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Effect of Internal Branching on Numbers of Monosubstituted Alkanes as Three-Dimensional Structures and as Graphs

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Itemized numbers of achiral and/or chiral monosubstituted alkanes (MSAs) as three-dimensional structures have been obtained by means of a newly developed method based on Fujita's proligand method (S. Fujita, *Theor. Chem. Acc.* **2005**, *113*, 73; **2005**, *113*, 80; **2006**, *115*, 37), where the itemization with respect to internal branching has been embodied by employing branching indicators (BIs), i.e., q for quaternary carbons, t for tertiary carbons, s for secondary carbons, and p for primary carbons. Each of the numbers appears as the coefficient of a branching monomial $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$, which is contained in a generating function to characterize MSAs having n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_q quaternary carbons ($k = n_q + n_t + n_s + n_p$). By following Fujita's proligand method, functional equations for recursive calculations have been obtained to treat respective cases, where previous approaches without considering BIs have been extended so as to incorporate BIs with no violation of consistency. The resulting functional equations have been used to obtain generating functions which give the numbers of achiral MSAs, chiral MSAs, total (achiral and chiral) MSAs. They have been compared with the corresponding numbers of MSAs as graphs. Thereby, difference between stereoisomers (3D structures) and constitutional isomers (graphs) has been discussed on a quantitative basis.

Difference between constitutional isomers (graphs) and stereoisomers (three-dimensional structures) is a key concept to be introduced in primary courses of organic stereochemistry, as found in most textbooks of organic chemistry[1–6] and of stereochemistry.[7–9] The difference is qualitatively clear and has been applied unquestioningly to solve stereochemical problems so that its central issues have been overlooked unconsciously. One of such issues is to grasp quantitative features of the difference, which have not been so fully investigated even in simple cases such as alkanes and monosubstituted alkanes.

For example, a typical question (Question 1) is how the number (N_{CI}) of inequivalent structures as constitutional isomers is related to the number (N_{SI}) of inequivalent three-dimensional (3D) structures as stereoisomers (achiral 3D structures and pairs of enantiomers) if a carbon content is given. Question 1 has not been pursued until recently because of no suitable methodology, although several chemical or mathematical approaches to enumerate constitutional isomers of alkanes (trees as graphs) or of monosubstituted alkanes (rooted or planted trees as graphs, mathematically speaking) were explored (e.g., Cayley,[10,11] Pólya,[12,13] and Otter[14]) and although an approach to enumerate stereoisomers of alkanes or monosubstituted alkanes appeared (e.g., Robinson et al.[15]). Quite recently, we have developed Fujita's proligand method[16–18] as a systematic approach for enumerating stereoisomers and applied it to obtain N_{SI}, e.g., the number of monosubstituted alkanes[19–21] and the number of alkanes.[22–24] The merit of Fujita's proligand method has been briefly emphasized in comparison with Pólya's theorem in an article of his own.[25] As for the difference between N_{CI} and N_{SI}, however, our discussion was yet based on case-by-case comparison between the corresponding structural formulas (graphs vs. 3D structures).

Another question (Question 2) is how the number N_{CI} is related to the number N_{SI}, if numbers of asymmetric and pseudoasymmetric carbons are given in addition to a carbon content. Although Pólya reported the effect of "asymmetric" carbons on enumeration,[12,13] his enumerated results were concerned with constitutional isomers (graphs, mathematically speaking), where pseudoasymmetry was not treated properly. Recently, we have enumerated achiral and chiral monosubstituted alkanes of carbon content k which have ℓ asymmetric carbons and m pseudoasymmetric carbons,[26,27] where Fujita's proligand method was applied to solve Question 2 after a clear distinction between asymmetric centers and pseudoasymmetric ones was realized by employing the classification scheme developed for *RS*-stereoisomers.[28] However, our discussion on the difference between N_{CI} and N_{SI} was yet based on case-by-case comparison between the corresponding structural formulas (graphs vs. 3D structural formulas), because pseudoasymmetry for evaluating N_{SI} vanishes in the evaluation of N_{CI}.

A more sophisticated question (Question 3) is how the number N_{CI} is related to the number N_{SI}, if a carbon content and degrees of branching are given. Henze and Blair took the branching of aliphatic alcohols into consideration,[29] where they obtained numbers (as graphs) of primary, secondary, and tertiary aliphatic alcohols of given carbon contents. Recently, we have calculated the numbers (as stereoisomers) of primary, secondary, and tertiary aliphatic alcohols of given carbon contents.[21] However, these enumeration results did not take the effect of internal branching into explicit consideration.

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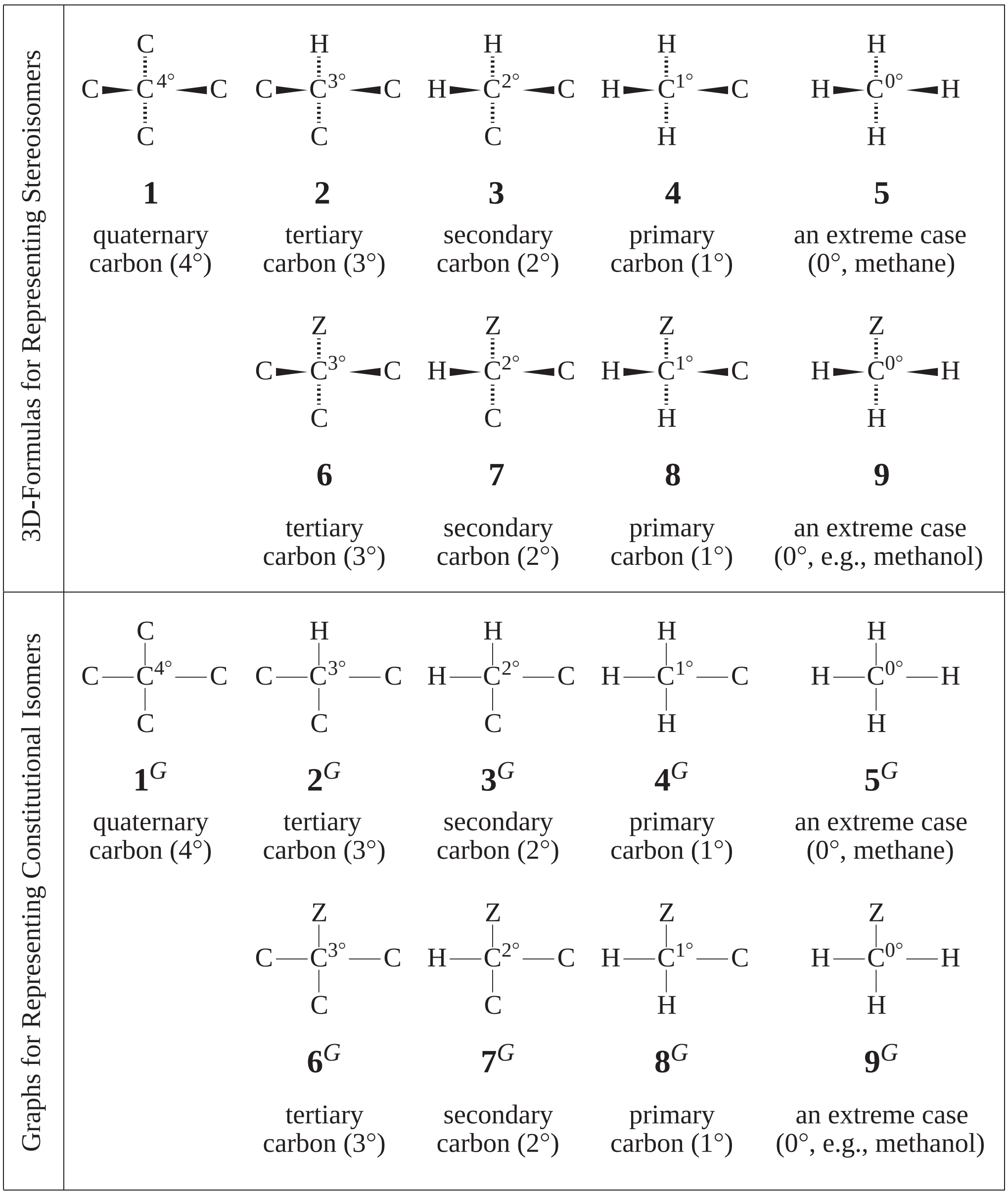


Figure 1. Degrees of branching for internal carbons (the first row) and and for external carbons (the second row), which characterize the constitutions of monosubstituted alkanes (e.g., aliphatic alcohols). Each central atom designated by 4°, 3°, 2°, or 1° is quaternary, tertiary, secondary, or primary.

In general, degrees of internal branching judged for a 3D structure, i.e., the numbers of primary, secondary, tertiary, and quaternary carbons, do not change even if the 3D structure (in the level of stereoisomers) is conceptually reduced into a graph (in the level of constitutional isomers). Hence, the solution of Question 3 will serve as a versatile clue to give a deeper insight of the above-mentioned difference between constitutional isomers and stereoisomers. The present paper will be devoted to develop theoretical methodology for solving Question 3. According to this methodology, we are able to obtain a categorization of alkanes and monosubstituted alkanes in a more detailed fashion than the conventional categorization of them, which has relied on a rather rough criterion, i.e., straight-chain and branched-chain compounds. Moreover, the present categorization is based on quantitative treatments so that its merit will be discussed in comparison with the conventional categorization whose discussion has a qualitative nature only and has been restricted to the domain of constitutional isomers.

Results

Branching Indicators. In order to discuss difference between stereoisomers (3D structures) and constitutional isomers (graphs), we use two representations, i.e., 3D structural formulas (wedge-dashed-line formulas) for representing stereoisomers and topological formulas for representing constitutional isomers. Degrees of branching in 3D structural formulas of alkanes and of monosubstituted alkanes (e.g., aliphatic alcohols when $Z = OH$) are depicted in the upper box of Figure 1, where each central atom of quaternary, tertiary, secondary, or primary branching is designated by 4°, 3°, 2°, or 1°. An extreme case (**5** for methane, **9** for methanol, etc.) indicates no branching designated by the symbol 0°. The corresponding topological expressions for graphs are also depicted in the lower box of Figure 1.

As found easily, the conceptual conversion of each 3D-structural formula into the corresponding graph (e.g., $\mathbf{1} \rightarrow \mathbf{1}^G$, $\mathbf{2} \rightarrow \mathbf{2}^G$, etc.) does not change the degree of branching in the central atom at issue. Hence, alkanes and monosubstituted alkanes as stereoisomers (3D structures) can be discussed in terms of such degrees of branching, by which they are correlated to the corresponding constitutional isomers (graphs). In other words, such degrees of branching serve as a common criterion to categorize stereoisomers as well as constitutional isomers, where resulting numbers are subdivided in more detail than when relying on carbon content only.

In previous papers,[19–21] we have applied Fujita's proligand method to the enumeration of monosubstituted alkanes, where such monosubstituted alkanes are considered to be alkyl ligands, which participate in recursive processes of substitution. In order to take account of internal branching in such recursive processes, we should cope with the fact that the degree of branching in a monosubstituted alkane (as an alkyl ligand) is changed after a recursive process, as exemplified in Figure 2. To treat such apparent changes of branching degrees, we shall tentatively consider preformed alkyl moieties (PAMs).

