s, p) = xp\{b(x, q, t, s, p) - 1\}. \quad (14)$$

The functions $a(x, q, t, s, p)$ and $b(x, q, t, s, p)$ in the right-hand sides have been obtained recursively by using the respective functional equations (eqs. 7 and 8). Note that eq. 9 is unnecessary because the recursiveness at this step is not taken into consideration. Hence, the functional equation $P^{(a)}(x, q, t, s, p)$ (eq. 13) counts achiral monosubstituted alkanes of primary type. By the functional equation $P^{(b)}(x, q, t, s, p)$ (eq. 14), on the other hand, each achiral monosubstituted alkane of primary type is counted once as well as each enantiomer of a enantiomeric pair is counted once. Thereby, we obtain the following equations:

$$P^{(a)}(x, q, t, s, p) = P^{(A)}(x, q, t, s, p) \quad (15)$$

$$P^{(b)}(x, q, t, s, p) = P^{(A)}(x, q, t, s, p) + 2P^{(C)}(x, q, t, s, p). \quad (16)$$

The total numbers of monosubstituted alkanes, in which each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once, satisfy the following equation:

$$P^{(B)}(x, q, t, s, p) = P^{(A)}(x, q, t, s, p) + P^{(C)}(x, q, t, s, p). \quad (17)$$

By starting from eqs. 15 and 16 as well as eq. 17, the generating functions represented by $P^{(A)}(x, q, t, s, p)$ (eq. 10), $P^{(C)}(x, q, t, s, p)$ (eq. 11), and $P^{(B)}(x, q, t, s, p)$ (eq. 12) are derived as follows:

$$P^{(A)}(x, q, t, s, p) = P^{(a)}(x, q, t, s, p) \quad (18)$$

$$P^{(C)}(x, q, t, s, p) = \frac{1}{2} \left\{ P^{(b)}(x, q, t, s, p) - P^{(a)}(x, q, t, s, p) \right\} \quad (19)$$

$$P^{(B)}(x, q, t, s, p) = \frac{1}{2} \left\{ P^{(a)}(x, q, t, s, p) + P^{(b)}(x, q, t, s, p) \right\}. \quad (20)$$

Table 2: Numbers of Achiral Monosubstituted Alkanes of Primary Type

The coefficient of x^k (cf. eqs. 10 and 18), i.e., $\sum_{knqn_n n_p} P^{(A)} q^n t^n s^n p^n$	
$k = 1$	0
$k = 2$	p^2
$k = 3$	sp^2
$k = 4$	$tp^3 + s^2p^2$
$k = 5$	$qp^4 + ts p^3 + s^3 p^2$
$k = 6$	$2qs p^4 + 2ts^2 p^3 + s^4 p^2$
$k = 7$	$qt p^5 + 4qs^2 p^4 + 2ts^3 p^3 + s^5 p^2$
$k = 8$	$q^2 p^6 + (t^3 + 2qts) p^5 + 6qs^3 p^4 + 3ts^4 p^3 + s^6 p^2$
$k = 9$	$(3q^2s + qt^2) p^6 + (t^3s + 5qt^2s) p^5 + 9qs^4 p^4 + 3ts^5 p^3 + s^7 p^2$
$k = 10$	$2q^2t p^7 + (8q^2s^2 + 2qt^2s) p^6 + (4t^3s^2 + 8qt^3s) p^5 + 12qs^5 p^4 + 4ts^6 p^3 + s^8 p^2$
$k = 11$	$2q^3 p^8 + (2qt^3 + 4q^2ts) p^7 + (6qt^2s^2 + 16q^2s^3) p^6 + (4t^3s^3 + 14qt^4s) p^5 + 16qs^6 p^4 + 4ts^7 p^3 + s^9 p^2$
$k = 12$	$(6q^3s + 2q^2t^2) p^8 + (4qt^3s + 2t^5 + 12q^2ts^2) p^7 + (10qt^2s^3 + 30q^2s^4) p^6 + (10t^3s^4 + 20qts^5) p^5 + 20qs^7 p^4 + 5ts^8 p^3 + s^{10} p^2$
$k = 13$	$3q^3t p^9 + (18q^3s^2 + 2qt^4 + 6q^2t^2s) p^8 + (14qt^3s^2 + 2t^5s + 22q^2t^2s^3) p^7 + (20qt^4s^4 + 50q^2s^5) p^6 + (10t^3s^5 + 30qts^6) p^5 + 25qs^8 p^4 + 5ts^9 p^3 + s^{11} p^2$
$k = 14$	$3q^4 p^{10} + (8q^3ts + 6q^2t^3) p^9 + (4qt^4s + 40q^3s^3 + 20q^2t^2s^2) p^8 + (24qt^3s^3 + 12t^5s^2 + 46q^2ts^4) p^7 + (30qt^2s^5 + 80q^2s^6) p^6 + (20t^3s^6 + 40qt^4s^7) p^5 + 30qs^9 p^4 + 6ts^{10} p^3 + s^{12} p^2$
$k = 15$	$(6q^3t^2 + 11q^4s) p^{10} + (12q^2t^3s + 26q^3ts^2 + 5qt^5) p^9 + (44q^2t^2s^3 + 16qt^4s^2 + 86q^3s^4) p^8 + (12t^5s^3 + 76q^2ts^5 + 54qt^3s^4) p^7 + (120q^2s^7 + 50qt^2s^6) p^6 + (20t^3s^7 + 55qts^8) p^5 + 36qs^{10} p^4 + 6ts^{11} p^3 + s^{13} p^2$ (omitted)
$k = 20$	$8q^6 p^{14} + (28q^4t^3 + 28q^5ts) p^{13} + (14q^2t^6 + 176q^4t^2s^2 + 58q^3t^4s + 208q^5s^3) p^{12} + (204q^2t^5s^2 + 296q^3t^3s^3 + 14t^9 + 28qt^7s + 332q^4ts^4) p^{11} + (360q^2t^4s^4 + 808q^3t^2s^5 + 90qt^6s^3 + 920q^4s^6) p^{10} + (180t^7s^4 + 852q^2t^3s^6 + 792q^3ts^7 + 360qt^5s^5) p^9 + (336qt^4s^7 + 924q^2t^2s^8 + 1284q^3s^9) p^8 + (678q^2ts^{10} + 252t^5s^8 + 504qt^3s^9) p^7 + (252qt^2s^{11} + 588q^2s^{12}) p^6 + (84t^3s^{12} + 168qts^{13}) p^5 + 72qs^{15} p^4 + 9ts^{16} p^3 + s^{18} p^2$ (omitted)

The generating function $P^{(A)}(x, q, t, s, p)$ (eq. 10) is obtained by using a functional equation (eq. 18) which is identical with eq. 13. The generating function $P^{(C)}(x, q, t, s, p)$ (eq. 11) can be written in the form of a functional equation (eq. 19) by starting eqs. 13 and 14, in which each pair of enantiomers is counted once. The generating function $P^{(B)}(x, q, t, s, p)$ (eq. 12) can be written in the form of a functional equation (eq. 20) by starting eqs. 13 and 14.

Because the functional equations represented by $a(x, q, t, s, p)$ (eq. 7), $b(x, q, t, s, p)$ (eq. 8), and $c(x^2, q^2, t^2, s^2, p^2)$ (eq. 9) have recursive nature, they are evaluated stepwise by increasing carbon content k one by one. The resulting intermediate series are introduced into eqs. 13 and 14. Then the resulting functions $P^{(a)}(x, q, t, s, p)$ and $P^{(b)}(x, q, t, s, p)$ are introduced into eqs.

Table 3: Numbers of Chiral Monosubstituted Alkanes of Primary Type^{a)}

The coefficient of x^k (cf. eqs. 11 and 19), i.e., $\sum P_{knq_n n_s n_p}^{(C)} q^n t^{n_s} s^{n_p}$	
$k = 1-4$	0
$k = 5$	$ts p^3$
$k = 6$	$t^2 p^4 + 2ts^2 p^3$
$k = 7$	$qt p^5 + 5t^2 s p^4 + 4ts^3 p^3$
$k = 8$	$(2t^3 + 6qts) p^5 + (qs^3 + 15t^2 s^2) p^4 + 6ts^4 p^3$
$k = 9$	$(q^2 s + 5qt^2) p^6 + (17t^3 s + 19qts^2) p^5 + (35t^2 s^3 + 2qs^4) p^4 + 9ts^5 p^3$
$k = 10$	$3q^2 t p^7 + (4q^2 s^2 + 7t^4 + 37qt^2 s) p^6 + (68t^3 s^2 + 50qts^3) p^5 + (70t^2 s^4 + 4qs^5) p^4 + 12ts^6 p^3$
$k = 11$	$(20qt^3 + 26q^2 ts) p^7 + (63t^4 s + 153qt^2 s^2 + 13q^2 s^3) p^6 + (208t^3 s^3 + 110qts^4) p^5 + (126t^2 s^5 + 7qs^6) p^4 + 16t^7 p^3$
$k = 12$	$(22q^2 t^2 + 4q^3 s) p^8 + (185qt^3 s + 20t^5 + 112q^2 t s^2) p^7 + (487qt^2 s^3 + 315t^4 s^2 + 33q^2 s^4) p^6 + (218qts^5 + 520t^3 s^4) p^5 + (11qs^7 + 210t^2 s^6) p^4 + 20ts^8 p^3$
$k = 13$	$10q^3 t p^9 + (78qt^4 + 207q^2 t^2 s + 21q^3 s^2) p^8 + (950qt^3 s^2 + 230t^5 s + 375q^2 t s^3) p^7 + (1295qt^2 s^4 + 1155t^4 s^3 + 74q^2 s^5) p^6 + (396qts^6 + 1150t^3 s^5) p^5 + (330t^2 s^7 + 16qs^8) p^4 + 25ts^9 p^3$
$k = 14$	$q^4 p^{10} + (102q^3 ts + 115q^2 t^3) p^9 + (870qt^4 s + 66t^6 + 1090q^2 t^2 s^2 + 81q^3 s^3) p^8 + (1380t^5 s^2 + 3636qt^3 s^3 + 1045q^2 t s^4) p^7 + (3465t^4 s^4 + 3039qt^2 s^5 + 149q^2 s^6) p^6 + (2300t^3 s^6 + 676qts^7) p^5 + (495t^2 s^8 + 23qs^9) p^4 + 30ts^{10} p^3$
$k = 15$	$(15q^4 s + 86q^3 t^2) p^{10} + (1317q^2 t^3 s + 298qt^5 + 552q^3 t s^2) p^9 + (858t^6 s + 5336qt^4 s^2 + 246q^3 s^4 + 4299q^2 t^2 s^3) p^8 + (6000t^5 s^3 + 11431qt^3 s^4 + 2578q^2 t s^5) p^7 + (9009t^4 s^5 + 279q^2 s^7 + 6473qt^2 s^6) p^6 + (4280t^3 s^7 + 1093qts^8) p^5 + (31qs^{10} + 715t^2 s^9) p^4 + 36ts^{11} p^3$
	(omitted)
$k = 20$	$10q^6 p^{14} + (2573q^4 t^3 + 1388q^5 ts) p^{13} + (11872q^2 t^6 + 52052q^3 t^4 s + 33472q^4 t^2 s^2 + 1794q^5 s^3) p^{12} + (333922q^2 t^5 s^2 + 2424t^9 + 305911q^3 t^3 s^3 + 75704qt^7 s + 46658q^4 t s^4) p^{11} + (1220392q^2 t^4 s^4 + 109395t^8 s^2 + 12083q^4 s^6 + 821667qt^6 s^3 + 383200q^3 t^2 s^5) p^{10} + (2095794qt^5 s^5 + 142380q^3 t s^7 + 1320600q^2 t^3 s^6 + 656280t^7 s^4) p^9 + (1225224t^6 s^6 + 522909q^2 t^2 s^8 + 1912128qt^4 s^7 + 13604q^3 s^9) p^8 + (720528qt^3 s^9 + 918792t^5 s^8 + 76499q^2 t s^{10}) p^7 + (306306t^4 s^{10} + 3060q^2 s^{12} + 115260qt^2 s^{11}) p^6 + (46368t^3 s^{12} + 7206qts^{13}) p^5 + (102qs^{15} + 3060t^2 s^{14}) p^4 + 72ts^{16} p^3$
	(omitted)

^{a)}Each pair of enantiomers is counted once.

Table 4: Numbers of Achiral and Chiral Monosubstituted Alkanes of Primary Type^{a)}

