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Categorization and Enumeration of Achiral and Chiral Alkanes of a Given Carbon Content by Considering Internal Branching

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Combinatorial enumeration of alkanes as three-dimensional structures has been investigated, where the degrees of internal branching have been taken into consideration by introducing branching indicators (BIs, i.e., q, t, s, and p). After generating functions for counting preformed alkyl moieties (PAMs) were calculated by following Fujita's proligand method (S. Fujita, *Theor. Chem. Acc.* **2005**, *113*, 73; **2005**, *113*, 80; **2006**, *115*, 37), they have been introduced into functional equations for counting alkanes so as to give the corresponding generating functions, where such alkanes of carbon content k have been categorized into four cases in terms of centroidal/bicentroidal nature and achirality/chirality. Thereby, the generating functions of the respective cases have given the numbers of alkanes, where each number appears as the coefficient of the term called a branching monomial (BM) $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$, when such an alkane contains n_q quaternary, n_t tertiary, n_s secondary, and n_q quaternary carbons ($k = n_q + n_t + n_s + n_p$). The results of the enumeration have been verified by drawing alkanes of several representative cases, where a mode of divergence, i.e., [n_q, n_t, n_s, and n_p], has been used for the purpose of qualitative discussions. Previous approaches without considering BIs have been derived by disregarding the effect of internal branching. Moreover, the functional equations for counting 3D structures have been systematically reduced into those for counting graphs, where graph-reduction conditions have been formulated to rationalize the reduction processes. Thereby, Pólya's theorem for counting graphs has been shown to be a special case of Fujita's proligand method for counting 3D structures. As a result, difference between stereoisomers (3D structures) and constitutional isomers (graphs) has been discussed by the common criterion due to BMs (or modes of divergence), which provides more detailed enumerations than previous enumerations due to carbon contents (or constitutions).

Enumeration of alkanes of a given carbon content has been a long-standing problem for about 130 years since the first epoch (the 1870s and 1880s), when Cayley a mathematician investigated the enumeration of rooted trees[1] and trees.[2,3] It was a fortunate start that the mathematical term trees and the chemical term alkanes (or the term isomers represented by a formula C_kH_{2k+2}[1]) were recognized to be essentially equivalent, just as Cayley himself was aware that his enumeration of trees was applicable to chemical combinatorics.[2] Because of such interdisciplinary nature, many mathematicians and a greater number of chemists have been engaged in solving the problem. Earlier accomplishments of solving the problem have been summarized in a book on graph theory.[4] Among them, we should refer to chemists' work by Henze and Blair,[5,6] where alcohols (rooted trees) and alkanes (trees) were enumerated after the development of recursive formulas. As for a mathematical foundation linking between rooted trees (or alcohols or monosubstituted alkanes) and trees (or alkanes), Jordan's work[7] on the dichotomy of centroidal and bicentroidal trees should be cited because Cayley's accomplishments relied on this dichotomy.

The second epoch of solving the problem was brought forth in the 1930s by a mathematician Pólya,[8] where trees (as mathematical objects) or alkanes (as chemical objects) were regarded as graphs or constitutional isomers. After his accomplishment, there appeared several extensions of Pólya's theorem and many applications to various graph-theoretical problems related to the problem described above. Such work on graph theory has been summarized in books[4,9–12] and reviews.[13–16] Among them, mention should be made of several pioneering works for preparing the next stage (e.g., Otter[17] and Robinson et al.[18]).

The third epoch of solving the problem has been marked by Fujita[19,20] for the first decade of this century, where trees or alkanes were investigated as three-dimensional (3D) structures on the basis of Fujita's proligand method,[21–23] which was in turn developed by starting from Fujita's unit-subduced-cycle-index (USCI) approach.[24–28] Thus, the concepts of sphericities and sphericity indices, which were originally assigned to orbits (equivalence classes) in Fujita's USCI approach, were modified to be assigned to cycles; and then, the modified concepts were combined with the concepts of proligands and promolecules[29] so as to develop Fujita's proligand method. The merits of Fujita's proligand method have been discussed in comparison with Pólya's theorem in an article of his own.[30] Further applications of Fujita's proligand method to more detailed enumerations have been reported.[31–36]

In all of these enumerations, however, trees or alkanes have been itemized with respect to carbon contents only, whether they were regarded as graphs (cf. the 1st and 2nd epochs) or 3D structures (cf. the 3rd epoch). Although several attempts of counting 3D structures have appeared to take account of the numbers of asymmetric and pseudoasymmetric carbons in addition to carbon contents,[37,38] they are not applicable to the enumeration of graphs, because the pseudoasymmetry cannot be theoretically considered in graph enumeration.[8,12] As a result, there have appeared no attempts to develop a common and more detailed criterion for categorizing alkanes as 3D structures and as graphs.

This situation (the absence of such a common and more detailed criterion) is not restricted to the fields of enumeration related to the problem, but is widely found in organic chemistry. In fact, whether alkanes were regarded as graphs or 3D structures, they have been usually categorized into straight-chain and branched-chain alkanes, as found in most textbooks on organic chemistry.[39–41] After the branching of carbon skeletons is referred to as being quaternary (4°), tertiary (3°), secondary (2°), or primary (1°), such straight-chain alkanes were explained to construct a series of homologs and such branched-chain alkanes were described to be constitutional isomers of straight-chain alkanes. From a viewpoint of solving the problem described above, the descriptions of the textbooks on organic chemistry imply that the number N_k of alkanes of a given carbon content (k) has been obtained so as to show that there exist one straight-chain alkane and $N_k - 1$ branched-chain alkanes, where no (or at most a poor) categorization of the $N_k - 1$ branched-chain alkanes is realized. A more detailed categorization of alkanes has not been discussed to the best of our knowledge, except that several alkanes have been discriminated by means of the prefixes due to internal branching such as iso (e.g., isopentane) and neo (e.g., neopentane). Even in the latter exceptional cases, the degrees of branching at the carbons of a straight-chain or branched-chain alkane have not been employed as a systematic clue for categorizing alkanes.

In an accompanying paper that will appear in a future issue of this journal,[42] we have enumerated monosubstituted alkanes as 3D structures and as graphs, 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 (divergence). This means that the criterion "per divergence" commonly applicable to 3D structures and graphs has been developed as a more detailed criterion than "per constitution" (i.e., per carbon content). Because the data of monosubstituted alkanes can be reagarded as those of alkyl ligands, they are capable of providing us with a basis of a wide variety of applications. As a continuation of the paper, the present paper deals with the enumerations of alkanes as 3D structures and as graphs where the effect of internal branching is evaluated by using the branching indicators after the alkanes are categorized into centroidal and bicentroidal ones. Thus, the number of achiral and/or chiral alkanes 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 obtained as the coefficient of the term named a branching monomial, i.e., $q^{n_q} t^{n_t} s^{n_s} p^{n_p} x^k$.

Preformed Alkyl Moieties (PAMs) as Substituents

In previous papers,[20,38] we have reported combinatorial enumeration of centroidal and bicentroidal alkanes by following Fujita's proligand method.[21–23] In order to consider the effect of internal branching in such centroidal and bicentroidal alkanes, we should briefly discuss the concept of preformed alkyl moieties (PAMs), which has been developed to count primary, secondary, and tertiary monosubstituted alkanes in the previous paper.[42]

Preformed Alkyl Moieties (PAMs) to Centroidal Alkanes. This subsection is devoted to examine how the internal branching affects a process of incorporating preformed alkyl moieties (PAMs) into centroidal alkanes. It should be commented here that the dichotomy of centroidal and bicentroidal trees has been first noted by Jordan[7] for the purpose of categorizing trees as graphs. This dichotomy has been used to solve the problem of counting trees by Cayley[3] in the first epoch and has been also applied to the systemtic enumeration of trees by Pólya[8] in the second epoch. The same dichotomy has been used by Fujita[20] in the enumeration of trees (alkanes) as 3D structures in the third epoch.

Let us consider a centroidal alkane of carbon content $k = 11$ (**5**) shown in Figure 1, where the symbol © represents a centroid. According to Jordan,[7] the carbon content (m) of each branch incident to the centroid satisfies $m < k/2 = 5.5$. The centroidal alkane **5** is constructed by a substitution process in which a tetrahedral skeleton accommodates a set of alkyl ligands (branchs) generated from monosubstituted alkanes **1**–**4**. As found by comparing **5** with its components **1**–**4**, the degree of branching in each of the components **1**–**4** is promoted by one (0° → 1°, 1° → 2°, etc.) after incorporated in the centroidal alkane **5**. Note that **1** is an extreme case so as to be denoted by 0°.

To cope with such promotion, we shall adopt the concept of preformed alkyl moieties (PAMs), which has been developed in order to assure recursive nature in the enumeration of monosubstituted alkanes. Thus, PAMs **1′**–**4′** are employed as substituents in place of monosubstituted alkanes **1**–**4**. Thereby, the branching degree of the principal carbon in each PAM (e.g., **1′** etc.) is not changed after incorporation in a centroidal alkane (e.g., **5**). In other words, the hypothetical process represented by $\mathbf{1'} + \mathbf{2'} + \mathbf{3'} + \mathbf{4'} \rightarrow \mathbf{5}$ accompanies no change of branching degrees.

Preformed Alkyl Moieties (PAMs) to Bicentroidal Alkanes. Let us consider a bicentroidal alkane of carbon content $k = 8$ (**7**) shown in Figure 2, where the symbol ©–© represents a bicentroid. The bicentroidal alkane **7** is divided into two branchs of carbon content $m = k/2 = 4$ at the bond of the bicentroid in agreement with Jordan's formulation.[7] With respect to degrees of branching, the same situation as for centroidal alkanes holds true in the generation of bicentroidal alkanes, as exemplified in Figure 2. The primary carbon of **6** which is attached by an atom or ligand (Z) is promoted in advance to be secondary (2°), as shown in the resulting PAM **6′**. Then the PAM is incorporated into a bicentroidal alkane **7**, where no change of branching degrees occurs. The tertiary carbon of **4** is incorporated into **7** via a PAM **4′** so as to be promoted in advance, finally giving a quaternary carbon (4°). The resulting alkane **7** is characterized by a bicentroid ©–©, the respective terminals of which are the principal nodes of an isobutyl ligand (carbon content 4) and of a t-butyl ligand (carbon content 4).

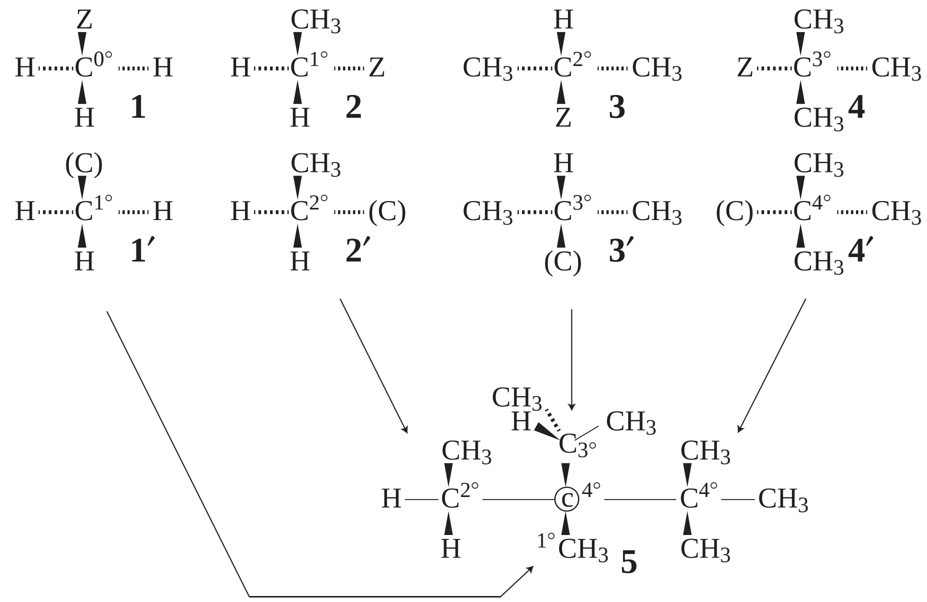


Figure 1. Degrees of branching (0°–4°) during the generation of a centroidal alkane **5**. Monosubstituted alkanes **1**–**4**, preformed alkyl moieties (PAMs, **1′**–**4′**), and a resulting centroidal alkane **5** during substitution are depicted. The degree of **1** is an extreme case so that it is tentatively denoted by the symbol 0°. The symbol © represents a centroid. Configurations are shown by wedged bonds and/or hashed dash bonds.

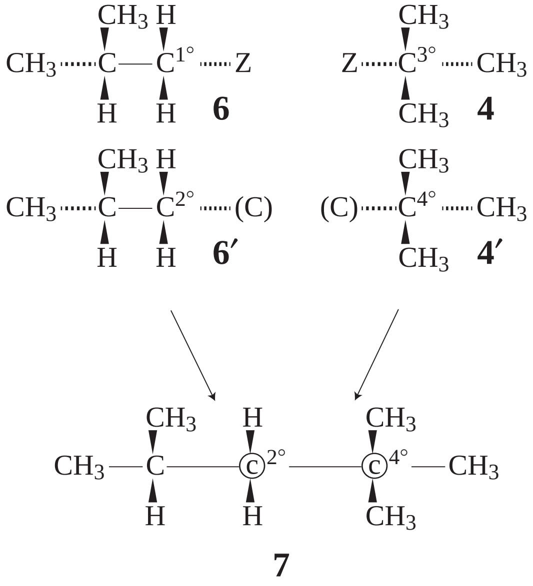


Figure 2. Degrees of branching during the generation of a bicentroidal alkane **7**. Monosubstituted alkanes **6** and **4**, preformed alkyl moieties (PAMs, **6′** and **4′**), and a resulting bicentroidal alkane **7** during substitution are depicted. The combined symbol ©–© represents a bicentroid. Configurations are shown by wedged bonds and/or hashed dash bonds.

Recursive Enumeration of Preformed Alkyl Moieties (PAMs). As exemplified by processes such as 2H + **1′** → **2′**, H + 2 × **1′** → **3′**, and 3 × **1′** → **4′** on the basis of a methyl skeleton (C_{3v}-symmetry), the generation of a PAM by starting from lower PAMs exhibits recursive nature with respect to degrees of branching as well as to carbon content. Note that the primary carbon (1°) in the starting PAM **1′** remains primary after it is incorporated into **2′**, **3′**, or **4′** (as an internal methyl ligand). In the next step of recursion, the resulting PAMs **2′**–**4′** as well as the starting PAM **1′** can be used to generate further PAMs of higher carbon content so that we are able to accomplish recursive generation of all PAMs.

More precisely speaking according to Fujita's proligand method[21–23] and its extension,[19,20] the recursiveness is concerned with the number of inequivalent achiral PAMs ($\alpha_{kn_qn_tn_sn_p}$), the number of inequivalent steric isomers of PAMs ($\beta_{kn_qn_tn_sn_p}$), and the number of inequivalent diploids of PAMs ($\gamma_{kn_qn_tn_sn_p}$), where each PAM of carbon content k has n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons ($k = n_q + n_t + n_s + n_p$ except an extreme case (CH_4)). For the terms "steric isomers" and "diploids," see Refs. 21–23.

By following Fujita's proligand method,[21–23] 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), where the number ($\alpha_{kn_qn_tn_sn_p}$, $\beta_{kn_qn_tn_sn_p}$, or $\gamma_{kn_qn_tn_sn_p}$) 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).

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

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

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

where the orders of the summations can be exchanged freely and where we put $\alpha_{00000} = \beta_{00000} = \gamma_{00000} = 1$ to treat the substitution of a hydrogen atom as an extreme case.

To evaluate the coefficients ($\alpha_{kn_qn_tn_sn_p}$, $\beta_{kn_qn_tn_sn_p}$, and $\gamma_{kn_qn_tn_sn_p}$) appearing in the generating functions (eqs 1–3), we should use the following functional equations:

$$\begin{aligned} a(x,q,t,s,p) &= 1 + xp + xs\{a(x,q,t,s,p) - 1\} \\ &\quad + xt\{c(x^2,q^2,t^2,s^2,p^2) - 1\} \\ &\quad + xq\{a(x,q,t,s,p) - 1\}\{c(x^2,q^2,t^2,s^2,p^2) - 1\} \end{aligned} \tag{4}$$

$$\begin{aligned} b(x,q,t,s,p) &= 1 + xp + xs\big\{b(x,q,t,s,p) - 1\big\} + xt\big\{b(x,q,t,s,p) - 1\big\}^2 \\ &\quad + \frac{xq}{3}\big\{[b(x,q,t,s,p) - 1]^3 + 2[b(x^3,q^3,t^3,s^3,p^3) - 1]\big\} \end{aligned} \tag{5}$$

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

where the first term (1) is added to treat a trivial case (a hydrogen atom) and the second term (xp or x^2p^2) is added to evaluate the contribution of a methyl ligand. These functional equations have been noted in the accompanying paper.[42] When the functions $a(x,q,t,s,p)$, $c(x^2,q^2,t^2,s^2,p^2)$, and $b(x,q,t,s,p)$ have been evaluated up to carbon content k in the form of series shown in eqs 1–3, these series are introduced into the right-hand sides of the functional equations (eqs 4–6) so that the resulting coefficients for carbon content $k+1$ are added to eqs 1–3 as the next terms. This process is repeated by increasing the carbon content k so as to construct eqs 1–3 stepwise.

Enumeration of Alkanes as 3D Structures

Enumeration of Centroidal Alkanes. According to the scheme for constructing centroidal alkanes (Subsection: **Preformed Alkyl Moieties (PAMs) to Centroidal Alkanes**), we shall first select respective skeletons for evaluating the degrees of branching. Then we shall derive functional equations for the substitution of PAMs on the basis of the selected skeletons.

Skeletons for Counting Centroidal Alkanes: Let the symbol $\widehat{A}_{kn_qn_tn_sn_p}$ be the number of inequivalent achiral alkanes of centroidal type, where k carbons in each alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons ($k = n_q + n_t + n_s + n_p$ except an extreme case ($\mathrm{CH_4}$)); the symbol $\widehat{C}_{kn_qn_tn_sn_p}$ be the number of inequivalent chiral alkanes of centroidal type under a similar categorization, where each pair of enantiomers is counted just once; and the symbol $\widehat{B}_{kn_qn_tn_sn_p}$ be the total number of inequivalent alkanes of centroidal type under a similar categorization, where each achiral 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:

$$\widehat{A}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{A}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^{k} \tag{7}$$

$$\widehat{C}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{C}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^{k} \tag{8}$$

$$\widehat{B}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{B}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^{k} \tag{9}$$

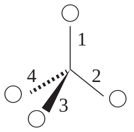
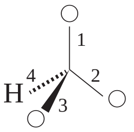
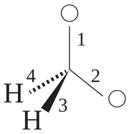
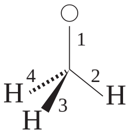
Because the generating functions for PAMs (eqs 1–3) have been already evaluated by using the functional equations (eqs 4–6),[42] we are able to derive the generating functions (eqs 7–9) by starting from eqs 1–3, where we adopt the idea described in Subsection: **Preformed Alkyl Moieties (PAMs) to Centroidal Alkanes**. To do this task, we should derive functional equations for generating such generating functions as eqs 7–9.

The task of the present section is to derive such functional equations for producing these generating functions (eqs 7–9), in which the number $\widehat{A}_{kn_qn_tn_sn_p}$, $\widehat{C}_{kn_qn_tn_sn_p}$, or $\widehat{B}_{kn_qn_tn_sn_p}$ appears as the coefficient of the term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$. It should be emphasized that categorization with respect to degrees of branching ("divergence") is a new matter to be investigated.