Suppose that a monosubstituted alkane **12** is generated by starting from other monosubstituted alkanes **10** and **11**. The primary carbon (1°) of **10** is changed into a secondary carbon (2°) appearing in the left part of **12**, while the secondary carbon (2°) of **11** is changed into a tertiary carbon (3°) appearing in the right part of **12**. Hence, it is convenient to consider a preformed alkyl moiety (PAM) **10′** (or **11′**), in which the carbon at issue is considered to be secondary (or tertiary) under the precondition that a further substitution shall occur on a carbon (as found in **12**). Moreover, the secondary carbon (2°) attached by Z in **12** is changed into a tertiary carbon (3°) in a preformed alkyl moiety (**12′**), which participates in a further substitution. It should be noted that, if we consider the change between the PAMs, i.e., $\mathbf{10'} + \mathbf{11'} \rightarrow \mathbf{12'}$, the degrees of branching do not change during the substitution. The conservation of branching degrees for PAMs assures recursive enumeration of PAMs (**12′**, etc.), which serves as basic data for enumerating monosubstituted alkanes (**12**, etc.).

Let us now introduce branching indicators (BIs), which are dummy variables for indicating degrees of branching: 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 the carbons is contained in a monosubstituted alkane (or a PAM) of carbon content k $(=n_q + n_t + n_s + n_p)$. Thereby, the monosubstituted alkane (or a PAM) 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 **12** is characterized by a BM $ts^2p^3x^6$, while the corresponding PAM **12′** is characterized by a BM $t^2sp^3x^6$. Note 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 px. Because we put $k = n_q + n_t + n_s + n_p$, we can omit x^k for the sake of simplicity, i.e., $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$.

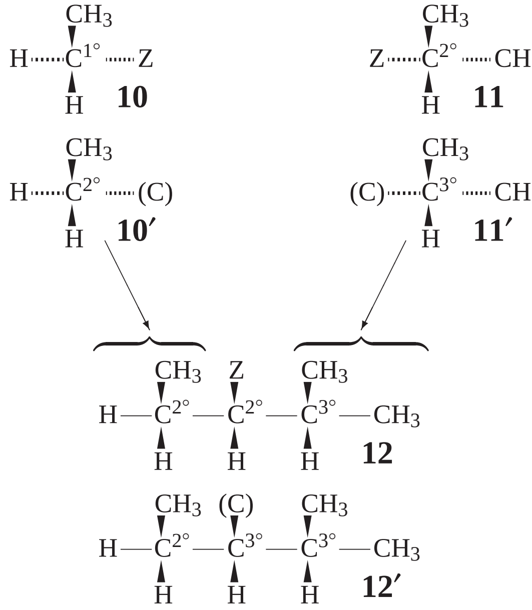


Figure 2. Degrees of branching during recursive processes of substitution. Monosubstituted alkanes **10**, **11**, and **12** vs. preformed alkyl moieties **10′**, **11′**, and **12′**.

Enumeration as Stereoisomers. Recursive Functional Equations for Preformed Alkyl Moieties (PAMs): In order to count preformed alkyl moieties (PAMs) of carbon content k which have n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons, let the symbol $\alpha_{kn_qn_tn_sn_p}$ be the number of inequivalent achiral PAMs; the symbol $\beta_{kn_qn_tn_sn_p}$ be the number of inequivalent steric isomers of PAMs; the symbol $\gamma_{kn_qn_tn_sn_p}$ be the number of inequivalent diploids of PAMs. Thereby, we are able to write down generating functions of these numbers by using the above-described BIs, (i.e., q, t, s, and p) as follows:

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

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

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

Note that $a(x, q, t, s, p)$ corresponds to homospheric cases (sphericity index: a_k), $b(x, q, t, s, p)$ corresponds to hemispheric cases (sphericity index: b_k), and $c(x, q, t, s, p)$ corresponds to enantiospheric cases (sphericity index: c_{2k}) in terms of the terminology developed by Fujita's USCI (unit-subduced-cycle-index) approach.[30]

For the purpose of obtaining these numbers ($\alpha_{kn_qn_tn_sn_p}$, $\beta_{kn_qn_tn_sn_p}$, and $\gamma_{kn_qn_tn_sn_p}$) as the coefficient of the term

$p^{n_p}s^{n_s}t^{n_t}q^{n_q}x^k$ (or $p^{2n_p}s^{2n_s}t^{2n_t}q^{2n_q}x^{2k}$), we shall develop functional equations to evaluate the effect of internal branching due to primary, secondary, tertiary, and quaternary carbons, which are contained in each PAM. We have already reported the enumeration of primary, secondary, and tertiary monosubstituted alkanes without explicit consideration of internal branching.[21] What we have to do is to evaluate the contribution of each case to internal branching when incorporated in PAMs.

First, we have obtained products of sphericity indices for primary monosubstituted alkanes (RH_2C–Z: R = alkyl) as follows: achiral a_1 (eq 13 of Ref. 21), steric b_1 (eq 12 of Ref. 21), and diploid c_2. The product of sphericity indices c_2 for treating diploids can be obtained from b_1 for treating steric cases.[19] If we have obtained $a(x,q,t,s,p)$ for treating achiral objects of carbon content k, the substitution of these achiral objects on a central carbon atom produces achiral objects of carbon content $k+1$, which are represented by a function $xs\{a(x,q,t,s,p)-1\}$, where xs shows that the central carbon results in the appearance of one secondary carbon when incorporated in PAMs (Z in **8** → (C) in **3** as a PAM. cf. Figure 1 coupled with Figure 2). Note that 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). On the same line, the above-described products of sphericities used to evaluate the effect of $b(x,q,t,s,p)$ for treating the substitution of steric objects and the effect of $c(x^2,q^2,t^2,s^2,p^2)$ for treating the substitution of diploids are as follows:

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

$$\text{steric}\quad xs\big\{b(x,q,t,s,p)-1\big\} \tag{5}$$

$$\text{diploid}\quad x^2s^2\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\} \tag{6}$$

Second, by starting from the products of sphericity indices for secondary monosubstituted alkanes (RR′HC–Z: R, R′ = alkyl), i.e., c_2 for achiral cases (eq 23 of Ref. 21), b_1^2 for steric cases (eq 22 of Ref. 21), and c_2^2 for diploid, we are able to obtain the following contributions of the respective cases:

$$\text{achiral}\quad xt\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\} \tag{7}$$

$$\text{steric}\quad xt\big\{b(x,q,t,s,p)-1\big\}^2 \tag{8}$$

$$\text{diploid}\quad x^2t^2\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\}^2 \tag{9}$$

where the $BI(t)$ for a tertiary carbon is used because the substituted position of the resulting PAM is tertiary (Z in **7** → (C) in **2** as a PAM. cf. Figure 1 coupled with Figure 2).

Third, the products of sphericity indices for tertiary monosubstituted alkanes (RR′R″C–Z: R, R′, R″ = alkyl), i.e., a_1c_2 for achiral cases (eq 33 of Ref. 21), $(b_1^3+2b_3)/3$ for steric cases (eq 32 of Ref. 21), and $(c_2^3+2c_6)/3$ for diploids, provide the following contributions of the respective cases:

$$\text{achiral}\quad xq\big\{a(x,q,t,s,p)-1\big\}\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\} \tag{10}$$

$$\text{steric}\quad \frac{xq}{3}\big\{[b(x,q,t,s,p)-1]^3+2[b(x^3,q^3,t^3,s^3,p^3)-1]\big\} \tag{11}$$

$$\text{diploid}\quad \frac{x^2q^2}{3}\big\{[c(x^2,q^2,t^2,s^2,p^2)-1]^3+2[c(x^6,q^6,t^6,s^6,p^6)-1]\big\} \tag{12}$$

where the $BI(q)$ for a quaternary carbon is used because the substituted position of the resulting PAM becomes quaternary (Z in **6** → (C) in **1** as a PAM. cf. Figure 1 coupled with Figure 2).

By summing up eqs 4, 7, and 10 for achiral cases, we obtain the following functional equation:

$$\begin{aligned} &a(x,q,t,s,p)\\ &\quad=1+xp+xs\big\{a(x,q,t,s,p)-1\big\}\\ &\qquad+xt\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\}\\ &\qquad+xq\big\{a(x,q,t,s,p)-1\big\}\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\}, \end{aligned} \tag{13}$$

where the first term (1) is added to treat a trivial case (a hydrogen atom) and the second term (xp) is added to evaluate the contribution of a methyl moiety. This functional equation can be used to evaluate the generating function represented by eq 1.

On a similar line, by summing up eqs 5, 8, and 11 for steric cases, we obtain the following functional equation:

$$\begin{aligned} &b(x,q,t,s,p)\\ &\quad=1+xp+xs\big\{b(x,q,t,s,p)-1\big\}\\ &\qquad+xt\big\{b(x,q,t,s,p)-1\big\}^2\\ &\qquad+\frac{xq}{3}\big\{[b(x,q,t,s,p)-1]^3\\ &\qquad+2[b(x^3,q^3,t^3,s^3,p^3)-1]\big\} \end{aligned} \tag{14}$$

where the first term (1) is added to treat a trivial case (a hydrogen atom) and the second term (xp) is added to evaluate the contribution of a methyl moiety. This functional equation can be used to evaluate the generating function represented by eq 2.

As for diploidal cases, we obtain a functional equation by summing up eqs 6, 9, and 12 as follows:

$$\begin{aligned} &c(x^2,q^2,t^2,s^2,p^2)\\ &\quad=1+x^2p^2+x^2s^2\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\}\\ &\qquad+x^2t^2\big\{c(x^2,q^2,t^2,s^2,p^2)-1\big\}^2\\ &\qquad+\frac{x^2q^2}{3}\big\{[c(x^2,q^2,t^2,s^2,p^2)-1]^3\\ &\qquad+2[c(x^6,q^6,t^6,s^6,p^6)-1]\big\} \end{aligned} \tag{15}$$

where the first term (1) is added to treat a trivial case (a hydrogen atom) and the second term (x^2p^2) is added to evaluate the contribution of a methyl moiety. The functional equation (eq 15) can be used to evaluate the generating function represented by eq 3.

The functional equations (eqs 13, 14, and 15) have a recursive nature so that the data of carbon content $k+1$ can be evaluated by using the data of carbon content k. Thereby, the generating functions for enumerating PAMs (eqs 1, 2, and 3) are obtained recursively.

Total Numbers of Monosubstituted Alkanes: The next task is to apply the data of eqs 1, 2, and 3 to the counting of monosubstituted alkanes by considering internal branching.

To evaluate the numbers of monosubstituted alkanes, the branching indicators p, s, t, and q used in eq 13 are converted as follows: $p \to 1$, $s \to p$, $t \to s$, and $q \to t$ in accord with the correspondence shown in Figures 1 and 2. Then, we obtain the following functional equation:

$$\begin{aligned} & B^{(a)}(x,q,t,s,p) \\ & \quad = 1 + x + xp\{a(x,q,t,s,p) - 1\} \\ & \qquad + xs\{c(x^2,q^2,t^2,s^2,p^2) - 1\} \\ & \qquad + xt\{a(x,q,t,s,p) - 1\}\{c(x^2,q^2,t^2,s^2,p^2) - 1\} \end{aligned} \tag{16}$$

Because each function appearing in the right-hand side of eq 16 has been evaluated recursively as above (cf. eq 13, 14, or 15), the function $B^{(a)}(x,q,t,s,p)$ can be obtained as a generating function (a polynomial concerning BMs).