	The coefficient of x^k (cf. eqs. 12 and 20), i.e., $\sum P_{knqn_n n_p}^{(B)} q^n t^{n_i} s^{n_s} p^{n_p}$
$k = 1$	0
$k = 2$	p^2
$k = 3$	sp^2
$k = 4$	$tp^3 + s^2 p^2$
$k = 5$	$qp^4 + 2ts p^3 + s^3 p^2$
$k = 6$	$(2qs + t^2) p^4 + 4ts^2 p^3 + s^4 p^2$
$k = 7$	$2qt p^5 + (4qs^2 + 5t^2 s) p^4 + 6ts^3 p^3 + s^5 p^2$
$k = 8$	$q^2 p^6 + (3t^3 + 8qts) p^5 + (15t^2 s^2 + 7qs^3) p^4 + 9ts^4 p^3 + s^6 p^2$
$k = 9$	$(4q^2 s + 6qt^2) p^6 + (18t^3 s + 24qts^2) p^5 + (35t^2 s^3 + 11qs^4) p^4 + 12ts^5 p^3 + s^7 p^2$
$k = 10$	$5q^2 t p^7 + (12q^2 s^2 + 39qt^2 s + 7t^4) p^6 + (72t^3 s^2 + 58qts^3) p^5 + (70t^2 s^4 + 16qs^5) p^4 + 16ts^6 p^3 + s^8 p^2$
$k = 11$	$2q^3 p^8 + (30q^2 ts + 22qt^3) p^7 + (159qt^2 s^2 + 63t^4 s + 29q^2 s^3) p^6 + (212t^3 s^3 + 124qts^4) p^5 + (126t^2 s^5 + 23qs^6) p^4 + 20ts^7 p^3 + s^9 p^2$
$k = 12$	$(24q^2 t^2 + 10q^3 s) p^8 + (189qt^3 s + 124q^2 ts^2 + 22t^5) p^7 + (497qt^2 s^3 + 315t^4 s^2 + 63q^2 s^4) p^6 + (238qts^5 + 530t^3 s^4) p^5 + (31qs^7 + 210t^2 s^6) p^4 + 25ts^8 p^3 + s^{10} p^2$
$k = 13$	$13q^3 t p^9 + (80qt^4 + 39q^3 s^2 + 213q^2 t^2 s) p^8 + (964qt^3 s^2 + 232t^5 s + 397q^2 ts^3) p^7 + (1315qt^2 s^4 + 1155t^4 s^3 + 124q^2 s^5) p^6 + (426qts^6 + 1160t^3 s^5) p^5 + (330t^2 s^7 + 41qs^8) p^4 + 30ts^9 p^3 + s^{11} p^2$
$k = 14$	$4q^4 p^{10} + (121q^2 t^3 + 110q^3 ts) p^9 + (874qt^4 s + 66t^6 + 1110q^2 t^2 s^2 + 121q^3 s^3) p^8 + (1392t^5 s^2 + 3660qt^3 s^3 + 1091q^2 ts^4) p^7 + (3465t^4 s^4 + 3069qt^2 s^5 + 229q^2 s^6) p^6 + (2320t^3 s^6 + 716qts^7) p^5 + (495t^2 s^8 + 53qs^9) p^4 + 36ts^{10} p^3 + s^{12} p^2$
$k = 15$	$(26q^4 s + 92q^3 t^2) p^{10} + (1329q^2 t^3 s + 578q^3 ts^2 + 303qt^5) p^9 + (858t^6 s + 5352qt^4 s^2 + 4343q^2 t^2 s^3 + 332q^3 s^4) p^8 + (6012t^5 s^3 + 11485qt^3 s^4 + 2654q^2 ts^5) p^7 + (9009t^4 s^5 + 6523qt^2 s^6 + 399q^2 s^7) p^6 + (4300t^3 s^7 + 1148qts^8) p^5 + (67qs^{10} + 715t^2 s^9) p^4 + 42ts^{11} p^3 + s^{13} p^2$
	(omitted)
$k = 20$	$18q^6 p^{14} + (2601q^4 t^3 + 1416q^5 ts) p^{13} + (11886q^2 t^6 + 52110q^3 t^4 s + 33648q^4 t^2 s^2 + 2002q^5 s^3) p^{12} + (334126q^2 t^5 s^2 + 2438t^9 + 306207q^3 t^3 s^3 + 46990q^4 t s^4 + 75732qt^7 s) p^{11} + (1220752q^2 t^4 s^4 + 109395t^8 s^2 + 13003q^4 s^6 + 384008q^3 t^2 s^5 + 821757qt^6 s^3) p^{10} + (2096154qt^5 s^5 + 1321452q^2 t^3 s^6 + 656460t^7 s^4 + 143172q^3 ts^7) p^9 + (1225224t^6 s^6 + 1912464qt^4 s^7 + 523833q^2 t^2 s^8 + 14888q^3 s^9) p^8 + (919044t^5 s^8 + 721032qt^3 s^9 + 77177q^2 ts^{10}) p^7 + (3648q^2 s^{12} + 306306t^4 s^{10} + 115512qt^2 s^{11}) p^6 + (46452t^3 s^{12} + 7374qts^{13}) p^5 + (174qs^{15} + 3060t^2 s^{14}) p^4 + 81ts^{16} p^3 + s^{18} p^2$
	(omitted)

^{a)}Each achiral compound or each pair of enantiomers is counted once.

18–20, which are expanded to give eqs. 10–12. This procedure is 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.

```
#AlkylPST8P.mpl
#Calculation of Primary Monosubstituted Alkanes

"Functional Equations for Inner Alkyl Ligands";
# (Part 1) H, methyl, primary, secondary, tertiary, quaternary
# --- internal alkyls for recursive calc.
ax := 1 + x*p + x*s*(a1-1) + x*t*(c2 -1) + x*q*(a1-1)*(c2-1);
cx := 1 + x^2*p^2 + x^2*s^2*(c2-1) + x^2*t^2*(c2-1)^2
      + ((x^2*q^2)/3)*((c2-1)^3 + 2*(c6-1));
bx := 1 + x*p + x*s*(b1-1) + x*t*(b1-1)^2
      + (x*q/3)*((b1-1)^3 + 2*(b3-1));

# (Part 2) Primary Monosubstituted Alkanes
# --- not for recursive calc.
#Methyl is not included.
Pax := x*p*(a1-1);
Pbx := x*p*(b1-1);

" (Part 3) Initial Values";
a1 := 1;
c2 := 1; c4 := 1; c6 := 1;
b1 := 1; b2 := 1; b3 := 1;
asum := 1: csum := 1: bsum := 1:
Pal := 1; Pc2 := 1; Pbl := 1;

"Recursive Calculation";
kmax := 30;
for k from 1 to kmax by 1 do
" k ="; k;

"(Part 4) Steric, Total, Primary, Secondary, Tertiary";
CPbx:= expand(coeff(Pbx,x^k)):
Pbl := Pbl + CPbx*x^k:

"(Part 5) Achiral Total, Primary, Secondary, Tertiary";
CPax:= expand(coeff(Pax,x^k)):
Pal := Pal + CPax*x^k:

"(Part 6) Steric";
Cbx:= expand(coeff(bx,x^k)):
Cb2x:= subs({p=p^2,s=s^2,t=t^2,q=q^2},
expand(coeff(bx,x^k))):
Cb3x:= subs({p=p^3,s=s^3,t=t^3,q=q^3},
expand(coeff(bx,x^k))):
Cbsum:= subs({p=1,s=1,t=1,q=1}, expand(coeff(bx,x^k))):
b1 := b1 + Cbx*x^k:
b2 := b2 + Cb2x*x^(2*k):
b3 := b3 + Cb3x*x^(3*k):
bsum := bsum + Cbsum*x^k:

"(Part 7) Diploid";
Ccx:= expand(coeff(cx,x^(2*k))):
Cc2x:= subs({p=p^2,s=s^2,t=t^2,q=q^2},
expand(coeff(cx,x^(2*k)))):
Cc3x:= subs({p=p^3,s=s^3,t=t^3,q=q^3},
expand(coeff(cx,x^(2*k)))):
Ccsum:= subs({p=1,s=1,t=1,q=1}, expand(coeff(cx,x^(2*k)))):
```

```

c2 := c2 + Ccx*x^(2*k):
c4 := c4 + Cc2x*x^(4*k):
c6 := c6 + Cc3x*x^(6*k):
csum := csum + Ccsum*x^(2*k):

"(Part 8) Achiral";
Cax:= expand(coeff(ax, x^k)):
Casum:= subs({p=1, s=1, t=1, q=1}, expand(coeff(ax, x^k))):
a1 := a1 + Cax*x^k:
asum := asum + Casum*x^k:
end do:

"(Part 9) Final Calculation";
#Primary (Achiral + Chiral)
BPx := (1/2)*(Pal + Pbl):
#Primary (Chiral)
CPx := (1/2)*(Pbl - Pal):

#(Part 10)#####

"Print Out of Pal (Achiral)";
for k from 1 to kmax by 1 do
carbon_content:= k:
NPa := collect(sort(expand(coeff(Pal, x^k)), [q, t, s, p]), p);
end do;

"Print Out of CPx (Chiral)";
for k from 1 to kmax by 1 do
carbon_content:= k:
Npc := collect(sort(expand(coeff(CPx, x^k)), [q, t, s, p]), p);
end do;

"Print Out of BPx (Total)";
for k from 1 to kmax by 1 do
carbon_content:= k:
Npt := collect(sort(expand(coeff(BPx, x^k)), [q, t, s, p]), p);
end do;

```

This code is stored in a file named “AlkyIPST8P.mpl”. In this code, the abbreviated symbols for functional equations are used as follows: a1 for $a(x, q, t, s, p)$ etc., b1 for $b(x, q, t, s, p)$ etc., and c2 for $c(x^2, q^2, t^2, s^2, p^2)$ etc. The symbols csum, csum, and bsum are used to store the series for $a(x)$ ($q = t = s = p = 1$), $b(x)$ ($q = t = s = p = 1$), and $c(x^2)$ ($q = t = s = p = 1$).

The first part (Part 1) of this code declares three functional equations ax for eq. 7, bx for eq. 8, and cx for eq. 9, which are calculated by using a1, b1, c2, etc. recursively. The second part (Part 2) declares two functional equations, i.e., Pax for $P^{(a)}(x, q, t, s, p)$ (eq. 13) and Pbx for $P^{(b)}(x, q, t, s, p)$ (eq. 14), which are calculated by using a1, b1, c2, etc. Note that they have no recursive nature. In Part 3 (“Initial Values”), the initial values are set for the initial (trivial) PAMs, and so on. The Part “Recursive Calculation” of the code shows a do loop for carbon content k , in which Parts 6–8 are the embodiment of recursive processes for PAMs. 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. In the do loop, Parts 4 and 5 store the results of Pax and Pbx (Part 2).

After escaping from the do loop for k , Part 9 (“Final Calculation”) declares the calculation of CPx for $P^{(C)}(x, q, t, s, p)$ (eq. 19) and CBx for $P^{(B)}(x, q, t, s, p)$ (eq. 20). Part 10 (“Print Out of ...”) of the code shows the print-out of the calculation results. The option $[q, t, s, p]$ of the Maple command sort specifies the order of branching indicators (q, t, s , and p) in the printing-

out format of each BM, i.e., the descending order of the branching degrees $4^\circ > 3^\circ > 2^\circ > 1^\circ$.

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

```
> restart;
> read "AlkylPST8P.mpl";
```

The above-mentioned code gives calculation results according to its print-out sections. Table 2 collects the data NP_a ($\sum_{k n_q n_t n_s n_p} P_{k n_q n_t n_s n_p}^{(A)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k (cf. eqs. 10 and 18), where the coefficient of the term $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$ indicates the number $P_{k n_q n_t n_s n_p}^{(A)}$. Table 3 collects the data NP_c ($\sum_{k n_q n_t n_s n_p} P_{k n_q n_t n_s n_p}^{(C)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k (cf. eqs. 11 and 19). Table 4 collects the data NP_t ($\sum_{k n_q n_t n_s n_p} P_{k n_q n_t n_s n_p}^{(B)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k (cf. eqs. 11 and 19). Note that the summations are concerned with $n_q, n_t, n_s,$ and n_p for each carbon content k .

3.2 Secondary Monosubstituted Alkanes

Let the symbol $S_{k n_q n_t n_s n_p}^{(A)}$ be the number of inequivalent achiral monosubstituted alkanes of secondary type, where k carbons in each monosubstituted alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons; the symbol $S_{k n_q n_t n_s n_p}^{(C)}$ be the number of inequivalent chiral monosubstituted alkanes of secondary type under a similar categorization, where each pair of enantiomers is counted once; and the symbol $S_{k n_q n_t n_s n_p}^{(B)}$ be the total number of inequivalent monosubstituted alkanes of secondary type under a similar categorization, where each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once. Thereby, we are able to write down generating functions of these numbers by using the above-described branching indicators (i.e., $q, t, s,$ and p) as follows:

$$S^{(A)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{k n_q n_t n_s n_p}^{(A)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (21)$$

$$S^{(C)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{k n_q n_t n_s n_p}^{(C)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (22)$$

$$S^{(B)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{k n_q n_t n_s n_p}^{(B)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (23)$$

By employing the term xs in place of xt used in the processes for deriving eq. 5 and so on, we obtain the following functional equations:

$$S^{(a)}(x, q, t, s, p) = xs \{c(x^2, q^2, t^2, s^2, p^2) - 1\} \quad (24)$$

$$S^{(b)}(x, q, t, s, p) = xs \{b(x, q, t, s, p) - 1\}^2. \quad (25)$$

Because $c(x^2, q^2, t^2, s^2, p^2)$ and $b(x, q, t, s, p)$ in the right-hand sides have been obtained recursively by using the respective functional equations (eqs. 9 and 8), the functional equation $S^{(a)}(x, q, t, s, p)$ (eq. 24) can be used to count achiral monosubstituted alkanes of secondary type. By means of the functional equation $S^{(b)}(x, q, t, s, p)$ (eq. 25), on the other hand, each

Table 5: Numbers of Achiral Monosubstituted Alkanes of Secondary Type

The coefficient of x^k (cf. eqs. 21 and 26), i.e., $\sum S_{kq_n n_s n_p}^{(A)} q^{n_q} t^{n_s} s^{n_s} p^{n_p}$	
$k = 1$	0
$k = 2$	0
$k = 3$	sp^2
$k = 4$	0
$k = 5$	$s^3 p^2$
$k = 6$	0
$k = 7$	$t^2 s p^4 + s^5 p^2$
$k = 8$	0
$k = 9$	$q^2 s p^6 + 3 t^2 s^3 p^4 + s^7 p^2$
$k = 10$	0
$k = 11$	$(2 q^2 s^3 + 2 t^4 s) p^6 + 6 t^2 s^5 p^4 + s^9 p^2$
$k = 12$	0
$k = 13$	$3 q^2 t^2 s p^8 + (4 q^2 s^5 + 10 t^4 s^3) p^6 + 10 t^2 s^7 p^4 + s^{11} p^2$
$k = 14$	0
$k = 15$	$q^4 s p^{10} + (5 t^6 s + 14 q^2 t^2 s^3) p^8 + (30 t^4 s^5 + 8 q^2 s^7) p^6 + 15 t^2 s^9 p^4 + s^{13} p^2$
$k = 16$	0
$k = 17$	$(5 q^4 s^3 + 11 q^2 t^4 s) p^{10} + (35 t^6 s^3 + 43 q^2 t^2 s^5) p^8 + (70 t^4 s^7 + 13 q^2 s^9) p^6 + 21 t^2 s^{11} p^4 + s^{15} p^2$
$k = 18$	0
$k = 19$	$8 q^4 t^2 s p^{12} + (16 q^4 s^5 + 76 q^2 t^4 s^3 + 14 t^8 s) p^{10} + (140 t^6 s^5 + 108 q^2 t^2 s^7) p^8 + (140 t^4 s^9 + 20 q^2 s^{11}) p^6 + 28 t^2 s^{13} p^4 + s^{17} p^2$
$k = 20$	0
	(omitted)

achiral monosubstituted alkane is counted once as well as each member of an enantiomeric pair is counted once. This means that we are able to obtain relationships similar to eqs. 15 and 16 for primary monosubstituted alkanes, where the letter “ P ” should be replaced by “ S ” for secondary monosubstituted alkanes. Hence, eqs. 21–23 are evaluated by the following functional equations:

$$S^{(A)}(x, q, t, s, p) = S^{(a)}(x, q, t, s, p) \tag{26}$$

$$S^{(C)}(x, q, t, s, p) = \frac{1}{2} \left\{ S^{(b)}(x, q, t, s, p) - S^{(a)}(x, q, t, s, p) \right\} \tag{27}$$

$$S^{(B)}(x, q, t, s, p) = \frac{1}{2} \left\{ S^{(a)}(x, q, t, s, p) + S^{(b)}(x, q, t, s, p) \right\}. \tag{28}$$

Note that the derivation of eqs. 26–28 from eqs. 24 and 25 is parallel to the derivation of eqs. 18–20 from eqs. 13 and 14 (via eqs. 15 and 16).