In the present enumeration, we use the term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$ or $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$, which is called a branching monomial (BM). Note that the component x^k can be omitted because we put $k = n_q + n_t + n_s + n_p$ except an extreme case ($\mathrm{CH_4}$). Hereafter, the exception of $\mathrm{CH_4}$ will be omitted in the description of the partition represented by $k = n_q + n_t + n_s + n_p$ if it is adequate for the sake of simplicity. For the purpose of qualitative discussions, it is convenient to introduce a symbol for indicating "a mode of divergence," which is defined to be a partition of carbon content k, i.e., [n_q, n_t, n_s, and n_p] in accord with the corresponding BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$. Thereby, an alkane (as a 3D structure or as a graph) is characterized by a BM $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$ or a mode of divergence [n_q, n_t, n_s, and n_p].

Such degrees of branching (divergence) have not been taken into consideration, although combinatorial enumeration of centroidal and bicentroidal alkanes as 3D structures (3D trees) was investigated as stereochemical models of alkanes

Table 1. Skeletons for Generating Centroidal Alkanes as 3D Structures (or 3D Trees) with a Quaternary, Tertiary, Secondary, or Primary Centroid[a)]

Skeletons for centroidal alkanes		Cycle index with chirality fittingness		
(as 3D trees)	CR	(CI-CF)		
 **8**	Quaternary (4°) $T_d(/C_{3v})$	Achiral	$\frac{1}{2}(a_1^2c_2 + c_4)$	(10)
		Chiral	$\frac{1}{24}(b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 - 6c_4)$	(11)
		Total	$\frac{1}{24}(b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4)$	(12)
 **9**	Tertiary (3°) $C_{3v}(/C_s)$	Achiral	a_1c_2	(13)
		Chiral	$\frac{1}{6}(b_1^3 + 2b_3 - 3a_1c_2)$	(14)
		Total	$\frac{1}{6}(b_1^3 + 2b_3 + 3a_1c_2)$	(15)
 **10**	Secondary (2°) $C_{2v}(/C_s)$	Achiral	$\frac{1}{2}(a_1^2 + c_2)$	(16)
		Chiral	$\frac{1}{4}(b_1^2 + b_2 - a_1^2 - c_2)$	(17)
		Total	$\frac{1}{4}(b_1^2 + b_2 + a_1^2 + c_2)$	(18)
 **11**	Primary (1°) $C_{3v}(/C_{3v})$	Achiral	a_1	(19)
		Chiral	$\frac{1}{2}(b_1 - a_1)$	(20)
		Total	$\frac{1}{2}(b_1 + a_1)$	(21)

a) The corresponding cycle indices with chirality fittingness (CI-CFs) are listed. Each substitution position represented by the symbol ○ accommodates a preformed alkyl moiety (PAM).

in a previous paper.[20] In fact, a tetrahedral skeleton of T_d-symmetry was solely considered to be substituted by a set of substituents selected from hydrogen and alkyl ligands. In other words, the substitution of hydrogens was discussed on the same line as the substitution of alkyl ligands.

In order to take account of such degrees of branching, it is a crux to differentiate the substitution of hydrogens from the substitution of alkyl ligands, where the alkyl ligands are selected from such PAMs as described above. It follows that we should modify the tetrahedral skeleton of T_d-symmetry into respective skeletons belonging to its subgroups, which correspond to quaternary (**8**), tertiary (**9**), secondary (**10**), and primary cases (**11**), as shown in Table 1. These skeletons have been generated by stepwise substitutions of a hydrogen atom by starting the skeleton **8**. In addition, such a extreme case as methane (CH_4) should be taken into consideration. Note that the intersection of four valence bonds in each of the skeletons **8**–**11** represents a centroidal carbon atom, although the symbol © is omitted.

The quaternary skeleton **8** belongs to T_d-symmetry, where the four substitution positions (○) are governed by a coset representation $T_{2d}(/C_{3v})$. According to Fujita's USCI approach[24–28] or to Fujita's proligand method,[21–23] the corresponding cycle index with chirality fittingness (CI-CF) is obtained to be eq 12 shown in Table 1, which has been already noted in Ref. 20 (eq 1). By collecting the terms relevant to the rotoreflections appearing in eq 12 and then multiplying by two, we are able to obtain the CI-CF (eq 10) for counting achiral quaternary alkanes. The CI-CF (eq 10) has been already noted in a different context (eq 3 of Ref. 20). The CI-CF (eq 10) for counting chiral quaternary alkanes is obtained from eq 12 by changing the plus signs of the terms relevant to the rotoreflections into minus signs. The CI-CF (eq 10) is identical to eq 4 of Ref. 20. As a matter of course, the summation of eqs 10 and 11 provides eq 12. It should be noted that the present equations (eqs 10–12) do not allow the substitution of hydrogen atoms, while the equations of Ref. 20 (eqs 1, 3, and 4) allow the substitution of hydrogen atoms.

The sphericity indices appearing in eqs 10–12 (i.e., a_d for a homospheric cycle, c_d for an enantiospheric cycle, and b_d for a hemispheric cycle) are replaced by the respective functions, $a(x^d, q^d, t^d, s^d, p^d)$, $c(x^d, q^d, t^d, s^d, p^d)$, and $b(x^d, q^d, t^d, s^d, p^d)$, which have been recursively calculated by using eqs 4–6. Note that eqs 4–6 are obtained to be such generating functions as eqs 1–3. Thereby, eqs 10–12 are converted into the following functions for evaluating the generation of quaternary centroidal alkanes:

$$\text{achiral:} \quad \frac{xq}{2}\{[a(x,q,t,s,p) - 1]^2[c(x^2,q^2,t^2,s^2,p^2) - 1] + [c(x^4,q^4,t^4,s^4,p^4) - 1]\} \tag{22}$$

$$\begin{aligned}\text{chiral:}\quad & \frac{xq}{24}\{[b(x,q,t,s,p)-1]^4+3[b(x^2,q^2,t^2,s^2,p^2)-1]^2\\ & +8[b(x,q,t,s,p)-1][b(x^3,q^3,t^3,s^3,p^3)-1]\\ & -6[a(x,q,t,s,p)-1]^2[c(x^2,q^2,t^2,s^2,p^2)-1]\\ & -6[c(x^4,q^2,t^4,s^4,p^4)-1]\} \qquad (23)\end{aligned}$$

$$\begin{aligned}\text{total:}\quad & \frac{xq}{24}\{[b(x,q,t,s,p)-1]^4+3[b(x^2,q^2,t^2,s^2,p^2)-1]^2\\ & +8[b(x,q,t,s,p)-1][b(x^3,q^3,t^3,s^3,p^3)-1]\\ & +6[a(x,q,t,s,p)-1]^2[c(x^2,q^2,t^2,s^2,p^2)-1]\\ & +6[c(x^4,q^2,t^4,s^4,p^4)-1]\} \qquad (24)\end{aligned}$$

where the subtraction of 1 in each pair of brackets is to eliminate the substitution of a hydrogen atom. The multiplication of the term *xq* indicates an increase of carbon content by one (x^1), which corresponds to the increase of one quaternary carbon q^1 as a centroid.

The tertiary skeleton **9** belongs to C_{3v}-symmetry, where the three substitution positions (○) are governed by a coset representation $C_{3v}(/C_s)$. The corresponding CI-CFs are calculated to give eqs 13–15, which are essentially equivalent to eqs 4, 5, and 2 of Ref. 19 except that the present equations (eqs 13–15) do not allow the substitution of hydrogens.

The sphericity indices (a_d, c_d, and b_d) appearing in eqs 13–15 are replaced by the functions $a(x^d,q^d,t^d,s^d,p^d)$, $c(x^d,q^d,t^d,s^d,p^d)$, and $b(x^d,q^d,t^d,s^d,p^d)$. Thereby, the CI-CFs (eqs 13–15) are converted into the following functions for evaluating the generation of tertiary centroidal alkanes:

$$\text{achiral:}\quad xt[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1] \qquad (25)$$

$$\begin{aligned}\text{chiral:}\quad & \frac{xt}{6}\{[b(x,q,t,s,p)-1]^3+2[b(x^3,q^3,t^3,s^3,p^3)-1]\\ & -3[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1]\} \qquad (26)\end{aligned}$$

$$\begin{aligned}\text{total:}\quad & \frac{xt}{6}\{[b(x,q,t,s,p)-1]^3+2[b(x^3,q^3,t^3,s^2,p^3)-1]\\ & +3[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1]\} \qquad (27)\end{aligned}$$

where the subtraction of 1 in each pair of brackets is to eliminate the substitution of a hydrogen atom. The multiplication of the term *xt* indicates an increase of carbon content by one (x^1), which corresponds to the increase of one tertiary carbon t^1 as a centroid. The functions appearing in the right-hand sides of eqs 25–27 have been recursively calculated by using eqs 4–6.

The secondary skeleton **10** belongs to C_{2v}-symmetry, where the two substitution positions (○) are governed by a coset representation $C_{2v}(/C_s)$. According to Fujita's USCI approach,[27] the $C_{2v}(/C_s)$-row and the "sum" row of the USCI-CF table (Table E.5 in the Appendix E of Ref. 27) are combined to give the CI-CF (eq 18) shown in Table 1. According to Fujita's proligand method,[21–23] on the other hand, the coset representation, $C_{2v}(/C_s)=\{(1)(2),(1\ 2),\overline{(1)(2)},\overline{(1\ 2)}\}$, corresponds to a set of products of sphericity indices, i.e., b_1^2, b_2, a_1^2, and c_2, which are summed up and averaged by multiplying 1/4 so as to give the same CI-CF (eq 18). By collecting and averaging the products of sphericity indices corresponding to improper rotations (i.e., a_1^2 and c_2), we are able to obtain eq 16 for counting achiral secondary alkanes. By subtracting eq 16 from eq 18, we can obtain eq 17 for counting chiral secondary alkanes.

The sphericity indices (a_d, c_d, and b_d) appearing in eqs 16–18 are replaced by the functions $a(x^d,q^d,t^d,s^d,p^d)$, $c(x^d,q^d,t^d,s^d,p^d)$, and $b(x^d,q^d,t^d,s^d,p^d)$. Thereby, the CI-CFs (eqs 16–18) are converted into the following functions for evaluating the generation of secondary centroidal alkanes:

$$\text{achiral:}\quad \frac{xs}{2}\{[a(x,q,t,s,p)-1]^2+[c(x^2,q^2,t^2,s^2,p^2)-1]\} \qquad (28)$$

$$\begin{aligned}\text{chiral:}\quad & \frac{xs}{4}\{[b(x,q,t,s,p)-1]^2+[b(x^2,q^2,t^2,s^2,p^2)-1]\\ & -[a(x,q,t,s,p)-1]^2-[c(x^2,q^2,t^2,s^2,p^2)-1]\} \qquad (29)\end{aligned}$$

$$\begin{aligned}\text{total:}\quad & \frac{xs}{4}\{[b(x,q,t,s,p)-1]^2+[b(x^2,q^2,t^2,s^2,p^2)-1]\\ & +[a(x,q,t,s,p)-1]^2+[c(x^2,q^2,t^2,s^2,p^2)-1]\} \qquad (30)\end{aligned}$$

where the subtraction of 1 in each pair of brackets is to eliminate the substitution of a hydrogen atom. The multiplication of the term *xs* indicates an increase of carbon content by one (x^1), which corresponds to the increase of one secondary carbon s^1. The functions appearing in the right-hand sides (eqs 28–30) have been recursively calculated by using eqs 4–6.

The primary skeleton **11** belongs to C_{3v}-symmetry, where the one substitution positions (○) is governed by a coset representation $C_{3v}(/C_{3v})$. According to Fujita's USCI approach,[27] the $C_{3v}(/C_{3v})$-row and the "sum" row of the USCI-CF table (Table E.7 in the Appendix E of Ref. 27) are combined to give the CI-CF (eq 21) shown in Table 1. The same CI-CF as eq 21 can be alternative derived according to Fujita's proligand method.[21–23] Thus, the coset representation, $C_{3v}(/C_{3v})=\{(1),(1),\overline{(1)},\overline{(1)}\}$, corresponds to a set of products of sphericity indices, i.e., b_1, b_1, a_1, and a_1, which are summed up and averaged by multiplying 1/4 so as to give eq 21. By collecting and averaging the products of sphericity indices corresponding to improper rotations (i.e., a_1 and a_1), we are able to obtain eq 19 for counting achiral primary alkanes. By subtracting eq 19 from eq 21, we can obtain eq 20 for counting chiral primary alkanes.

The sphericity indices (a_d, c_d, and b_d) appearing in eqs 19–21 are replaced by the functions $a(x^d,q^d,t^d,s^d,p^d)$, $c(x^d,q^d,t^d,s^d,p^d)$, and $b(x^d,q^d,t^d,s^d,p^d)$. Thereby, the CI-CFs (eqs 19–21) are converted into the following functions for evaluating the generation of primary centroidal alkanes:

$$\text{achiral:}\quad xp[a(x,q,t,s,p)-1] \qquad (31)$$

$$\text{chiral:}\quad \frac{xp}{2}\left\{[b(x,q,t,s,p)-1]-[a(x,q,t,s,p)-1]\right\} \qquad (32)$$

$$\text{total:}\quad \frac{xp}{2}\left\{[b(x,q,t,s,p)-1]+[a(x,q,t,s,p)-1]\right\} \qquad (33)$$

where the subtraction of 1 in each pair of brackets is to eliminate the substitution of a hydrogen atom. The multiplication of the term xp at the top of each function (eqs 31–33) indicates an increase of carbon content by one (x^1), which is accompanied with the increase of one primary carbon p^1 as a centroid. The functions appearing in the right-hand sides of eqs 31–33 have been recursively calculated by using eqs 4–6. It should be noted, however, that the participation of eqs 31–33 is not realized even if they are incorporated in the functional equations to be derived. In other words, the participation of eqs 31–33 is automatically eliminated during the calculation processes of centroidal alkanes because of their definition.

Functional Equations for Counting Centroidal Alkanes: By summing up eqs 22, 25, 28, and 31 and by adding the term x for treating an extreme case (methane), we arrive at a functional equation for counting achiral centroidal alkanes:

$$\begin{aligned}
&\widehat{A}(x,q,t,s,p)\\
&\quad = x + xp[a(x,q,t,s,p)-1]\\
&\qquad + \frac{xs}{2}\{[a(x,q,t,s,p)-1]^2 + [c(x^2,q^2,t^2,s^2,p^2)-1]\}\\
&\qquad + xt[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad + \frac{xq}{2}\Big\{[a(x,q,t,s,p)-1]^2[c(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad + [c(x^4,q^4,t^4,s^4,p^4)-1]\Big\} \qquad (34)
\end{aligned}$$

This functional equation can be used to calculate the generating function represented by eq 7, where the branching degree of each internal carbon is taken into consideration.

The summing-up of eqs 23, 26, 29, and 32 produces a functional equation for counting chiral centroidal alkanes:

$$\begin{aligned}
&\widehat{C}(x,q,t,s,p)\\
&\quad = \frac{xp}{2}\Big\{[b(x,q,t,s,p)-1] - [a(x,q,t,s,p)-1]\Big\}\\
&\qquad + \frac{xs}{4}\{[b(x,q,t,s,p)-1]^2 + [b(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad - [a(x,q,t,s,p)-1]^2 - [c(x^2,q^2,t^2,s^2,p^2)-1]\}\\
&\qquad + \frac{xt}{6}\{[b(x,q,t,s,p)-1]^3 + 2[b(x^3,q^3,t^3,s^3,p^3)-1]\\
&\qquad - 3[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1]\}\\
&\qquad + \frac{xq}{24}\{[b(x,q,t,s,p)-1]^4 + 3[b(x^2,q^2,t^2,s^2,p^2)-1]^2\\
&\qquad + 8[b(x,q,t,s,p)-1][b(x^3,q^3,t^3,s^3,p^3)-1]\\
&\qquad - 6[a(x,q,t,s,p)-1]^2[c(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad - 6[c(x^4,q^2,t^4,s^4,p^4)-1]\} \qquad (35)
\end{aligned}$$

where the branching degree of each internal carbon is taken into consideration. This functional equation can be used to calculate the generating function represented by eq 8. According to the present formulation, each pair of enantiomers is counted just once, just as each achiral alkane is counted once.

By summing up eqs 24, 27, 30, and 33, we arrive at a functional equation for counting total (achiral plus chiral) centroidal alkanes:

$$\begin{aligned}
&\widehat{B}(x,q,t,s,p)\\
&\quad = x + \frac{xp}{2}\Big\{[b(x,q,t,s,p)-1] + [a(x,q,t,s,p)-1]\Big\}\\
&\qquad + \frac{xs}{4}\{[b(x,q,t,s,p)-1]^2 + [b(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad + [a(x,q,t,s,p)-1]^2 + [c(x^2,q^2,t^2,s^2,p^2)-1]\}\\
&\qquad + \frac{xt}{6}\{[b(x,q,t,s,p)-1]^3 + 2[b(x^3,q^3,t^3,s^3,p^3)-1]\\
&\qquad + 3[a(x,q,t,s,p)-1][c(x^2,q^2,t^2,s^2,p^2)-1]\}\\
&\qquad + \frac{xq}{24}\{[b(x,q,t,s,p)-1]^4 + 3[b(x^2,q^2,t^2,s^2,p^2)-1]^2\\
&\qquad + 8[b(x,q,t,s,p)-1][b(x^3,q^3,t^3,s^3,p^3)-1]\\
&\qquad + 6[a(x,q,t,s,p)-1]^2[c(x^2,q^2,t^2,s^2,p^2)-1]\\
&\qquad + 6[c(x^4,q^2,t^4,s^4,p^4)-1]\} \qquad (36)
\end{aligned}$$

where the term x is added to treat an extreme case (methane). This functional equation can be used to calculate the generating function represented by eq 9, where the branching degree of each internal carbon is taken into consideration.

Obviously, eqs 34–36 satisfy the following relationship:

$$\widehat{B}(x,q,t,s,p) = \widehat{A}(x,q,t,s,p) + \widehat{C}(x,q,t,s,p) \qquad (37)$$

In accord with this equation, the coefficients of the term $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$ appearing in eqs 7–9 satisfy the following relationship:

$$\widehat{B}_{kn_qn_tn_sn_p} = \widehat{A}_{kn_qn_tn_sn_p} + \widehat{C}_{kn_qn_tn_sn_p} \qquad (38)$$

where we put $k = n_q + n_t + n_s + n_p$ except an extreme case (CH_4).

Our target is to evaluate eqs 34–36 by using eqs 4–6 under the criterion for counting centroidal alkanes as 3D structures (3D trees). To pursue the target, we are able to focus our attention on the stepwise increase of carbon content k without the explicit consideration of n_q, n_t, n_s, and n_p, because we put $k = n_q + n_t + n_s + n_p$. Hence, the methodology described in a previous paper[34] is adopted here after slight modification due to branching indicators. Let examine the coefficient of the term x^k appearing in series generated from eq 34, 35, or 36. The criterion for specifying centroidal alkanes (3D trees) means that the maximum number (m), which is the number of non-terminal vertices in the largest PAM, is restricted to satisfy the following condition:

$$\frac{1}{2}k - 1 \le m < \frac{1}{2}k \qquad (39)$$

or equivalently

$$2m < k \le 2m + 2 \qquad (40)$$

It should be noted that the coefficient of the term x^k is a polynomial composed of branching indicators (q, t, s, and p) and that the numbers k and m can be selected as numbers common to every monomials contained in the polynomial in accord with the relationship $k = n_q + n_t + n_s + n_p$ and with a relevant relationship concerning m (eq 40).