On a similar line, by starting from eq 14, we obtain the following functional equation:

$$\begin{aligned} & B^{(b)}(x,q,t,s,p) \\ & \quad = 1 + x + xp\{b(x,q,t,s,p) - 1\} \\ & \qquad + xs\{b(x,q,t,s,p) - 1\}^2 \\ & \qquad + \frac{xt}{3}\{[b(x,q,t,s,p) - 1]^3 \\ & \qquad + 2[b(x^3,q^3,t^3,s^3,p^3) - 1]\} \end{aligned} \tag{17}$$

which can be evaluated by using eqs 13, 14, and 15.

As for diploidal cases, we obtain a functional equation by starting from eq 15 as follows:

$$\begin{aligned} & B^{(c)}(x^2,q^2,t^2,s^2,p^2) \\ & \quad = 1 + x^2 + x^2p^2\{c(x^2,q^2,t^2,s^2,p^2) - 1\} \\ & \qquad + x^2s^2\{c(x^2,q^2,t^2,s^2,p^2) - 1\}^2 \\ & \qquad + \frac{x^2t^2}{3}\{[c(x^2,q^2,t^2,s^2,p^2) - 1]^3 \\ & \qquad + 2[c(x^6,q^6,t^6,s^6,p^6) - 1]\} \end{aligned} \tag{18}$$

which can be also evaluated by using eqs 13, 14, and 15.

Let the symbol $B^{(A)}_{kn_qn_tn_sn_p}$ be the number of inequivalent monosubstituted alkanes, 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 $B^{(C)}_{kn_qn_tn_sn_p}$ be the number of inequivalent monosubstituted alkanes under a similar categorization, where each pair of enantiomers is counted once; and the symbol $B^{(B)}_{kn_qn_tn_sn_p}$ be the total number of inequivalent monosubstituted alkanes 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:

$$B^{(A)}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(A)}_{kn_qn_tn_sn_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{19}$$

$$B^{(C)}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(C)}_{kn_qn_tn_sn_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{20}$$

$$B^{(B)}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(B)}_{kn_qn_tn_sn_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{21}$$

The generating function $B^{(A)}(x,q,t,s,p)$ (eq 19) is obtained by using a functional equation (eq 22) which is identical with eq 16. On the other hand, $B^{(b)}(x,q,t,s,p)$ (eq 17) is equal to the sum of $B^{(A)}(x,q,t,s,p) + 2B^{(C)}(x,q,t,s,p)$. Thus, we obtain the following equations:

$$B^{(A)}(x,q,t,s,p) = B^{(a)}(x,q,t,s,p) \tag{22}$$

$$B^{(C)}(x,q,t,s,p) = \frac{1}{2}\left\{B^{(b)}(x,q,t,s,p) - B^{a}(x,q,t,s,p)\right\} \tag{23}$$

$$B^{(B)}(x,q,t,s,p) = \frac{1}{2}\left\{B^{(a)}(x,q,t,s,p) + B^{(b)}(x,q,t,s,p)\right\} \tag{24}$$

The generating function $B^{(C)}(x,q,t,s,p)$ (eq 20) can be written in the form of a functional equation (eq 23) by starting eqs 16 and 17, in which each pair of enantiomers is counted once. The generating function $B^{(B)}(x,q,t,s,p)$ (eq 21) can be written in the form of a functional equation (eq 24) by starting eqs 16 and 17. Note that, in these total numbers of monosubstituted alkanes, each achiral monosubstituted alkane is counted once as well as each pair of enantiomers is counted once.

Implementation and Results for Stereoisomers: The functional equations represented by $a(x,q,t,s,p)$ (eq 13), $b(x,q,t,s,p)$ (eq 14), and $c(x^2,q^2,t^2,s^2,p^2)$ (eq 15) exhibit recursive nature so that they are implemented by mean of the Maple programming language as follows. The upper limit of the carbon content (k) is tentatively fixed to be 30, but it can be freely selected as far as the capacity of a computer permits.

```
#AlkylPST8B.mpl
#Calculation of Total (Achiral + Chiral) Alkyls

"Functional Equations for Inner Alkyl Ligands";
#(Part 1) H, methyl, primary, secondary, tertiary, quaternary
#--- inner alkyl (preformed alkyl moieties)
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));

"Functional Equations for Alkyl Ligands Substituted by OH etc.";
#(Part2) H, methyl, primary, secondary, tertiary
#--- alcoholic alkyl
Bax := 1 + x + x*p*(a1-1) + x*s*(c2 -1) + x*t*(a1-1)*(c2-1);
Bcx := 1 + x^2 + x^2*p^2*(c2-1) + x^2*s^2*(c2-1)^2
+ ((x^2*t^2)/3)*((c2-1)^3 + 2*(c6-1));
Bbx := 1 + x + x*p*(b1-1) + x*s*(b1-1)^2
+ (x*t/3)*((b1-1)^3 + 2*(b3-1));

"(Part3) Initial Values";
a1 := 1;
c2 := 1; c4 := 1; c6 := 1;
b1 := 1; b2 := 1; b3 := 1;
asum := 1: csum := 1: bsum := 1:
Ba1 := 1; Bc2 := 1; Bb1 := 1;

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

"(Part 4) Total":
CBbx:= expand(coeff(Bbx,x^k)):
Bb1 := Bb1 + CBbx*x^k:

"(Part 5) Achiral":
CBax:= expand(coeff(Bax,x^k)):
```

```
Ba1 := Ba1 + CBax*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";
#Total Numbers
BBx := (1/2)*(expand(Ba1) + expand(Bb1)):
#Chiral
CCx := (1/2)*(expand(Bb1) - expand(Ba1)):

EBBx := expand(BBx):
ECCx := expand(CCx):

#(Part 10)###################################

"Print Out of Ba1 (Achiral)";
for k from 1 to kmax by 1 do
carbon_content:= k:
Na := collect(expand(coeff(Ba1,x^k)),p):
end do;

"Print Out of ECCx (Chiral)";
for k from 1 to kmax by 1 do
carbon_content:= k:
Nc := collect(expand(coeff(ECCx,x^k)),p):
end do;

"Print Out of EBBx (Total)";
for k from 1 to kmax by 1 do
carbon_content:= k:
Nt := collect(expand(coeff(EBBx,x^k)),p):
end do;
```

This code is stored in a file named "AlkylPST8B.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 `asum`, `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 13, `bx` for eq 14, and `cx` for eq 15, which are calculated by using `a1`, `b1`, `c2`, etc. recursively. The second part (Part 2) declares three functional equations, i.e., `Bax` for $B^{(a)}(x, q, t, s, p)$ (eq 16) and `Bbx` for $B^{(b)}(x, q, t, s, p)$ (eq 17), `Bcx` for $B^{(c)}(x^2, q^2, t^2, s^2, p^2)$ (eq 18), which are calculated by using `a1`, `b1`, `c2`, etc. Note that they are not recursive. 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 enumerating 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 `Bbx` and `Bax` (cf. Part 2) in `Bb1` and `Ba1`.

After escaping from the `do` loop for k, Part 9 ("Final Calculation") declares the calculation of `BBx` for $B^{(B)}(x, q, t, s, p)$ (eq 21) and `CCx` for $B^{(C)}(x, q, t, s, p)$ (eq 20). Part 10 ("Print Out of $\cdots$") of the code shows the print-out of the calculation results.

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

```
> restart;
> read "AlkylPST8B.mpl";
```

The above-mentioned code gives calculation results according to its print-out sections.

Table 1 collects the data `Na` ($\sum B^{(A)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k appearing in eqs 19 and 22. Note that the summation is concerned with n_q, n_t, n_s, and n_p for each carbon content k although a single summation symbol is used. Thus, each row of Table 1 shows the numbers of achiral monosubstituted alkanes of carbon content k, which emerge as the coefficients of the term $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$. For example, the ($k = 4$)-row of Table 1 lists the polynomial $s^2p^2 + 2tp^3$ as the coefficient of x^4, This polynomial shows that there exist one achiral 3D structure of the BM s^2p^2 (i.e., $CH_3CH_2CH_2CH_2Z$ containing two secondary carbons and two primary carbons) and two achiral 3D structures of the BM tp^3 (i.e, $(CH_3)_3CZ$ and $(CH_3)_2CHCH_2Z$ containing one tertiary carbon and three primary carbons).

Table 2 collects the data `Nc` ($\sum B^{(C)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k appearing in eqs 20 and 23. Each row of Table 2 shows the numbers of chiral monosubstituted alkanes of carbon content k, which are itemized by means of BMs ($q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), where each pair of enantiomers is counted just once. For example, the ($k = 4$)-row of Table 2 lists the term s^2p^2 as the coefficient of x^4, which shows the existence of one pair of enantiomers, i.e., one pair of *R*- and *S*-$CH_3CH_2CH(CH_3)Z$.

Table 3 collects the data `Nt` ($\sum B^{(B)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k appearing in eqs 21 and 24. Each row of Table 3 shows the numbers of achiral plus chiral monosubstituted alkanes of carbon content k, which are itemized by means of BMs ($q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), where each pair of enantiomers is counted just once if chiral. As a matter of course, Table 3 is obtained by summing up Tables 1 and 2. For example, the ($k = 4$)-row of Table 3 lists the term $2s^2p^2 + 2tp^3$, which is obtained by adding the term $s^2p^2 + 2tp^3$ of Table 1 to the term s^2p^2 of Table 2.

To verify the results collected in Tables 1–3, structural formulas of monosubstituted alkanes of lower carbon contents ($k = 1$–5) are depicted in Figure 3, where they are categorized by means of branching monomials. Because each pair of enantiomers is counted once according to the present methodology, either one of them is depicted as a representative. It is easy to grasp a resemblance between monosubstituted alkanes of the same branching monomials, if we replace each substituent Z by a hydrogen or in other words, if we note carbon skeletons only.