The generating function $S^{(A)}(x, q, t, s, p)$ (eq. 21) is obtained by using a functional equation (eq. 26) which is identical with eq. 24. The generating function $S^{(C)}(x, q, t, s, p)$ (eq. 22) can be written in the form of a functional equation (eq. 27) by starting eqs. 24 and 25, in which

Table 6: Numbers of Chiral Monosubstituted Alkanes of Secondary Type^{a)}

The coefficient of x^k (cf. eqs. 22 and 27), i.e., $\sum_{k, n_q, n_t, n_s, n_p} S_k^{(C)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$	
$k = 1-3$	0
$k = 4$	$s^2 p^2$
$k = 5$	$ts p^3 + s^3 p^2$
$k = 6$	$q s p^4 + 4 t s^2 p^3 + 2 s^4 p^2$
$k = 7$	$(3 q s^2 + 2 t^2 s) p^4 + 10 t s^3 p^3 + 2 s^5 p^2$
$k = 8$	$4 q t s p^5 + (7 q s^3 + 15 t^2 s^2) p^4 + 20 t s^4 p^3 + 3 s^6 p^2$
$k = 9$	$q^2 s p^6 + (7 t^3 s + 22 q t s^2) p^5 + (51 t^2 s^3 + 15 q s^4) p^4 + 35 t s^5 p^3 + 3 s^7 p^2$
$k = 10$	$(8 q^2 s^2 + 16 q t^2 s) p^6 + (56 t^3 s^2 + 76 q t s^3) p^5 + (140 t^2 s^4 + 28 q s^5) p^4 + 56 t s^6 p^3 + 4 s^8 p^2$
$k = 11$	$12 q^2 t s p^7 + (27 q^2 s^3 + 124 q t^2 s^2 + 20 t^4 s) p^6 + (252 t^3 s^3 + 210 q t s^4) p^5 + (312 t^2 s^5 + 48 q s^6) p^4 + 84 t s^7 p^3 + 4 s^9 p^2$
$k = 12$	$3 q^3 s p^8 + (92 q^2 t s^2 + 64 q t^3 s) p^7 + (560 q t^2 s^3 + 210 t^4 s^2 + 80 q^2 s^4) p^6 + (840 t^3 s^4 + 498 q t s^5) p^5 + (630 t^2 s^6 + 78 q s^7) p^4 + 120 t s^8 p^3 + 5 s^{10} p^2$
$k = 13$	$(70 q^2 t^2 s + 23 q^3 s^2) p^8 + (628 q t^3 s^2 + 420 q^2 t s^3 + 66 t^5 s) p^7 + (1920 q t^2 s^4 + 1150 t^4 s^3 + 195 q^2 s^5) p^6 + (1056 q t s^6 + 2310 t^3 s^5) p^5 + (120 q s^8 + 1150 t^2 s^7) p^4 + 165 t s^9 p^3 + 5 s^{11} p^2$
$k = 14$	$36 q^3 t s p^9 + (251 q t^4 s + 106 q^3 s^3 + 706 q^2 t^2 s^2) p^8 + (3482 q t^3 s^3 + 792 t^5 s^2 + 1476 q^2 t s^4) p^7 + (5500 q t^2 s^5 + 4620 t^4 s^4 + 436 q^2 s^6) p^6 + (2058 q t s^7 + 5544 t^3 s^6) p^5 + (1980 t^2 s^8 + 177 q s^9) p^4 + 220 t s^{10} p^3 + 6 s^{12} p^2$
$k = 15$	$7 q^4 s p^{10} + (378 q^2 t^3 s + 356 q^3 t s^2) p^9 + (2993 q t^4 s^2 + 212 t^6 s + 3958 q^2 t^2 s^3 + 380 q^3 s^4) p^8 + (5148 t^5 s^3 + 14268 q t^3 s^4 + 4364 q^2 t s^5) p^7 + (15000 t^4 s^5 + 13832 q t^2 s^6 + 886 q^2 s^7) p^6 + (12012 t^3 s^7 + 3750 q t s^8) p^5 + (3210 t^2 s^9 + 253 q s^{10}) p^4 + 286 t s^{11} p^3 + 6 s^{13} p^2$
	(omitted)
$k = 20$	$342 q^5 t s p^{13} + (1402 q^5 s^3 + 11214 q^3 t^4 s + 15500 q^4 t^2 s^2) p^{12} + (142124 q^2 t^5 s^2 + 44892 q^4 t s^4 + 208076 q^3 t^3 s^3 + 14986 q t^7 s) p^{11} + (461200 q^3 t^2 s^5 + 1113684 q^2 t^4 s^4 + 43758 t^8 s^2 + 18972 q^4 s^6 + 529372 q t^6 s^3) p^{10} + (1961280 q^2 t^3 s^6 + 258592 q^3 t s^7 + 583440 t^7 s^4 + 2467116 q t^5 s^5) p^9 + (1141296 q^2 t^2 s^8 + 1837836 t^6 s^6 + 3502344 q t^4 s^7 + 36312 q^3 s^9) p^8 + (235176 q^2 t s^{10} + 1919820 q t^3 s^9 + 2100384 t^5 s^8) p^7 + (434588 q t^2 s^{11} + 1021020 t^4 s^{10} + 14168 q^2 s^{12}) p^6 + (222768 t^3 s^{12} + 38688 q t s^{13}) p^5 + (21420 t^2 s^{14} + 1050 q s^{15}) p^4 + 816 t s^{16} p^3 + 9 s^{18} p^2$
	(omitted)

^{a)}Each achiral compound or each pair of enantiomers is counted once.

Table 7: Numbers of Achiral and Chiral Monosubstituted Alkanes of Secondary Type^{a)}

The coefficient of x^k (cf. eqs. 23 and 28), i.e., $\sum_{kn,qt,s,p} \binom{B}{kn,qt,s,p} q^{nq} t^{nt} s^{ns} p^{np}$	
$k = 1$	0
$k = 2$	0
$k = 3$	sp^2
$k = 4$	s^2p^2
$k = 5$	$ts p^3 + 2s^3p^2$
$k = 6$	$qs p^4 + 4ts^2p^3 + 2s^4p^2$
$k = 7$	$(3qs^2 + 3t^2s) p^4 + 10ts^3p^3 + 3s^5p^2$
$k = 8$	$4qts p^5 + (7q^3s^3 + 15t^2s^2) p^4 + 20ts^4p^3 + 3s^6p^2$
$k = 9$	$2q^2s p^6 + (7t^3s + 22qts^2) p^5 + (54t^2s^3 + 15qs^4) p^4 + 35ts^5p^3 + 4s^7p^2$
$k = 10$	$(8q^2s^2 + 16qt^2s) p^6 + (56t^3s^2 + 76qts^3) p^5 + (140t^2s^4 + 28qs^5) p^4 + 56ts^6p^3 + 4s^8p^2$
$k = 11$	$12q^2ts p^7 + (29q^2s^3 + 124qt^2s^2 + 22t^4s) p^6 + (252t^3s^3 + 210qts^4) p^5 + (318t^2s^5 + 48qs^6) p^4 + 84ts^7p^3 + 5s^9p^2$
$k = 12$	$3q^3s p^8 + (92q^2ts^2 + 64qt^3s) p^7 + (560qt^2s^3 + 210t^4s^2 + 80q^2s^4) p^6 + (840t^3s^4 + 498qts^5) p^5 + (630t^2s^6 + 78qs^7) p^4 + 120ts^8p^3 + 5s^{10}p^2$
$k = 13$	$(73q^2t^2s + 23q^3s^2) p^8 + (628qt^3s^2 + 420q^2ts^3 + 66t^5s) p^7 + (1920qt^2s^4 + 1160t^4s^3 + 199q^2s^5) p^6 + (1056qts^6 + 2310t^3s^5) p^5 + (120qs^8 + 1160t^2s^7) p^4 + 165ts^9p^3 + 6s^{11}p^2$
$k = 14$	$36q^3ts p^9 + (251qt^4s + 106q^3s^3 + 706q^2t^2s^2) p^8 + (3482qt^3s^3 + 792t^5s^2 + 1476q^2ts^4) p^7 + (5500qt^2s^5 + 4620t^4s^4 + 436q^2s^6) p^6 + (2058qts^7 + 5544t^3s^6) p^5 + (1980t^2s^8 + 177qs^9) p^4 + 220ts^{10}p^3 + 6s^{12}p^2$
$k = 15$	$8q^4s p^{10} + (378q^2t^3s + 356q^3ts^2) p^9 + (2993qt^4s^2 + 217t^6s + 3972q^2t^2s^3 + 380q^3s^4) p^8 + (5148t^5s^3 + 14268qt^3s^4 + 4364q^2ts^5) p^7 + (15030t^4s^5 + 13832qt^2s^6 + 894q^2s^7) p^6 + (12012t^3s^7 + 3750qts^8) p^5 + (3225t^2s^9 + 253qs^{10}) p^4 + 286ts^{11}p^3 + 7s^{13}p^2$ (omitted)
$k = 20$	$342q^5ts p^{13} + (1402q^5s^3 + 11214q^3t^4s + 15500q^4t^2s^2) p^{12} + (142124q^2t^5s^2 + 44892q^4ts^4 + 208076q^3t^3s^3 + 14986qt^7s) p^{11} + (461200q^3t^2s^5 + 1113684q^2t^4s^4 + 43758t^8s^2 + 18972q^4s^6 + 529372qt^6s^3) p^{10} + (1961280q^2t^3s^6 + 258592q^3ts^7 + 583440t^7s^4 + 2467116qt^5s^5) p^9 + (1141296q^2t^2s^8 + 1837836t^6s^6 + 3502344qt^4s^7 + 36312q^3s^9) p^8 + (235176q^2ts^{10} + 1919820qt^3s^9 + 2100384t^5s^8) p^7 + (434588qt^2s^{11} + 1021020t^4s^{10} + 14168q^2s^{12}) p^6 + (222768t^3s^{12} + 38688qts^{13}) p^5 + (21420t^2s^{14} + 1050qs^{15}) p^4 + 816ts^{16}p^3 + 9s^{18}p^2$ (omitted)

^{a)} Each achiral compound or each pair of enantiomers is counted once.

each pair of enantiomers is counted once. The generating function $S^{(B)}(x, q, t, s, p)$ (eq. 23) can be written in the form of a functional equation (eq. 28) by starting eqs. 24 and 25. Note that the total numbers of monosubstituted alkanes are obtained under the condition that each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once.

A program named “AlkylPST8S.mpl” for counting secondary monosubstituted alkanes is written by using the Maple programming language. Several of the parts for counting primary monosubstituted alkanes (“AlkylPST8P.mpl” described above) are revised to treat secondary ones. Part 2 is replaced by the following code in accord with eqs. 24 and 25:

```
#(Part 2) Secondary Monosubstituted Alkanes
# --- not for recursive calc.
Sax := x*s*(c2-1);
Sbx := x*s*(b1-1)^2;
```

Parts 3–5 are rewritten on the same line. Parts 6–8 as well as Part 1 are used without changes. Part 9 is replaced by the following code in accord with eqs. 27 and 28:

```
"(Part 9) Final Calculation";
#Secondary Alkyls (Achiral + Chiral)
BSx := (1/2)*(Sal + Sbl);
#Secondary Alkyls (Chiral)
CSx := (1/2)*(Sbl - Sal);
```

where each character “P” (primary) involved in the symbols of variables is changed into “S” (secondary). Part 10 is also rewritten in order to print out the data at issue.

The modified program (“AlkylPST8S.mpl”) is executed to print out calculation results according to its print-out sections, as collected in Table 5 for the data NSa ($\sum S_{knqn_tn_s n_p}^{(A)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 26 and 21), in Table 6 for the data NSc ($\sum S_{knqn_tn_s n_p}^{(C)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 27 and 22), and in Table 7 for the data NSt ($\sum S_{knqn_tn_s n_p}^{(B)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 28 and 23). Although a single summation is used to save space, it is concerned with n_q , n_t , n_s , and n_p for each carbon content k . Thus, each of the polynomials concerning the branching indicators (q , t , s , and p) which appear in the k -rows of the respective tables is the coefficient of x^k .

3.3 Tertiary Monosubstituted Alkanes

The symbols for tertiary monosubstituted alkanes, i.e., $T_{knqn_tn_s n_p}^{(A)}$ (achiral), $T_{knqn_tn_s n_p}^{(C)}$ (chiral), and $T_{knqn_tn_s n_p}^{(B)}$ (achiral plus chiral), are used on the same line as the primary and secondary counterparts described above. Thereby, we are able to write down generating functions of these numbers by using the above-mentioned branching indicators, (i.e., q , t , s , and p) as follows:

$$T^{(A)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{knqn_tn_s n_p}^{(A)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (29)$$

$$T^{(C)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{knqn_tn_s n_p}^{(C)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k \quad (30)$$

$$T^{(B)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{knqn_tn_s n_p}^{(B)} P^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (31)$$