Suppose that eqs 4–6 have been evaluated up to the term x^m so that eqs 1–3 are represented as follows:

$$a(x,q,t,s,p)^{(m)} = \sum_{k=0}^{m}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\alpha_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{41}$$

$$b(x,q,t,s,p)^{(m)} = \sum_{k=0}^{m}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\beta_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{42}$$

$$c(x^2,q^2,t^2,s^2,p^2)^{(m)} = \sum_{k=0}^{m}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\gamma_{kn_qn_tn_sn_p}p^{2n_p}\right)s^{2n_s}\right)t^{2n_t}\right)q^{2n_q}\right)x^{2k} \tag{43}$$

where the superscript (m) represents the use of eqs 1–3 by fixing m. The upper limits for n_q, n_t, n_s, and n_p are specified to be infinite but practically to be m because we put $k = n_q + n_t + n_s + n_p$ where k runs from 0 to m. After m is tentatively fixed, eqs 41–43 are introduced into the right-hand sides of eqs 34–36. Then the resulting equations are expanded to give respective series for $\widehat{A}(x,q,t,s,p)^{(m)}$ (cf. eq 7), $\widehat{C}(x,q,t,s,p)^{(m)}$ (cf. eq 8), and $\widehat{B}(x,q,t,s,p)^{(m)}$ (cf. eq 9), where the superscript (m) represents the use of eqs 41–43 by fixing m. In accord with eq 40, the coefficients of the terms x^{2m+1} and x^{2m+2} in the series are effective to determine $\widehat{A}_{2m+1,n_qn_tn_sn_p}$ and $\widehat{A}_{2m+2,n_qn_tn_sn_p}$; $\widehat{C}_{2m+1,n_qn_tn_sn_p}$ and $\widehat{C}_{2m+2,n_qn_tn_sn_p}$; as well as $\widehat{B}_{2m+1,n_qn_tn_sn_p}$ and $\widehat{B}_{2m+2,n_qn_tn_sn_p}$. The operator "coeff" is used to select the coefficient of the term x^k contained in a counting series $f(x)$, e.g., $\mathrm{coeff}(f(x),x^k)$. Let the symbol $\widehat{A}_{2m+1}(q,t,s,p)$ be the coefficient polynomial of the term x^{2m+1} appearing in $\widehat{A}(x,q,t,s,p)^{(m)}$, and so on. Thereby, we obtain the following equations for evaluating such coefficients as polynomials composed of branching indicators (q, t, s, and p):

$$\begin{aligned}\widehat{A}_{2m+1}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{A}_{2m+1,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{A}(x,q,t,s,p)^{(m)},x^{2m+1})\end{aligned} \tag{44}$$

$$\begin{aligned}\widehat{C}_{2m+1}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{C}_{2m+1,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{C}(x,q,t,s,p)^{(m)},x^{2m+1})\end{aligned} \tag{45}$$

$$\begin{aligned}\widehat{B}_{2m+1}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{B}_{2m+1,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{B}(x,q,t,s,p)^{(m)},x^{2m+1})\end{aligned} \tag{46}$$

for odd carbon contents where we put $2m+1 = n_q + n_t + n_s + n_p$. The upper limits for n_q, n_t, n_s, and n_p are specified to be infinite but practically to be $2m+1$.

On a similar line, we obtain the following coefficients:

$$\begin{aligned}\widehat{A}_{2m+2}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{A}_{2m+2,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{A}(x,q,t,s,p)^{(m)},x^{2m+2})\end{aligned} \tag{47}$$

$$\begin{aligned}\widehat{C}_{2m+2}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{C}_{2m+2,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{C}(x,q,t,s,p)^{(m)},x^{2m+2})\end{aligned} \tag{48}$$

$$\begin{aligned}\widehat{B}_{2m+2}(q,t,s,p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{B}_{2m+2,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\ &= \mathrm{coeff}(\widehat{B}(x,q,t,s,p)^{(m)},x^{2m+2})\end{aligned} \tag{49}$$

for even carbon contents where we put $2m+2 = n_q + n_t + n_s + n_p$. The upper limits for n_q, n_t, n_s, and n_p are specified to be infinite but practically to be $2m+2$.

Implementation and Results for Centroidal Alkanes: Because the functional equations represented by $a(x,q,t,s,p)$ (eq 4), $b(x,q,t,s,p)$ (eq 5), and $c(x^2,q^2,t^2,s^2,p^2)$ (eq 6) exhibit recursiveness, they are evaluated stepwise by increasing carbon content k one by one. When we have calculated up to $k = m$, the resulting intermediate series are introduced into eqs 34–36. Then the resulting functions $\widehat{A}(x,q,t,s,p)^{(m)}$ (cf. eq 7), $\widehat{C}(x,q,t,s,p)^{(m)}$ (cf. eq 8), and $\widehat{B}(x,q,t,s,p)^{(m)}$ (cf. eq 9) are examined according to eqs 44–46 and eqs 47–49. Thereby, the coefficients of x^{2m+1} and x^{2m+2} are picked up in the forms of polynomials concerning branching indicators (q, t, s, and p), i.e., $\widehat{A}_{2m+1}(q,t,s,p)$ (eq 44) and $\widehat{A}_{2m+2}(q,t,s,p)$ (eq 47) for achiral centroidal alkanes (3D trees); $\widehat{C}_{2m+1}(q,t,s,p)$ (eq 45) and $\widehat{C}_{2m+2}(q,t,s,p)$ (eq 48) for chiral centroidal alkanes (3D trees); and $\widehat{B}_{2m+1}(q,t,s,p)$ (eq 46) and $\widehat{B}_{2m+2}(q,t,s,p)$ (eq 49) for total (achiral plus chiral) centroidal alkanes (3D trees).

To exemplify recursive processes based on the functional equations (eqs 4–6) and subsequent non-recursive processes based on the functional equations (eqs 34–36), let us examine the case in which m is tentatively fixed to be 4. Suppose that eqs 4–6 for counting PAMs have been calculated up to carbon content 4 as follows:

$$\begin{aligned}a(x,q,t,s,p)^{(4)} &= 1 + px + spx^2 + (s^2p + tp^2)x^3\\ &\quad + (s^3p + tsp^2 + qp^3)x^4\end{aligned} \tag{50}$$

$$\begin{aligned}b(x,q,t,s,p)^{(4)} &= 1 + px + spx^2 + (s^2p + tp^2)x^3\\ &\quad + (s^3p + 3\,tsp^2 + qp^3)x^4\end{aligned} \tag{51}$$

$$\begin{aligned}c(x^2,q^2,t^2,s^2,p^2)^{(4)} &= 1 + p^2x^2 + s^2p^2x^4 + (s^4p^2 + t^2p^4)x^6 +\\ &\quad + (s^6p^2 + 3\,t^2s^2p^4 + q^2p^6)x^8\end{aligned} \tag{52}$$

These equations correspond to eqs 41–43 when we put $m = 4$. These equations (eqs 50–52) are introduced into eq 34 and the resulting functional equation $\widehat{A}(x,q,t,s,p)^{(4)}$ is expanded to give the following generating function:

$$
\begin{aligned}
&\widehat{A}(x,q,t,s,p)^{(4)} \\
&\quad = \ldots + \left\{\left(2\,q^2 s + q t^2\right)p^6 + \left(t^3 s + 5\,q t s^2\right)p^5 \right. \\
&\qquad \left. + \left(3\,t^2 s^3 + 5\,q s^4\right)p^4 + 3\,t s^5 p^3 + s^7 p^2\right\}x^9 \\
&\qquad\quad + \{2\,q^2 t p^7 + \left(2\,q^2 s^2 + t^4 + 2\,q t^2 s\right)p^6 + \left(4\,t^3 s^2 + 4\,q t s^3\right)p^5 \\
&\qquad\qquad + \left(t^2 s^4 + 4\,q s^5\right)p^4 + 2\,t s^6 p^3\}x^{10} + \ldots
\end{aligned}
\tag{53}
$$

The expansion to give the right-hand side of eq 53 may be manually cumbersome but can be easily conducted by using such personal computer software as the Maple system. In eq 53, the coefficients of the terms x^9 $(9 = 2 \times 4 + 1)$ and x^{10} $(10 = 2 \times 4 + 2)$ are shown because they are effective at this step of calculation according to eqs 44 and 47. As a result, the generating function (eq 7) turns out to be evaluated up to 10.

This procedure is implemented by mean of the Maple programming language as follows. Although the upper limit of the carbon content (k) in the present recursive process is tentatively fixed to be 15, we are able to obtain the data of centroidal alkanes up to 32. The limit can be freely selected as far as the capacity of the computer permits.

```
#AlkaneBI02.mpl
#Centroidal Alkanes by Considering Internal Branching

"(Part 1) Functional Equations for Inner Alkyl Ligands
(Preformed Alkyl Moieties)";
# hydrogen and internal alkyls
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) Functional Equations for Alkanes
as Centroidal 3D Structures";
#an extreme case, primary, secondary, tertiary, quaternary
Axbi := x + x*p*(a1-1) + (x*s/2)*((a1-1)^2 + (c2-1))
    + (x*t)*(a1-1)*(c2-1)
    + (x*q/2)*((a1-1)^2*(c2-1) + (c4-1));
Cxbi := (x*p/2)*((b1-1) - (a1-1))
    + (x*s/4)*((b1-1)^2 + (b2-1) - (a1-1)^2 - (c2-1))
    + (x*t/6)*((b1-1)^3 + 2*(b3-1) - 3*(a1-1)*(c2-1))
    + (x*q/24)*((b1-1)^4 + 3*(b2-1)^2 + 8*(b1-1)*(b3-1)
              - 6*(a1-1)^2*(c2-1) - 6*(c4-1));
Bxbi := x + (x*p/2)*((b1-1) + (a1-1))
    + (x*s/4)*((b1-1)^2 + (b2-1) + (a1-1)^2 + (c2-1))
    + (x*t/6)*((b1-1)^3 + 2*(b3-1) + 3*(a1-1)*(c2-1))
    + (x*q/24)*((b1-1)^4 + 3*(b2-1)^2 + 8*(b1-1)*(b3-1)
              + 6*(a1-1)^2*(c2-1) + 6*(c4-1));

#(Part 3) Validity Check
ValidityCheck:= expand(Axbi + Cxbi - Bxbi);

"(Part 4) Initial Values";
a1 := 1;
c2 := 1; c4 := 1; c6 := 1;
b1 := 1; b2 := 1; b3 := 1;
Abi := x; Cbi := 0; Bbi := x;

"(Part 5) Recursive Calculation";
kmax := 15;
for k from 1 to kmax by 1 do
"k ="; 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))):
b1 := b1 + Cbx*x^k;
b2 := b2 + Cb2x*x^(2*k);
b3 := b3 + Cb3x*x^(3*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))));
c2 := c2 + Ccx*x^(2*k):
c4 := c4 + Cc2x*x^(4*k):
c6 := c6 + Cc3x*x^(6*k):

"(Part 8) Achiral":
Cax:= expand(coeff(ax,x^k)):
a1 := a1 + Cax*x^k:

#(Part 9) Centroidal Alkanes
kk := 2*k +1:
Abi := Abi + coeff(expand(Axbi),x^kk)*x^kk
          + coeff(expand(Axbi),x^(kk+1))*x^(kk+1):
Cbi := Cbi + coeff(expand(Cxbi),x^kk)*x^kk
          + coeff(expand(Cxbi),x^(kk+1))*x^(kk+1):
Bbi := Bbi + coeff(expand(Bxbi),x^kk)*x^kk
          + coeff(expand(Bxbi),x^(kk+1))*x^(kk+1):

##"Validity Check";
#CheckB := expand(Bbi - Abi - Cbi);
end do:

#(Part 10) Print-Out
"Print Out of Abi (Achiral)";
for k from 1 to 2*kmax by 1 do
carbon_content:= k:
NAbi := collect(sort(expand(coeff(Abi,x^k)),[q,t,s,p]),p);
end do;

"Print Out of Abi (Chiral)";
for k from 1 to 2*kmax by 1 do
carbon_content:= k:
NCbi := collect(sort(expand(coeff(Cbi,x^k)),[q,t,s,p]),p);
end do;

"Print Out of Bbi (Chiral + Achiral)";
for k from 1 to 2*kmax by 1 do
carbon_content:= k:
NBbi := collect(sort(expand(coeff(Bbi,x^k)),[q,t,s,p]),p);
end do;
```

In this program named "AlkaneBI02.mpl," the abbreviated symbols for functional equations are used as follows: `a1` for $a(x,q,t,s,p)$, `b1` for $b(x,q,t,s,p)$, `c2` for $c(x^2,q^2,t^2,s^2,p^2)$, and so on, which serve as series for storing the stepwise data of PAMs.

The first part (Part 1) of this program declares three functional equations `ax` for eq 4, `bx` for eq 5, and `cx` for eq 6, which are recursively calculated by using `a1`, `b1`, `c2`, and so on. The second part (Part 2) declares three functional equations, i.e., `Axbi` for $\widehat{A}(x,q,t,s,p)$ (eq 34), `Cxbi` for $\widehat{C}(x,q,t,s,p)$ (eq 35), and `Bxbi` for $\widehat{A}(x,q,t,s,p)$ (eq 36), which exhibit no recursive nature. Part 3 is inserted to check the validity of `Axbi`, `Cxbi`, and `Bxbi`. In Part 4 ("Initial Values"), the initial values are set for the initial (trivial) PAMs, and so on. Part 5 ("Recursive Calculation") of the program shows a `do` loop with respect to carbon content k, in which Parts 6–8 provide recursive processes for counting 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. Part 9 serves as warehouses for the data of centroidal alkanes, i.e., `Abi` for storing the results of $\widehat{A}(x,q,t,s,p)$ (cf. eqs 44 and 47), `Cbi` for storing the results

Table 2. Numbers of Achiral Centroidal Alkanes as 3D Structures[a)]

	The coefficient of x^k (cf. eqs 7 and 34), i.e., $\sum \widehat{A}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k=1$	1
$k=2$	0
$k=3$	sp^2
$k=4$	tp^3
$k=5$	$qp^4 + tsp^3 + s^3p^2$
$k=6$	$qsp^4 + ts^2p^3$
$k=7$	$qtp^5 + (2\,qs^2 + t^2s)p^4 + 2\,ts^3p^3 + s^5p^2$
$k=8$	$(t^3 + qts)p^5 + (2\,qs^3 + t^2s^2)p^4 + 2\,ts^4p^3$
$k=9$	$(2\,q^2s + qt^2)p^6 + (t^3s + 5\,qts^2)p^5 + (3\,t^2s^3 + 5\,qs^4)p^4 + 3\,ts^5p^3 + s^7p^2$
$k=10$	$2\,q^2tp^7 + (2\,q^2s^2 + t^4 + 2\,qt^2s)p^6 + (4\,t^3s^2 + 4\,qts^3)p^5 + (t^2s^4 + 4\,qs^5)p^4 + 2\,ts^6p^3$
$k=11$	$q^3p^8 + (4\,q^2ts + 2\,qt^3)p^7 + (6\,qt^2s^2 + 2\,t^4s + 9\,q^2s^3)p^6 + (4\,t^3s^3 + 14\,qts^4)p^5 +$ $(6\,t^2s^5 + 8\,qs^6)p^4 + 4\,ts^7p^3 + s^9p^2$
$k=12$	$(2\,q^2t^2 + 3\,q^3s)p^8 + (4\,qt^3s + 2\,t^5 + 8\,q^2ts^2)p^7 + (8\,qt^2s^3 + 5\,t^4s^2 + 7\,q^2s^4)p^6 +$ $(11\,qts^5 + 10\,t^3s^4)p^5 + (6\,qs^7 + 3\,t^2s^6)p^4 + 3\,ts^8p^3$
$k=13$	$3\,q^3tp^9 + (3\,qt^4 + 9\,q^3s^2 + 7\,q^2t^2s)p^8 + (14\,qt^3s^2 + 2\,t^5s + 22\,q^2ts^3)p^7 +$ $(20\,qt^2s^4 + 10\,t^4s^3 + 27\,q^2s^5)p^6 + (30\,qts^6 + 10\,t^3s^5)p^5 + (10\,t^2s^7 + 13\,qs^8)p^4 + 5\,ts^9p^3 +$ $s^{11}p^2$
$k=14$	$q^4p^{10} + (6\,q^3ts + 5\,q^2t^3)p^9 + (3\,qt^4s + 2\,t^6 + 17\,q^2t^2s^2 + 14\,q^3s^3)p^8 +$ $(12\,t^5s^2 + 18\,qt^3s^3 + 31\,q^2ts^4)p^7 + (12\,t^4s^4 + 24\,qt^2s^5 + 21\,q^2s^6)p^6 +$ $(19\,t^3s^6 + 20\,qts^7)p^5 + (3\,t^2s^8 + 9\,qs^9)p^4 + 3\,ts^{10}p^3$
$k=15$	$(6\,q^4s + 5\,q^3t^2)p^{10} + (12\,q^2t^3s + 26\,q^3ts^2 + 5\,qt^5)p^9 +$ $(5\,t^6s + 20\,qt^4s^2 + 44\,q^2t^2s^3 + 43\,q^3s^4)p^8 + (12\,t^5s^3 + 54\,qt^3s^4 + 76\,q^2ts^5)p^7 +$ $(30\,t^4s^5 + 50\,qt^2s^6 + 64\,q^2s^7)p^6 + (20\,t^3s^7 + 55\,qts^8)p^5 + (18\,qs^{10} + 15\,t^2s^9)p^4 +$ $6\,ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k=20$	$2\,q^6p^{14} + (24\,q^4t^3 + 20\,q^5ts)p^{13} + (28\,q^2t^6 + 46\,q^3t^4s + 110\,q^4t^2s^2 + 72\,q^5s^3)p^{12} +$ $(192\,q^2t^5s^2 + 14\,t^9 + 232\,q^3t^3s^3 + 28\,qt^7s + 240\,q^4ts^4)p^{11} +$ $(364\,q^2t^4s^4 + 63\,t^8s^2 + 300\,q^4s^6 + 118\,qt^6s^3 + 426\,q^3t^2s^5)p^{10} +$ $(336\,qt^5s^5 + 496\,q^3ts^7 + 672\,q^2t^3s^6 + 180\,t^7s^4)p^9 +$ $(202\,t^6s^6 + 537\,q^2t^2s^8 + 356\,qt^4s^7 + 384\,q^3s^9)p^8 + (414\,qt^3s^9 + 252\,t^5s^8 + 386\,q^2ts^{10})p^7 +$ $(110\,t^4s^{10} + 150\,q^2s^{12} + 190\,qt^2s^{11})p^6 + (80\,t^3s^{12} + 90\,qts^{13})p^5 + (20\,qs^{15} + 10\,t^2s^{14})p^4 +$ $5\,ts^{16}p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of achiral centroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

of $\widehat{C}(x, q, t, s, p)$ (cf. eqs 45 and 48), and `Bbi` for storing the results of $\widehat{B}(x, q, t, s, p)$ (cf. eqs 46 and 49). After escaping from the `do` loop for k, Part 10 ("Print Out of $\cdots$") of the program 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° > 3° > 2° > 1°.

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

```
> restart;
> read "AlkaneBIO2.mpl";
```

The results are collected in Table 2 for the numbers of achiral centroidal alkanes (eq 7), in Table 3 for the numbers of chiral centroidal alkanes (eq 8), and in Table 4 for the total numbers of achiral and chiral centroidal alkanes (eq 9), where each polynomial $\sum \widehat{A}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, $\sum \widehat{C}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, or $\sum \widehat{B}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$ is the coefficient of the term x^k. Although such single summations are used in these tables, they should be read as full multiple summations.

Enumeration of Bicentroidal Alkanes. The skeleton for constructing bicentroidal alkanes is easily formulated according to the discussion described in Subsection: **Preformed Alkyl Moieties (PAMs) to Bicentroidal Alkanes**. On the basis of the selected skeleton, we shall derive functional equations for examining the effect of branching in the substitution of PAMs.