Enumeration as Constitutional Isomers. Recursive Functional Equations for PAMs as Graphs: Let the symbol $R_{kn_qn_tn_sn_p}$ be the number of inequivalent PAMs (as graphs)

Table 1. Total Numbers of Achiral Monosubstituted Alkanes

	The coefficient of x^k (cf. eqs 19 and 22), i.e., $\sum B^{(A)}_{kn_q n_t n_s n_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$	1 (methanol as an extreme case)
$k = 2$	p^2
$k = 3$	$2\,sp^2$
$k = 4$	$s^2p^2 + 2\,tp^3$
$k = 5$	$2\,s^3p^2 + 2\,tsp^3 + qp^4$
$k = 6$	$(2\,qs + t^2)p^4 + 4\,ts^2p^3 + s^4p^2$
$k = 7$	$2\,qtp^5 + (4\,qs^2 + 2\,t^2s)p^4 + 4\,ts^3p^3 + 2\,s^5p^2$
$k = 8$	$q^2p^6 + (4\,qts + 2\,t^3)p^5 + (6\,qs^3 + 3\,t^2s^2)p^4 + 6\,ts^4p^3 + s^6p^2$
$k = 9$	$(4\,q^2s + 2\,qt^2)p^6 + (2\,t^3s + 10\,qts^2)p^5 + (9\,qs^4 + 6\,t^2s^3)p^4 + 6\,ts^5p^3 + 2\,s^7p^2$
$k = 10$	$4\,q^2tp^7 + (8\,q^2s^2 + 4\,qt^2s + 2\,t^4)p^6 + (16\,qts^3 + 8\,t^3s^2)p^5 + (12\,qs^5 + 6\,t^2s^4)p^4 + 8\,ts^6p^3 +$ s^8p^2
$k = 11$	$2\,q^3p^8 + (4\,qt^3 + 8\,q^2ts)p^7 + (12\,qt^2s^2 + 18\,q^2s^3 + 4\,t^4s)p^6 + (28\,qts^4 + 8\,t^3s^3)p^5 +$ $(16\,qs^6 + 12\,t^2s^5)p^4 + 8\,ts^7p^3 + 2\,s^9p^2$
$k = 12$	$(6\,q^3s + 5\,q^2t^2)p^8 + (24\,q^2ts^2 + 4\,t^5 + 8\,qt^3s)p^7 + (30\,q^2s^4 + 10\,t^4s^2 + 20\,qt^2s^3)p^6 +$ $(40\,qts^5 + 20\,t^3s^4)p^5 + (10\,t^2s^6 + 20\,qs^7)p^4 + 10\,ts^8p^3 + s^{10}p^2$
$k = 13$	$6\,q^3tp^9 + (18\,q^3s^2 + 5\,qt^4 + 14\,q^2t^2s)p^8 + (28\,qt^3s^2 + 44\,q^2ts^3 + 4\,t^5s)p^7 +$ $(20\,t^4s^3 + 54\,q^2s^5 + 40\,qt^2s^4)p^6 + (20\,t^3s^5 + 60\,qts^6)p^5 + (25\,qs^8 + 20\,t^2s^7)p^4 +$ $10\,ts^9p^3 + 2\,s^{11}p^2$
$k = 14$	$3\,q^4p^{10} + (12\,q^2t^3 + 16\,q^3ts)p^9 + (10\,qt^4s + 40\,q^3s^3 + 5\,t^6 + 38\,q^2t^2s^2)p^8 +$ $(48\,qt^3s^3 + 24\,t^5s^2 + 92\,q^2ts^4)p^7 + (30\,t^4s^4 + 80\,q^2s^6 + 60\,qt^2s^5)p^6 +$ $(40\,t^3s^6 + 80\,qts^7)p^5 + (30\,qs^9 + 15\,t^2s^8)p^4 + 12\,ts^{10}p^3 + s^{12}p^2$
$k = 15$	$(12\,q^4s + 10\,q^3t^2)p^{10} + (24\,q^2t^3s + 52\,q^3ts^2 + 10\,qt^5)p^9 +$ $(88\,q^2t^2s^3 + 40\,qt^4s^2 + 86\,q^3s^4 + 10\,t^6s)p^8 + (152\,q^2ts^5 + 108\,qt^3s^4 + 24\,t^5s^3)p^7 +$ $(100\,qt^2s^6 + 60\,t^4s^5 + 128\,q^2s^7)p^6 + (110\,qts^8 + 40\,t^3s^7)p^5 + (36\,qs^{10} + 30\,t^2s^9)p^4 +$ $12\,ts^{11}p^3 + 2\,s^{13}p^2$
	(omitted)
$k = 20$	$8\,q^6p^{14} + (56\,q^5ts + 56\,q^4t^3)p^{13} + (260\,q^4t^2s^2 + 208\,q^5s^3 + 108\,q^3t^4s + 60\,q^2t^6)p^{12} +$ $(408\,q^2t^5s^2 + 664\,q^4ts^4 + 592\,q^3t^3s^3 + 56\,qt^7s + 28\,t^9)p^{11} +$ $(852\,q^2t^4s^4 + 126\,t^8s^2 + 920\,q^4s^6 + 252\,qt^6s^3 + 1156\,q^3t^2s^5)p^{10} +$ $(1704\,q^2t^3s^6 + 1584\,q^3ts^7 + 360\,t^7s^4 + 720\,qt^5s^5)p^9 +$ $(420\,t^6s^6 + 840\,qt^4s^7 + 1494\,q^2t^2s^8 + 1284\,q^3s^9)p^8 +$ $(504\,t^5s^8 + 1356\,q^2ts^{10} + 1008\,qt^3s^9)p^7 + (504\,qt^2s^{11} + 588\,q^2s^{12} + 252\,t^4s^{10})p^6 +$ $(168\,t^3s^{12} + 336\,qts^{13})p^5 + (72\,qs^{15} + 36\,t^2s^{14})p^4 + 18\,ts^{16}p^3 + s^{18}p^2$ (omitted)

of carbon content k which have n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons. Thereby, we are able to write down generating functions of these numbers by using the above-described BIs (i.e., q, t, s, and p) as follows:

$$r(x, q, t, s, p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} R_{kn_q n_t n_s n_p} p^{n_p}\right) s^{n_s}\right) t^{n_t}\right) q^{n_q}\right) x^k \tag{25}$$

In order to evaluate eq 25, on one hand, we can directly extend Pólya's theorem[12,13] to involve BIs (i.e., q, t, s, and p) as a new matter, where we stick to the domain of graphs without considering 3D structures. On the other hand, we here take an alternative way in order to understand more clearly the difference between 3D structures and graphs. Thus, we start from the functional equations for counting PAMs as 3D structures (eqs 13 and 14), where we reduce 3D structures into graphs after we enumerate achiral and chiral 3D structures by using $(1/2)\{a(x, q, t, s, p) + b(x, q, t, s, p)\}$ (cf. eq 24). By dividing the sum of eqs 13 and 14 by 2, we obtain

$$\begin{aligned}
&\frac{1}{2}\{a(x, q, t, s, p) + b(x, q, t, s, p)\} \\
&\quad = 1 + xp + \frac{xs}{2}\big\{[a(x, q, t, s, p) - 1] + [b(x, q, t, s, p) - 1]\big\} \\
&\qquad + \frac{xt}{2}\big\{[b(x, q, t, s, p) - 1]^2 + [c(x^2, q^2, t^2, s^2, p^2) - 1]\big\} \\
&\qquad + \frac{xq}{6}\big\{[b(x, q, t, s, p) - 1]^3 + 2[b(x^3, q^3, t^3, s^3, p^3) - 1] \\
&\qquad + 3[a(x, q, t, s, p) - 1][c(x^2, q^2, t^2, s^2, p^2) - 1]\big\}
\end{aligned} \tag{26}$$

which counts PAMs as stereoisomers, where each achiral ligand or each pair of enantiomeric ligands is counted once. In order to count these PAMs as graphs, we shall equalize all of the functions appearing in eq 26 as follows:

$$\begin{aligned}
a(x^k, q^k, t^k, s^k, p^k) &= b(x^k, q^k, t^k, s^k, p^k) \\
&= c(x^k, q^k, t^k, s^k, p^k) = r(x^k, q^k, t^k, s^k, p^k).
\end{aligned} \tag{27}$$

Thereby, eq 26 is converted into the following functional equation:

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

Table 2. Total Numbers of Chiral Monosubstituted Alkanes[a)]

	The coefficient of x^k (cf. eqs 20 and 23), i.e., $\sum B^{(C)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$–3	0
$k = 4$	s^2p^2
$k = 5$	$2\,tsp^3 + s^3p^2$
$k = 6$	$(t^2 + qs)p^4 + 6\,ts^2p^3 + 2\,s^4p^2$
$k = 7$	$qtp^5 + (3\,qs^2 + 9\,t^2s)p^4 + 15\,ts^3p^3 + 2\,s^5p^2$
$k = 8$	$(11\,qts + 3\,t^3)p^5 + (36\,t^2s^2 + 8\,qs^3)p^4 + 27\,ts^4p^3 + 3\,s^6p^2$
$k = 9$	$(2\,q^2s + 7\,qt^2)p^6 + (44\,qts^2 + 34\,t^3s)p^5 + (17\,qs^4 + 102\,t^2s^3)p^4 + 46\,ts^5p^3 + 3\,s^7p^2$
$k = 10$	$3\,q^2tp^7 + (12\,q^2s^2 + 68\,qt^2s + 11\,t^4)p^6 + (164\,t^3s^2 + 135\,qts^3)p^5 +$ $(242\,t^2s^4 + 32\,qs^5)p^4 + 71\,ts^6p^3 + 4\,s^8p^2$
$k = 11$	$(42\,q^2ts + 30\,qt^3)p^7 + (40\,q^2s^3 + 124\,t^4s + 336\,qt^2s^2)p^6 + (584\,t^3s^3 + 340\,qts^4)p^5 +$ $(55\,qs^6 + 498\,t^2s^5)p^4 + 104\,ts^7p^3 + 4\,s^9p^2$
$k = 12$	$(7\,q^3s + 29\,q^2t^2)p^8 + (342\,qt^3s + 221\,q^2ts^2 + 34\,t^5)p^7 +$ $(113\,q^2s^4 + 730\,t^4s^2 + 1230\,qt^2s^3)p^6 + (757\,qts^5 + 1670\,t^3s^4)p^5 + (89\,qs^7 + 940\,t^2s^6)p^4 +$ $145\,ts^8p^3 + 5\,s^{10}p^2$
$k = 13$	$11\,q^3tp^9 + (44\,q^3s^2 + 346\,q^2t^2s + 123\,qt^4)p^8 + (460\,t^5s + 2041\,qt^3s^2 + 855\,q^2ts^3)p^7 +$ $(3071\,t^4s^3 + 3690\,qt^2s^4 + 269\,q^2s^5)p^6 + (4148\,t^3s^5 + 1527\,qts^6)p^5 +$ $(1640\,t^2s^7 + 136\,qs^8)p^4 + 197\,ts^9p^3 + 5\,s^{11}p^2$
$k = 14$	$q^4p^{10} + (165\,q^2t^3 + 152\,q^3st)p^9 + (187\,q^3s^3 + 2140\,q^2t^2s^2 + 1617\,qt^4s + 113\,t^6)p^8 +$ $(3156\,t^5s^2 + 8851\,qt^3s^3 + 2686\,q^2ts^4)p^7 + (9636\,qt^2s^5 + 585\,q^2s^6 + 10380\,t^4s^4)p^6 +$ $(2864\,qts^7 + 9220\,t^3s^6)p^5 + (200\,qs^9 + 2715\,t^2s^8)p^4 + 258\,ts^{10}p^3 + 6\,s^{12}p^2$
$k = 15$	$(22\,q^4s + 111\,q^3t^2)p^{10} + (2254\,q^2t^3s + 984\,q^3ts^2 + 486\,qt^5)p^9 +$ $(1711\,t^6s + 9571\,q^2t^2s^3 + 626\,q^3s^4 + 11304\,qt^4s^2)p^8 +$ $(15432\,t^5s^3 + 7349\,q^2ts^5 + 31047\,qt^3s^4)p^7 + (30000\,t^4s^5 + 1165\,q^2s^7 + 22610\,qt^2s^6)p^6 +$ $(5054\,qts^8 + 18856\,t^3s^7)p^5 + (4275\,t^2s^9 + 284\,qs^{10})p^4 + 332\,ts^{11}p^3 + 6\,s^{13}p^2$
	(omitted)
$k = 20$	$10\,q^6p^{14} + (1887\,q^5ts + 3424\,q^4t^3)p^{13} +$ $(56680\,q^4t^2s^2 + 3196\,q^5s^3 + 85613\,q^3t^4s + 18937\,q^2t^6)p^{12} +$ $(653287\,q^2t^5s^2 + 97050\,q^4ts^4 + 618071\,q^3t^3s^3 + 142989\,qt^7s + 4406\,t^9)p^{11} +$ $(2892182\,q^2t^4s^4 + 240606\,t^8s^2 + 31055\,q^4s^6 + 1880185\,qt^6s^3 + 937346\,q^3t^2s^5)p^{10} +$ $(3775422\,q^2t^3s^6 + 419368\,q^3ts^7 + 1750140\,t^7s^4 + 5798808\,qt^5s^5)p^9 +$ $(3981768\,t^6s^6 + 6418941\,qt^4s^7 + 1808265\,q^2t^2s^8 + 49916\,q^3s^9)p^8 +$ $(3675420\,t^5s^8 + 323285\,q^2ts^{10} + 2961886\,qt^3s^9)p^7 +$ $(589518\,qt^2s^{11} + 17228\,q^2s^{12} + 1531404\,t^4s^{10})p^6 + (296940\,t^3s^{12} + 47313\,qts^{13})p^5 +$ $(1152\,qs^{15} + 25992\,t^2s^{14})p^4 + 909\,ts^{16}p^3 + 9\,s^{18}p^2$
	(omitted)