Table 8: Numbers of Achiral Monosubstituted Alkanes of Tertiary Type

	The coefficient of x^k (cf. eqs. 29 and 34), i.e., $\sum T_{kn, q^n, t^n, s^n, p}^{(A)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1-3$	0
$k = 4$	tp^3
$k = 5$	tsp^3
$k = 6$	$t^2p^4 + 2ts^2p^3$
$k = 7$	$qt p^5 + t^2s p^4 + 2ts^3 p^3$
$k = 8$	$(2qts + t^3) p^5 + 3t^2s^2 p^4 + 3ts^4 p^3$
$k = 9$	$qt^2 p^6 + (5qt s^2 + t^3s) p^5 + 3t^2s^3 p^4 + 3ts^5 p^3$
$k = 10$	$2q^2t p^7 + (2t^4 + 2qt^2s) p^6 + (4t^3s^2 + 8qt s^3) p^5 + 6t^2s^4 p^4 + 4ts^6 p^3$
$k = 11$	$(4q^2ts + 2qt^3) p^7 + (2t^4s + 6qt^2s^2) p^6 + (4t^3s^3 + 14qt s^4) p^5 + 6t^2s^5 p^4 + 4ts^7 p^3$
$k = 12$	$3q^2t^2 p^8 + (12q^2ts^2 + 4qt^3s + 2t^5) p^7 + (10t^4s^2 + 10qt^2s^3) p^6 + (10t^3s^4 + 20qt s^5) p^5 + 10t^2s^6 p^4 + 5ts^8 p^3$
$k = 13$	$3q^3t p^9 + (5q^2t^2s + 3qt^4) p^8 + (14qt^3s^2 + 2t^5s + 22q^2ts^3) p^7 + (10t^4s^3 + 20qt^2s^4) p^6 + (10t^3s^5 + 30qt s^6) p^5 + 10t^2s^7 p^4 + 5ts^9 p^3$
$k = 14$	$(6q^2t^3 + 8q^3ts) p^9 + (6qt^4s + 18q^2t^2s^2 + 5t^6) p^8 + (24qt^3s^3 + 12t^5s^2 + 46q^2ts^4) p^7 + (30qt^2s^5 + 30t^4s^4) p^6 + (40qt s^7 + 20t^3s^6) p^5 + 15t^2s^8 p^4 + 6ts^{10} p^3$
$k = 15$	$4q^3t^2 p^{10} + (5qt^5 + 26q^3ts^2 + 12q^2t^3s) p^9 + (24qt^4s^2 + 5t^6s + 30q^2t^2s^3) p^8 + (54qt^3s^4 + 12t^5s^3 + 76q^2ts^5) p^7 + (50qt^2s^6 + 30t^4s^5) p^6 + (20t^3s^7 + 55qt s^8) p^5 + 15t^2s^9 p^4 + 6ts^{11} p^3$
	(omitted)
$k = 20$	$(28q^5ts + 28q^4t^3) p^{13} + (50q^3t^4s + 84q^4t^2s^2 + 46q^2t^6) p^{12} + (28qt^7s + 296q^3t^3s^3 + 332q^4ts^4 + 204q^2t^5s^2 + 14t^9) p^{11} + (162qt^6s^3 + 126t^8s^2 + 348q^3t^2s^5 + 492q^2t^4s^4) p^{10} + (180t^7s^4 + 360qt^5s^5 + 792q^3ts^7 + 852q^2t^3s^6) p^9 + (504qt^4s^7 + 420t^6s^6 + 570q^2t^2s^8) p^8 + (252t^5s^8 + 504qt^3s^9 + 678q^2ts^{10}) p^7 + (252t^4s^{10} + 252qt^2s^{11}) p^6 + (84t^3s^{12} + 168qt s^{13}) p^5 + 36t^2s^{14} p^4 + 9ts^{16} p^3$
	(omitted)

By employing the term xt in place of xq used in the processes for deriving eq. 6 and so on, we obtain the following functional equations:

$$T^{(a)}(x, q, t, s, p) = xt \{a(x, q, t, s, p) - 1\} \{c(x^2, q^2, t^2, s^2, p^2) - 1\} \quad (32)$$

$$T^{(b)}(x, q, t, s, p) = \frac{xt}{3} \{ [b(x, q, t, s, p) - 1]^3 + 2[b(x^3, q^3, t^3, s^3, p^3) - 1] \}. \quad (33)$$

where $a(x, q, t, s, p)$, $c(x^2, q^2, t^2, s^2, p^2)$, $b(x, q, t, s, p)$, and $b(x^3, q^3, t^3, s^3, p^3)$ in the right-hand sides have been obtained recursively by using the respective functional equations (eqs. 8–9).

The functional equation $T^{(a)}(x, q, t, s, p)$ (eq. 32) counts achiral monosubstituted alkanes of tertiary type. By the functional equation $T^{(b)}(x, q, t, s, p)$ (eq. 33), on the other hand, each achiral monosubstituted alkane of tertiary type is counted once as well as each enantiomers of a chiral pair is counted once. See eqs. 15 and 16 for primary monosubstituted alkanes, where the letter “ P ” should be replaced by “ T ” for tertiary monosubstituted alkanes.

Table 9: Numbers of Chiral Monosubstituted Alkanes of Tertiary Type^{a)}

The coefficient of x^k (cf. eqs. 30 and 35), i.e., $\sum T_{knqnnsnp}^{(C)} q^n t^n s^n p^n$	
$k = 1-6$	0
$k = 7$	$2t^2sp^4 + ts^3p^3$
$k = 8$	$(qts + t^3)p^5 + 6t^2s^2p^4 + ts^4p^3$
$k = 9$	$2qt^2p^6 + (3qts^2 + 10t^3s)p^5 + 16t^2s^3p^4 + 2ts^5p^3$
$k = 10$	$(4t^4 + 15qt^2s)p^6 + (40t^3s^2 + 9qts^3)p^5 + 32t^2s^4p^4 + 3ts^6p^3$
$k = 11$	$(4q^2ts + 10qt^3)p^7 + (41t^4s + 59qt^2s^2)p^6 + (124t^3s^3 + 20qts^4)p^5 + 60t^2s^5p^4 + 4ts^7p^3$
$k = 12$	$7q^2t^2p^8 + (17q^2ts^2 + 93qt^3s + 14t^5)p^7 + (205t^4s^2 + 183qt^2s^3)p^6 + (310t^3s^4 + 41qts^5)p^5 + 100t^2s^6p^4 + 5ts^8p^3$
$k = 13$	$q^3t^2p^9 + (69q^2t^2s + 45qt^4)p^8 + (463qt^3s^2 + 164t^5s + 60q^2ts^3)p^7 + (766t^4s^3 + 475qt^2s^4)p^6 + (688t^3s^5 + 75qts^6)p^5 + 160t^2s^7p^4 + 7ts^9p^3$
$k = 14$	$(50q^2t^3 + 14q^3ts)p^9 + (496qt^4s + 344q^2t^2s^2 + 47t^6)p^8 + (1733qt^3s^3 + 984t^5s^2 + 165q^2ts^4)p^7 + (1097qt^2s^5 + 2295t^4s^4)p^6 + (130qts^7 + 1376t^3s^6)p^5 + 240t^2s^8p^4 + 8ts^{10}p^3$
$k = 15$	$25q^3t^2p^{10} + (188qt^5 + 76q^3ts^2 + 559q^2t^3s)p^9 + (2975qt^4s^2 + 641t^6s + 1314q^2t^2s^3)p^8 + (5348qt^3s^4 + 4284t^5s^3 + 407q^2ts^5)p^7 + (2305qt^2s^6 + 5991t^4s^5)p^6 + (2564t^3s^7 + 211qts^8)p^5 + 350t^2s^9p^4 + 10ts^{11}p^3$ (omitted)
$k = 20$	$(157q^5ts + 851q^4t^3)p^{13} + (22347q^3t^4s + 7708q^4t^2s^2 + 7065q^2t^6)p^{12} + (52299qt^7s + 104084q^3t^3s^3 + 5500q^4ts^4 + 177241q^2t^5s^2 + 1982t^9)p^{11} + (529146qt^6s^3 + 87453t^8s^2 + 92946q^3t^2s^5 + 558106q^2t^4s^4)p^{10} + (510420t^7s^4 + 1235898qt^5s^5 + 18396q^3ts^7 + 493542q^2t^3s^6)p^9 + (1004469qt^4s^7 + 918708t^6s^6 + 144060q^2t^2s^8)p^8 + (656244t^5s^8 + 321538qt^3s^9 + 11610q^2ts^{10})p^7 + (204078t^4s^{10} + 39670qt^2s^{11})p^6 + (27804t^3s^{12} + 1419qts^{13})p^5 + 1512t^2s^{14}p^4 + 21ts^{16}p^3$ (omitted)

^{a)}Each achiral compound or each pair of enantiomers is counted once.

The generating function $T^{(A)}(x, q, t, s, p)$ (eq. 29) is obtained by using a functional equation (eq. 34) which is identical with eq. 32. The generating function $T^{(C)}(x, q, t, s, p)$ (eq. 30) can be written in the form of a functional equation (eq. 35) by starting eqs. 32 and 33, in which each pair of enantiomers is counted once. The generating function $T^{(B)}(x, q, t, s, p)$ (eq. 31) can be written in the form of a functional equation (eq. 36) by starting eqs. 32 and 33. Note that the total numbers of monosubstituted alkanes are obtained under the condition that each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once.

$$T^{(A)}(x, q, t, s, p) = T^{(a)}(x, q, t, s, p) \quad (34)$$

$$T^{(C)}(x, q, t, s, p) = \frac{1}{2} \left\{ T^{(b)}(x, q, t, s, p) - T^{(a)}(x, q, t, s, p) \right\} \quad (35)$$

$$T^{(B)}(x, q, t, s, p) = \frac{1}{2} \left\{ T^{(a)}(x, q, t, s, p) + T^{(b)}(x, q, t, s, p) \right\}. \quad (36)$$

Table 10: Numbers of Achiral and Chiral Monosubstituted Alkanes of Tertiary Type^{a)}

The coefficient of x^k (cf. eqs. 31 and 36), i.e., $\sum T_{kn_1n_2n_3}^{(B)} q^{n_1} t^{n_2} s^{n_3} p^n$	
$k = 1-3$	0
$k = 4$	tp^3
$k = 5$	$ts p^3$
$k = 6$	$t^2 p^4 + 2ts^2 p^3$
$k = 7$	$qt p^5 + 3t^2 s p^4 + 3ts^3 p^3$
$k = 8$	$(3qts + 2t^3) p^5 + 9t^2 s^2 p^4 + 4ts^4 p^3$
$k = 9$	$3qt^2 p^6 + (8qts^2 + 11t^3 s) p^5 + 19t^2 s^3 p^4 + 5ts^5 p^3$
$k = 10$	$2q^2 t p^7 + (6t^4 + 17qt^2 s) p^6 + (44t^3 s^2 + 17qts^3) p^5 + 38t^2 s^4 p^4 + 7ts^6 p^3$
$k = 11$	$(8q^2 ts + 12qt^3) p^7 + (43t^4 s + 65qt^2 s^2) p^6 + (128t^3 s^3 + 34qts^4) p^5 + 66t^2 s^5 p^4 + 8ts^7 p^3$
$k = 12$	$10q^2 t^2 p^8 + (29q^2 ts^2 + 97qt^3 s + 16t^5) p^7 + (215t^4 s^2 + 193qt^2 s^3) p^6 + (320t^3 s^4 + 61qts^5) p^5 + 110t^2 s^6 p^4 + 10ts^8 p^3$
$k = 13$	$4q^3 t p^9 + (74q^2 t^2 s + 48qt^4) p^8 + (477qt^3 s^2 + 166t^5 s + 82q^2 ts^3) p^7 + (776t^4 s^3 + 495qt^2 s^4) p^6 + (698t^3 s^5 + 105qts^6) p^5 + 170t^2 s^7 p^4 + 12ts^9 p^3$
$k = 14$	$(56q^2 t^3 + 22q^3 ts) p^9 + (502qt^4 s + 362q^2 t^2 s^2 + 52t^6) p^8 + (1757qt^3 s^3 + 996t^5 s^2 + 211q^2 ts^4) p^7 + (1127qt^2 s^5 + 2325t^4 s^4) p^6 + (170qts^7 + 1396t^3 s^6) p^5 + 255t^2 s^8 p^4 + 14ts^{10} p^3$
$k = 15$	$29q^3 t^2 p^{10} + (193qt^5 + 102q^3 ts^2 + 571q^2 t^3 s) p^9 + (2999qt^4 s^2 + 646t^6 s + 1344q^2 t^2 s^3) p^8 + (5402qt^3 s^4 + 4296t^5 s^3 + 483q^2 ts^5) p^7 + (2355qt^2 s^6 + 6021t^4 s^5) p^6 + (2584t^3 s^7 + 266qts^8) p^5 + 365t^2 s^9 p^4 + 16ts^{11} p^3$ (omitted)
$k = 20$	$(185q^5 ts + 879q^4 t^3) p^{13} + (22397q^3 t^4 s + 7792q^4 t^2 s^2 + 7111q^2 t^6) p^{12} + (52327qt^7 s + 104380q^3 t^3 s^3 + 5832q^4 ts^4 + 177445q^2 t^5 s^2 + 1996t^9) p^{11} + (529308qt^6 s^3 + 87579t^8 s^2 + 93294q^3 t^2 s^5 + 558598q^2 t^4 s^4) p^{10} + (510600t^7 s^4 + 1236258qt^5 s^5 + 19188q^3 ts^7 + 494394q^2 t^3 s^6) p^9 + (1004973qt^4 s^7 + 919128t^6 s^6 + 144630q^2 t^2 s^8) p^8 + (656496t^5 s^8 + 322042qt^3 s^9 + 12288q^2 ts^{10}) p^7 + (204330t^4 s^{10} + 39922qt^2 s^{11}) p^6 + (27888t^3 s^{12} + 1587qts^{13}) p^5 + 1548t^2 s^{14} p^4 + 30ts^{16} p^3$ (omitted)

^{a)}Each achiral compound or each pair of enantiomers is counted once.

A program named “AlkylPST8T.mpl” for counting tertiary monosubstituted alkanes is written by using the Maple programming language. The program “AlkylPST8P.mpl” for counting primary monosubstituted alkanes (described above) is modified to treat tertiary counterparts. Part 2 is replaced by the following code in accord with eqs. 32 and 33:

```
#(Part 2) Tertiary Monosubstituted Alkanes
# ---not for recursive calc.
Tax := x*t*(a1-1)*(c2-1);
Tbx := (x*t/3)*((b1-1)^3 + 2*(b3-1));
```

Parts 3–5 are rewritten on the same line. Parts 6–8 as well as Part 1 are used without changes. Part 9 is replaced by the following code in accord with eqs. 35 and 36:

```
"(Part 9) Final Calculation";
#Tertiary (Chiral + Achiral)
BTx := (1/2)*(Tal + Tbl);
#Tertiary (Chiral)
CTx := (1/2)*(Tbl - Tal);
```

where each character “P” (primary) involved in the symbols of variables is changed into “T” (tertiary). Part 10 is also rewritten in order to print out the data at issue.

The modified program (“AlkylPST8T.mpl”) is executed to give calculation results, which are collected in Table 8 for the data NT_a ($\sum T_{knqn_tn_s n_p}^{(A)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 34 and 29), in Table 9 for the data NT_c ($\sum T_{knqn_tn_s n_p}^{(C)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 35 and 30), and in Table 10 for the data NT_t ($\sum T_{knqn_tn_s n_p}^{(B)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, cf. eqs. 36 and 31). Although a single summation is used to save space, it is concerned with n_q , n_t , n_s , and n_p for each carbon content k . Thus, each of the polynomials concerning the branching indicators (q , t , s , and p) which appear in the k -rows of the respective tables is the coefficient of x^k .