Skeleton for Counting Bicentroidal Alkanes: Let the symbol $\widetilde{A}_{kn_qn_tn_sn_p}$ be the number of inequivalent achiral alkanes of bicentroidal type, where k carbons in each alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons ($k = n_q + n_t + n_s + n_p$); the symbol $\widetilde{C}_{kn_qn_tn_sn_p}$ be the number of inequivalent chiral alkanes of bicentroidal type under a similar categorization, where each pair of enantiomers is counted once; and the symbol $\widetilde{B}_{kn_qn_tn_sn_p}$ be the total number of inequivalent alkanes of bicentroidal type under a similar categorization, where each achiral 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:

Table 3. Numbers of Chiral Centroidal Alkanes as 3D Structures[a)]

	The coefficient of x^k (cf. eqs 8 and 35), i.e., $\sum \widehat{C}_{kn_q n_t n_s n_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$–6	0
$k = 7$	$t^2 s p^4 + t s^3 p^3$
$k = 8$	$t^2 s^2 p^4$
$k = 9$	$q t^2 p^6 + (3\,q t s^2 + 3\,t^3 s) p^5 + 8\,t^2 s^3 p^4 + 2\,t s^5 p^3$
$k = 10$	$5\,q t^2 s p^6 + (5\,q t s^3 + 6\,t^3 s^2) p^5 + 7\,t^2 s^4 p^4 + t s^6 p^3$
$k = 11$	$(3\,q t^3 + 4\,q^2 t s) p^7 + (10\,t^4 s + 29\,q t^2 s^2 + q^2 s^3) p^6 + (40\,t^3 s^3 + 20\,q t s^4) p^5 +$ $(30\,t^2 s^5 + q s^6) p^4 + 4\,t s^7 p^3$
$k = 12$	$q^2 t^2 p^8 + (15\,q t^3 s + 13\,q^2 t s^2 + 2\,t^5) p^7 + (55\,q t^2 s^3 + 25\,t^4 s^2 + 3\,q^2 s^4) p^6 +$ $(24\,q t s^5 + 50\,t^3 s^4) p^5 + (q s^7 + 21\,t^2 s^6) p^4 + t s^8 p^3$
$k = 13$	$q^3 t p^9 + (11\,q t^4 + 33\,q^2 t^2 s + 2\,q^3 s^2) p^8 + (150\,q t^3 s^2 + 32\,t^5 s + 60\,q^2 t s^3) p^7 +$ $(235\,q t^2 s^4 + 191\,t^4 s^3 + 8\,q^2 s^5) p^6 + (75\,q t s^6 + 226\,t^3 s^5) p^5 + (80\,t^2 s^7 + 2\,q s^8) p^4 + 7\,t s^9 p^3$
$k = 14$	$(8\,q^3 t s + 13\,q^2 t^3) p^9 + (89\,q t^4 s + t^6 + 7\,q^3 s^3 + 104\,q^2 t^2 s^2) p^8 +$ $(344\,q t^3 s^3 + 109\,q^2 t s^4 + 117\,t^5 s^2) p^7 + (309\,t^4 s^4 + 319\,q t^2 s^5 + 11\,q^2 s^6) p^6 +$ $(225\,t^3 s^6 + 73\,q t s^7) p^5 + (51\,t^2 s^8 + 2\,q s^9) p^4 + 2\,t s^{10} p^3$
$k = 15$	$(q^4 s + 12\,q^3 t^2) p^{10} + (183\,q^2 t^3 s + 36\,q t^5 + 76\,q^3 t s^2) p^9 +$ $(106\,t^6 s + 742\,q t^4 s^2 + 29\,q^3 s^4 + 646\,q^2 t^2 s^3) p^8 + (852\,t^5 s^3 + 1766\,q t^3 s^4 + 407\,q^2 t s^5) p^7 +$ $(1494\,t^4 s^5 + 36\,q^2 s^7 + 1145\,q t^2 s^6) p^6 + (848\,t^3 s^7 + 211\,q t s^8) p^5 + (5\,q s^{10} + 175\,t^2 s^9) p^4 +$ $10\,t s^{11} p^3$
	(omitted)
$k = 20$	$(236\,q^4 t^3 + 105\,q^5 t s) p^{13} + (734\,q^2 t^6 + 4282\,q^3 t^4 s + 158\,q^5 s^3 + 2724\,q^4 t^2 s^2) p^{12} +$ $(214\,t^9 + 25355\,q^2 t^5 s^2 + 4833\,q t^7 s + 24605\,q^3 t^3 s^3 + 4136\,q^4 t s^4) p^{11} +$ $(6939\,t^8 s^2 + 95819\,q^2 t^4 s^4 + 996\,q^4 s^6 + 59746\,q t^6 s^3 + 32991\,q^3 t^2 s^5) p^{10} +$ $(12754\,q^3 t s^7 + 161562\,q t^5 s^5 + 111330\,q^2 t^3 s^6 + 46380\,t^7 s^4) p^9 +$ $(47235\,q^2 t^2 s^8 + 93076\,t^6 s^6 + 159929\,q t^4 s^7 + 1246\,q^3 s^9) p^8 +$ $(65642\,q t^3 s^9 + 75960\,t^5 s^8 + 7462\,q^2 t s^{10}) p^7 +$ $(27497\,t^4 s^{10} + 11655\,q t^2 s^{11} + 283\,q^2 s^{12}) p^6 + (4496\,t^3 s^{12} + 801\,q t s^{13}) p^5 +$ $(310\,t^2 s^{14} + 11\,q s^{15}) p^4 + 5\,t s^{16} p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$) represents the number of chiral centroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once.

$$\widetilde{A}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{A}_{kn_q n_t n_s n_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{54}$$

$$\widetilde{C}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{C}_{kn_q n_t n_s n_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{55}$$

$$\widetilde{B}(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{B}_{kn_q n_t n_s n_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{56}$$

Functional Equations for Bicentroidal Alkanes: In order to evaluate these generating functions (eqs 54–56), it is necessary to derive functional equations. Bicentroidal alkanes as 3D structures (3D trees) are characterized by the following criterion:

$$m = \frac{1}{2}k \tag{57}$$

or

$$2m = k \tag{58}$$

which is essentially equivalent to bicentroidal trees as graphs described by Jordan.[7] Compare eq 57 (or eq 58) with eq 39 (or eq 40) for specifying centroidal alkanes.

The criterion (eq 58) means that two PAMs of the same carbon content m occupy the two substitution positions of a dumbbell skeleton **12**. The two substitution positions of **12** construct an orbit governed by a CR $\mathbf{K}(/\mathbf{K}')$, where we take account of a factor group $\mathbf{K} = D_{\infty h}/C_{\infty}$ and its subgroup $\mathbf{K}' = D_{\infty h}/C_{\infty v}$. The concrete form of the CR $\mathbf{K}(/\mathbf{K}')$ is obtained as follows:

$$\mathbf{K}(/\mathbf{K}') = \{(1)(2), (1\ 2), \overline{(1)(2)}, \overline{(1\ 2)}\} \tag{62}$$

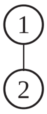
where the numbers 1 and 2 are given to show the substitution positions of the skeleton **12**. The cycles contained in eq 62 correspond to respective products of sphericity indices, i.e., b_1^2, b_2, a_1^2, and c_2, which are summed up and averaged by multiplying 1/4. Thereby, we obtain the CI-CF represented by eq 61 (Table 5) according to Fujita's proligand method.[21–23] This is also obtained by using Theorem 1 of Ref. 23 on the basis of the fact that the CR $\mathbf{K}(/\mathbf{K}')$ is isomorphic to $C_{2v}(/C_s)$. An equation equivalent to eq 61 has been reported previously on the basis of Fujita's USCI approach.[43] The CI-CF (eq 59) for counting achiral bicentroi-

Table 4. Numbers of Achiral Plus Chiral Centroidal Alkanes as 3D Structures^{a)}

	The coefficient of x^k (cf. eqs 9 and 36), i.e., $\sum \widehat{B}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k=1$	1
$k=2$	0
$k=3$	sp^2
$k=4$	tp^3
$k=5$	$qp^4 + tsp^3 + s^3p^2$
$k=6$	$qsp^4 + ts^2p^3$
$k=7$	$qtp^5 + (2qs^2 + 2t^2s)p^4 + 3ts^3p^3 + s^5p^2$
$k=8$	$(t^3 + qts)p^5 + (2qs^3 + 2t^2s^2)p^4 + 2ts^4p^3$
$k=9$	$(2q^2s + 2qt^2)p^6 + (4t^3s + 8qts^2)p^5 + (11t^2s^3 + 5qs^4)p^4 + 5ts^5p^3 + s^7p^2$
$k=10$	$2q^2tp^7 + (2q^2s^2 + t^4 + 7qt^2s)p^6 + (10t^3s^2 + 9qts^3)p^5 + (8t^2s^4 + 4qs^5)p^4 + 3ts^6p^3$
$k=11$	$q^3p^8 + (8q^2ts + 5qt^3)p^7 + (35qt^2s^2 + 12t^4s + 10q^2s^3)p^6 + (44t^3s^3 + 34qts^4)p^5 +$ $(36t^2s^5 + 9qs^6)p^4 + 8ts^7p^3 + s^9p^2$
$k=12$	$(3q^2t^2 + 3q^3s)p^8 + (19qt^3s + 4t^5 + 21q^2ts^2)p^7 + (63qt^2s^3 + 30t^4s^2 + 10q^2s^4)p^6 +$ $(35qts^5 + 60t^3s^4)p^5 + (7qs^7 + 24t^2s^6)p^4 + 4ts^8p^3$
$k=13$	$4q^3tp^9 + (14qt^4 + 11q^3s^2 + 40q^2t^2s)p^8 + (164qt^3s^2 + 34t^5s + 82q^2ts^3)p^7 +$ $(255qt^2s^4 + 201t^4s^3 + 35q^2s^5)p^6 + (105qts^6 + 236t^3s^5)p^5 + (90t^2s^7 + 15qs^8)p^4 +$ $12ts^9p^3 + s^{11}p^2$
$k=14$	$q^4p^{10} + (14q^3ts + 18q^2t^3)p^9 + (92qt^4s + 3t^6 + 121q^2t^2s^2 + 21q^3s^3)p^8 +$ $(129t^5s^2 + 362qt^3s^3 + 140q^2ts^4)p^7 + (321t^4s^4 + 343qt^2s^5 + 32q^2s^6)p^6 +$ $(244t^3s^6 + 93qts^7)p^5 + (54t^2s^8 + 11qs^9)p^4 + 5ts^{10}p^3$
$k=15$	$(7q^4s + 17q^3t^2)p^{10} + (195q^2t^3s + 102q^3ts^2 + 41qt^5)p^9 +$ $(111t^6s + 762qt^4s^2 + 690q^2t^2s^3 + 72q^3s^4)p^8 + (864t^5s^3 + 1820qt^3s^4 + 483q^2ts^5)p^7 +$ $(1524t^4s^5 + 1195qt^2s^6 + 100q^2s^7)p^6 + (868t^3s^7 + 266qts^8)p^5 +$ $(23qs^{10} + 190t^2s^9)p^4 + 16ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k=20$	$2q^6p^{14} + (260q^4t^3 + 125q^5ts)p^{13} + (762q^2t^6 + 4328q^3t^4s + 2834q^4t^2s^2 + 230q^5s^3)p^{12} +$ $(25547q^2t^5s^2 + 228t^9 + 24837q^3t^3s^3 + 4861qt^7s + 4376q^4ts^4)p^{11} +$ $(96183q^2t^4s^4 + 7002t^8s^2 + 1296q^4s^6 + 59864qt^6s^3 + 33417q^3t^2s^5)p^{10} +$ $(161898qt^5s^5 + 13250q^3ts^7 + 112002q^2t^3s^6 + 46560t^7s^4)p^9 +$ $(93278t^6s^6 + 47772q^2t^2s^8 + 160285qt^4s^7 + 1630q^3s^9)p^8 +$ $(66056qt^3s^9 + 76212t^5s^8 + 7848q^2ts^{10})p^7 +$ $(27607t^4s^{10} + 433q^2s^{12} + 11845qt^2s^{11})p^6 + (4576t^3s^{12} + 891qts^{13})p^5 +$ $(31qs^{15} + 320t^2s^{14})p^4 + 10ts^{16}p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$) represents the number of achiral and chiral centroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once, just as each achiral alkane is counted once.

Table 5. Skeleton for Generating Bicentroidal Alkanes as 3D Structures (or 3D Trees)^{a)}

Skeleton for bicentroid alkanes		Cycle index with chirality fittingness		
(as 3D trees)	CR	(CI-CF)		
 **12**	**K**(/**K′**)	Achiral	$\frac{1}{2}(a_1^2 + c_2)$	(59)
		Chiral	$\frac{1}{4}(b_1^2 + b_2 - a_1^2 - c_2)$	(60)
		Total	$\frac{1}{4}(b_1^2 + b_2 + a_1^2 + c_2)$	(61)

a) The corresponding cycle indices with chirality fittingness (CI-CFs) are listed. Each of the two substitution positions accommodates a preformed alkyl moiety (PAM).

dal alkanes as 3D structures is derived by using the first proposition of Theorem 4 of Ref. 23. The CI-CF (eq 60) for counting chiral bicentroidal alkanes as 3D structures is derived by using the second proposition of Theorem 4 of Ref. 23.

The sphericity indices (a_d, c_d, and b_d) appearing in the CI-CFs (eqs 59–61) are replaced by the functions $a(x^d, q^d, t^d, s^d, p^d)$, $c(x^d, q^d, t^d, s^d, p^d)$, and $b(x^d, q^d, t^d, s^d, p^d)$ after one is subtracted to eliminate the substitution of a hydrogen. Thereby, the CI-CFs are converted into the following functions for evaluating the generation of bicentroidal alkanes as 3D structures:

$$\widetilde{A}(x, q, t, s, p) = \frac{1}{2}\{[a(x, q, t, s, p) - 1]^2 + [c(x^2, q^2, t^2, s^2, p^2) - 1]\} \quad (63)$$

$$\begin{aligned}&\widetilde{C}(x,q,t,s,p)\\&=\frac{1}{4}\{[b(x,q,t,s,p)-1]^2+[b(x^2,q^2,t^2,s^2,p^2)-1]\\&\quad-[a(x,q,t,s,p)-1]^2-[c(x^2,q^2,t^2,s^2,p^2)-1]\}\end{aligned}\tag{64}$$

$$\begin{aligned}&\widetilde{B}(x,q,t,s,p)\\&=\frac{1}{4}\{[b(x,q,t,s,p)-1]^2+[b(x^2,q^2,t^2,s^2,p^2)-1]\\&\quad+[a(x,q,t,s,p)-1]^2+[c(x^2,q^2,t^2,s^2,p^2)-1]\}\end{aligned}\tag{65}$$

Suppose that we have obtained $a(x,q,t,s,p)$, $b(x,q,t,s,p)$, and $c(x^2,q^2,t^2,s^2,p^2)$ (eqs 1–3) up to $k=m$. In other words, suppose that eqs 41–43 have been evaluated at such a fixed m. After m is tentatively fixed, eqs 41–43 are introduced into the right-hand sides of eqs 63–65. Then the resulting equations are expanded to give respective series for $\widetilde{A}(x,q,t,s,p)^{(m)}$ (cf. eq 54), $\widetilde{C}(x,q,t,s,p)^{(m)}$ (cf. eq 55), and $\widetilde{B}(x,q,t,s,p)^{(m)}$ (cf. eq 56), where the superscript (m) represents the use of eqs 41–43 by fixing m. In accord with eq 58, the coefficients of the term x^{2m} in the series are effective to determine $\widetilde{A}_{2m,n_qn_tn_sn_p}$, $\widetilde{C}_{2m,n_qn_tn_sn_p}$, and $\widetilde{B}_{2m,n_qn_tn_sn_p}$. The operator "coeff" is used to select the coefficient of the term x^k contained in a counting series. Thereby, we obtain the following equations for evaluating such coefficients as polynomials composed of branching indicators (q, t, s, and p):

$$\begin{aligned}&\widetilde{A}_{2m}(q,t,s,p)\\&=\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{A}_{2m,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\&=\mathrm{coeff}(\widetilde{A}(x,q,t,s,p)^{(m)},x^{2m})\end{aligned}\tag{66}$$

$$\begin{aligned}&\widetilde{C}_{2m}(q,t,s,p)\\&=\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{C}_{2m,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\&=\mathrm{coeff}(\widetilde{C}(x,q,t,s,p)^{(m)},x^{2m})\end{aligned}\tag{67}$$

$$\begin{aligned}&\widetilde{B}_{2m}(q,t,s,p)\\&=\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{B}_{2m,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\\&=\mathrm{coeff}(\widetilde{B}(x,q,t,s,p)^{(m)},x^{2m})\end{aligned}\tag{68}$$

where we put $2m=n_q+n_t+n_s+n_p$. The upper limits for n_q, n_t, n_s, and n_p are specified to be infinite but practically to be $2m$.

Implementation and Results for Bicentroidal Alkanes: Let us first exemplify the procedure described above by using the data of PAMs calculated up to 4 (eqs 50–52). These generating functions for counting PAMs are introduced into the right-hand side of the functional equation $\widetilde{A}(x,q,t,s,p)$ (eq 63) to give an intermediate generating function $\widetilde{A}(x,q,t,s,p)^{(4)}$ (cf. eq 54) as follows:

$$\begin{aligned}&\widetilde{A}(x,q,t,s,p)^{(4)}\\&=\cdots+\left\{q^2p^6+qtsp^5+\left(qs^3+2\,t^2s^2\right)p^4+ts^4p^3+s^6p^2\right\}x^8\end{aligned}\tag{69}$$

where the coefficient of the term x^8 ($8=2\times4$) is shown because it is effective at this step of calculation according to eq 66. As a result, the generating function (eq 54) turns out to be evaluated up to 8.

To implement this exemplified procedure by a computer, the same code for evaluating $a(x,q,t,s,p)$, $b(x,q,t,s,p)$, and $c(x^2,q^2,t^2,s^2,p^2)$ (eqs 1–3) in the above-mentioned program "AlkaneBI02.mpl" can be used to treat bicentroidal alkanes. Part 2 of "AlkaneBI02.mpl" is replaced by the following counterpart for declaring functional equations for bicentroidal alkanes.

```
"(Part 2) Functional Equations for Alkanes
as Bicentroidal 3D Structures";
Abxbi := (1/2)*((a1-1)^2 + (c2-1));
Cbxbi := (1/4)*((b1-1)^2 + (b2-1) - (a1-1)^2 - (c2-1));
Bbxbi := (1/4)*((b1-1)^2 + (b2-1) + (a1-1)^2 + (c2-1));
```

where we use `Abxbi` for $\widetilde{A}(x,q,t,s,p)$ (eq 63), `Cbxbi` for $\widetilde{C}(x,q,t,s,p)$ (eq 64), and `Bbxbi` for $\widetilde{B}(x,q,t,s,p)$ (eq 65). In accord with eqs 66–68, Part 9 of "AlkaneBI02.mpl" is replaced by the following code:

```
#(Part 9) Bicentroidal Alkanes
kk := 2*k:
Abbi := Abbi + coeff(expand(Abxbi),x^kk)*x^kk;
Cbbi := Cbbi + coeff(expand(Cbxbi),x^kk)*x^kk;
Bbbi := Bbbi + coeff(expand(Bbxbi),x^kk)*x^kk;
```

The printing section (Part 10) is modified to print out `Abbi`, `Cbbi`, and `Bbbi` in place of `Abi`, `Cbi`, and `Bbi`.