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

$$
+ \frac{xq}{6}\left\{[r(x,q,t,s,p) - 1]^3 + 2[r(x^3,q^3,t^3,s^3,p^3) - 1] \right.
$$
$$
\left. + 3[r(x,q,t,s,p) - 1][r(x^2,q^2,t^2,s^2,p^2) - 1]\right\} \qquad (28)
$$

which can be used to evaluate the generating function represented by eq 25. It should be noted that eq 28 has a recursive nature, because PAMs are regarded as graphs.

Total Numbers of Monosubstituted Alkanes as Graphs: Let the symbol $B^{(R)}_{kn_qn_tn_sn_p}$ be the number of inequivalent monosubstituted alkanes (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. Then, we evaluate the number $B^{(R)}_{kn_qn_tn_sn_p}$ in the form of a generating function:

$$
B^{(R)}(x,q,t,s,p)
$$
$$
= \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(R)}_{kn_qn_tn_sn_p} p^{n_p}\right) s^{n_s}\right) t^{n_t}\right) q^{n_q}\right) x^k \qquad (29)
$$

By introducing eqs 16 and 17 into eq 24, we obtain the following result:

$$
B^{(B)}(x,q,t,s,p)
$$
$$
= 1 + x + \frac{xp}{2}\left\{[a(x,q,t,s,p) - 1] + [b(x,q,t,s,p) - 1]\right\}
$$
$$
+ \frac{xs}{2}\left\{[b(x,q,t,s,p) - 1]^2 + [c(x^2,q^2,t^2,s^2,p^2) - 1]\right\}
$$
$$
+ \frac{xt}{6}\left\{[b(x,q,t,s,p) - 1]^3 + 2[b(x^3,q^3,t^3,s^3,p^3) - 1] \right.
$$
$$
\left. + 3[a(x,q,t,s,p) - 1][c(x^2,q^2,t^2,s^2,p^2) - 1]\right\} \qquad (30)
$$

where the right-hand side is a functional equation for counting monosubstituted alkanes as stereoisomers. In order to count graphs, $B^{(B)}(x,q,t,s,p)$ is replaced by $B^{(R)}(x,q,t,s,p)$ under the condition represented by eq 27. Thereby, we obtain:

$$
B^{(R)}(x,q,t,s,p)
$$
$$
= 1 + x + xp\left\{r(x,q,t,s,p) - 1\right\}
$$
$$
+ \frac{xs}{2}\left\{[r(x,q,t,s,p) - 1]^2 + [r(x^2,q^2,t^2,s^2,p^2) - 1]\right\}
$$

Table 3. Total Numbers of Achiral and Chiral Monosubstituted Alkanes[a)]

	The coefficient of x^k (cf. eqs 21 and 24), i.e., $\sum B^{(B)}_{kn_q n_t n_s n_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$	1 (methanol as an extreme case)
$k = 2$	p^2
$k = 3$	$2\,sp^2$
$k = 4$	$2\,s^2p^2 + 2\,tp^3$
$k = 5$	$4\,tsp^3 + qp^4 + 3\,s^3p^2$
$k = 6$	$(2\,t^2 + 3\,qs)p^4 + 10\,ts^2p^3 + 3\,s^4p^2$
$k = 7$	$3\,qtp^5 + (7\,qs^2 + 11\,t^2s)p^4 + 19\,ts^3p^3 + 4\,s^5p^2$
$k = 8$	$q^2p^6 + (15\,qts + 5\,t^3)p^5 + (14\,qs^3 + 39\,t^2s^2)p^4 + 33\,ts^4p^3 + 4\,s^6p^2$
$k = 9$	$(6\,q^2s + 9\,qt^2)p^6 + (54\,qts^2 + 36\,t^3s)p^5 + (26\,qs^4 + 108\,t^2s^3)p^4 + 52\,ts^5p^3 + 5\,s^7p^2$
$k = 10$	$7\,q^2tp^7 + (20\,q^2s^2 + 72\,qt^2s + 13\,t^4)p^6 + (172\,t^3s^2 + 151\,qts^3)p^5 +$ $(248\,t^2s^4 + 44\,qs^5)p^4 + 79\,ts^6p^3 + 5\,s^8p^2$
$k = 11$	$2\,q^3p^8 + (50\,q^2ts + 34\,qt^3)p^7 + (58\,s^3q^2 + 128\,t^4s + 348\,qt^2s^2)p^6 +$ $(592\,t^3s^3 + 368\,qts^4)p^5 + (71\,qs^6 + 510\,t^2s^5)p^4 + 112\,ts^7p^3 + 6\,s^9p^2$
$k = 12$	$(13\,q^3s + 34\,q^2t^2)p^8 + (350\,qt^3s + 245\,q^2ts^2 + 38\,t^5)p^7 +$ $(143\,q^2s^4 + 740\,t^4s^2 + 1250\,qt^2s^3)p^6 + (797\,qts^5 + 1690\,t^3s^4)p^5 +$ $(109\,qs^7 + 950\,t^2s^6)p^4 + 155\,ts^8p^3 + 6\,s^{10}p^2$
$k = 13$	$17\,q^3tp^9 + (62\,q^3s^2 + 360\,q^2t^2s + 128\,qt^4)p^8 + (464\,t^5s + 2069\,qt^3s^2 + 899\,q^2ts^3)p^7 +$ $(3091\,t^4s^3 + 3730\,qs^4t^2 + 323\,q^2s^5)p^6 + (4168\,t^3s^5 + 1587\,qts^6)p^5 +$ $(1660\,t^2s^7 + 161\,qs^8)p^4 + 207\,ts^9p^3 + 7\,s^{11}p^2$
$k = 14$	$4\,q^4p^{10} + (177\,q^2t^3 + 168\,q^3ts)p^9 + (227\,q^3s^3 + 2178\,q^2t^2s^2 + 1627\,qt^4s + 118\,t^6)p^8 +$ $(3180\,t^5s^2 + 8899\,qt^3s^3 + 2778\,q^2ts^4)p^7 + (9696\,qt^2s^5 + 665\,q^2s^6 + 10410\,t^4s^4)p^6 +$ $(2944\,qts^7 + 9260\,t^3s^6)p^5 + (230\,qs^9 + 2730\,t^2s^8)p^4 + 270\,ts^{10}p^3 + 7\,s^{12}p^2$
$k = 15$	$(34\,q^4s + 121\,q^3t^2)p^{10} + (2278\,q^2t^3s + 1036\,q^3ts^2 + 496\,qt^5)p^9 +$ $(1721\,t^6s + 9659\,q^2t^2s^3 + 712\,q^3s^4 + 11344\,qt^4s^2)p^8 +$ $(15456\,t^5s^3 + 7501\,q^2ts^5 + 31155\,qt^3s^4)p^7 + (30060\,t^4s^5 + 1293\,q^2s^7 + 22710\,qt^2s^6)p^6 +$ $(5164\,qts^8 + 18896\,t^3s^7)p^5 + (4305\,t^2s^9 + 320\,qs^{10})p^4 + 344\,ts^{11}p^3 + 8\,s^{13}p^2$
	(omitted)
$k = 20$	$18\,q^6p^{14} + (1943\,q^5ts + 3480\,q^4t^3)p^{13} +$ $(56940\,q^4t^2s^2 + 3404\,q^5s^3 + 85721\,q^3t^4s + 18997\,q^2t^6)p^{12} +$ $(653695\,q^2t^5s^2 + 97714\,q^4ts^4 + 618663\,q^3t^3s^3 + 143045\,qt^7s + 4434\,t^9)p^{11} +$ $(2893034\,q^2t^4s^4 + 240732\,t^8s^2 + 31975\,q^4s^6 + 1880437\,qt^6s^3 + 938502\,q^3t^2s^5)p^{10} +$ $(3777126\,q^2t^3s^6 + 420952\,q^3ts^7 + 1750500\,t^7s^4 + 5799528\,qt^5s^5)p^9 +$ $(3982188\,t^6s^6 + 6419781\,qt^4s^7 + 1809759\,q^2t^2s^8 + 51200\,q^3s^9)p^8 +$ $(3675924\,t^5s^8 + 324641\,q^2ts^{10} + 2962894\,qt^3s^9)p^7 +$ $(590022\,qt^2s^{11} + 17816\,q^2s^{12} + 1531656\,t^4s^{10})p^6 + (297108\,t^3s^{12} + 47649\,qts^{13})p^5 +$ $(1224\,qs^{15} + 26028\,t^2s^{14})p^4 + 927\,ts^{16}p^3 + 10\,s^{18}p^2$
	(omitted)

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

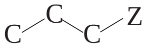
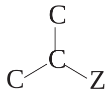
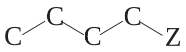
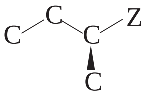
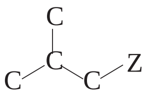
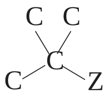
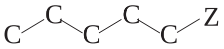
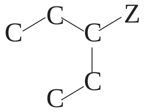
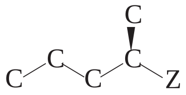
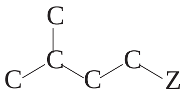
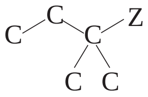
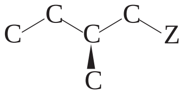
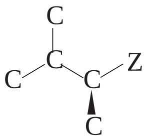
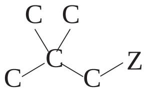
$$+ \frac{xt}{6}\left\{[r(x,q,t,s,p) - 1]^3 + 2[r(x^3,q^3,t^3,s^3,p^3) - 1]\right.$$

$$\left. + 3[r(x,q,t,s,p) - 1][r(x^2,q^2,t^2,s^2,p^2) - 1]\right\} \qquad (31)$$

which is a functional equation to give the generating function represented by eq 29.