4 Enumeration as Constitutional Isomers

4.1 Recursive Functional Equations for PAMs as Graphs

Let the symbol $R_{knqn_tn_s n_p}$ be the number of inequivalent PAMs (as graphs) of carbon content k which have n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons. Then the generating function of the number $R_{knqn_tn_s n_p}$ is represented by using the above-mentioned branching indicators (i.e., q , t , s , and p) as follows:

$$r(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} R_{knqn_tn_s n_p} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (37)$$

By summing up eqs. 7 and 8, we obtain

$$\begin{aligned} & \frac{1}{2} \{a(x, q, t, s, p) + b(x, q, t, s, p)\} \\ &= 1 + xp + \frac{xs}{2} \{[a(x, q, t, s, p) - 1] + [b(x, q, t, s, p) - 1]\} \\ & \quad + \frac{xt}{2} \{[b(x, q, t, s, p) - 1]^2 + [c(x^2, q^2, t^2, s^2, p^2) - 1]\} \\ & \quad + \frac{xq}{6} \{[b(x, q, t, s, p) - 1]^3 + 2[b(x^3, q^3, t^3, s^3, p^3) - 1] \\ & \quad + 3[a(x, q, t, s, p) - 1][c(x^2, q^2, t^2, s^2, p^2) - 1]\}, \end{aligned} \quad (38)$$

which counts PAMs as stereoisomers, where each achiral PAM or each pair of enantiomeric PAMs is counted once. In order to count these PAMs as graphs, we shall equalize all of the functions appearing in eq. 38 as follows:

$$a(x^k, q^k, t^k, s^k, p^k) = b(x^k, q^k, t^k, s^k, p^k) = c(x^k, q^k, t^k, s^k, p^k) = r(x^k, q^k, t^k, s^k, p^k), \quad (39)$$

which is here called a *graph-reduction condition*. Thereby, eq. 38 is converted into the following functional equation:

$$\begin{aligned} r(x, q, t, s, p) = & 1 + xp + xs \{r(x, q, t, s, p) - 1\} \\ & + \frac{xt}{2} \{[r(x, q, t, s, p) - 1]^2 + [r(x^2, q^2, t^2, s^2, p^2) - 1]\} \\ & + \frac{xq}{6} \{[r(x, q, t, s, p) - 1]^3 + 2[r(x^3, q^3, t^3, s^3, p^3) - 1] \\ & + 3[r(x, q, t, s, p) - 1][r(x^2, q^2, t^2, s^2, p^2) - 1]\}, \end{aligned} \quad (40)$$

which can be used to evaluate the generating function represented by eq. 37. It should be noted that eq. 40 has recursive nature, because PAMs are regarded as graphs.

4.2 Primary Monosubstituted Alkanes as Graphs

Let the symbol $P_{kn_qn_tn_s n_p}^{(R)}$ be the number of inequivalent monosubstituted alkanes of primary type (as graphs), where k carbons in each monosubstituted alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons. The number $P_{kn_qn_tn_s n_p}^{(R)}$ is obtained as the coefficient of the term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$ appearing in the following generating function:

$$P^{(R)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_s n_p}^{(R)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (41)$$

By introducing eq. 13 and 14 into eq. 20, we obtain the following equation:

$$P^{(B)}(x, q, t, s, p) = \frac{xp}{2} \{[a(x, q, t, s, p) - 1] + [b(x, q, t, s, p) - 1]\}, \quad (42)$$

which is a concrete form of evaluating the number of achiral and chiral primary monosubstituted alkanes as 3D structures. For the purpose of reducing such 3D structures into graphs, we should cease the different treatments between achiral and chiral 3D structures. Hence, in order to count graphs, the functions which appear in the right-hand side of eq. 42 are rewritten under the graph-reduction condition represented by eq. 39 as well as the function $P^{(B)}(x, q, t, s, p)$ which appears in the left-hand side of eq. 42 is replaced by $P^{(R)}(x, q, t, s, p)$. Thereby we obtain:

$$P^{(R)}(x, q, t, s, p) = xp \{r(x, q, t, s, p) - 1\}, \quad (43)$$

which can be used to evaluate the generating function represented by eq. 41.

The recursive process using eq. 40 and the calculation using eq. 43 are programmed by the Maple language as follows:

Table 11: Numbers of Monosubstituted Alkanes of Primary Type as Graphs

The coefficient of x^k (cf. eqs. 41 and 43), i.e., $\sum P_{kn,qn,n_s,n_p}^{(R)} q^n t^{n_s} s^{n_s} p^{n_p}$	
$k = 1$	0
$k = 2$	p^2
$k = 3$	sp^2
$k = 4$	$tp^3 + s^2p^2$
$k = 5$	$qp^4 + 2ts p^3 + s^3p^2$
$k = 6$	$(2qs + t^2)p^4 + 4ts^2p^3 + s^4p^2$
$k = 7$	$2qt p^5 + (4qs^2 + 4t^2s)p^4 + 6ts^3p^3 + s^5p^2$
$k = 8$	$q^2p^6 + (2t^3 + 8qts)p^5 + (11t^2s^2 + 7qs^3)p^4 + 9ts^4p^3 + s^6p^2$
$k = 9$	$(4q^2s + 5qt^2)p^6 + (9t^3s + 23qts^2)p^5 + (24t^2s^3 + 11qs^4)p^4 + 12ts^5p^3 + s^7p^2$
$k = 10$	$5q^2t p^7 + (12q^2s^2 + 27qt^2s + 3t^4)p^6 + (32t^3s^2 + 53qts^3)p^5 + (46t^2s^4 + 16qs^5)p^4 + 16ts^6p^3 + s^8p^2$
$k = 11$	$2q^3p^8 + (27q^2ts + 12qt^3)p^7 + (99qt^2s^2 + 20t^4s + 29q^2s^3)p^6 + (86t^3s^3 + 108qts^4)p^5 + (80t^2s^5 + 23qs^6)p^4 + 20ts^7p^3 + s^9p^2$
$k = 12$	$(17q^2t^2 + 10q^3s)p^8 + (82qt^3s + 103q^2ts^2 + 6t^5)p^7 + (283qt^2s^3 + 86t^4s^2 + 62q^2s^4)p^6 + (199qts^5 + 203t^3s^4)p^5 + (31qs^7 + 130t^2s^6)p^4 + 25ts^8p^3 + s^{10}p^2$
$k = 13$	$12q^3t p^9 + (28qt^4 + 38q^3s^2 + 124q^2t^2s)p^8 + (365qt^3s^2 + 46t^5s + 306q^2ts^3)p^7 + (697q^2t^4s^4 + 283t^4s^3 + 120q^2s^5)p^6 + (343qts^6 + 423t^3s^5)p^5 + (200t^2s^7 + 41qs^8)p^4 + 30ts^9p^3 + s^{11}p^2$
$k = 14$	$4q^4p^{10} + (55q^2t^3 + 87q^3ts)p^9 + (237qt^4s + 11t^6 + 572q^2t^2s^2 + 114q^3s^3)p^8 + (234t^5s^2 + 1247qt^3s^3 + 786q^2ts^4)p^7 + (786t^4s^4 + 1530qt^2s^5 + 217q^2s^6)p^6 + (816t^3s^6 + 558qts^7)p^5 + (295t^2s^8 + 53qs^9)p^4 + 36ts^{10}p^3 + s^{12}p^2$
$k = 15$	$(25q^4s + 56q^3t^2)p^{10} + (483q^2t^3s + 408q^3ts^2 + 66qt^5)p^9 + (106t^6s + 1241qt^4s^2 + 2025q^2t^2s^3 + 300q^3s^4)p^8 + (892t^5s^3 + 3596qt^3s^4 + 1797q^2ts^5)p^7 + (1923t^4s^5 + 3088qt^2s^6 + 370q^2s^7)p^6 + (1466t^3s^7 + 869qts^8)p^5 + (67qs^{10} + 420t^2s^9)p^4 + 42ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k = 20$	$17q^6p^{14} + (833q^4t^3 + 840q^5ts)p^{13} + (1316q^2t^6 + 9810q^3t^4s + 12116q^4t^2s^2 + 1464q^5s^3)p^{12} + (39499q^2t^5s^2 + 98t^9 + 70875q^3t^3s^3 + 22745q^4ts^4 + 4909qt^7s)p^{11} + (186634q^2t^4s^4 + 4304t^8s^2 + 8959q^4s^6 + 123410q^3t^2s^5 + 62338qt^6s^3)p^{10} + (215036qt^5s^5 + 288855q^2t^3s^6 + 32386t^7s^4 + 68658q^3ts^7)p^9 + (85925t^6s^6 + 290287qt^4s^7 + 174937q^2t^2s^8 + 10824q^3s^9)p^8 + (99790t^5s^8 + 172626qt^3s^9 + 41344q^2ts^{10})p^7 + (3045q^2s^{12} + 54836t^4s^{10} + 45881qt^2s^{11})p^6 + (14410t^3s^{12} + 5031qts^{13})p^5 + (174qs^{15} + 1716t^2s^{14})p^4 + 81ts^{16}p^3 + s^{18}p^2$
	(omitted)

```

#GraphAlkylPST1P.mpl
#Calculation of Primary Alkyls (Graphs)

"Functional Equations for Inner Alkyl Ligands (as Graphs)";
# H, methyl, primary, secondary, tertiary, quaternary
# --- internal alkyl
rx := 1 + x*p + x*s*(r1-1) + (x*t/2)*((r1-1)^2 + (r2-1))
+ (x*q/6)*((r1-1)^3 + 2*(r3-1) + 3*(r1-1)*(r2-1));

#Primary Monosubstituted Alkanes
Prx := x*p*(r1-1);

"Initial Values";
r1 := 1; r2 := 1; r3 := 1;
rsum := 1;
Pr1 := 1;

"Recursive Calculation";
kmax := 30;
for k from 1 to kmax by 1 do
"k ="; k;

"Primary Graphs";
CPrx:= expand(coeff(Prx,x^k)):
Pr1 := Pr1 + CPrx*x^k:

"Graphs";
Crx:= expand(coeff(rx,x^k)):
Cr2x:= subs({p=p^2,s=s^2,t=t^2,q=q^2}, expand(coeff(rx,x^k))):
Cr3x:= subs({p=p^3,s=s^3,t=t^3,q=q^3}, expand(coeff(rx,x^k))):
Crsum:= subs({p=1,s=1,t=1,q=1}, expand(coeff(rx,x^k))):
r1 := r1 + Crx*x^k:
r2 := r2 + Cr2x*x^(2*k):
r3 := r3 + Cr3x*x^(3*k):
rsum := rsum + Crsum*x^k:
end do:

#####
"Print Out of Pr1 (Primary Graphs)";
for k from 1 to kmax by 1 do
carbon_content:= k:
NPr := collect(sort(expand(coeff(Pr1,x^k)), [q,t,s,p]), p);
end do;

```

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

```

> restart;
> read "GraphAlkylPST1P.mpl";

```

Table 11 collects the data NP_r ($\sum_{kn_qn_tn_sn_p} P^{(R)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k (cf. eqs. 41 and 43).

4.3 Secondary Monosubstituted Alkanes as Graphs

Let the symbol $S_{kn_qn_tn_sn_p}^{(R)}$ be the number of inequivalent monosubstituted alkanes of secondary type (as graphs), where k carbons in each monosubstituted alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary

carbons. Suppose that the number $S_{kn_qn_tn_sn_p}^{(R)}$ is evaluated in the form of a generating function represented by:

$$S^{(R)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{kn_qn_tn_sn_p}^{(R)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (44)$$

The introduction of eq. 24 and 25 into eq. 28 provides us with the following equation:

$$S^{(B)}(x, q, t, s, p) = \frac{xs}{2} \{ [b(x, q, t, s, p) - 1]^2 + [c(x^2, q^2, t^2, s^2, p^2) - 1] \}, \quad (45)$$

which is a concrete form of $S^{(B)}(x, q, t, s, p)$ for counting 3D structures. In order to count graphs, $S^{(B)}(x, q, t, s, p)$ is replaced by $S^{(R)}(x, q, t, s, p)$ under the graph-reduction condition (eq. 39). Thereby we obtain:

$$S^{(R)}(x, q, t, s, p) = \frac{xs}{2} \{ [r(x, q, t, s, p) - 1]^2 + [r(x^2, q^2, t^2, s^2, p^2) - 1] \}, \quad (46)$$

which is used to produce the generating function (eq. 44).

The calculation using the functional equation (eq. 46) has been programmed by means of the Maple language on the same line as the program "GraphAlkylPST1P.mpl". The resulting program, which is named "GraphAlkylPST1S.mpl", was executed to give the data of secondary monosubstituted alkanes as graphs ($\sum S_{kn_qn_tn_sn_p}^{(R)} p^{n_p} s^{n_s} t^{n_t} q^{n_q}$). Table 12 collects the respective coefficients of x^k for secondary cases (cf. eqs. 44 and 46).

4.4 Tertiary Monosubstituted Alkanes as Graphs

Let the symbol $T_{kn_qn_tn_sn_p}^{(R)}$ be the number of inequivalent monosubstituted alkanes of tertiary type (as graphs), where k carbons in each monosubstituted alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons. The corresponding generating function is represented as follows:

$$T^{(R)}(x, q, t, s, p) = \sum_{k=0}^{\infty} \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{kn_qn_tn_sn_p}^{(R)} p^{n_p} \right) s^{n_s} \right) t^{n_t} \right) q^{n_q} \right) x^k. \quad (47)$$

By introducing eqs. 32 and 33 into eq. 36, we obtain the following functional equation:

$$T^{(B)}(x, q, t, s, p) = \frac{xt}{6} \{ [b(x, q, t, s, p) - 1]^3 + 2[b(x^3, q^3, t^3, s^3, p^3) - 1] + 3[a(x, q, t, s, p) - 1][c(x^2, q^2, t^2, s^2, p^2) - 1] \}, \quad (48)$$

which is a concrete form for counting tertiary monosubstituted alkanes as 3D structures. In order to count graphs, the function $T^{(B)}(x, q, t, s, p)$ which appears in the left-hand side of eq. 48 is replaced by $T^{(R)}(x, q, t, s, p)$ and the functions which appear in the right-hand side of eq. 48 are modified under the graph-reduction condition represented by eq. 39. Thereby eq. 48 for 3D structures is reduced into the following functional equation for graphs:

$$T^{(R)}(x, q, t, s, p) = \frac{xt}{6} \{ [r(x, q, t, s, p) - 1]^3 + 2[r(x^3, q^3, t^3, s^3, p^3) - 1] + 3[r(x, q, t, s, p) - 1][r(x^2, q^2, t^2, s^2, p^2) - 1] \}, \quad (49)$$