The results of executing this program are collected in Table 6 for the numbers of achiral bicentroidal alkanes, in Table 7 for the numbers of chiral bicentroidal alkanes, and in Table 8 for the total numbers of achiral and chiral bicentroidal alkanes, where each polynomial, i.e., $\sum\widetilde{A}_{kn_qn_tn_sn_p}q^{n_q}t^{n_t}s^{n_s}p^{n_p}$, $\sum\widetilde{C}_{kn_qn_tn_sn_p}q^{n_q}t^{n_t}s^{n_s}p^{n_p}$, or $\sum\widetilde{B}_{kn_qn_tn_sn_p}q^{n_q}t^{n_t}s^{n_s}p^{n_p}$ is the coefficient of the term x^k.

Total Number of Alkanes as 3D Structures. The values of $\widehat{A}_{kn_qn_tn_sn_p}$ (eq 7), $\widehat{C}_{kn_qn_tn_sn_p}$ (eq 8), and $\widehat{B}_{kn_qn_tn_sn_p}$ (eq 9) for centroidal alkanes as 3D structures have been evaluated and collected in Tables 2–4. On the other hand, the data of $\widetilde{A}_{kn_qn_tn_sn_p}$ (eq 54), $\widetilde{C}_{kn_qn_tn_sn_p}$ (eq 55), and $\widetilde{B}_{kn_qn_tn_sn_p}$ (eq 56) for bicentroidal alkanes as 3D structures have been evaluated and collected in Tables 6–8. It follows that the corresponding total numbers of alkanes as 3D structures are obtained by their summations, which are respectively represented by the symbols $\widehat{\widetilde{A}}_{kn_qn_tn_sn_p}$, $\widehat{\widetilde{C}}_{kn_qn_tn_sn_p}$, and $\widehat{\widetilde{B}}_{kn_qn_tn_sn_p}$. Then, they appear as the coefficients of the following generating functions:

$$\begin{aligned}&\widehat{\widetilde{A}}(x,q,t,s,p)\\&=\sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{\widetilde{A}}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k\end{aligned}\tag{70}$$

$$\begin{aligned}&\widehat{\widetilde{C}}(x,q,t,s,p)\\&=\sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{\widetilde{C}}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k\end{aligned}\tag{71}$$

Table 6. Numbers of Achiral Bicentroidal Alkanes as 3D Structures[a)]

	The coefficient of x^k (cf. eqs 54 and 66), i.e., $\sum \widetilde{A}_{kn_qn_tn_sn_p} q^{n_q}t^{n_t}s^{n_s}p^{n_p}$
$k = 1$	0
$k = 2$	p^2
$k = 3$	0
$k = 4$	s^2p^2
$k = 5$	0
$k = 6$	$t^2p^4 + ts^2p^3 + s^4p^2$
$k = 7$	0
$k = 8$	$q^2p^6 + qtsp^5 + (qs^3 + 2\,t^2s^2)p^4 + ts^4p^3 + s^6p^2$
$k = 9$	0
$k = 10$	$(t^4 + 3\,q^2s^2)p^6 + 4\,qts^3p^5 + (5\,t^2s^4 + 2\,qs^5)p^4 + 2\,ts^6p^3 + s^8p^2$
$k = 11$	0
$k = 12$	$2\,q^2t^2p^8 + 4\,q^2ts^2p^7 + (10\,q^2s^4 + 5\,t^4s^2 + 2\,qt^2s^3)p^6 + 9\,qts^5p^5 + (7\,t^2s^6 + 4\,qs^7)p^4 + 2\,ts^8p^3 + s^{10}p^2$
$k = 13$	0
$k = 14$	$q^4p^{10} + (2\,q^3ts + q^2t^3)p^9 + (2\,qt^4s + 3\,t^6 + 9\,q^2t^2s^2 + 6\,q^3s^3)p^8 + (6\,qt^3s^3 + 15\,q^2ts^4)p^7 + (18\,t^4s^4 + 6\,qt^2s^5 + 23\,q^2s^6)p^6 + (t^3s^6 + 20\,qts^7)p^5 + (12\,t^2s^8 + 6\,qs^9)p^4 + 3\,ts^{10}p^3 + s^{12}p^2$
$k = 15$	0
	(omitted)
$k = 20$	$3\,q^6p^{14} + (4\,q^4t^3 + 8\,q^5ts)p^{13} + (23\,q^2t^6 + 48\,q^4t^2s^2 + 8\,q^3t^4s + 32\,q^5s^3)p^{12} + (12\,q^2t^5s^2 + 64\,q^3t^3s^3 + 92\,q^4ts^4)p^{11} + (218\,q^2t^4s^4 + 63\,t^8s^2 + 152\,q^3t^2s^5 + 181\,q^4s^6 + 8\,qt^6s^3)p^{10} + (24\,qt^5s^5 + 180\,q^2t^3s^6 + 296\,q^3ts^7)p^9 + (64\,qt^4s^7 + 327\,q^2t^2s^8 + 218\,t^6s^6 + 258\,q^3s^9)p^8 + (90\,qt^3s^9 + 292\,q^2ts^{10})p^7 + (142\,t^4s^{10} + 62\,qt^2s^{11} + 159\,q^2s^{12})p^6 + (4\,t^3s^{12} + 78\,qts^{13})p^5 + (26\,t^2s^{14} + 16\,qs^{15})p^4 + 4\,ts^{16}p^3 + s^{18}p^2$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of achiral bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

Table 7. Numbers of Chiral Bicentroidal Alkanes as 3D Structures[a)]

	The coefficient of x^k (cf. eqs 55 and 67), i.e., $\sum \widetilde{C}_{kn_qn_tn_sn_p} q^{n_q}t^{n_t}s^{n_s}p^{n_p}$
$k = 1$–7	0
$k = 8$	$qtsp^5 + 2\,t^2s^2p^4 + ts^4p^3$
$k = 9$	0
$k = 10$	$(t^4 + 2\,qt^2s)p^6 + (6\,t^3s^2 + 4\,qts^3)p^5 + 9\,t^2s^4p^4 + 2\,ts^6p^3$
$k = 11$	0
$k = 12$	$2\,q^2t^2p^8 + (4\,q^2ts^2 + 15\,qt^3s)p^7 + (25\,t^4s^2 + 34\,qt^2s^3)p^6 + (50\,t^3s^4 + 17\,qts^5)p^5 + 29\,t^2s^6p^4 + 4\,ts^8p^3$
$k = 13$	0
$k = 14$	$(6\,q^3ts + 2\,q^2t^3)p^9 + (34\,qt^4s + 6\,t^6 + q^3s^3 + 63\,q^2t^2s^2)p^8 + (227\,qt^3s^3 + 56\,q^2ts^4 + 75\,t^5s^2)p^7 + (261\,t^4s^4 + 222\,qt^2s^5 + 7\,q^2s^6)p^6 + (227\,t^3s^6 + 57\,qts^7)p^5 + (69\,t^2s^8 + qs^9)p^4 + 6\,ts^{10}p^3$
$k = 15$	0
	(omitted)
$k = 20$	$(52\,q^5ts + 40\,q^4t^3)p^{13} + (440\,q^2t^6 + 1298\,q^3t^4s + 26\,q^5s^3 + 1086\,q^4t^2s^2)p^{12} + (10074\,q^2t^5s^2 + 1364\,q^4ts^4 + 2646\,qt^7s + 10006\,q^3t^3s^3)p^{11} + (3969\,t^8s^2 + 43625\,q^2t^4s^4 + 13280\,q^3t^2s^5 + 391\,q^4s^6 + 28472\,qt^6s^3)p^{10} + (52920\,q^2t^3s^6 + 26460\,t^7s^4 + 85542\,qt^5s^5 + 5642\,q^3ts^7)p^9 + (24564\,q^2t^2s^8 + 91066\,qt^4s^7 + 59972\,t^6s^6 + 502\,q^3s^9)p^8 + (55188\,t^5s^8 + 41376\,qt^3s^9 + 4148\,q^2ts^{10})p^7 + (174\,q^2s^{12} + 23491\,t^4s^{10} + 8117\,qt^2s^{11})p^6 + (4744\,t^3s^{12} + 618\,qts^{13})p^5 + (7\,qs^{15} + 446\,t^2s^{14})p^4 + 16\,ts^{16}p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of chiral bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once.

Table 8. Numbers of Total (Achiral Plus Chiral) Bicentroidal Alkanes as 3D Structures[a)]

	The coefficient of x^k (cf. eqs 56 and 68), i.e., $\sum \widetilde{B}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$	0
$k = 2$	p^2
$k = 3$	0
$k = 4$	s^2p^2
$k = 5$	0
$k = 6$	$t^2p^4 + ts^2p^3 + s^4p^2$
$k = 7$	0
$k = 8$	$q^2p^6 + 2\,qtsp^5 + (qs^3 + 4\,t^2s^2)p^4 + 2\,ts^4p^3 + s^6p^2$
$k = 9$	0
$k = 10$	$(3\,q^2s^2 + 2\,qt^2s + 2\,t^4)p^6 + (6\,t^3s^2 + 8\,qts^3)p^5 + (14\,t^2s^4 + 2\,qs^5)p^4 + 4\,ts^6p^3 + s^8p^2$
$k = 11$	0
$k = 12$	$4\,q^2t^2p^8 + (8\,q^2ts^2 + 15\,qt^3s)p^7 + (36\,qt^2s^3 + 30\,t^4s^2 + 10\,q^2s^4)p^6 +$ $(50\,t^3s^4 + 26\,qts^5)p^5 + (36\,t^2s^6 + 4\,qs^7)p^4 + 6\,ts^8p^3 + s^{10}p^2$
$k = 13$	0
$k = 14$	$q^4p^{10} + (3\,q^2t^3 + 8\,q^3ts)p^9 + (36\,qt^4s + 9\,t^6 + 72\,q^2t^2s^2 + 7\,q^3s^3)p^8 +$ $(75\,t^5s^2 + 233\,qt^3s^3 + 71\,q^2ts^4)p^7 + (279\,t^4s^4 + 228\,qt^2s^5 + 30\,q^2s^6)p^6 +$ $(228\,t^3s^6 + 77\,qts^7)p^5 + (81\,t^2s^8 + 7\,qs^9)p^4 + 9\,ts^{10}p^3 + s^{12}p^2$
$k = 15$	0
	(omitted)
$k = 20$	$3\,q^6p^{14} + (44\,q^4t^3 + 60\,q^5ts)p^{13} + (463\,q^2t^6 + 1306\,q^3t^4s + 1134\,q^4t^2s^2 + 58\,q^5s^3)p^{12} +$ $(10086\,q^2t^5s^2 + 10070\,q^3t^3s^3 + 2646\,qt^7s + 1456\,q^4ts^4)p^{11} +$ $(43843\,q^2t^4s^4 + 4032\,t^8s^2 + 572\,q^4s^6 + 28480\,qt^6s^3 + 13432\,q^3t^2s^5)p^{10} +$ $(85566\,qt^5s^5 + 26460\,t^7s^4 + 53100\,q^2t^3s^6 + 5938\,q^3ts^7)p^9 +$ $(24891\,q^2t^2s^8 + 91130\,qt^4s^7 + 60190\,t^6s^6 + 760\,q^3s^9)p^8 +$ $(55188\,t^5s^8 + 41466\,qt^3s^9 + 4440\,q^2ts^{10})p^7 + (333\,q^2s^{12} + 23633\,t^4s^{10} + 8179\,qt^2s^{11})p^6 +$ $(4748\,t^3s^{12} + 696\,qts^{13})p^5 + (472\,t^2s^{14} + 23\,qs^{15})p^4 + 20\,ts^{16}p^3 + s^{18}p^2$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of achiral and chiral bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once, just as each achiral alkane is counted once.

$$\widehat{\widetilde{B}}(x, q, t, s, p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{\widetilde{B}}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{72}$$

The following relationships are obvious by the definitions of the respective numbers.

$$\widehat{\widetilde{A}}_{kn_qn_tn_sn_p} = \widehat{A}_{kn_qn_tn_sn_p} + \widetilde{A}_{kn_qn_tn_sn_p} \tag{73}$$

$$\widehat{\widetilde{C}}_{kn_qn_tn_sn_p} = \widehat{C}_{kn_qn_tn_sn_p} + \widetilde{C}_{kn_qn_tn_sn_p} \tag{74}$$

$$\widehat{\widetilde{B}}_{kn_qn_tn_sn_p} = \widehat{B}_{kn_qn_tn_sn_p} + \widetilde{B}_{kn_qn_tn_sn_p} \tag{75}$$

The two sets of generating functions, i.e., eqs 7–9 and eqs 54–56, are summed up so as to give the generating functions defined by eqs 70–72. Under the condition that the two sets of generating functions have been evaluated as series, we obtain the total numbers by using the following relationships:

$$\widehat{\widetilde{A}}(x, q, t, s, p) = \widehat{A}(x, q, t, s, p) + \widetilde{A}(x, q, t, s, p) \tag{76}$$

$$\widehat{\widetilde{C}}(x, q, t, s, p) = \widehat{C}(x, q, t, s, p) + \widetilde{C}(x, q, t, s, p) \tag{77}$$

$$\widehat{\widetilde{B}}(x, q, t, s, p) = \widehat{B}(x, q, t, s, p) + \widetilde{B}(x, q, t, s, p) \tag{78}$$

It should be noted, however, that eqs 76–78 are not concerned with the set of functional equations (eqs 34–36) for centroidal alkanes and the other set (eqs 63–65) for bicentroidal alkanes. Simple summations of the two sets of functional equations (eq 34 + eq 63; eq 35 + eq 64; and eq 36 + eq 65) give erroneous results, because the integer m runs according to eq 40 for the former set and differently according to eq 58 for the latter set.

The results are collected in Table 9 for the numbers of achiral centroidal and bicentroidal alkanes, in Table 10 for the numbers of chiral centroidal and bicentroidal alkanes, and in Table 11 for the total numbers of achiral and chiral centroidal and bicentroidal alkanes, where each polynomial $\sum \widehat{\widetilde{A}}_{kn_qn_tn_sn_p} q^{n_q}t^{n_t}s^{n_s}p^{n_p}$, $\sum \widehat{\widetilde{C}}_{kn_qn_tn_sn_p} q^{n_q}t^{n_t}s^{n_s}p^{n_p}$, or $\sum \widehat{\widetilde{B}}_{kn_qn_tn_sn_p} q^{n_q}t^{n_t}s^{n_s}p^{n_p}$ is the coefficient of the term x^k. Obviously, Table 9 can be obtained by summing up Tables 2 and 6; Table 10 can be obtained by summing up Tables 3 and 7; and Table 11 can be obtained by summing up Tables 4 and 8; where these relationships are in agreement with eq 76–78.

Enumeration of Alkanes as Graphs

If our discussions are restricted to alkanes as graphs, Pólya's theorem can be used to cope with the effect of branching, where cycle indices (CIs) (without chirality fittingness) are modified by BIs introduced as a new matter. Such CIs can be alternatively obtained by starting from the above-mentioned results concerning 3D structures, where cycle indices with

Table 9. Numbers of Achiral Alkanes (Centroidal & Bicentroidal) as 3D Structures[a)]

	The coefficient of x^k (cf. eq 70), i.e., $\sum \widehat{\widetilde{A}}_{kn_q n_t n_s n_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k=1$	1
$k=2$	p^2
$k=3$	sp^2
$k=4$	$tp^3 + s^2p^2$
$k=5$	$qp^4 + tsp^3 + s^3p^2$
$k=6$	$(qs + t^2)p^4 + 2\,ts^2p^3 + s^4p^2$
$k=7$	$qtp^5 + (2\,qs^2 + t^2s)p^4 + 2\,ts^3p^3 + s^5p^2$
$k=8$	$q^2p^6 + (t^3 + 2\,qts)p^5 + (3\,t^2s^2 + 3\,qs^3)p^4 + 3\,ts^4p^3 + s^6p^2$
$k=9$	$(2\,q^2s + qt^2)p^6 + (t^3s + 5\,qts^2)p^5 + (3\,t^2s^3 + 5\,qs^4)p^4 + 3\,ts^5p^3 + s^7p^2$
$k=10$	$2\,q^2tp^7 + (5\,q^2s^2 + 2\,qt^2s + 2\,t^4)p^6 + (4\,t^3s^2 + 8\,qts^3)p^5 + (6\,t^2s^4 + 6\,qs^5)p^4 + 4\,ts^6p^3 + s^8p^2$
$k=11$	$q^3p^8 + (4\,q^2ts + 2\,qt^3)p^7 + (6\,qt^2s^2 + 2\,t^4s + 9\,q^2s^3)p^6 + (4\,t^3s^3 + 14\,qts^4)p^5 + (6\,t^2s^5 + 8\,qs^6)p^4 + 4\,ts^7p^3 + s^9p^2$
$k=12$	$(4\,q^2t^2 + 3\,q^3s)p^8 + (4\,qt^3s + 12\,q^2ts^2 + 2\,t^5)p^7 + (10\,qt^2s^3 + 10\,t^4s^2 + 17\,q^2s^4)p^6 + (20\,qts^5 + 10\,t^3s^4)p^5 + (10\,qs^7 + 10\,t^2s^6)p^4 + 5\,ts^8p^3 + s^{10}p^2$
$k=13$	$3\,q^3tp^9 + (3\,qt^4 + 9\,q^3s^2 + 7\,q^2t^2s)p^8 + (14\,qt^3s^2 + 2\,t^5s + 22\,q^2ts^3)p^7 + (20\,qt^2s^4 + 10\,t^4s^3 + 27\,q^2s^5)p^6 + (30\,qts^6 + 10\,t^3s^5)p^5 + (10\,t^2s^7 + 13\,qs^8)p^4 + 5\,ts^9p^3 + s^{11}p^2$
$k=14$	$2\,q^4p^{10} + (6\,q^2t^3 + 8\,q^3ts)p^9 + (5\,qt^4s + 5\,t^6 + 26\,q^2t^2s^2 + 20\,q^3s^3)p^8 + (12\,t^5s^2 + 24\,qt^3s^3 + 46\,q^2ts^4)p^7 + (30\,t^4s^4 + 30\,qt^2s^5 + 44\,q^2s^6)p^6 + (20\,t^3s^6 + 40\,qts^7)p^5 + (15\,t^2s^8 + 15\,qs^9)p^4 + 6\,ts^{10}p^3 + s^{12}p^2$
$k=15$	$(6\,q^4s + 5\,t^2q^3)p^{10} + (12\,q^2t^3s + 26\,q^3ts^2 + 5\,t^5q)p^9 + (5\,t^6s + 20\,qt^4s^2 + 44\,q^2t^2s^3 + 43\,q^3s^4)p^8 + (12\,t^5s^3 + 54\,qt^3s^4 + 76\,q^2ts^5)p^7 + (30\,t^4s^5 + 50\,qt^2s^6 + 64\,q^2s^7)p^6 + (20\,t^3s^7 + 55\,qts^8)p^5 + (18\,qs^{10} + 15\,t^2s^9)p^4 + 6\,ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k=20$	$5\,q^6p^{14} + (28\,q^4t^3 + 28\,q^5ts)p^{13} + (51\,t^6q^2 + 54\,q^3t^4s + 158\,q^4t^2s^2 + 104\,q^5s^3)p^{12} + (204\,q^2t^5s^2 + 14\,t^9 + 296\,q^3t^3s^3 + 332\,q^4ts^4 + 28\,qt^7s)p^{11} + (582\,q^2t^4s^4 + 126\,t^8s^2 + 481\,q^4s^6 + 578\,q^3t^2s^5 + 126\,qt^6s^3)p^{10} + (360\,qt^5s^5 + 852\,q^2t^3s^6 + 180\,t^7s^4 + 792\,q^3ts^7)p^9 + (420\,t^6s^6 + 420\,qt^4s^7 + 864\,q^2t^2s^8 + 642\,q^3s^9)p^8 + (252\,t^5s^8 + 504\,qt^3s^9 + 678\,q^2ts^{10})p^7 + (309\,q^2s^{12} + 252\,t^4s^{10} + 252\,qt^2s^{11})p^6 + (84\,t^3s^{12} + 168\,qts^{13})p^5 + (36\,qs^{15} + 36\,t^2s^{14})p^4 + 9\,ts^{16}p^3 + s^{18}p^2$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of achiral centroidal & bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

chirality fittingness (CI-CFs) derived by Fujita's proligand method are systematically reduced into the corresponding CIs for graphs. The following discussions rely mainly on the latter systematic derivation due to the reduction from 3D structures to graphs. Throughout our discussions, we put emphasis on the fact that Pólya's theorem for manipulating graphs can be regarded as a special case of Fujita's proligand method for manipulating 3D structures.