Implementation and Results for Constitutional Isomers: The functional equation represented by $r(x,q,t,s,p)$ (eq 28) has a recursive nature so as to be implemented (as a program named "GraphAlkylPST1.mpl") by mean of the Maple programming language. 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. It should be noted that the recursive enumeration as graphs requires only one functional equation $r(x,q,t,s,p)$ (eq 28) whereas the corresponding recursive enumeration as stereoisomers requires three functional equations, i.e., $a(x,q,t,s,p)$ (eq 13), $b(x,q,t,s,p)$ (eq 14), and $c(x^2,q^2,t^2,s^2,p^2)$ (eq 15), as described above (cf. the program "AlkylPST8B.mpl").

```
#GraphAlkylPST1.mpl
#Calculation of Total Numbers of Alkyls as Graphs

"Functional Equations for Inner Alkyl Ligands (as Graphs)";
#(Part 1) H, methyl, primary, secondary, tertiary, quaternary
# --- inner alkyl (preformed alkyl moiety)
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));

#"Functional Equations for Alkyl Ligands Substituted by OH etc.";
#(Part 2) H, methyl, primary, secondary, tertiary
# --- alcoholic alkyl
Brx := 1 + x + x*p*(r1-1) + (x*s/2)*((r1-1)^2 + (r2-1))
+ (x*t/6)*((r1-1)^3 + 2*(r3-1) + 3*(r1-1)*(r2-1));

"(Part 3)Initial Values";
r1 := 1; r2 := 1; r3 := 1;
rsum := 1:
Br1 := 1;

"(Part 4) Recursive Calculation";
kmax := 30;
for k from 1 to kmax by 1 do
"k ="; k;

"(Part 5) Total Number of Tertiary Alkyls as Graphs";
CBrx:= expand(coeff(Brx,x^k));
```

CC[a)]	BM[b)]	Achiral	Chiral
$k = 1$	1	C—Z **13**	
$k = 2$	p^2	C—C—Z **14**	
$k = 3$	sp^2	 **15**  **16**	
$k = 4$	s^2p^2	 **17**	 **18**
	tp^3	 **19**  **20**	
$k = 5$	s^3p^2	 **21**  **22**	 **23**
	tsp^3	 **24**  **25**	 **26**  **27**
	qp^4	 **28**	

a) CC: carbon content. b) BM: branching monomial.

Figure 3. Monosubstituted alkanes of lower carbon contents (k = 1–5), which are categorized by means of branching monomials. Either one of two enantiomers is depicted as a representative.

```
Br1 := Br1 + CBrx*x^k;

"(Part 6) 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:

#(Part 7)###################################
"Print Out of Br1 (Total Graphs)";
for k from 1 to kmax by 1 do
carbon_content:= k:
NBr := collect(expand(coeff(Br1,x^k)),p):
end do;
```

This code employs abbreviated symbols for functional equations, i.e., `r1` for $r(x, q, t, s, p)$, `r2` for $r(x^2, q^2, t^2, s^2, p^2)$, and so on. The symbol `rsum` is used to store the series for $r(x)$ ($q = t = s = p = 1$). The first part (Part 1) of this code declares a functional equation `rx` for eq 28, which is calculated by using `r1` etc. recursively. The second part (Part 2) declares a functional equation `Brx` for $B^{(R)}(x, q, t, s, p)$ (eq 31), which is non-recursively calculated by using `r1` and so on. In Part 3 ("Initial Values"), the initial values are set for the initial (trivial) PAMs, and so on. Part 4 ("Recursive Calculation") of the code shows a `do` loop for carbon content k, in which Part 6 is the embodiment of the recursive process for PAMs as graphs. In each step of the `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, Part 5 stores the result of `Brx` (cf. Part 2) in `Br1`.

After escaping from the `do` loop for k, Part 7 ("Print Out of Br1 ...") of the code shows the print-out of `NBr`, which is the coefficient of x^k appearing in `Br1` for $B^{(R)}(x, q, t, s, p)$ (cf. eqs 29 and 31).

Table 4. Numbers of Monosubstituted Alkanes as Graphs

	The coefficient of x^k (cf. eqs 29 and 31), i.e., $\sum B^{(R)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k=1$	1 (methanol for an extreme case)
$k=2$	p^2
$k=3$	$2\,sp^2$
$k=4$	$2\,s^2p^2 + 2\,tp^3$
$k=5$	$3\,s^3p^2 + 4\,tsp^3 + qp^4$
$k=6$	$(3\,qs + 2\,t^2)p^4 + 9\,ts^2p^3 + 3\,s^4p^2$
$k=7$	$3\,qtp^5 + (7\,qs^2 + 9\,t^2s)p^4 + 16\,ts^3p^3 + 4\,s^5p^2$
$k=8$	$q^2p^6 + (14\,qts + 4\,t^3)p^5 + (14\,qs^3 + 26\,t^2s^2)p^4 + 26\,ts^4p^3 + 4\,s^6p^2$
$k=9$	$(6\,q^2s + 8\,qt^2)p^6 + (45\,qts^2 + 20\,t^3s)p^5 + (25\,qs^4 + 63\,t^2s^3)p^4 + 39\,ts^5p^3 + 5\,s^7p^2$
$k=10$	$7\,q^2tp^7 + (7\,t^4 + 19\,q^2s^2 + 50\,qt^2s)p^6 + (115\,qts^3 + 76\,t^3s^2)p^5 + (130\,t^2s^4 + 41\,qs^5)p^4 +$ $57\,ts^6p^3 + 5\,s^8p^2$
$k=11$	$2\,q^3p^8 + (21\,qt^3 + 43\,q^2ts)p^7 + (46\,t^4s + 53\,q^2s^3 + 201\,qt^2s^2)p^6 +$ $(221\,t^3s^3 + 256\,qts^4)p^5 + (64\,qs^6 + 247\,t^2s^5)p^4 + 78\,ts^7p^3 + 6\,s^9p^2$
$k=12$	$(26\,q^2t^2 + 13\,q^3s)p^8 + (181\,q^2ts^2 + 160\,qt^3s + 13\,t^5)p^7 +$ $(123\,q^2s^4 + 208\,t^4s^2 + 626\,qt^2s^3)p^6 + (513\,qts^5 + 558\,t^3s^4)p^5 + (95\,qs^7 + 430\,t^2s^6)p^4 +$ $105\,ts^8p^3 + 6\,s^{10}p^2$
$k=13$	$16\,q^3tp^9 + (212\,q^2t^2s + 56\,q^3s^2 + 52\,qt^4)p^8 + (106\,t^5s + 588\,q^2ts^3 + 767\,qt^3s^2)p^7 +$ $(263\,q^2s^5 + 727\,t^4s^3 + 1660\,qt^2s^4)p^6 + (1246\,t^3s^5 + 953\,qts^6)p^5 +$ $(713\,t^2s^7 + 136\,qs^8)p^4 + 137\,ts^9p^3 + 7\,s^{11}p^2$
$k=14$	$4\,q^4p^{10} + (129\,q^3ts + 90\,q^2t^3)p^9 + (478\,qt^4s + 1058\,q^2t^2s^2 + 188\,q^3s^3 + 25\,t^6)p^8 +$ $(566\,t^5s^2 + 2806\,qt^3s^3 + 1633\,q^2ts^4)p^7 + (3907\,qt^2s^5 + 2133\,t^4s^4 + 511\,q^2s^6)p^6 +$ $(2558\,t^3s^6 + 1664\,qts^7)p^5 + (1120\,t^2s^8 + 189\,qs^9)p^4 + 175\,ts^{10}p^3 + 7\,s^{12}p^2$
$k=15$	$(80\,q^3t^2 + 32\,q^4s)p^{10} + (865\,q^2t^3s + 664\,q^3ts^2 + 128\,qt^5)p^9 +$ $(2665\,qt^4s^2 + 540\,q^3s^4 + 4037\,q^2t^2s^3 + 248\,t^6s)p^8 +$ $(8613\,qt^3s^4 + 2274\,t^5s^3 + 4014\,q^2ts^5)p^7 + (8405\,qt^2s^6 + 5522\,t^4s^5 + 942\,q^2s^7)p^6 +$ $(4885\,t^3s^7 + 2766\,qts^8)p^5 + (1702\,t^2s^9 + 256\,qs^{10})p^4 + 219\,ts^{11}p^3 + 8\,s^{13}p^2$
	(omitted)
$k=20$	$17\,q^6p^{14} + (1229\,q^4t^3 + 1138\,q^5ts)p^{13} +$ $(19707\,q^4t^2s^2 + 17148\,q^3t^4s + 2451\,q^2t^6 + 2167\,q^5s^3)p^{12} +$ $(225\,t^9 + 40286\,q^4ts^4 + 10539\,qt^7s + 134803\,q^3t^3s^3 + 79881\,q^2t^5s^2)p^{11} +$ $(144338\,qt^6s^3 + 409774\,q^2t^4s^4 + 255634\,q^3t^2s^5 + 10525\,t^8s^2 + 17263\,q^4s^6)p^{10} +$ $(541962\,qt^5s^5 + 155918\,q^3ts^7 + 85383\,t^7s^4 + 693720\,q^2t^3s^6)p^9 +$ $(464802\,q^2t^2s^8 + 27181\,q^3s^9 + 806494\,qt^4s^7 + 248246\,t^6s^6)p^8 +$ $(123339\,q^2ts^{10} + 321539\,t^5s^8 + 537358\,qt^3s^9)p^7 +$ $(10382\,q^2s^{12} + 163377\,qt^2s^{11} + 201534\,t^4s^{10})p^6 + (21075\,qts^{13} + 62164\,t^3s^{12})p^5 +$ $(885\,qs^{15} + 9060\,t^2s^{14})p^4 + 555\,ts^{16}p^3 + 10\,s^{18}p^2$
	(omitted)

The above-described code is executed by inputting the following command on the Maple inputting window:

```
> restart;
> read "GraphAlkylPST1.mpl";
```

The calculation results are obtained according to its print-out sections. Table 4 collects the data `NBr` ($\sum B^{(R)}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$), which is the coefficient of x^k (cf. eqs 29 and 31). Note that the summation is concerned with n_q, n_t, n_s, and n_p for each carbon content k.

Discussion

Achiral and Chiral Monosubstituted Alkanes. One of the merits of the present enumeration stems from the categorization of monosubstituted alkanes into achiral and chiral 3D structures, as found in Table 1 (cf. $B^{(A)}(x,q,t,s,p)$ of eq 22) and Table 2 (cf. $B^{(C)}(x,q,t,s,p)$ of eq 23). By starting from eqs 22–24, we obtain the following relationship:

$$B^{(B)}(x,q,t,s,p) = B^{(A)}(x,q,t,s,p) + B^{(C)}(x,q,t,s,p) \quad (32)$$

This relationship is converted into a relevant one:

$$B^{(B)}_{kn_qn_tn_sn_p} = B^{(A)}_{kn_qn_tn_sn_p} + B^{(C)}_{kn_qn_tn_sn_p} \quad (33)$$

with respect to their coefficients which appear in eqs 19–21. The relationships (eqs 32 and 33) are confirmed by examining the respective coefficients which appear in each term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$ of a given k in Tables 1–3. For example, the ($k=5$)-row of Table 3 lists the term $3s^3p^2$, which is obtained by adding the term $2s^3p^2$ of Table 1 (cf. **21** and **22** in Figure 3) to the term s^3p^2 of Table 2 (cf. **23** in Figure 3).