Table 12: Numbers of Monosubstituted Alkanes of Secondary Type as Graphs

The coefficient of x^k (cf. eqs. 44 and 46), i.e., $\sum_{kn, q, n, n, p} s_{kn, q, n, n, p}^{(R)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$	
$k = 1$	0
$k = 2$	0
$k = 3$	sp^2
$k = 4$	s^2p^2
$k = 5$	$tsp^3 + 2s^3p^2$
$k = 6$	$qsp^4 + 3ts^2p^3 + 2s^4p^2$
$k = 7$	$(3qs^2 + 2t^2s)p^4 + 7ts^3p^3 + 3s^5p^2$
$k = 8$	$3qts p^5 + (7qs^3 + 7t^2s^2)p^4 + 13ts^4p^3 + 3s^6p^2$
$k = 9$	$2q^2s p^6 + (3t^3s + 14qts^2)p^5 + (23t^2s^3 + 14qs^4)p^4 + 22ts^5p^3 + 4s^7p^2$
$k = 10$	$(7q^2s^2 + 8qt^2s)p^6 + (17t^3s^2 + 45qts^3)p^5 + (54t^2s^4 + 25qs^5)p^4 + 34ts^6p^3 + 4s^8p^2$
$k = 11$	$8q^2ts p^7 + (24q^2s^3 + 50qt^2s^2 + 6t^4s)p^6 + (66t^3s^3 + 115qts^4)p^5 + (117t^2s^5 + 41qs^6)p^4 + 50ts^7p^3 + 5s^9p^2$
$k = 12$	$3q^3s p^8 + (50q^2ts^2 + 21qt^3s)p^7 + (201qt^2s^3 + 40t^4s^2 + 61q^2s^4)p^6 + (197t^3s^4 + 256qts^5)p^5 + (220t^2s^6 + 64qs^7)p^4 + 70ts^8p^3 + 5s^{10}p^2$
$k = 13$	$(31q^2t^2s + 18q^3s^2)p^8 + (160qt^3s^2 + 206q^2ts^3 + 11t^5s)p^7 + (626qt^2s^4 + 188t^4s^3 + 143q^2s^5)p^6 + (513qts^6 + 503t^3s^5)p^5 + (95qs^8 + 393t^2s^7)p^4 + 95ts^9p^3 + 6s^{11}p^2$
$k = 14$	$21q^3ts p^9 + (52qt^4s + 74q^3s^3 + 239q^2t^2s^2)p^8 + (767qt^3s^3 + 95t^5s^2 + 661q^2t^4s)p^7 + (1660qt^2s^5 + 658t^4s^4 + 294q^2s^6)p^6 + (953qts^7 + 1137t^3s^6)p^5 + (650t^2s^8 + 136qs^9)p^4 + 125ts^{10}p^3 + 6s^{12}p^2$
$k = 15$	$7q^4s p^{10} + (101q^2t^3s + 166q^3ts^2)p^9 + (478qt^4s^2 + 23t^6s + 1184q^2t^2s^3 + 240q^3s^4)p^8 + (514t^5s^3 + 2806qt^3s^4 + 1812q^2ts^5)p^7 + (1961t^4s^5 + 3907qt^2s^6 + 572q^2s^7)p^6 + (2352t^3s^7 + 1664qts^8)p^5 + (1037t^2s^9 + 189qs^{10})p^4 + 161ts^{11}p^3 + 7s^{13}p^2$ (omitted)
$k = 20$	$149q^5ts p^{13} + (703q^5s^3 + 1549q^3t^4s + 3758q^4t^2s^2)p^{12} + (11736q^2t^5s^2 + 13781q^4ts^4 + 31583q^3t^3s^3 + 763qt^7s)p^{11} + (92589q^3t^2s^5 + 109953q^2t^4s^4 + 1278t^8s^2 + 8304q^4s^6 + 27394qt^6s^3)p^{10} + (264592q^2t^3s^6 + 75346q^3ts^7 + 19123t^7s^4 + 160886qt^5s^5)p^9 + (228126q^2t^2s^8 + 79845t^6s^6 + 322465qt^4s^7 + 16357q^3s^9)p^8 + (73826q^2ts^{10} + 269253qt^3s^9 + 134275t^5s^8)p^7 + (98292qt^2s^{11} + 103414t^4s^{10} + 7337q^2s^{12})p^6 + (37838t^3s^{12} + 14799qts^{13})p^5 + (6384t^2s^{14} + 711qs^{15})p^4 + 444ts^{16}p^3 + 9s^{18}p^2$ (omitted)

Table 13: Numbers of Monosubstituted Alkanes of Tertiary Type as Graphs

The coefficient of x^k (cf. eqs. 47 and 49), i.e., $\sum T_{knq_n t_n s_n p}^{(R)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$	
$k = 1-3$	0
$k = 4$	tp^3
$k = 5$	$ts p^3$
$k = 6$	$t^2 p^4 + 2ts^2 p^3$
$k = 7$	$qt p^5 + 3t^2 s p^4 + 3ts^3 p^3$
$k = 8$	$(3qts + 2t^3) p^5 + 8t^2 s^2 p^4 + 4ts^4 p^3$
$k = 9$	$3qt^2 p^6 + (8qts^2 + 8t^3 s) p^5 + 16t^2 s^3 p^4 + 5ts^5 p^3$
$k = 10$	$2q^2 t p^7 + (4t^4 + 15qt^2 s) p^6 + (27t^3 s^2 + 17qt s^3) p^5 + 30t^2 s^4 p^4 + 7ts^6 p^3$
$k = 11$	$(8q^2 t s + 9qt^3) p^7 + (20t^4 s + 52qt^2 s^2) p^6 + (69t^3 s^3 + 33qt s^4) p^5 + 50t^2 s^5 p^4 + 8ts^7 p^3$
$k = 12$	$9q^2 t^2 p^8 + (28q^2 t s^2 + 57qt^3 s + 7t^5) p^7 + (82t^4 s^2 + 142qt^2 s^3) p^6 + (158t^3 s^4 + 58qts^5) p^5 + 80t^2 s^6 p^4 + 10ts^8 p^3$
$k = 13$	$4q^3 t p^9 + (57q^2 t^2 s + 24qt^4) p^8 + (242qt^3 s^2 + 49t^5 s + 76q^2 t s^3) p^7 + (256t^4 s^3 + 337qt^2 s^4) p^6 + (320t^3 s^5 + 97qt s^6) p^5 + 120t^2 s^7 p^4 + 12ts^9 p^3$
$k = 14$	$(35q^2 t^3 + 21q^2 t s) p^9 + (189qt^4 s + 247q^2 t^2 s^2 + 14t^6) p^8 + (792qt^3 s^3 + 237t^5 s^2 + 186q^2 t s^4) p^7 + (717qt^2 s^5 + 689t^4 s^4) p^6 + (153qts^7 + 605t^3 s^6) p^5 + 175t^2 s^8 p^4 + 14ts^{10} p^3$
$k = 15$	$24q^3 t^2 p^{10} + (62qt^5 + 90q^3 t s^2 + 281q^2 t^3 s) p^9 + (946qt^4 s^2 + 119t^6 s + 828q^2 t^2 s^3) p^8 + (2211qt^3 s^4 + 868t^5 s^3 + 405q^2 t s^5) p^7 + (1410qt^2 s^6 + 1638t^4 s^5) p^6 + (1067t^3 s^7 + 233qts^8) p^5 + 245t^2 s^9 p^4 + 16ts^{11} p^3$
	(omitted)
$k = 20$	$(149q^2 t s + 396q^4 t^3) p^{13} + (5789q^3 t^4 s + 3833q^4 t^2 s^2 + 1135q^2 t^6) p^{12} + (4867qt^7 s + 32345q^3 t^3 s^3 + 3760q^4 t s^4 + 28646q^2 t^5 s^2 + 127t^9) p^{11} + (54606qt^6 s^3 + 4943t^8 s^2 + 39635q^3 t^2 s^5 + 113187q^2 t^4 s^4) p^{10} + (33874t^7 s^4 + 166040qt^5 s^5 + 11914q^3 t s^7 + 140273q^2 t^3 s^6) p^9 + (193742qt^4 s^7 + 82476t^6 s^6 + 61739q^2 t^2 s^8) p^8 + (87474t^5 s^8 + 95479qt^3 s^9 + 8169q^2 t s^{10}) p^7 + (43284t^4 s^{10} + 19204qt^2 s^{11}) p^6 + (9916t^3 s^{12} + 1245qts^{13}) p^5 + 960t^2 s^{14} p^4 + 30ts^{16} p^3$
	(omitted)

which is used to evaluate eq. 47.

The calculation using the functional equation (eq. 49) has been programmed by means of the Maple language on the same line as the code “GraphAlkylPST1P.mpl”. The resulting code was stored under the name “GraphAlkylPST1T.mpl” and executed to give the data of tertiary monosubstituted alkanes as graphs. Table 13 collects the results of the calculation, i.e., the polynomials ($\sum T_{knq_n t_n s_n p}^{(R)} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$) which appear as the coefficients of x^k (cf. eqs. 47 and 49).

5 Discussions

5.1 Cases of Lower Carbon Contents

To verify the results collected in Tables 2–10, the 3D structures of monosubstituted alkanes of carbon contents 1–5 are depicted in Fig. 2, where their structure skeletons are shown in place of full 3D structures with hydrogen atoms. A monosubstituted methane ($\text{CH}_3\text{—Z}$, e.g., methanol)

is added to the “primary” column of Fig. 2, although it is an extreme case other than primary, secondary, and tertiary monosubstituted alkanes.

According to Tables 2–10, the 3D structures collected in Fig. 2 are categorized in terms of achirality/chirality on one hand and in terms of primary/secondary/tertiary on the other hand, where further categorization due to branching monomials (BMs) are embodied as a new matter by means of the present method. For example, the “achiral-primary” column of Fig. 2 is in agreement with the results ($k = 1$ –5) of Table 2. Thus, the coefficient (1) of the term p^2 appearing in the ($k = 2$)-row of Table 2 corresponds to a monosubstituted ethane (**6**, e.g., ethanol). The coefficient (1) of the term sp^2 appearing in the ($k = 3$)-row of Table 2 corresponds to a 1-monosubstituted propane (**7**, e.g., propan-1-ol). The term $tp^3 + s^2p^2$ in the ($k = 4$)-row of Table 2 indicates the presence of **9** (e.g., butan-1-ol) and **11** (e.g., 2-methylpropan-1-ol or isobutyl alcohol). The term $qp^4 + tsp^3 + s^3p^2$ in the ($k = 5$)-row of Table 2 corresponds to the presence of **13** (e.g., pentan-1-ol), **16** (e.g., 3-methylbutan-1-ol), and **20** (e.g., 2,2-dimethylpropan-1-ol). It should be noted that the appearance of branching indicators in each branching monomial (BM) in Fig. 2 as well as in Table 2 follows the order printed out by the Maple programs described above, i.e., in the descending order of branching degrees ($q > t > s > p$).

Similarly, the “achiral-secondary” column and the “achiral-tertiary” column of Fig. 2 are respectively depicted to verify the results ($k = 1$ –5) of Table 5 and those of Table 8. The “chiral-primary” column and the “chiral-secondary” column of Fig. 2 correspond to the data of Table 3 and those of Table 6. Table 9 indicates the absence of chiral and tertiary monosubstituted alkanes of carbon content $k = 1$ –6, so that the “chiral-tertiary” column is omitted in Fig. 2.



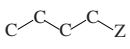
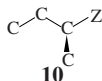


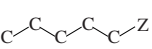
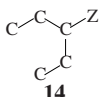
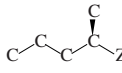
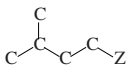
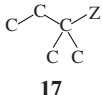
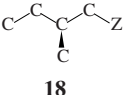
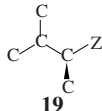

5.2 3D Structures and Graphs

In the present method, each pair of two enantiomers is counted just once. This means that the numbers of 3D structures are equal to those of graphs if they contain one or less asymmetric carbon. Up to carbon content 5, each monosubstituted alkane contain one or less asymmetric carbon so that this conclusion is verified for primary monosubstituted alkanes (Table 4 vs. Table 11), for secondary monosubstituted alkanes (Table 7 vs. Table 12), and for tertiary monosubstituted alkanes (Table 10 vs. Table 13), as depicted in Fig. 2. Because graphs conceptually lack the concept of achirality/chirality, the data of chiral plus achiral 3D structures (Tables 4, Table 7, and Table 10) are employed for this type of comparison.

All of the 3D structures of carbon content 6 are depicted according to the data collected in Tables 2–10 and listed in Fig. 3, where they are categorized in terms of achirality/chirality, primary/secondary/tertiary, and internal branching. Achiral monosubstituted alkanes of secondary type do not exist when carbon content is even so that the “achiral-secondary” column is omitted in Fig. 3. Because chiral monosubstituted alkanes of tertiary type are absent when carbon content is 6 or less, the corresponding column is omitted in Fig. 3.

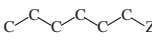
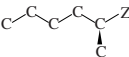
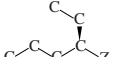
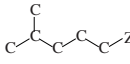
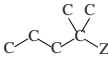
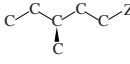
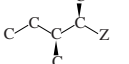
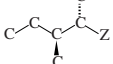
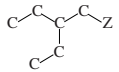

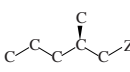
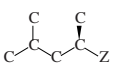
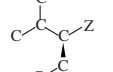

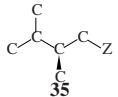
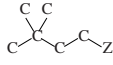

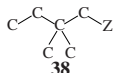
The data collected for secondary monosubstituted alkanes (Table 7 vs. Table 12) show that the lowest case exhibiting the difference between 3D structures and graphs appears in the $k = 6$ rows of the respective tables, i.e., $4stp^3x^6$ in Table 7 and $3stp^3x^6$ in Table 12. The term $4stp^3x^6$ in Table 7 shows the existence of four 3D structures, i.e., **27** (and its enantiomer), **28** (and its enantiomer), **32** (and its enantiomer), and **33** (and its enantiomer). Among them, **27** (and its enantiomer) and **28** (and its enantiomer) coalesce into a single graph, which is in agreement with the term $3stp^3x^6$ in Table 12.

Among the 3D structures of carbon content 7, those corresponding to the BM ts^3p^3 are depicted in Fig. 4, where they are categorized in terms of achirality/chirality and primary/second-

CC ^{a)}	BM ^{b)}	Achiral ^{c)}			Chiral ^{d)}	
		Primary (Table 2)	Secondary (Table 5)	Tertiary (Table 8)	Primary (Table 3)	Secondary (Table 6)
$k = 1$	1	(C-Z) ^{e)} 5				
$k = 2$	p^2	C-C-Z 6				
$k = 3$	sp^2	 7	 8			
$k = 4$	s^2p^2	 9				 10
	tp^3	 11		 12		
$k = 5$	s^3p^2	 13	 14			 15
	ts^2p^3	 16		 17	 18	 19
	qp^4	 20				

a) CC: carbon content. b) BM: branching monomial. c) Achiral monosubstituted alkanes of secondary type do not exist when carbon content is even. d) Chiral monosubstituted alkanes of tertiary type are absent when carbon content is 6 or less. e) Methanol (an extreme case, not primary).