Recursive Functional Equations for PAMs as Graphs. Let the symbol $R_{kn_q n_t n_s n_p}$ 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. A generating function for obtaining this number can be written by using the above-described BIs (q, t, s, and p) as follows:

$$r(x,q,t,s,p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} R_{kn_q n_t n_s n_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{79}$$

According to the treatment described in an accompanying paper that will appear in a future issue of this journal,[42] the sum $(1/2)\{a(x,q,t,s,p) + b(x,q,t,s,p)\}$ (eq 4 plus eq 5) for counting achiral plus chiral PAMs as 3D structures can be reduced into the corresponding functional equation for counting PAMS as graphs:

$$\begin{aligned} r(x,q,t,s,p) &= 1 + xp + xs\{r(x,q,t,s,p) - 1\} \\ &\quad + \frac{xt}{2}\{[r(x,q,t,s,p) - 1]^2 + [r(x^2,q^2,t^2,s^2,p^2) - 1]\} \\ &\quad + \frac{xq}{6}\{[r(x,q,t,s,p) - 1]^3 + 2[r(x^3,q^3,t^3,s^3,p^3) - 1] \\ &\quad + 3[r(x,q,t,s,p) - 1][r(x^2,q^2,t^2,s^2,p^2) - 1]\} \end{aligned} \tag{80}$$

where we use a graph-reduction condition:

$$\begin{aligned} a(x^d,q^d,t^d,s^d,p^d) = b(x^d,q^d,t^d,s^d,p^d) &= c(x^d,q^d,t^d,s^d,p^d) \\ &= r(x^d,q^d,t^d,s^d,p^d) \end{aligned} \tag{81}$$

Equation 80 can be used to evaluate the generating function represented by eq 79. Note that eq 80 has a recursive nature, because PAMs are regarded as graphs.

Table 10. Numbers of Chiral Alkanes (Centroidal & Bicentroidal) as 3D Structures[a)]

	The coefficient of x^k (cf. eq 71), i.e., $\sum \widehat{\widetilde{C}}_{kn_q n_t n_s n_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$–6	0
$k = 7$	$t^2sp^4 + ts^3p^3$
$k = 8$	$qtsp^5 + 3\,t^2s^2p^4 + ts^4p^3$
$k = 9$	$qt^2p^6 + (3\,qts^2 + 3\,t^3s)p^5 + 8\,t^2s^3p^4 + 2\,ts^5p^3$
$k = 10$	$(t^4 + 7\,qt^2s)p^6 + (12\,t^3s^2 + 9\,qts^3)p^5 + 16\,t^2s^4p^4 + 3\,ts^6p^3$
$k = 11$	$(3\,qt^3 + 4\,q^2ts)p^7 + (10\,t^4s + 29\,qt^2s^2 + q^2s^3)p^6 + (40\,t^3s^3 + 20\,qts^4)p^5 +$ $(30\,t^2s^5 + qs^6)p^4 + 4\,ts^7p^3$
$k = 12$	$3\,q^2t^2p^8 + (30\,qt^3s + 17\,q^2ts^2 + 2\,t^5)p^7 + (89\,qt^2s^3 + 50\,t^4s^2 + 3\,q^2s^4)p^6 +$ $(41\,qts^5 + 100\,t^3s^4)p^5 + (qs^7 + 50\,t^2s^6)p^4 + 5\,ts^8p^3$
$k = 13$	$q^3tp^9 + (11\,qt^4 + 33\,q^2t^2s + 2\,q^3s^2)p^8 + (150\,qt^3s^2 + 32\,t^5s + 60\,q^2ts^3)p^7 +$ $(235\,qt^2s^4 + 191\,t^4s^3 + 8\,q^2s^5)p^6 + (75\,qts^6 + 226\,t^3s^5)p^5 + (80\,t^2s^7 + 2\,qs^8)p^4 + 7\,ts^9p^3$
$k = 14$	$(14\,q^3ts + 15\,q^2t^3)p^9 + (123\,qt^4s + 7\,t^6 + 8\,q^3s^3 + 167\,q^2t^2s^2)p^8 +$ $(571\,qt^3s^3 + 165\,q^2ts^4 + 192\,t^5s^2)p^7 + (570\,t^4s^4 + 541\,qt^2s^5 + 18\,q^2s^6)p^6 +$ $(452\,t^3s^6 + 130\,qts^7)p^5 + (120\,t^2s^8 + 3\,qs^9)p^4 + 8\,ts^{10}p^3$
$k = 15$	$(q^4s + 12\,t^2q^3)p^{10} + (183\,q^2t^3s + 36\,t^5q + 76\,q^3ts^2)p^9 +$ $(106\,t^6s + 742\,qt^4s^2 + 29\,q^3s^4 + 646\,q^2t^2s^3)p^8 + (852\,t^5s^3 + 1766\,qt^3s^4 + 407\,q^2ts^5)p^7 +$ $(1494\,t^4s^5 + 36\,q^2s^7 + 1145\,qt^2s^6)p^6 + (848\,t^3s^7 + 211\,qts^8)p^5 + (5\,qs^{10} + 175\,t^2s^9)p^4 +$ $10\,ts^{11}p^3$
	(omitted)
$k = 20$	$(276\,q^4t^3 + 157\,q^5ts)p^{13} + (1174\,t^6q^2 + 5580\,q^3t^4s + 184\,q^5s^3 + 3810\,q^4t^2s^2)p^{12} +$ $(214\,t^9 + 35429\,q^2t^5s^2 + 7479\,qt^7s + 34611\,q^3t^3s^3 + 5500\,q^4ts^4)p^{11} +$ $(10908\,t^8s^2 + 139444\,q^2t^4s^4 + 1387\,q^4s^6 + 88218\,qt^6s^3 + 46271\,q^3t^2s^5)p^{10} +$ $(18396\,q^3ts^7 + 247104\,qt^5s^5 + 164250\,q^2t^3s^6 + 72840\,t^7s^4)p^9 +$ $(71799\,q^2t^2s^8 + 153048\,t^6s^6 + 250995\,qt^4s^7 + 1748\,q^3s^9)p^8 +$ $(107018\,qt^3s^9 + 131148\,t^5s^8 + 11610\,q^2ts^{10})p^7 +$ $(50988\,t^4s^{10} + 19772\,qt^2s^{11} + 457\,q^2s^{12})p^6 + (9240\,t^3s^{12} + 1419\,qts^{13})p^5 +$ $(756\,t^2s^{14} + 18\,qs^{15})p^4 + 21\,ts^{16}p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$) represents the number of chiral centroidal & bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once.

Enumeration of Centroidal Alkanes as Graphs. Functional Equations for Counting Centroidal Alkanes as Graphs: Let the symbol $\widehat{R}_{kn_q n_t n_s n_p}$ be the number of inequivalent centroidal alkanes as graphs, where k carbons in each alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons ($k = n_q + n_t + n_s + n_p$). Thereby, we are able to write down a generating function for obtaining this number by using the above-described BIs (q, t, s, and p) as follows:

$$\widehat{R}(x, q, t, s, p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} \widehat{R}_{kn_q n_t n_s n_p} p^{n_p}\right) s^{n_s}\right) t^{n_t}\right) q^{n_q}\right) x^k \tag{82}$$

The generation function (eq 82) for counting alkanes as graphs can be evaluated by adopting skeletons shown in Table 12, which is drawn on a similar line as Table 1 for counting 3D structures.

Four skeletons depicted as graphs in Table 12, i.e., a quaternary skeleton **13**, a tertiary skeleton **14**, a secondary skeleton **15**, and a primary skeleton **16**, correspond to the four skeletons **8**–**11** depicted as 3D structures in Table 1. Pólya's theorem[8] is applied to their permutation groups (the symmetric groups of degree 4 ($\mathscr{S}^{[4]}$), 3 ($\mathscr{S}^{[3]}$), 2 ($\mathscr{S}^{[2]}$), and 1 ($\mathscr{S}^{[1]}$) so as to provide the corresponding cycle indices (CIs without chirality fittingness), as collected in the rightmost column of Table 12 (eqs 83–86). These equations (CIs) can be alternatively derived by the reduction of the CI-CFs (eqs 12, 15, 18, and 21) under a graph-reduction condition $a_d = b_d = c_d = r_d$ (cf. eq 81). After the variable r_d is replaced by the function $r(x^d, q^d, t^d, s^d, p^d) - 1$, a similar treatment to the derivation of eq 36 is employed in the treatment of eqs 83–86. Thereby, we obtain a functional equation for counting centroidal alkanes as graphs:

$$\begin{aligned}
\widehat{R}(x, q, t, s, p) &\\
= x &+ xp[r(x, q, t, s, p) - 1] \\
&+ \frac{xs}{2}\{[r(x, q, t, s, p) - 1]^2 + [r(x^2, q^2, t^2, s^2, p^2) - 1]\} \\
&+ \frac{xt}{6}\{[r(x, q, t, s, p) - 1]^3 + 2[r(x^3, q^3, t^3, s^3, p^3) - 1] \\
&\quad + 3[r(x, q, t, s, p) - 1][r(x^2, q^2, t^2, s^2, p^2) - 1]\} \\
&+ \frac{xq}{24}\{[r(x, q, t, s, p) - 1]^4 + 3[r(x^2, q^2, t^2, s^2, p^2) - 1]^2 \\
&\quad + 8[r(x, q, t, s, p) - 1][r(x^3, q^3, t^3, s^3, p^3) - 1] \\
&\quad + 6[r(x, q, t, s, p) - 1]^2[r(x^2, q^2, t^2, s^2, p^2) - 1] \\
&\quad + 6[r(x^4, q^2, t^4, s^4, p^4) - 1]\}
\end{aligned} \tag{87}$$

Table 11. Numbers of Achiral and Chiral Alkanes (Centroidal & Bicentroidal) as 3D Structures[a)]

	The coefficient of x^k (cf. eq 72), i.e., $\sum \widehat{\widetilde{B}}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$
$k = 1$	1
$k = 2$	p^2
$k = 3$	sp^2
$k = 4$	$tp^3 + s^2p^2$
$k = 5$	$qp^4 + tsp^3 + s^3p^2$
$k = 6$	$(qs + t^2)p^4 + 2\,ts^2p^3 + s^4p^2$
$k = 7$	$qtp^5 + (2\,qs^2 + 2\,t^2s)p^4 + 3\,ts^3p^3 + s^5p^2$
$k = 8$	$q^2p^6 + (t^3 + 3\,qts)p^5 + (6\,t^2s^2 + 3\,qs^3)p^4 + 4\,ts^4p^3 + s^6p^2$
$k = 9$	$(2\,q^2s + 2\,qt^2)p^6 + (4\,t^3s + 8\,qts^2)p^5 + (11\,t^2s^3 + 5\,qs^4)p^4 + 5\,ts^5p^3 + s^7p^2$
$k = 10$	$2\,q^2tp^7 + (5\,q^2s^2 + 9\,qt^2s + 3\,t^4)p^6 + (16\,t^3s^2 + 17\,qts^3)p^5 + (22\,t^2s^4 + 6\,qs^5)p^4 +$ $7\,ts^6p^3 + s^8p^2$
$k = 11$	$q^3p^8 + (8\,q^2ts + 5\,qt^3)p^7 + (35\,qt^2s^2 + 12\,t^4s + 10\,q^2s^3)p^6 + (44\,t^3s^3 + 34\,qts^4)p^5 +$ $(36\,t^2s^5 + 9\,qs^6)p^4 + 8\,ts^7p^3 + s^9p^2$
$k = 12$	$(7\,q^2t^2 + 3\,q^3s)p^8 + (34\,qt^3s + 29\,q^2ts^2 + 4\,t^5)p^7 + (99\,qt^2s^3 + 60\,t^4s^2 + 20\,q^2s^4)p^6 +$ $(61\,qts^5 + 110\,t^3s^4)p^5 + (11\,qs^7 + 60\,t^2s^6)p^4 + 10\,ts^8p^3 + s^{10}p^2$
$k = 13$	$4\,q^3tp^9 + (14\,qt^4 + 11\,q^3s^2 + 40\,q^2t^2s)p^8 + (164\,qt^3s^2 + 34\,t^5s + 82\,q^2ts^3)p^7 +$ $(255\,qt^2s^4 + 201\,t^4s^3 + 35\,q^2s^5)p^6 + (105\,qts^6 + 236\,t^3s^5)p^5 + (90\,t^2s^7 + 15\,qs^8)p^4 +$ $12\,ts^9p^3 + s^{11}p^2$
$k = 14$	$2\,q^4p^{10} + (21\,q^2t^3 + 22\,q^3ts)p^9 + (128\,qt^4s + 12\,t^6 + 193\,q^2t^2s^2 + 28\,q^3s^3)p^8 +$ $(204\,t^5s^2 + 595\,qt^3s^3 + 211\,q^2ts^4)p^7 + (600\,t^4s^4 + 571\,qt^2s^5 + 62\,q^2s^6)p^6 +$ $(472\,t^3s^6 + 170\,qts^7)p^5 + (135\,t^2s^8 + 18\,qs^9)p^4 + 14\,ts^{10}p^3 + s^{12}p^2$
$k = 15$	$(7\,q^4s + 17\,t^2q^3)p^{10} + (195\,q^2t^3s + 102\,q^3ts^2 + 41\,t^5q)p^9 +$ $(111\,t^6s + 762\,qt^4s^2 + 690\,q^2t^2s^3 + 72\,q^3s^4)p^8 + (864\,t^5s^3 + 1820\,qt^3s^4 + 483\,q^2ts^5)p^7 +$ $(1524\,t^4s^5 + 1195\,qt^2s^6 + 100\,q^2s^7)p^6 + (868\,t^3s^7 + 266\,qts^8)p^5 +$ $(23\,qs^{10} + 190\,t^2s^9)p^4 + 16\,ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k = 20$	$5\,q^6p^{14} + (304\,q^4t^3 + 185\,q^5ts)p^{13} +$ $(1225\,t^6q^2 + 5634\,q^3t^4s + 3968\,q^4t^2s^2 + 288\,q^5s^3)p^{12} +$ $(35633\,q^2t^5s^2 + 228\,t^9 + 34907\,q^3t^3s^3 + 5832\,q^4ts^4 + 7507\,qt^7s)p^{11} +$ $(140026\,q^2t^4s^4 + 11034\,t^8s^2 + 1868\,q^4s^6 + 46849\,q^3t^2s^5 + 88344\,qt^6s^3)p^{10} +$ $(247464\,qt^5s^5 + 165102\,q^2t^3s^6 + 73020\,t^7s^4 + 19188\,q^3ts^7)p^9 +$ $(153468\,t^6s^6 + 251415\,qt^4s^7 + 72663\,q^2t^2s^8 + 2390\,q^3s^9)p^8 +$ $(131400\,t^5s^8 + 107522\,qt^3s^9 + 12288\,q^2ts^{10})p^7 +$ $(766\,q^2s^{12} + 51240\,t^4s^{10} + 20024\,qt^2s^{11})p^6 + (9324\,t^3s^{12} + 1587\,qts^{13})p^5 +$ $(54\,qs^{15} + 792\,t^2s^{14})p^4 + 30\,ts^{16}p^3 + s^{18}p^2$ (omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the total number of centroidal & bicentroidal alkanes having n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons. Each pair of enantiomers is counted just once, just as each achiral alkane is counted once.

This functional equation can be used to calculate the generating function represented by eq 9, where the branching degree of each internal carbon is taken into consideration.

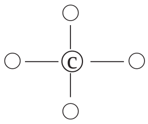
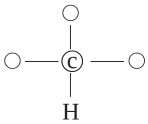
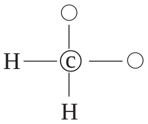
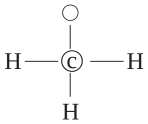
As found easily, the functional equation (eq 87) can be alternatively obtained by modifying the functional equation described above, i.e., $\widehat{B}(x, q, t, s, p)$ (eq 36), under the the graph-reduction condition (eq 81). Thus, eq 36 for counting total (achiral plus chiral) centroidal alkanes as 3D structures is converted into the corresponding functional equation (eq 87). Note that the achirality/chirality of 3D structures vanishes in reduction processes from 3D structures to graphs.

Let us now evaluate eq 87 by using eq 80 under the condition for specifying centroidal alkanes (eq 40). Suppose that eq 80 has been evaluated up to the term x^m so that eq 79 is represented as follows:

$$r(x, q, t, s, p)^{(m)} = \sum_{k=0}^{m}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{R}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{88}$$

where the superscript (m) represents the use of eq 80 by fixing m. The upper limits for n_q, n_t, n_s, and n_p are specified to be infinite but practically to be m because we put $k = n_q + n_t + n_s + n_p$ where k runs from 0 to m. After m is tentatively fixed, eq 88 is introduced into the right-hand sidee of eq 87. Then the resulting equation is expanded to give a series for $\widehat{R}(x, q, t, s, p)^{(m)}$ (cf. eq 82), where the superscript (m) represents the use of eqs 88 by fixing m. In accord with eq 40, the coefficients of the terms x^{2m+1} and x^{2m+2} in the series are effective to determine $\widehat{R}_{2m+1,n_qn_tn_sn_p}$ and $\widehat{R}_{2m+2,n_qn_tn_sn_p}$.

Table 12. Skeletons for Generating Centroidal Alkanes as Graphs (or Trees) with a Quaternary, Tertiary, Secondary, or Primary Centroid[a)]

Skeleton for centroidal alkanes		Cycle index (without chirality fittingness)	
(trees as graphs)	Permutation group	(CI)	
 **13**	Quaternary (4°) $\mathcal{S}^{[4]}$	$\frac{1}{24}(r_1^4 + 3r_2^2 + 8r_1r_3 + 6r_1^2r_2 + 6r_4)$	(83)
 **14**	Tertiary (3°) $\mathcal{S}^{[3]}$	$\frac{1}{6}(r_1^3 + 2r_3 + 3r_1r_2)$	(84)
 **15**	Secondary (2°) $\mathcal{S}^{[2]}$	$\frac{1}{2}(r_1^2 + r_2)$	(85)
 **16**	Primary (1°) $\mathcal{S}^{[1]}$	r_1	(86)

a) The corresponding cycle indices (CIs) are listed. Each substitution position represented by ○ accommodates a preformed alkyl moiety (PAM).

Hence, we can obtain the following polynomials:

$$\widehat{R}_{2m+1}(q,t,s,p) = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{R}_{2m+1,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q} = \mathrm{coeff}(\widehat{R}(x,q,t,s,p)^{(m)}, x^{2m+1}) \quad (89)$$

$$\widehat{R}_{2m+2}(q,t,s,p) = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{R}_{2m+2,n_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q} = \mathrm{coeff}(\widehat{R}(x,q,t,s,p)^{(m)}, x^{2m+2}) \quad (90)$$

where we put $2m+1 = n_q + n_t + n_s + n_p$ (eq 89) or $2m+2 = n_q + n_t + n_s + n_p$ (eq 90).