3D-Structures without Branching Indicators. Previous results[19,20] can be regarded as special cases of the present enumeration, where the effect of internal branching has not been taken into consideration. This section is devoted to show that the previous formulation and results can be derived by omitting the branching indicators developed for the the present enumeration.

Let the symbol A_k be the summation of $B^{(A)}_{kn_qn_tn_sn_p}$ at a given carbon content k; the symbol C_k be the summation of $B^{(C)}_{kn_qn_tn_sn_p}$

at a given carbon content k; and the symbol B_k be the summation of $B^{(B)}_{kn_qn_tn_sn_p}$ at a given carbon content k. It follows that eqs 19–21 give the following equations:

$$A_k = \left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(A)}_{kn_qn_tn_sn_p}\right)\right)\right)\right) \tag{34}$$

$$C_k = \left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(C)}_{kn_qn_tn_sn_p}\right)\right)\right)\right) \tag{35}$$

$$B_k = \left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(B)}_{kn_qn_tn_sn_p}\right)\right)\right)\right) \tag{36}$$

where we do not take the effect of branching into consideration. Obviously, the value A_k can be obtained by adding relevant coefficients appearing in the k-th row of Table 1. For example, we obtain $A_7 = 2 + 4 + 2 + 4 + 2 = 14$, where these coefficients appear in the ($k = 7$)-th row of Table 1. On the same line, the values C_k and B_k can be obtained by starting from the data collected in Tables 2 and 3. The following equation can easily be derived from eq 33:

$$B_k = A_k + C_k \tag{37}$$

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

$$\begin{aligned} A(x) &= \sum_{k=0}^{\infty} A_k x^k \\ &= B^{(A)}(x, 1, 1, 1, 1) \end{aligned} \tag{38}$$

$$\begin{aligned} C(x) &= \sum_{k=0}^{\infty} C_k x^k \\ &= B^{(C)}(x, 1, 1, 1, 1) \end{aligned} \tag{39}$$

$$\begin{aligned} B(x) &= \sum_{k=0}^{\infty} B_k x^k \\ &= B^{(B)}(x, 1, 1, 1, 1), \end{aligned} \tag{40}$$

which can be obtained by putting $q = t = s = p = 1$ in eqs 19–21. Because the above-described program "AlkylPST8B.mpl" has calculated the generating functions, $B^{(A)}(x, q, t, s, p)$, $B^{(C)}(x, q, t, s, p)$, and $B^{(B)}(x, q, t, s, p)$, and stored them respectively as the series designated by `Ba1`, `ECCx` (or `CCx`), and `EBBx` (or `BBx`), we are able to calculate $A(x)$, $C(x)$, and $B(x)$ by adding the following code for calculating them:

```
GrossAA := subs({p=1,s=1,t=1,q=1}, expand(Ba1));
GrossCC := subs({p=1,s=1,t=1,q=1}, ECCx);
GrossBB := subs({p=1,s=1,t=1,q=1}, EBBx);
```

Thereby, we obtain the following generating functions:

$$\begin{aligned} A(x) &= B^{(A)}(x, 1, 1, 1, 1) \\ &= 1 + x + x^2 + 2x^3 + 3x^4 + 5x^5 + 8x^6 + 14x^7 \\ &\quad + 23x^8 + 41x^9 + 69x^{10} + 122x^{11} + \\ &\quad + 208x^{12} + 370x^{13} + 636x^{14} \\ &\quad + 1134x^{15} + \ldots + 19059x^{20} + \ldots \end{aligned} \tag{41}$$

$$\begin{aligned} C(x) &= B^{(C)}(x, 1, 1, 1, 1) \\ &= x^4 + 3x^5 + 10x^6 + 30x^7 + 88x^8 \\ &\quad + 255x^9 + 742x^{10} + 2157x^{11} + \\ &\quad + 6312x^{12} + 18563x^{13} + 54932x^{14} \\ &\quad + 163479x^{15} + \ldots + 41140608x^{20} + \ldots \end{aligned} \tag{42}$$

$$\begin{aligned} B(x) &= B^{(B)}(x, 1, 1, 1, 1) \\ &= 1 + x + x^2 + 2x^3 + 4x^4 + 8x^5 + 18x^6 + 44x^7 \\ &\quad + 111x^8 + 296x^9 + 811x^{10} + 2279x^{11} + \\ &\quad + 6520x^{12} + 18933x^{13} + 55568x^{14} \\ &\quad + 164613x^{15} + \ldots + 41159667x^{20} + \ldots \end{aligned} \tag{43}$$

These values are identical to those reported in previous papers (Table 2 of Ref. 19 for up to carbon content 20 and Table 1 of Ref. 20 for up to carbon content 100). Hence, these 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 13–15. Thereby we obtain the following functional equations without branching monomials:

$$a(x) = 1 + xa(x)c(x^2) \tag{44}$$

$$b(x) = 1 + \frac{x}{3}\left\{b(x)^3 + 2b(x^3)\right\} \tag{45}$$

$$c(x^2) = 1 + \frac{x^2}{3}\left\{c(x^2)^3 + 2c(x^6)\right\} \tag{46}$$

They are identical respectively with eqs 21, 17, and 19 of Ref. 19.

Because the program "AlkylPST8B.mpl" described above has calculated $a(x) = a(x, 1, 1, 1, 1)$, $b(x) = b(x, 1, 1, 1, 1)$, and $c(x^2) = c(x^2, 1, 1, 1, 1)$ (cf. eqs 13–15) and stored them in the variables `asum`, `bsum`, and `csum`, we are able to calculate $A(x)$, $C(x)$, and $B(x)$ alternatively by adding the following code for calculating them:

```
GrossA := sort(expand(asum),x);
GrossC := sort((1/2)*(expand(bsum) - expand(asum)),x);
GrossB := sort((1/2)*(expand(asum) + expand(bsum)),x);
```

The results are identical to those described above (eqs 41–43).

Graphs without Branching Indicators. Let the symbol R_k be the summation of $B^{(R)}_{kn_qn_tn_sn_p}$ at a given carbon content k. It follows that eq 29 gives the following equation:

$$R_k = \left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} B^{(R)}_{kn_qn_tn_sn_p}\right)\right)\right)\right) \tag{47}$$

where we do not take the effect of branching into consideration. Obviously, the value R_k can be obtained by adding relevant coefficients appearing in the k-th row of Table 4. For example, we obtain $R_7 = 3 + 7 + 9 + 16 + 4 = 39$, where these coefficients appear in the ($k = 7$)-th row of Table 4.

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

$$r(x) = \sum_{k=0}^{\infty} R_k x^k = B^{(R)}(x, 1, 1, 1, 1) \quad (48)$$

which can be obtained by putting $q = t = s = p = 1$ in eq 29. Because the above-described program "GraphAlkylPST1.mpl" has calculated the generating function $B^{(R)}(x, q, t, s, p)$ and stored as the series designated by `Br1`, we are able to calculate $r(x)$ by adding the following code:

```
GrossRR := subs({p=1,s=1,t=1,q=1}, expand(Br1));
```

Thereby, we obtain the following generating function:

$$\begin{aligned} r(x) &= B^{(R)}(x, 1, 1, 1, 1) \\ &= 1 + x + x^2 + 2x^3 + 4x^4 + 8x^5 + 17x^6 \\ &\quad + 39x^7 + 89x^8 + 211x^9 + 507x^{10} + 1238x^{11} + \\ &\quad + 3057x^{12} + 7639x^{13} + 19241x^{14} \\ &\quad + 48865x^{15} + \ldots + 5622109x^{20} + \ldots \end{aligned} \quad (49)$$

These values are identical to those reported in previous papers (Table 2 of Ref. 19 for up to carbon content 20 and Table 2 of Ref. 20 for up to carbon content 100). Hence, these 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 $q = t = s = p = 1$ and $r(x) = r(x, 1, 1, 1, 1)$ in eq 28. Thereby we obtain the following functional equation without branching monomials:

$$r(x) = 1 + \frac{x}{6}\left\{r(x)^3 + 2r(x^3) + 3r(x)r(x^2)\right\}, \quad (50)$$

which has been once noted in Ref. 19 (eq 39).

Because $r(x) = r(x, 1, 1, 1, 1)$ (cf. eq 28) has been calculated and stored in the variable `rsum` during the execution of the program "GraphAlkylPST1.mpl" described above, we are able to calculate $r(x)$ alternatively by adding the following code:

```
GrossR := sort(expand(rsum),x);
```

The result is identical to those described above (eq 49).

3D-Structures and Graphs. Throughout the present enumeration as stereoisomers, a pair of enantiomers is counted just once. This means that two enantiomers of each pair having one asymmetric carbon are equalized in terms of the achiral point group that governs the common skeleton of the two enantiomers or an achiral point group (e.g., C_s) that governs an appropriate pairwise arrangement of the two enantiomers. The phrase "as stereoisomers" is used to emphasize the presumption that equivalence classes are judged by means of such an achiral point group. Thus, just as each achiral compound constructs an equivalence class, each pair of enantiomers constructs an equivalence class. For example, a tetrahedral molecule C(ABXY) and its enantiomeric molecule C(BAXY) have a tetrahedral skeleton as a common skeleton of the T_d-point group. The enantiomers, C(ABXY) and C(BAXY), are equalized under the T_d-point group. It follows that the numbers of inequivalent compounds as stereoisomers are equal to the corresponding numbers as graphs (constitutional isomers) if they have one or fewer asymmetric carbon. Accordingly, the data of lower carbon contents ($k = 1$–5) collected in Table 3 (as stereoisomers) are equal to the corresponding ones collected in Table 4 (as graphs).

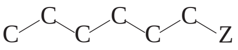
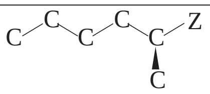
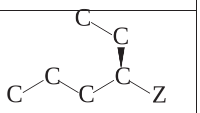
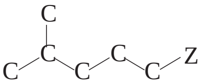
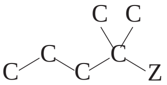
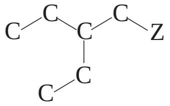
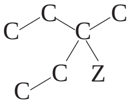
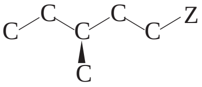
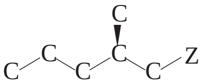
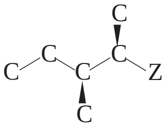
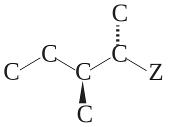
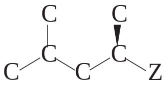
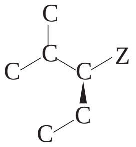
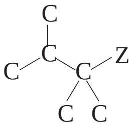
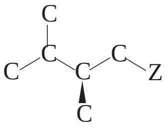
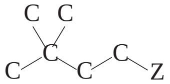
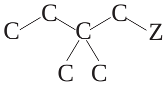
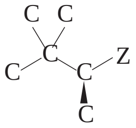
As the lowest case in which the number as stereoisomers is different from the number as graphs, we can find a case of carbon content 6, i.e., $10ts^2p^3$ in Table 3 (as stereoisomers) and $9ts^2p^3$ in Table 4 (as graphs). They are depicted in Figure 4 (**32**–**41**) as well as other monosubstituted alkanes of carbon content 6. Among the ten compounds **32**–**41** corresponding to the term $10ts^2p^3$ in Table 3, two diastereomers **38** and **39** coalesce with each other to give a single graph. This coalescence results in the coefficient 9 of the term $9ts^2p^3$ in Table 4.