Figure 2: Monosubstituted alkanes of lower carbon contents ($k = 1-5$), which are categorized by means of branching monomials. The symbol Z represents an atom (other than carbon and hydrogen) or an achiral univalent ligand (e.g., a hydroxyl ligand for alcohols). Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

CC ^{a)}	BM ^{b)}	Achiral ^{c)}		Chiral ^{d)}		
		Primary (Table 2)	Tertiary (Table 8)	Primary (Table 3)	Secondary (Table 6)	
k = 6	$s^4 p^2$	 21			 22	 23
	$ts^2 p^3$	 24	 25	 26	 27	 28
		 29	 30	 31	 32	 33
	$t^2 p^4$		 34	 35		
qsp^4	 36			 37		
		 38				

^{a)} CC: carbon content. ^{b)} BM: branching monomial without the term x^6 . ^{c)} Achiral monosubstituted alkanes of secondary type do not exist when carbon content is even. ^{d)} Chiral monosubstituted alkanes of tertiary type are absent when carbon content is 6 or less.

Figure 3: Monosubstituted alkanes of carbon content $k = 6$, which are categorized by means of branching monomials. The symbol Z represents an atom (other than carbon and hydrogen) or an achiral univalent ligand (e.g., a hydroxyl ligand for alcohols). Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

Achiral ^{a)}		Chiral		
Primary ($2ts^3p^3$ in Table 2)	Tertiary ($2ts^3p^3$ in Table 8)	Primary ($4ts^3p^3$ in Table 3)	Secondary ($10ts^3p^3$ in Table 6)	Tertiary (ts^3p^3 in Table 9)

^{a)} Achiral monosubstituted alkanes of secondary type are absent for the term $ts^3p^3x^7$.

Figure 4: Monosubstituted alkanes of carbon content 7 with the branching monomial ts^3p^3 . The symbol Z represents an atom (other than carbon and hydrogen) or an achiral univalent ligand (e.g., a hydroxyl ligand for alcohols). Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

ary/tertiary according to the data collected in Tables 2–10. Achiral monosubstituted alkanes of secondary type are absent so that the “achiral-secondary” column is omitted in Fig. 4.

The term $10ts^3p^3$ in the ($k = 7$)-row of Table 6 shows the existence of ten 3D structures, i.e., **47–56** (and their respective enantiomers). Among them, each of three sets of diastereomers (i.e., **51** (and its enantiomer) and **52** (and its enantiomer); **53** (and its enantiomer) and **54** (and its enantiomer); **55** (and its enantiomer) and **56** (and its enantiomer)) coalesces into a single graph. The three sets of coalescence results in a decrease by 3, which is in agreement with the term $7ts^3p^3$ in the ($k = 7$)-row of Table 12, because $10ts^3p^3 - 3ts^3p^3 = 7ts^3p^3$.

5.3 Pseudoasymmetric Cases

The coefficient 3 of the term $3t^2s^3p^4$ appearing in the ($k = 9$)-row of Table 5 shows the existence of three achiral monosubstituted alkanes of carbon content 9 (**59–61**), as depicted in Fig. 5. Among them, a set of diastereomers, **59** and **60**, exhibits a pseudoasymmetric nature. Figure 5 also involves other two monosubstituted alkanes (**58** and **62**), which correspond to the terms s^7p^2 and q^2sp^6 appearing in the ($k = 9$)-row of Table 5.

The two monosubstituted alkanes of the pseudoasymmetric case (**59** and **60**) are represented by $p\bar{p}\text{CHOH}$, if we consider a pair of enantiomeric ligands, $p = R\text{-CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ and $\bar{p} = S\text{-CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$. Note that the R - and S -configurations of such isolated ligands are assigned tentatively by regarding each vacant bond as having the lowest priority. Let us restrict our domain of thinking to the substitution of p , \bar{p} and a hydrogen atom in order to examine the

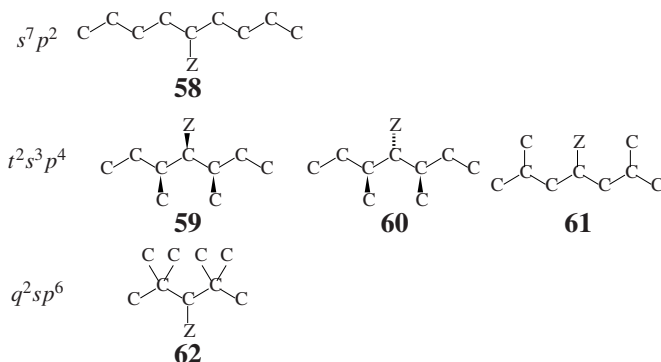


Figure 5: Achiral secondary monosubstituted alkanes of carbon content 9. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

pseudoasymmetric case more intimately.

Suppose that p and \bar{p} are considered to be such PAMs as characterized by a BM $ts\bar{p}^2x^4$. Then, eqs. 7–9 for the present restricted case are obtained as follows:

$$a(x, q, t, s, p) = 1 \quad (50)$$

$$b(x, q, t, s, p) = 1 + ts\bar{p}^2x^4 + t\bar{s}p^2x^4 = 1 + 2ts\bar{p}^2x^4 \quad (51)$$

$$c(x^2, q^2, t^2, s^2, p^2) = 1 + 2(ts\bar{p}^2x^4)(t\bar{s}p^2x^4) = 1 + 2t^2s^2p^4x^8, \quad (52)$$

where the concept of sphericity indices [19] is applied to this case. Note that the first term 1 in each right-hand side is added to treat the substitution of a hydrogen as an extreme case. For the purpose of evaluating secondary monosubstituted alkanes, eqs. 50–52 are introduced into eqs. 24 and 25 to give:

$$S^{(a)}(x, q, t, s, p) = xs \times 2t^2s^2p^4x^8 = 2t^2s^3p^4x^9 \quad (53)$$

$$S^{(b)}(x, q, t, s, p) = xs \times (2ts\bar{p}^2x^4)^2 = 4t^2s^3p^4x^9. \quad (54)$$

Then, eqs. 53 and 54 are introduced into eqs. 26–28 to give:

$$S^{(A)}(x, q, t, s, p) = 2t^2s^3p^4x^9 \quad (55)$$

$$S^{(C)}(x, q, t, s, p) = t^2s^3p^4x^9 \quad (56)$$

$$S^{(B)}(x, q, t, s, p) = 3t^2s^3p^4x^9 \quad (57)$$

The term $2t^2s^3p^4x^9$ appearing in the right-hand side of eq. 55 shows the presence of two achiral monosubstituted alkanes (**59** and **60**) characterized by $p\bar{p}\text{CHOH}$. On the other hand, the term $t^2s^3p^4x^9$ appearing in the right-hand side of eq. 56 corresponds to one pair of enantiomers ($pp\text{CHOH}$ and $\bar{p}\bar{p}\text{CHOH}$), which is counted just once.

5.4 Without Branching Indicators

5.4.1 Primary Monosubstituted Alkanes Without Introducing Branching Indicators

By disregarding the effect of internal branching, we are able to derive previous results [9] as special cases of the present enumeration. This section is devoted to show how the previous formulation and results are derived by omitting the branching indicators developed for the the present enumeration.

Let the symbol $P_k^{(A)}$ be the summation of $P_{kn_qn_tn_s n_p}^{(A)}$ at a given carbon content k ; the symbol $P_k^{(C)}$ be the summation of $P_{kn_qn_tn_s n_p}^{(C)}$ at a given carbon content k ; and the symbol $P_k^{(B)}$ be the summation of $P_{kn_qn_tn_s n_p}^{(B)}$ at a given carbon content k ; where the carbon content k is given to satisfy $k = n_q + n_t + n_s + n_p$. It follows that eqs. 10–12 give the following generating functions:

$$P_k^{(A)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_s n_p}^{(A)} \right) \right) \right) \right) \quad (58)$$

$$P_k^{(C)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_s n_p}^{(C)} \right) \right) \right) \right) \quad (59)$$

$$P_k^{(B)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} P_{kn_qn_tn_s n_p}^{(B)} \right) \right) \right) \right), \quad (60)$$

where we disregard the effect of branching by putting $q = t = s = p = 1$. Obviously, the value $P_k^{(A)}$ can be obtained by adding relevant coefficients appearing in the k -row of Table 2. For example, we obtain $P_7^{(A)} = 1 + 2 + 4 + 1 = 8$, where these coefficients appear in the ($k = 7$)-row of Table 2. On the same line, the values $P_k^{(C)}$ and $P_k^{(B)}$ can be obtained by starting from the data collected in Tables 3 and 4.

These summed numbers are more systematically obtained as the coefficients of the following generating functions:

$$P^{(A)}(x) = \sum_{k=0}^{\infty} P_k^{(A)} x^k = P^{(A)}(x, 1, 1, 1, 1) \quad (61)$$

$$P^{(C)}(x) = \sum_{k=0}^{\infty} P_k^{(C)} x^k = P^{(C)}(x, 1, 1, 1, 1) \quad (62)$$

$$P^{(B)}(x) = \sum_{k=0}^{\infty} P_k^{(B)} x^k = P^{(B)}(x, 1, 1, 1, 1), \quad (63)$$

which can be obtained by putting $q = t = s = p = 1$ in eqs. 18–20. The following equation can easily be derived from eq. 17:

$$P_k^{(B)} = P_k^{(A)} + P_k^{(C)}. \quad (64)$$

The generating functions, $P^{(A)}(x, q, t, s, p)$, $P^{(C)}(x, q, t, s, p)$, and $P^{(B)}(x, q, t, s, p)$, has been already calculated by the above-described program “AlkyIPST8P.mpl” and stored respectively in the form of the series designated by Pa1, CPx, and BPx. It follows that we are able to calculate $P^{(A)}(x)$, $P^{(C)}(x)$, and $P^{(B)}(x)$ (eqs. 61–63) by adding the following code for calculating them:

```
"Primary achiral";
NPa:= sort(subs({p=1,s=1,t=1,q=1}, expand(Pal,x^k)));
"Primary chiral";
NPc:= sort(subs({p=1,s=1,t=1,q=1}, expand(CPx,x^k)));
"Primary chiral+achiral";
NPb:= sort(subs({p=1,s=1,t=1,q=1}, expand(BPx,x^k)));
```

Thereby, we obtain the following generating functions:

$$P^{(A)}(x) = 1 + x^2 + x^3 + 2x^4 + 3x^5 + 5x^6 + 8x^7 + 14x^8 + 23x^9 + 41x^{10} + 69x^{11} + 122x^{12} + 208x^{13} + 370x^{14} + 636x^{15} + \dots + 10908x^{20} + \dots \quad (65)$$

$$P^{(C)}(x) = x^5 + 3x^6 + 10x^7 + 30x^8 + 88x^9 + 255x^{10} + 742x^{11} + 2157x^{12} + 6312x^{13} + 18563x^{14} + 54932x^{15} + \dots + 13500689x^{20} + \dots \quad (66)$$

$$P^{(B)}(x) = 1 + x^2 + x^3 + 2x^4 + 4x^5 + 8x^6 + 18x^7 + 44x^8 + 111x^9 + 296x^{10} + 811x^{11} + 2279x^{12} + 6520x^{13} + 18933x^{14} + 55568x^{15} + \dots + 13511597x^{20} + \dots \quad (67)$$

These values are identical with those reported in previous papers (Table 1 of Ref. [9] for up to carbon content 100). Hence, the previous results can be regarded as special cases of the present enumeration, where the effect of internal branching is disregarded.

This conclusion can be more generally obtained by putting $q = t = s = p = 1$, $a(x) = a(x, 1, 1, 1, 1)$, $b(x) = b(x, 1, 1, 1, 1)$, and $c(x^2) = c(x^2, 1, 1, 1, 1)$ in eqs. 7–9. They are introduced into eqs. 13 and 14 and the resulting $P^{(a)}(x, 1, 1, 1, 1)$ and $P^{(b)}(x, 1, 1, 1, 1)$ are further introduced into eqs. 18–19, where we put $q = t = s = p = 1$. Thereby we obtain the following functional equations without BMs:

$$P^{(A)}(x) = x\{a(x) - 1\} \quad (68)$$

$$P^{(C)}(x) = \frac{x}{2}\{(b(x) - 1) - (a(x) - 1)\} \quad (69)$$

$$P^{(B)}(x) = \frac{x}{2}\{(a(x) - 1) + (b(x) - 1)\}. \quad (70)$$

These equations (eqs. 68–70) correspond to eq. 19, 20, and 18 of Ref. [9] except that an extreme case (e.g., methanol) is treated differently.

When we consider primary monosubstituted alkanes to be graphs, we put $P^{(R)}(x, 1, 1, 1, 1) = P^{(R)}(x)$ in eq. 43. The resulting equation is expanded to give the following generating function:

$$P^{(R)}(x) = 1 + x^2 + x^3 + 2x^4 + 4x^5 + 8x^6 + 17x^7 + 39x^8 + 89x^9 + 211x^{10} + 507x^{11} + 1238x^{12} + 3057x^{13} + 7639x^{14} + 19241x^{15} + \dots + 2156010x^{20} + \dots, \quad (71)$$

where the coefficient of each term x^k indicates the number of graphs of carbon content k . The results are identical with those collected in Table 5 of Ref. [9].

5.4.2 Secondary Monosubstituted Alkanes Without Introducing Branching Indicators

At a given carbon content k , let the symbol $S_k^{(A)}$ be the summation of $S_{knqn_r n_s n_p}^{(A)}$; the symbol $S_k^{(C)}$ be the summation of $S_{knqn_r n_s n_p}^{(C)}$; and the symbol $S_k^{(B)}$ be the summation of $S_{knqn_r n_s n_p}^{(B)}$, where

$k = n_q + n_t + n_s + n_p$. It follows that eqs. 21–23 give the following equations:

$$S_k^{(A)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{kn_q n_t n_s n_p}^{(A)} \right) \right) \right) \right) \quad (72)$$

$$S_k^{(C)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{kn_q n_t n_s n_p}^{(C)} \right) \right) \right) \right) \quad (73)$$

$$S_k^{(B)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} S_{kn_q n_t n_s n_p}^{(B)} \right) \right) \right) \right), \quad (74)$$

where we do not take the effect of branching into consideration ($q = t = s = p = 1$). Obviously, the value $S_k^{(A)}$ can be obtained by adding relevant coefficients appearing in the k -row of Table 5. On the same line, the values $S_k^{(C)}$ and $S_k^{(B)}$ can be obtained by starting from the data collected in Tables 6 and 7.