Implementation and Results for Centroidal Alkanes as Graphs: The functional equation represented by $r(x,q,t,s,p)$ (eq 80) has a recursive nature, which is implemented by mean of the do loop of the Maple programming language. The program is stored in a file named "GraphCAlkane1.mpl," as shown below. The upper limit of the carbon content (k) is tentatively fixed to be 15 so that we are able to calculate the numbers of centroidal alkanes up to 32 in accord with eqs 89 and 90. The upper limit 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 a single functional equation $r(x,q,t,s,p)$ (eq 80). This feature presents a sharp contrast to the corresponding recursive enumeration as 3D structures, which requires three functional equations, i.e., $a(x,q,t,s,p)$ (eq 4), $b(x,q,t,s,p)$ (eq 5), and $c(x^2,q^2,t^2,s^2,p^2)$ (eq 6), as coded in the above-described program "AlkaneBI02.mpl."

```
#GraphCAlkane1.mpl
#Total Numbers of Centroidal Alkanes as Graphs

"(Part 1) Functional Equations
for Internal 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));

"(Part 2) Functional Equations for Centroidal Alkanes";
Rxbi := 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))
    + (x*q/24)*((r1-1)^4 + 3*(r2-1)^2 + 8*(r1-1)*(r3-1)
                + 6*(r1-1)^2*(r2-1) + 6*(r4-1));
"(Part 3) Initial Values";
r1 := 1; r2 := 1; r3 := 1; r4 := 1;
rsum := 1:
Rbi := x;

"(Part 4) Recursive Calculation";
kmax := 15;
for k from 1 to kmax by 1 do
"k ="; k;

"(Part 5) PAMs as 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))):
Cr4x:= subs({p=p^4,s=s^4,t=t^4,q=q^4}, 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):
r4 := r4 + Cr4x*x^(4*k):
rsum := rsum + Crsum*x^k:

"(Part 6) Centroidal Alkanes as Graphs";
kk := 2*k +1:
Rbi := Rbi + coeff(expand(Rxbi),x^kk)*x^kk
          + coeff(expand(Rxbi),x^(kk+1))*x^(kk+1):
end do:

"(Part 7) Print Out of Rbi (Total)";
for k from 1 to 2*kmax by 1 do
carbon_content:= k:
NRbi := collect(sort(expand(coeff(Rbi,x^k)),[q,t,s,p]),p);
end do;
```

The abbreviated symbols for functional equations, i.e., `r1` for the power 1 of $r(x, q, t, s, p)$, `r2` for the power 2 of $r(x^2, q^2, t^2, s^2, p^2)$, and so on are employed in this program. The symbol `rsum` is used to store the series for $r(x)$ $(q = t = s = p = 1)$.

The first part (Part 1) of this program declares a functional equation `rx` for eq 80, which is calculated by using `r1` etc. recursively. The second part (Part 2) declares a functional equation `Rxbi` for $\widehat{R}(x, q, t, s, p)$ (eq 87), which are 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. The Part 4 ("Recursive Calculation") shows a `do` loop for carbon content k, in which Part 5 shows the recursive process for PAMs as graphs. Part 6 calculates and stores the result of `Rxbi` (cf. Part 2) in a series named `Rbi`, where the next two coefficients are calculated by using a Maple command `coeff` and added to the end of respective functional equations in each step of the `do` loop.

After escaping from the `do` loop for k, Part 7 shows the print-out of `NRbi`, which is the coefficient of x^k stored in `Rbi` for $\widehat{R}(x, q, t, s, p)$ (cf. eq 87). Note that each coefficient is a polynomial of branching indicators (q, t, s, and p). 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 format of each BM, i.e., the descending order of the branching degrees $4^\circ > 3^\circ > 2^\circ > 1^\circ$.

The above-described program is executed by inputting the following command in the Maple input window:

```
> restart;
> read "GraphCAlkane1.mpl";
```

The calculation results are obtained according to its printout sections. The data stored in the series `Rbi`, i.e., $\sum \widehat{R}_{kn_qn_tn_sn_p} p^{n_p} s^{n_s} t^{n_t} q^{n_q}$ which is the coefficient of x^k (cf. eqs 82, 89, and 90), are shown in Table 13. Note that the summation is concerned with n_q, n_t, n_s, and n_p for each carbon content k.

Enumeration of Bicentroidal Alkanes as Graphs. Let the symbol $\widetilde{R}_{kn_qn_tn_sn_p}$ be the number of inequivalent bicentroidal alkanes as graphs where k carbons in each alkane (except trivial cases) are categorized into n_q quaternary carbons, n_t tertiary carbons, n_s secondary carbons, and n_p primary carbons $(k = n_q + n_t + n_s + n_p)$. Thereby, we are able to write down a generating function of the number by using the above-described branching indicators, (i.e., q, t, s, and p) as follows:

$$\widetilde{R}(x, q, t, s, p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{R}_{kn_qn_tn_sn_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{91}$$

In a similar way to the treatment of 3D structures, the dumbbell skeleton **17** shown in Table 14 is used to treat bicentroidal alkanes as graphs. Note that **17** is regarded as belonging to the symmetric group of degree 2 ($\mathcal{S}^{[2]}$):

$$\mathcal{S}^{[2]} = \{(1)(2), (1\ 2)\} \tag{93}$$

whereas the seemingly same skeleton **12** for treating 3D structures belongs to the CR $\mathbf{K}(/\mathbf{K}')$ (eq 62). The cycles contained in eq 93 correspond to variables r_1^2 and r_2, which are summed up and averaged by multiplying 1/2. Thereby, we obtain the CI represented by eq 92 (Table 14) according to Pólya's method.[8] The same CI can be alternatively derived by the reduction of the CI-CF (eq 61) under a graph-reduction condition $a_d = b_d = c_d = r_d$ (cf. eq 81). This means that the Pólya's method[8] is a special case of Fujita's proligand method.[21–23]

After the variable r_d is replaced by the function $r(x^d, q^d, t^d, s^d, p^d) - 1$, a similar treatment to the derivation of eq 65 is employed in the treatment of eq 92. Thereby, we obtain a functional equation for counting bicentroidal alkanes as graphs:

$$\widetilde{R}(x, q, t, s, p) = \frac{1}{2}\left\{[r(x, q, t, s, p) - 1]^2 + [r(x^2, q^2, t^2, s^2, p^2) - 1]\right\} \tag{94}$$

The criterion (eq 58) is employed so that the two substitution positions of the dumbbell skeleton **17** accommodate two PAMs of the same carbon content m. Suppose that we have obtained $r(x, q, t, s, p)$ (eqs 80) up to $k = m$. After m is tentatively fixed, eq 80 is introduced into the right-hand side of eq 94. Then the resulting equation is expanded to give a series for $\widetilde{R}(x, q, t, s, p)^{(m)}$ (cf. eq 91), where the superscript (m) represents the use of eq 80 by fixing m. In accord with eq 58, the coefficient of the term x^{2m} in the series is effective to determine $\widetilde{R}_{2m,n_qn_tn_sn_p}$. Thereby, we obtain the following equation for evaluating such a coefficient as a polynomial composed of branching indicators (q, t, s, and p):

$$\begin{aligned}\widetilde{R}_{2m}(q, t, s, p) &= \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{R}_{2m,n_qn_tn_sn_p} p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q} \\ &= \mathrm{coeff}(\widetilde{R}(x, q, t, s, p)^{(m)}, x^{2m})\end{aligned} \tag{95}$$

where we put $2m = n_q + n_t + n_s + n_p$.

The numbers of bicentroidal alkanes as graphs for each carbon content are shown in Table 15 as the coefficients of the BMs appearing in a polynomial $\sum \widetilde{R}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$.

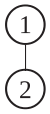
Total Number of Alkanes as Graphs. The values of $\widehat{R}_{kn_qn_tn_sn_p}$ (eq 82) for centroidal alkanes as graphs have been evaluated and collected in Table 13, while the data of $\widetilde{R}_{kn_qn_tn_sn_p}$ (eq 91) for bicentroidal alkanes as graphs have been evaluated and collected in Table 15. Hence, the total number

Table 13. Numbers of Centroidal Alkanes as Graphs[a)]

	The coefficient of x^k (cf. eqs 82, 89, and 90), i.e., $\sum \widehat{R}_{kn_qn_tn_sn_p} p^{n_p} s^{n_s} t^{n_t} q^{n_q}$
$k = 1$	1 (methane for an extreme case)
$k = 2$	0
$k = 3$	sp^2
$k = 4$	tp^3
$k = 5$	$qp^4 + tsp^3 + s^3p^2$
$k = 6$	$qsp^4 + ts^2p^3$
$k = 7$	$qtp^5 + (2\,qs^2 + 2\,t^2s)p^4 + 3\,ts^3p^3 + s^5p^2$
$k = 8$	$(t^3 + qts)p^5 + (2\,qs^3 + 2\,t^2s^2)p^4 + 2\,ts^4p^3$
$k = 9$	$(2\,q^2s + 2\,qt^2)p^6 + (3\,t^3s + 8\,qts^2)p^5 + (9\,t^2s^3 + 5\,qs^4)p^4 + 5\,ts^5p^3 + s^7p^2$
$k = 10$	$2\,q^2tp^7 + (2\,q^2s^2 + t^4 + 6\,qt^2s)p^6 + (6\,t^3s^2 + 9\,qts^3)p^5 + (6\,t^2s^4 + 4\,qs^5)p^4 + 3\,ts^6p^3$
$k = 11$	$q^3p^8 + (8\,q^2ts + 4\,qt^3)p^7 + (28\,qt^2s^2 + 6\,t^4s + 10\,q^2s^3)p^6 + (24\,t^3s^3 + 33\,qts^4)p^5 + (27\,t^2s^5 + 9\,qs^6)p^4 + 8\,ts^7p^3 + s^9p^2$
$k = 12$	$(3\,q^2t^2 + 3\,q^3s)p^8 + (13\,qt^3s + 2\,t^5 + 20\,q^2ts^2)p^7 + (45\,qt^2s^3 + 14\,t^4s^2 + 10\,q^2s^4)p^6 + (32\,qts^5 + 31\,t^3s^4)p^5 + (7\,qs^7 + 18\,t^2s^6)p^4 + 4\,ts^8p^3$
$k = 13$	$4\,q^3tp^9 + (8\,qt^4 + 11\,q^3s^2 + 31\,q^2t^2s)p^8 + (86\,qt^3s^2 + 11\,t^5s + 76\,q^2ts^3)p^7 + (174\,qt^2s^4 + 69\,t^4s^3 + 35\,q^2s^5)p^6 + (97\,qts^6 + 109\,t^3s^5)p^5 + (63\,t^2s^7 + 15\,qs^8)p^4 + 12\,ts^9p^3 + s^{11}p^2$
$k = 14$	$q^4p^{10} + (13\,q^3ts + 12\,q^2t^3)p^9 + (36\,qt^4s + t^6 + 85\,q^2t^2s^2 + 21\,q^3s^3)p^8 + (30\,t^5s^2 + 173\,qt^3s^3 + 121\,q^2ts^4)p^7 + (99\,t^4s^4 + 215\,qt^2s^5 + 32\,q^2s^6)p^6 + (105\,t^3s^6 + 82\,qts^7)p^5 + (36\,t^2s^8 + 11\,qs^9)p^4 + 5\,ts^{10}p^3$
$k = 15$	$(7\,q^4s + 14\,q^3t^2)p^{10} + (101\,q^2t^3s + 90\,q^3ts^2 + 15\,qt^5)p^9 + (23\,t^6s + 254\,qt^4s^2 + 428\,q^2t^2s^3 + 71\,q^3s^4)p^8 + (182\,t^5s^3 + 759\,qt^3s^4 + 405\,q^2ts^5)p^7 + (423\,t^4s^5 + 717\,qt^2s^6 + 98\,q^2s^7)p^6 + (360\,t^3s^7 + 233\,qts^8)p^5 + (23\,qs^{10} + 127\,t^2s^9)p^4 + 16\,ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k = 20$	$2\,q^6p^{14} + (122\,q^4t^3 + 95\,q^5ts)p^{13} + (145\,q^2t^6 + 1185\,q^3t^4s + 1405\,q^4t^2s^2 + 200\,q^5s^3)p^{12} + (4352\,q^2t^5s^2 + 18\,t^9 + 7924\,q^3t^3s^3 + 523\,qt^7s + 2761\,q^4ts^4)p^{11} + (20056\,q^2t^4s^4 + 465\,t^8s^2 + 1098\,q^4s^6 + 6526\,qt^6s^3 + 14115\,q^3t^2s^5)p^{10} + (22429\,qt^5s^5 + 8121\,q^3ts^7 + 31864\,q^2t^3s^6 + 3305\,t^7s^4)p^9 + (8715\,t^6s^6 + 20108\,q^2t^2s^8 + 31211\,qt^4s^7 + 1396\,q^3s^9)p^8 + (19469\,qt^3s^9 + 10412\,t^5s^8 + 5078\,q^2ts^{10})p^7 + (5944\,t^4s^{10} + 400\,q^2s^{12} + 5543\,qt^2s^{11})p^6 + (1636\,t^3s^{12} + 677\,qts^{13})p^5 + (31\,qs^{15} + 200\,t^2s^{14})p^4 + 10\,ts^{16}p^3$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of centroidal alkanes as graphs, which have n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

Table 14. Skeleton for Generating Bicentroidal Alkanes as Graphs (or Trees)[a)]

Skeleton for bicentroid alkanes		Cycle index (without chirality fittingness)	
(as trees or graphs)	Permutation group	(CI)	
 **17**	$\mathcal{S}^{[2]}$	$\frac{1}{2}(r_1^2 + r_2)$	(92)

a) The corresponding cycle index (CI) without chirality fittingness is listed. Each of the two substitution positions accommodates a preformed alkyl moiety (PAM).

of alkanes as graphs are obtained by their summation. Let the summation be represented by the symbol $\widehat{\widetilde{R}}_{kn_qn_tn_sn_p}$. Then, the following relationship is obvious by the definitions of the respective numbers:

$$\widehat{\widetilde{R}}_{kn_qn_tn_sn_p} = \widehat{R}_{kn_qn_tn_sn_p} + \widetilde{R}_{kn_qn_tn_sn_p} \tag{96}$$

where the term in the left-hand side satisfies the following generating function:

$$\widehat{\widetilde{R}}(x, q, t, s, p) = \sum_{k=0}^{\infty}\left(\sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{\widetilde{R}}_{kn_qn_tn_sn_p}p^{n_p}\right)s^{n_s}\right)t^{n_t}\right)q^{n_q}\right)x^k \tag{97}$$

The two generating functions (eq 82 and eq 91) are summed up so as to give the generating function defined by eq 96 under

Table 15. Numbers of Bicentroidal Alkanes as Graphs[a)]

	The coefficient of x^k (cf. eqs 91, 94, and 95), i.e., $\sum \widetilde{R}_{kn_qn_tn_sn_p} p^{n_p} s^{n_s} t^{n_t} q^{n_q}$
$k = 1$	0
$k = 2$	p^2
$k = 3$	0
$k = 4$	$s^2 p^2$
$k = 5$	0
$k = 6$	$t^2 p^4 + ts^2 p^3 + s^4 p^2$
$k = 7$	0
$k = 8$	$q^2 p^6 + 2\, qtsp^5 + (qs^3 + 3\, t^2 s^2)p^4 + 2\, ts^4 p^3 + s^6 p^2$
$k = 9$	0
$k = 10$	$(3\, q^2 s^2 + 2\, qt^2 s + t^4)p^6 + (4\, t^3 s^2 + 8\, qts^3)p^5 + (11\, t^2 s^4 + 2\, qs^5)p^4 + 4\, ts^6 p^3 + s^8 p^2$
$k = 11$	0
$k = 12$	$3\, q^2 t^2 p^8 + (8\, q^2 ts^2 + 8\, qt^3 s)p^7 + (28\, qt^2 s^3 + 10\, t^4 s^2 + 10\, q^2 s^4)p^6 + (24\, t^3 s^4 + 26\, qts^5)p^5 +$ $(25\, t^2 s^6 + 4\, qs^7)p^4 + 6\, ts^8 p^3 + s^{10} p^2$
$k = 13$	0
$k = 14$	$q^4 p^{10} + (2\, q^2 t^3 + 8\, q^3 ts)p^9 + (16\, qt^4 s + 3\, t^6 + 47\, q^2 t^2 s^2 + 7\, q^3 s^3)p^8 +$ $(22\, t^5 s^2 + 102\, qt^3 s^3 + 65\, q^2 ts^4)p^7 + (84\, t^4 s^4 + 149\, qt^2 s^5 + 29\, q^2 s^6)p^6 +$ $(101\, t^3 s^6 + 71\, qts^7)p^5 + (56\, t^2 s^8 + 7\, qs^9)p^4 + 9\, ts^{10} p^3 + s^{12} p^2$
$k = 15$	0
	(omitted)
$k = 20$	$3\, q^6 p^{14} + (24\, q^4 t^3 + 54\, q^5 ts)p^{13} + (78\, q^2 t^6 + 364\, q^3 t^4 s + 576\, q^4 t^2 s^2 + 58\, q^5 s^3)p^{12} +$ $(1728\, q^2 t^5 s^2 + 3193\, q^3 t^3 s^3 + 240\, qt^7 s + 999\, q^4 ts^4)p^{11} +$ $(9148\, q^2 t^4 s^4 + 210\, t^8 s^2 + 481\, q^4 s^6 + 3012\, qt^6 s^3 + 5947\, q^3 t^2 s^5)p^{10} +$ $(11634\, qt^5 s^5 + 1720\, t^7 s^4 + 15622\, q^2 t^3 s^6 + 3793\, q^3 ts^7)p^9 +$ $(11023\, q^2 t^2 s^8 + 17908\, qt^4 s^7 + 5341\, t^6 s^6 + 669\, q^3 s^9)p^8 +$ $(7280\, t^5 s^8 + 12610\, qt^3 s^9 + 3091\, q^2 ts^{10})p^7 + (305\, q^2 s^{12} + 4980\, t^4 s^{10} + 4099\, qt^2 s^{11})p^6 +$ $(1686\, t^3 s^{12} + 568\, qts^{13})p^5 + (290\, t^2 s^{14} + 23\, qs^{15})p^4 + 20\, ts^{16} p^3 + s^{18} p^2$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q} t^{n_t} s^{n_s} p^{n_p}$) represents the number of bicentroidal alkanes as graphs, which have n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

the condition that the two generating functions have already been evaluated as series. Thus, we can write down the total numbers by using the following relationship:

$$\widetilde{\widehat{R}}(x, q, t, s, p) = \widehat{R}(x, q, t, s, p) + \widetilde{R}(x, q, t, s, p) \tag{98}$$

if the two generating functions in the right-hand side have already been evaluated as series. Just like the counterpart (eqs 76–78) for 3D structures, the relationship (eq 98) for graphs means that simple summation of the functional equations (eqs 87 and 94) gives erroneous results, because the integer m runs according to eq 40 for eq 87 and differently according to eq 58 for eq 94.

The total numbers of centroidal and bicentroidal alkanes as graphs for each carbon content are shown in Table 16, where the polynomial of each row (k), i.e., $\sum \widetilde{\widehat{R}}_{kn_qn_tn_sn_p} q^{n_q} t^{n_t} s^{n_s} p^{n_p}$, indicates the numbers $\widetilde{\widehat{R}}_{kn_qn_tn_sn_p}$ as the coefficients of the BMs. Obviously, Table 16 can be obtained by summing up Tables 13 and 15 in accord with eq 98.

Discussion

Cases of Lower Carbon Contents. To verify the results listed in Tables 2–4 and 6–11, the 3D structures of alkanes of carbon contents 1–6 are depicted in Figure 3. It is convenient to pay attention to the feature that the power n_p of the term p^{n_p} represents the number of terminal methyl ligands. This feature can be used to check 3D structures at issue, as found easily in Figure 3.