Internal Branching vs. Branching at a Substituted Carbon. In general, the degree of branching at a carbon substituted by Z does not change if the substituent Z is replaced by a hydrogen (cf. Figure 1). It follows that the branching monomial (BM) of each monosubstituted alkane is the same as the BM of the corresponding alkane. For example, The ten compounds **32**–**41** corresponding to the term $10ts^2p^3$ in Figure 4 are correlated to two alkanes **47** and **48** shown in Figure 5. Because the alkane **47** has five inequivalent carbons, there emerge five monosubstituted alkanes as graphs, which correspond to five compounds as stereoisomers **32**, **33**, **35**, **36**, and **41**. On the other hand, the alkane **48** has four inequivalent carbons, there emerge four monosubstituted alkanes as graphs, which correspond to five compounds **34**, **36**, **37**, **38**, and **39** as stereoisomers. The last two, **38** and **39**, are in a diastereomeric relationship so that they are reduced to a single graph.

As a more complicated example, Figure 6 collects monosubstituted alkanes of carbon content $k = 7$ and a branching monomial ts^3p^3. According to Table 3 (as stereoisomers), there are 19 monosubstituted alkanes, which are categorized into four achiral ones (cf. Table 1) and 15 pairs of enantiomers (cf. Table 2). In agreement with this categorization, Figure 6 shows that **49**–**52** are achiral, while **53**–**67** are pairs of enantiomers, where an arbitrary enantiomer for each pair is depicted as a representative. The coefficient 16 of the term ts^3p^3 appearing at the ($k = 7$)-th row of Table 4 indicates that there are 16 inequivalent graphs, because there exist three sets of diastereomers, i.e., (**62**, **63**), (**64**, **65**), and (**66**, **67**), each set of which coalesces to give a single graph.

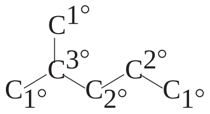
The 19 monosubstituted alkanes (four achiral ones and 15 pairs of enantiomers) can be subdivided into three categories by means of their carbon skeletons (i.e., **68**–**70**) which are produced by converting Z into a hydrogen, as shown in Figure 7. The carbon skeletons (i.e., **68**–**70**) are characterized by the BM (ts^3p^3). Because the skeleton **68** has six inequivalent carbons, there emerge six monosubstituted alkanes as graphs, which correspond to six compounds as stereoisomers **49**, **51**, **54**, **55**, **57**, and **60**. The skeleton **69** has seven inequivalent carbons so that there emerge seven monosubstituted alkanes as graphs, which correspond to ten compounds **53**, **58**, **59**, **61**, **62**, **63**, **64**, **65**, **66**, and **67**. The skeleton **70** has three inequivalent carbons so as to give three monosubstituted alkanes as graphs, which correspond to three compounds, i.e., **50**, **52**, and **56**.

Extreme Cases. Monosubstituted alkanes characterized by carbon content k and the BM $s^{k-2}p^2$ construct an extreme case in which the number of them can be calculated algebraically.

CC[a)]	BM[b)]	Achiral	Chiral
$k = 6$	s^4p^2	 **29**	 **30**  **31**
	ts^2p^3	 **32**  **33**  **36**  **37**	 **34**  **35**  **38**  **39**  **40**  **41**
	t^2p^4	 **42**	 **43**
	qsp^4	 **44**  **45**	 **46**

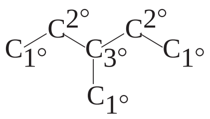
a) CC: carbon content. b) BM: branching monomial.

Figure 4. Monosubstituted alkanes of carbon content $k = 6$, which are categorized by means of branching monomials. Either one of two enantiomers is depicted as a representative.



47

$\Longrightarrow$ **32**, **33**, **35**, **36**, **41**



48

$\Longrightarrow$ **34**, **36**, **37**, $\underbrace{\mathbf{38}, \mathbf{39}}$

Figure 5. Carbon skeletons to give monosubstituted alkanes of branching monomial ts^2p^3 (**32**–**41**). They have the same branching monomial ts^2p^3.

Obviously, there exists one achiral monosubstituted alkanes represented by the following formula (a straight-chained monosubstituted alkane): $C^{1^\circ}H_3$–$(C^{2^\circ}H_2)_\alpha$–$C^{1^\circ}H_2$–Z, which is characterized by the BM $s^{k-2}p^2$ when $\alpha = k - 2$. On the other hand, there exist monosubstituted alkanes represented by the following formula (a secondary monosubstituted alkane): $C^{1^\circ}H_3$–$(C^{2^\circ}H_2)_\alpha$–$C^{2^\circ}H(Z)$–$(C^{2^\circ}H_2)_\beta$–$C^{1^\circ}H_3$, which is also characterized by the BM $s^{k-2}p^2$.

When k is odd, the latter formula shows that there is one achiral monosubstituted alkane of $\alpha = \beta = (k - 3)/2$. Moreover, there exist the number $(k - 3)/2$ of chiral monosubstituted alkanes ($\alpha < \beta$) of the latter formula. Hence, the total number is calculated to be

$$1 + 1 + \frac{k-3}{2} = \frac{k+1}{2} \tag{51}$$

When k is even, there is no achiral monosubstituted alkane of the latter formula but there are the number $(k - 2)/2$ of chiral monosubstituted alkanes ($\alpha < \beta$) of the latter formula. Hence, the total number is calculated to be

$$1 + \frac{k-2}{2} = \frac{k}{2} \tag{52}$$

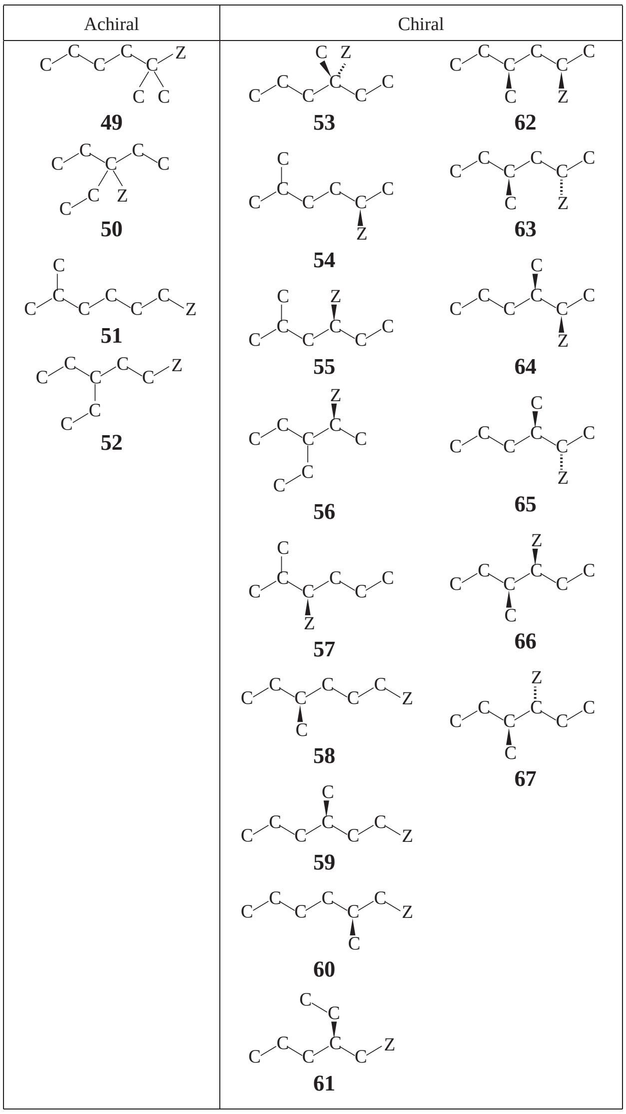


Figure 6. Monosubstituted alkanes of carbon content 7 and the branching monomial ts^3p^3. Either one of two enantiomers is depicted as a representative.

Hence, the coefficients of the term $s^{k-2}p^2$ are summarized as follows:

$$\begin{array}{lccc} & \text{achiral} & \text{chiral} & \text{total} \\ \hline k\text{: odd} & 2 & \frac{k-3}{2} & \frac{k+1}{2} \\ k\text{: even} & 1 & \frac{k-2}{2} & \frac{k}{2} \\ \hline & \text{Table 1} & \text{Table 2} & \text{Table 3} \end{array} \tag{53}$$

These results are confirmed by referring to Tables 1–3.

Conclusion

Branching indicators (BIs, i.e., q, t, s, and p) have been developed as a versatile tool to evaluate the effect of internal branching on the numbers of achiral and/or chiral monosubstituted alkanes (MSAs) as three-dimensional structures and on the numbers of MSAs as graphs. By following Fujita's proligand method,[16–18] functional equations for recursive calculations have been obtained to treat respective cases, where previous approaches[19–21] without considering BIs have been extended so as to incorporate BIs with no violation of consistency. Such functional equations have been used to obtain generating functions, in which each number of objects having n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_q quaternary carbons appears as the coefficient of a branching monomial $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$. The numbers of achiral MSAs, chiral MSAs, total (achiral and chiral) MSAs have been obtained as such generating functions. They have been compared with the corresponding numbers of MSAs as graphs. Thereby, difference between stereoisomers (3D structures) and constitutional isomers (graphs) has been discussed fruitfully.

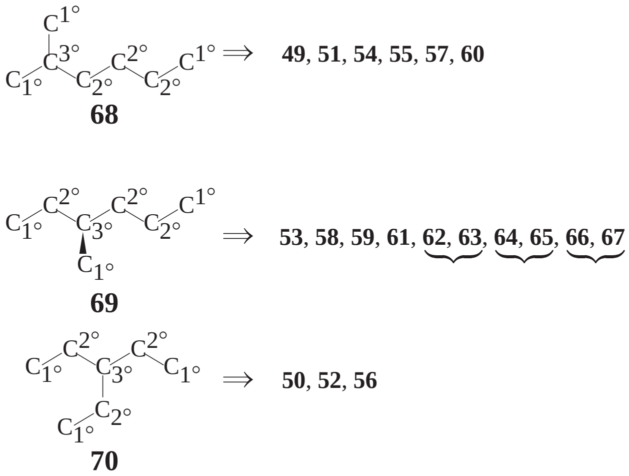


Figure 7. Carbon skeletons to give monosubstituted alkanes of branching monomial ts^3p^3 (**49**–**67**). They have the same branching monomial ts^3p^3.

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27 It is a great honor that our article[26] has been selected as a BCSJ award article of *Bull. Chem. Soc. Jpn.* Vol. 81 (No. 2).

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