These summed numbers are more systematically obtained as the coefficients of the following generating functions:

$$S^{(A)}(x) = \sum_{k=0}^{\infty} S_k^{(A)} x^k = S^{(A)}(x, 1, 1, 1, 1) \quad (75)$$

$$S^{(C)}(x) = \sum_{k=0}^{\infty} S_k^{(C)} x^k = S^{(C)}(x, 1, 1, 1, 1) \quad (76)$$

$$S^{(B)}(x) = \sum_{k=0}^{\infty} S_k^{(B)} x^k = S^{(B)}(x, 1, 1, 1, 1), \quad (77)$$

which can be obtained by putting $q = t = s = p = 1$ in eqs. 21–23. The following equation can easily be derived:

$$S_k^{(B)} = S_k^{(A)} + S_k^{(C)}. \quad (78)$$

The generating functions, $S^{(A)}(x, q, t, s, p)$, $S^{(C)}(x, q, t, s, p)$, and $S^{(B)}(x, q, t, s, p)$, have been calculated by the program “GraphAlkylPST1S.mpl” and they have been stored respectively as the series designated by `Sa1`, `CSx` and `BSx`. Hence, the derived functional equations $S^{(A)}(x)$, $S^{(C)}(x)$, and $S^{(B)}(x)$ (eqs. 75–77) can be evaluated by adding the following code for calculating them:

```
"Secondary achiral";
NSa:= sort(subs({p=1, s=1, t=1, q=1}, expand(Sa1, x^k)));
"Secondary chiral";
NSc:= sort(subs({p=1, s=1, t=1, q=1}, expand(CSx, x^k)));
"Secondary chiral+achiral";
NSb:= sort(subs({p=1, s=1, t=1, q=1}, expand(BSx, x^k)));
```

Thereby, we obtain the following generating functions:

$$S^{(A)}(x) = x^3 + x^5 + 2x^7 + 5x^9 + 11x^{11} + 28x^{13} + 74x^{15} + \dots \quad (79)$$

$$S^{(C)}(x) = x^4 + 2x^5 + 7x^6 + 17x^7 + 49x^8 + 134x^9 + 384x^{10} + 1093x^{11} + 3180x^{12} + 9278x^{13} + 27390x^{14} + 81299x^{15} + \dots + 20403645x^{20} + \dots \quad (80)$$

$$S^{(B)}(x) = x^3 + x^4 + 3x^5 + 7x^6 + 19x^7 + 49x^8 + 139x^9 + 384x^{10} + 1104x^{11} + 3180x^{12} + 9306x^{13} + 27390x^{14} + 81373x^{15} + \dots + 20403645x^{20} + \dots \quad (81)$$

These values are identical with those reported in previous papers (Table 2 of Ref. [9] for up to carbon content 100). Hence, the previous results can be regarded as special cases of the present enumeration, where the effect of internal branching is disregarded.

The conclusion described in the preceding paragraph can be more generally obtained by putting $q = t = s = p = 1$, $a(x) = a(x, 1, 1, 1, 1)$, $b(x) = b(x, 1, 1, 1, 1)$, and $c(x^2) = c(x^2, 1, 1, 1, 1)$ in eqs. 7–9. They are introduced into eqs. 24 and 25 and the resulting $S^{(a)}(x, 1, 1, 1, 1)$ and $S^{(b)}(x, 1, 1, 1, 1)$ are further introduced into eqs. 26–27, where we put $q = t = s = p = 1$. Thereby we obtain the following functional equations without BMs:

$$S^{(A)}(x) = x\{c(x^2) - 1\} \quad (82)$$

$$S^{(C)}(x) = \frac{x}{2}\{(b(x) - 1)^2 - (c(x^2) - 1)\} \quad (83)$$

$$S^{(B)}(x) = \frac{x}{2}\{(b(x) - 1)^2 + (c(x^2) - 1)\}. \quad (84)$$

These equations (eqs. 82–84) are identical with eqs. 29, 30, and 28 of Ref. [9].

As for secondary monosubstituted alkanes as graphs, we put $S^{(R)}(x, 1, 1, 1, 1) = S^{(R)}(x)$ in eq. 46, which is expanded to give the following generating function:

$$S^{(R)}(x) = x^3 + x^4 + 3x^5 + 6x^6 + 15x^7 + 33x^8 + 82x^9 + 194x^{10} + 482x^{11} + 1188x^{12} + 2988x^{13} + 7528x^{14} + 19181x^{15} + \dots + 2216862x^{20} + \dots, \quad (85)$$

where the coefficient of each term x^k indicates the number of graphs of carbon content k . The results are identical with those collected in Table 5 of Ref. [9].

5.4.3 Tertiary Monosubstituted Alkanes Without Introducing Branching Indicators

Let the symbol $T_k^{(A)}$ be the summation of $T_{kn_qn_tn_s n_p}^{(A)}$; the symbol $T_k^{(C)}$ be the summation of $T_{kn_qn_tn_s n_p}^{(C)}$; and the symbol $T_k^{(B)}$ be the summation of $T_{kn_qn_tn_s n_p}^{(B)}$; where the carbon content k is given to satisfy $k = n_q + n_t + n_s + n_p$. It follows that eqs. 29–31 give the following equations:

$$T_k^{(A)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{kn_qn_tn_s n_p}^{(A)} \right) \right) \right) \right) \quad (86)$$

$$T_k^{(C)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{kn_qn_tn_s n_p}^{(C)} \right) \right) \right) \right) \quad (87)$$

$$T_k^{(B)} = \left(\sum_{n_q=0}^{\infty} \left(\sum_{n_t=0}^{\infty} \left(\sum_{n_s=0}^{\infty} \left(\sum_{n_p=0}^{\infty} T_{kn_qn_tn_s n_p}^{(B)} \right) \right) \right) \right), \quad (88)$$

where we disregard the effect of branching into consideration by putting $q = t = s = p = 1$. Obviously, the values $T_k^{(A)}$, $T_k^{(C)}$, and $T_k^{(B)}$ can be obtained by starting from the data collected in Tables 5, 6, and 7.

These summed numbers are more systematically obtained as the coefficients of the following generating functions:

$$T(x)^{(A)} = \sum_{k=0}^{\infty} T_k^{(A)} x^k = T^{(A)}(x, 1, 1, 1, 1) \quad (89)$$

$$T(x)^{(C)} = \sum_{k=0}^{\infty} T_k^{(C)} x^k = T^{(C)}(x, 1, 1, 1, 1) \quad (90)$$

$$T(x)^{(B)} = \sum_{k=0}^{\infty} T_k^{(B)} x^k = T^{(B)}(x, 1, 1, 1, 1). \quad (91)$$

which can be obtained by putting $q = t = s = p = 1$ in eqs. 29–31. The following equation can easily be derived.

$$T_k^{(B)} = T_k^{(A)} + T_k^{(C)}. \quad (92)$$

The generating functions, $T^{(A)}(x, q, t, s, p)$, $T^{(C)}(x, q, t, s, p)$, and $T^{(B)}(x, q, t, s, p)$ (eqs. 89–91), have been calculated and stored respectively as the series designated by `Tal`, `CTx` and `BTx`. Hence, the derived functional equations $T^{(A)}(x)$, $T^{(C)}(x)$, and $T^{(B)}(x)$ can be evaluated by adding the following code for calculating them:

```
"Tertiary achiral";
NTa:= sort(subs({p=1, s=1, t=1, q=1}, expand(Tal, x^k)));
"Tertiary chiral";
NTc:= sort(subs({p=1, s=1, t=1, q=1}, expand(CTx, x^k)));
"Tertiary chiral+achiral";
NTb:= sort(subs({p=1, s=1, t=1, q=1}, expand(BTx, x^k)));
```

Thereby, we obtain the following generating functions:

$$T^{(A)}(x) = x^4 + x^5 + 3x^6 + 4x^7 + 9x^8 + 13x^9 + 28x^{10} + 42x^{11} + 86x^{12} + 134x^{13} + 266x^{14} + 424x^{15} + \dots + 8151x^{20} + \dots \quad (93)$$

$$T^{(C)}(x) = 3x^7 + 9x^8 + 33x^9 + 103x^{10} + 322x^{11} + 975x^{12} + 2973x^{13} + 8979x^{14} + 27248x^{15} + \dots + 7236274x^{20} + \dots \quad (94)$$

$$T^{(B)}(x) = x^4 + x^5 + 3x^6 + 7x^7 + 18x^8 + 46x^9 + 131x^{10} + 364x^{11} + 1061x^{12} + 3107x^{13} + 9245x^{14} + 27672x^{15} + \dots + 7244425x^{20} + \dots \quad (95)$$

The coefficients of the respective terms x^k appearing in the right-hand sides of eqs. 93–95 are identical with those reported in previous papers (Table 3 of Ref. [9] for up to carbon content 100). Hence, the present enumeration emphasizing the effect of internal branching involves the previous enumeration as a special case.

This conclusion can be more generally obtained by putting $q = t = s = p = 1$, $a(x) = a(x, 1, 1, 1, 1)$, $b(x) = b(x, 1, 1, 1, 1)$, and $c(x^2) = c(x^2, 1, 1, 1, 1)$ in eqs. 7–9. They are introduced into eqs. 32 and 33 and the resulting $T^{(a)}(x, 1, 1, 1, 1)$ and $T^{(b)}(x, 1, 1, 1, 1)$ are further introduced into eqs. 34–35, where we put $q = t = s = p = 1$. Thereby we obtain the following functional equations without BMs:

$$T^{(A)}(x) = x(a(x) - 1)(c(x^2) - 1) \quad (96)$$

$$T^{(C)}(x) = \frac{x}{6} \{ (b(x) - 1)^3 + 2(b(x^3) - 1) - 3(a(x) - 1)(c(x^2) - 1) \} \quad (97)$$

$$T^{(B)}(x) = \frac{x}{6} \{ (b(x) - 1)^3 + 2(b(x^3) - 1) + 3(a(x) - 1)(c(x^2) - 1) \}. \quad (98)$$

These equations (eqs. 96–98) are identical with eqs. 39, 40 ($b(x)$ in the second term should be replaced by $b(x^3)$), and 38 ($b(x)$ in the second term should be replaced by $b(x^3)$) of Ref. [9].

As graphs for tertiary monosubstituted alkanes, we put $T^{(R)}(x, 1, 1, 1, 1) = T^{(R)}(x)$ in eq. 49, which is expanded to give the following generating function:

$$T^{(R)}(x) = x^4 + x^5 + 3x^6 + 7x^7 + 17x^8 + 40x^9 + 102x^{10} + 249x^{11} + 631x^{12} + 1594x^{13} + 4074x^{14} + 10443x^{15} + \dots + 1249237x^{20} + \dots, \quad (99)$$

where the coefficient of each term x^k indicates the number of graphs of carbon content k . The results are identical with those collected in Table 5 of Ref. [9].

5.5 “Per Divergence” vs. “Per Constitution”

So long as we do not employ branching indicators for evaluating “divergence” due to internal branching, we have to rely on carbon content (“constitution”) as an only clue for categorizing 3D structures and graphs. For example, the coefficient 19 of the term $19x^7$ appearing in $S^{(B)}(x)$ (eq. 81) indicates the presence of 19 secondary monosubstituted alkanes as 3D structures. On the other hand, the coefficient 15 of the term $15x^7$ appearing in $S^{(R)}(x)$ (eq. 85) indicates the presence of 15 secondary monosubstituted alkanes as graphs. The difference ($4 = 19 - 15$) between them demonstrates the contribution of stereoisomers of carbon content 7.

In contrast, the present method due to branching indicators for evaluating “divergence” provides us with a versatile clue for categorizing 3D structures and graphs. The generating function $S^{(B)}(x, q, t, s, p)$ indicates that the 19 secondary monosubstituted alkanes as 3D structures are categorized by means of the polynomial of BMs, $(3qs^2p^4 + 3t^2sp^4 + 10ts^3p^3 + 3s^5p^2)x^7$, as listed in the ($k = 7$)-row of Table 7. The generating function $S^{(R)}(x, q, t, s, p)$ indicates that 15 of the corresponding graphs are categorized by a polynomial appearing at the ($k = 7$)-row of Table 12, i.e., $(3qs^2p^4 + 2t^2sp^4 + 7ts^3p^3 + 3s^5p^2)x^7$. The latter polynomial subtracted from the former leaves a difference $(t^2sp^4 + 3ts^3p^3)x^7$, which is an itemized characterization of the above-described difference 4 ($= 19 - 15$). The BM $t^2sp^4x^7$ corresponds to a set of diastereomers of 3,4-dimethylpentan-2-ol, which coalesce to give a single graph. The BM $3ts^3p^3x^7$ corresponds to the three sets of diastereomers depicted in Fig. 4 (**51/52**, **53/54**, and **55/56**), which coalesce to give three graphs.

In most textbooks on organic chemistry [20, 21], aliphatic alcohols have been categorized into primary, secondary, tertiary alcohols, where there are no systematic treatments of such “divergence” as discussed in the present article. It should be here emphasized that the concept of “divergence” serves as a common clue for characterizing 3D structures and graphs, where the “divergence” is embodied on the basis of BMs, which are composed of branching indicators (q, t, s , and p). Because the conventional concept “constitution” corresponds to carbon content k in the present enumeration and because we put $k = q + t + s + p$ for each carbon content k , the present clue “divergence” provides us with more detailed categorization than the conventional clue “constitution”.

6 Conclusion

Primary, secondary, and tertiary monosubstituted alkanes are counted as three-dimensional (3D) structures by means of Fujita’s prolignand method [4, 8, 9], where the effect of inner branching is taken into consideration by means of branching indicators. Thus, each monosubstituted alkane of carbon content k is characterized by the product of branching indicators (named a *branching*

monomial), $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$, which is composed of such branching indicators as q for n_q quaternary carbons, t for n_t tertiary carbons, s for n_s secondary carbons, and p for n_p primary carbons ($k = n_q + n_t + n_s + n_p$). According to cycle indices with chirality fittingness (CI-CFs), three kinds of sphericity indices (SIs), i.e., a_d for homospheric cycles, c_d for enantiospheric cycles, and b_d for hemispheric cycles, are replaced by $a(x^d, q^d, t^d, s^d, p^d)$, $c(x^d, q^d, t^d, s^d, p^d)$, and $b(x^d, q^d, t^d, s^d, p^d)$ so as to produce functional equations for recursive calculation. Respective functional equations for counting primary, secondary, and tertiary monosubstituted alkanes are derived and used to produce generating functions in which the number of 3D structures is calculated as the coefficient of the term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$. The calculation procedures are programmed by means of the Maple programming language and executed to calculate values up to carbon content 15. The respective results are collected in tabular forms, where the numbers of monosubstituted alkanes as 3D structures are further itemized into achiral and chiral ones. By omitting the sphericity concept, the functional equations for 3D structures are transformed into the counterparts for graphs, which are applied to the enumeration of primary, secondary, and tertiary monosubstituted alkanes as graphs (chemically, constitutional isomers).

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