Each structure appearing in the "centroidal achiral" column of Figure 3 verifies the coefficient of the corresponding BM ($p^{n_p} s^{n_s} t^{n_t} q^{n_q}$) which is involved in polynomials collected in Table 2. The symbol © in each 3D structure of Figure 3 indicates a centroid, where the criterion for centroidal alkanes (eq 40) is satisfied. Figure 3 does not contain chiral centroidal alkanes in agreement with Table 3.

The case of carbon content 1 is an extreme case, i.e., methane (**18**), which is characterized by a trivial BM 1 ($=q^0 t^0 s^0 p^0$ or strictly speaking $q^0 t^0 s^0 p^0 1^1$) or a trivial mode of divergence [0,0,0,0]. Because the carbon of methane is characterized to be 0°, the branching indicator corresponding to such an extreme case (0°) is not defined but regarded as being equal to 1 for the sake of simplicity. For a practical purpose, the carbon of methane is tentatively considered to be primary so that the mode of divergence is denoted as [0,0,0,(1)], where the symbol (1) represents the contribution of such a tentative primary carbon.

Each structure appearing in the "bicentroidal achiral" column of Figure 3 verifies the coefficient of the corresponding BM (Table 6). The symbol ©–© in each 3D structure of Figure 3 indicates a bicentroid, where the criterion for characterizing bicentroidal alkanes (eq 58) is satisfied. Figure 3 does not contain chiral bicentroidal alkanes in agreement with Table 7.

The 3D structures of alkanes of carbon content 7 are depicted in Figure 4, which contains centroidal alkanes only. Wheth-

Table 16. Total Numbers of Alkanes (Centroidal & Bicentroidal) as Graphs[a)]

	The coefficient of x^k (cf. eq 97), i.e., $\sum \widehat{\widetilde{\boldsymbol{R}}}_{kn_q n_t n_s n_p} p^{n_p} s^{n_s} t^{n_t} q^{n_q}$
$k=1$	1
$k=2$	p^2
$k=3$	sp^2
$k=4$	$tp^3 + s^2p^2$
$k=5$	$qp^4 + tsp^3 + s^3p^2$
$k=6$	$(qs + t^2)p^4 + 2\,ts^2p^3 + s^4p^2$
$k=7$	$qtp^5 + (2\,qs^2 + 2\,t^2s)p^4 + 3\,ts^3p^3 + s^5p^2$
$k=8$	$q^2p^6 + (t^3 + 3\,qts)p^5 + (5\,t^2s^2 + 3\,qs^3)p^4 + 4\,ts^4p^3 + s^6p^2$
$k=9$	$(2\,q^2s + 2\,t^2q)p^6 + (3\,t^3s + 8\,qts^2)p^5 + (9\,t^2s^3 + 5\,qs^4)p^4 + 5\,ts^5p^3 + s^7p^2$
$k=10$	$2\,q^2tp^7 + (5\,q^2s^2 + 8\,qt^2s + 2\,t^4)p^6 + (10\,t^3s^2 + 17\,qts^3)p^5 + (17\,t^2s^4 + 6\,qs^5)p^4 + 7\,ts^6p^3 + s^8p^2$
$k=11$	$q^3p^8 + (8\,q^2ts + 4\,t^3q)p^7 + (28\,qt^2s^2 + 6\,t^4s + 10\,q^2s^3)p^6 + (24\,t^3s^3 + 33\,qts^4)p^5 + (27\,t^2s^5 + 9\,qs^6)p^4 + 8\,ts^7p^3 + s^9p^2$
$k=12$	$(6\,t^2q^2 + 3\,q^3s)p^8 + (21\,qt^3s + 28\,q^2ts^2 + 2\,t^5)p^7 + (73\,qt^2s^3 + 24\,t^4s^2 + 20\,q^2s^4)p^6 + (58\,qts^5 + 55\,t^3s^4)p^5 + (11\,qs^7 + 43\,t^2s^6)p^4 + 10\,ts^8p^3 + s^{10}p^2$
$k=13$	$4\,q^3tp^9 + (8\,t^4q + 11\,q^3s^2 + 31\,q^2t^2s)p^8 + (86\,qt^3s^2 + 11\,t^5s + 76\,q^2ts^3)p^7 + (174\,qt^2s^4 + 69\,t^4s^3 + 35\,q^2s^5)p^6 + (97\,qts^6 + 109\,t^3s^5)p^5 + (63\,t^2s^7 + 15\,qs^8)p^4 + 12\,ts^9p^3 + s^{11}p^2$
$k=14$	$2\,q^4p^{10} + (14\,q^2t^3 + 21\,q^3ts)p^9 + (52\,qt^4s + 4\,t^6 + 132\,q^2t^2s^2 + 28\,q^3s^3)p^8 + (52\,t^5s^2 + 275\,qt^3s^3 + 186\,q^2ts^4)p^7 + (183\,t^4s^4 + 364\,qt^2s^5 + 61\,q^2s^6)p^6 + (206\,t^3s^6 + 153\,qts^7)p^5 + (92\,t^2s^8 + 18\,qs^9)p^4 + 14\,ts^{10}p^3 + s^{12}p^2$
$k=15$	$(7\,q^4s + 14\,t^2q^3)p^{10} + (101\,q^2t^3s + 90\,q^3ts^2 + 15\,t^5q)p^9 + (23\,t^6s + 254\,qt^4s^2 + 428\,q^2t^2s^3 + 71\,q^3s^4)p^8 + (182\,t^5s^3 + 759\,qt^3s^4 + 405\,q^2ts^5)p^7 + (423\,t^4s^5 + 717\,qt^2s^6 + 98\,q^2s^7)p^6 + (360\,t^3s^7 + 233\,qts^8)p^5 + (23\,qs^{10} + 127\,t^2s^9)p^4 + 16\,ts^{11}p^3 + s^{13}p^2$
	(omitted)
$k=20$	$5\,q^6p^{14} + (146\,q^4t^3 + 149\,q^5ts)p^{13} + (223\,q^2t^6 + 1549\,q^3t^4s + 1981\,q^4t^2s^2 + 258\,q^5s^3)p^{12} + (6080\,q^2t^5s^2 + 18\,t^9 + 11117\,q^3t^3s^3 + 3760\,q^4ts^4 + 763\,qt^7s)p^{11} + (29204\,q^2t^4s^4 + 675\,t^8s^2 + 1579\,q^4s^6 + 20062\,q^3t^2s^5 + 9538\,qt^6s^3)p^{10} + (34063\,qt^5s^5 + 47486\,q^2t^3s^6 + 5025\,t^7s^4 + 11914\,q^3ts^7)p^9 + (14056\,t^6s^6 + 49119\,qt^4s^7 + 31131\,q^2t^2s^8 + 2065\,q^3s^9)p^8 + (17692\,t^5s^8 + 32079\,qt^3s^9 + 8169\,q^2ts^{10})p^7 + (705\,q^2s^{12} + 10924\,t^4s^{10} + 9642\,qt^2s^{11})p^6 + (3322\,t^3s^{12} + 1245\,qts^{13})p^5 + (54\,qs^{15} + 490\,t^2s^{14})p^4 + 30\,ts^{16}p^3 + s^{18}p^2$
	(omitted)

a) The coefficient of each branching monomial (BM, $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) represents the number of centroidal and bicentroidal alkanes as graphs, which have n_q quaternary, n_t tertiary, n_s secondary, and n_p primary carbons.

er achiral or chiral, there are no bicentroidal alkanes of carbon content 7 (odd in general) in agreement with Tables 6 and 7. The 3D structures depicted in the "centroidal achiral" column of Figure 4 correspond to the data shown in the ($k = 7$)-row of Table 2, i.e., $qtp^5 + (2\,qs^2 + t^2s)p^4 + 2\,ts^3p^3 + s^5p^2$. On the other hand, the 3D structures depicted in the "centroidal chiral" column of Figure 4 correspond to the data shown in the ($k = 7$)-row of Table 3, i.e., $t^2sp^4 + ts^3p^3$, where an arbitrary one of two enantiomers is depicted as a representative.

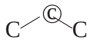
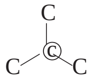
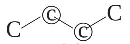
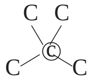
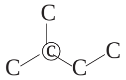
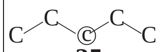
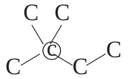
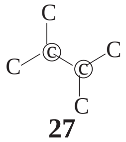
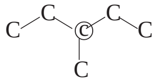
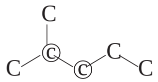
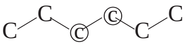
Meso and Related Cases. Figure 5 collects centroidal and bicentroidal alkanes of carbon content 8, which are depicted as achiral and chiral 3D structures. In particular, there appears meso-3,4-dimethylhexane (**50**) as the lowest case of bicentroidal alkanes of meso type.

The 3D structures depicted in the "centroidal achiral" column of Figure 5 are consistent with the data shown in the ($k = 8$)-row of Table 2, i.e., $(t^3 + qts)p^5 + (2\,qs^3 + t^2s^2)p^4 + 2\,ts^4p^3$, where the coefficient of each BM represents the number of alkanes as 3D structures.

The "centroidal chiral" column of Figure 5 involves only one 3D structure **49** corresponding to the BM $t^2s^2p^4$, which appears in the ($k = 8$)-row of Table 3. Note that an arbitrary enantiomer is depicted as a representative, because the present enumeration counts each pair of enantiomers just once.

The 3D structures depicted in the "bicentroidal achiral" column of Figure 5 correspond to the data shown in the ($k = 8$)-row of Table 6, i.e., $q^2p^6 + qtsp^5 + (qs^3 + 2\,t^2s^2)p^4 + ts^4p^3 + s^6p^2$. Among them, one isomer of 3,4-dimethylhexane (**50**) characterized by BM $t^2s^2p^4$ exhibits meso character, where an *R*-1-methylpropyl ligand is linked with an *S*-1-methylpropyl ligand so as to give an achiral bicentroidal alkane (suppose that the R or S descriptor in each alkane is maintained even in isolation).

The other isomer of 3,4-dimethylhexane (**52** or its enantiomer) is also characterized by BM $t^2s^2p^4$ but appears in the the "bicentroidal chiral" column of Figure 5. The chiral alkane **52** belongs to C_2 at the highest attainable symmetry so that it is counted just once in spite of the presence of two

CC[a]	BM[b] divergence	Centroidal Alkanes (Table 4)		Bicentroidal Alkanes (Table 8)	
		Achiral (Table 2)	Chiral[c] (Table 3)	Achiral (Table 6)	Chiral[d] (Table 7)
$k = 1$	1 [0,0,0,(1)]	(C)[e] **18**			
$k = 2$	p^2 [0,0,0,2]			©—© **19**	
$k = 3$	sp^2 [0,0,1,2]	 **20**			
$k = 4$	tp^3 [0,1,0,3]	 **21**			
	s^2p^2 [0,0,2,2]			 **22**	
$k = 5$	qp^4 [1,0,0,4]	 **23**			
	tsp^3 [0,1,1,3]	 **24**			
	s^3p^2 [0,0,3,2]	 **25**			
$k = 6$	qsp^4 [1,0,1,4]	 **26**			
	t^2p^4 [0,2,0,4]			 **27**	
	ts^2p^3 [0,1,2,3]	 **28**		 **29**	
	s^4p^2 [0,0,4,2]			 **30**	

[a] CC: carbon content. [b] BM: branching monomial. [c] Absence of chiral centroidal alkanes. [d] Absence of chiral bicentroidal alkanes. [e] Methane (an extreme case).

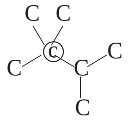
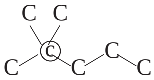
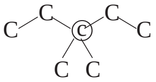
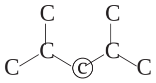
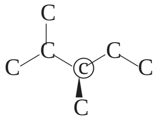
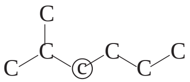
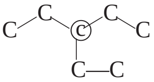
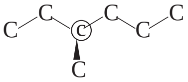
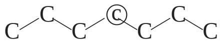
Figure 3. Alkanes of lower carbon contents ($k = 1$–6), which are categorized by means of branching monomials. The symbol © indicates a centroid, while the symbol ©–© indicates a bicentroid.

asymmetric carbons.

In addition of **52**, the "bicentroidal chiral" column of Figure 5 contains the remaining alkanes as 3D structures, which are consistent with the data shown in the ($k = 8$)-row of Table 7, i.e., $qtsp^5 + 2\,t^2s^2p^4 + ts^4p^3$. Because each pair of enantiomers is counted just once in the present enumeration, an arbitrary one is selected from the pair and depicted as a representative.

3D Structures vs. Graphs. The *meso*-3,4-dimethylhexane (**50**) and the relevant chiral alkane **52** (Figure 5) should further be commented from a viewpoint of the difference between 3D structures and graphs. Because graphs cannot deal with chirality/achirality, the 3D structural data of achiral plus chiral alkanes (Tables 4, 8, and 11) should be compared with Tables 13, 15, and 16.

Compare the ($k = 8$)-row of Table 8 (i.e., $q^2p^6 + 2\,qtsp^5 + (qs^3 + 4\,t^2s^2)p^4 + 2\,ts^4p^3 + s^6p^2$) with the ($k = 8$)-row of Table 15 (i.e., $q^2p^6 + 2\,qtsp^5 + (qs^3 + 3\,t^2s^2)p^4 + 2\,ts^4p^3 +$

CC[a]	BM[b] divergence	Centroidal Alkanes (Table 4)		Bicentroidal Alkanes (Table 8)	
		Achiral (Table 2)	Chiral (Table 3)	Achiral[c] (Table 6)	Chiral[d] (Table 7)
$k = 7$	qtp^5 [1,1,0,5]	 **31**			
	qs^2p^4 [1,0,2,4]	 **32**  **33**			
	t^2sp^4 [0,2,1,4]	 **34**	 **35**		
	ts^3p^3 [0,1,3,3]	 **36**  **37**	 **38**		
	s^5p^2 [0,0,5,2]	 **39**			

[a] CC: carbon content. [b] BM: branching monomial. [c] Absence of achiral bicentroidal alkanes. [d] Absence of chiral bicentroidal alkanes.

Figure 4. Alkanes of carbon content 7, which are categorized by means of branching monomials. Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds. The symbol © indicates a centroid.

s^6p^2). The difference between them is found in the BM $4\,t^2s^2p^4$ for 3D structures vs. the BM $3\,t^2s^2p^4$ for graphs. The coefficient 4 of the former BM, which corresponds to the four bicentroidal alkanes **50**–**53**, is reduced into the value 3 of the latter BM. The decrease by one ($4\,t^2s^2p^4 - 3\,t^2s^2p^4 = t^2s^2p^4$) stems from the fact that the *meso*-alkane **50** and the relevant alkane **52** coalesce into a single graph.

The 3D structures of alkanes characterized by carbon content 9 and by BM $t^2s^3p^4$ are depicted in Figure 6. Whether achiral or chiral, there are no bicentroidal alkanes of carbon content 9 (odd in general) in agreement with Tables 6 and 7. Hence Figure 6 contains centroidal alkanes only.

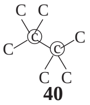
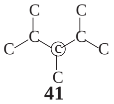
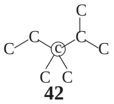
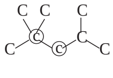
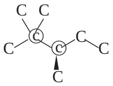
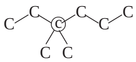
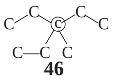
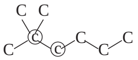
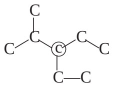
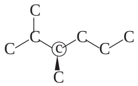
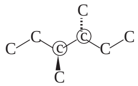
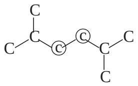
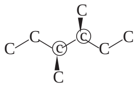
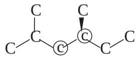
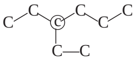
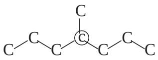
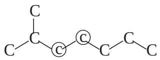
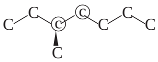
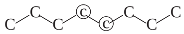
The three 3D structures depicted in the "centroidal achiral" column of Figure 6 are consistent with the coefficient 3 of the term $3t^2s^3p^4$ which appears in the ($k = 9$)-row of Table 2. On the other hand, the eight 3D structures depicted in the "centroidal chiral" column of Figure 6 correspond to the coefficient 8 of the term $8t^2s^3p^4$ found in the ($k = 9$)-row of Table 3.

The total number 11 (=3 + 8) of the 3D structures collected in Figure 6 is in agreement with the coefficient 11 of the term $11t^2s^3p^4$ which appears in the ($k = 9$)-row of Table 4. The corresponding number of graphs is found to be 9, which appears as the coefficient of the term $9t^2s^3p^4$ in the ($k = 9$)-row of Table 13. Among the 3D structures listed in Figure 6, a diastereomeric pair of **60** (an achiral 3D structure) and **65** (a chiral 3D structure) coalesces into a single graph, just as a diastereomeric pair of two chiral 3D structures, **66** and **67**, coalesces into a single graph. The two modes of coalescence well explain the above-mentioned decrease by 2 (the 11 of 3D structures reduced into the 9 of graphs).

The achiral alkane **60** having two asymmetric carbons should be pointed out because its internal compensation of chirality is akin to that of the *meso*-alkane **50**. When we focus our attention on the reduction from 3D structures to graphs, we find that the diastereomeric relationship between **60** and **65** is akin to the diastereomeric relationship between **50** and **52**.

The comparisons between Table 1 and Table 12 and between Table 5 and Table 14 provide us with an insight to methodological differences between Fujita's proligand method aiming at 3D structures and Pólya's method aiming at graphs. There are at least two predominant differences between them:

1. Symmetries of Skeletons: The 3D skeletons collected in Table 1 are considered to be governed by such coset representations (CRs) as $T_d(/C_{3v})$ which are derived from appropriate point groups (e.g., T_d) and their subgroups (e.g., C_{3v}). It should be emphasized that both the continuous nature of 3D structures and their discrete nature are systematically treated by considering point groups (for discussions on continuous objects) and their CRs (for discussions on discrete objects).

CC[a]	BM[b] divergence	Centroidal Alkanes (Table 4)		Bicentroidal Alkanes (Table 8)	
		Achiral (Table 2)	Chiral (Table 3)	Achiral (Table 6)	Chiral (Table 7)
$k = 8$	q^2p^6 [2,0,0,6]			 **40**	
	t^3p^5 [0,3,0,5]	 **41**			
	$qtsp^5$ [1,1,1,5]	 **42**		 **43**	 **44**
	qs^3p^4 [1,0,3,4]	 **45**  **46**		 **47**	
	$t^2s^2p^4$ [0,2,2,4]	 **48**	 **49**	 **50**  **51**	 **52**  **53**
	ts^4p^3 [0,1,4,3]	 **54**  **55**		 **56**	 **57**
	s^6p^2 [0,0,6,2]			 **58**	

[a] CC: carbon content. [b] BM: branching monomial.

Figure 5. Alkanes of carbon content 8, which are categorized by means of branching monomials. The symbol © indicates a centroid, while the symbol ©–© indicates a bicentroid. Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

In contrast, the graph skeletons collected in Table 12 are considered to belong to such permutation groups as the symmetric group of degree 4 ($\mathcal{S}^{[4]}$). This means that graphs are abstract objects to consider their discrete nature only.

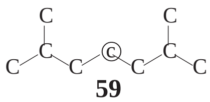
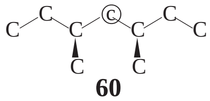
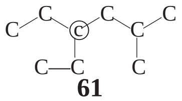
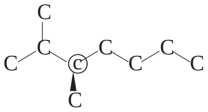
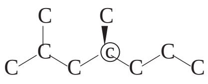
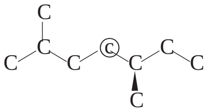
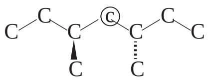
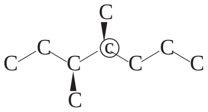
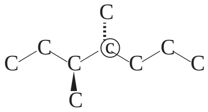
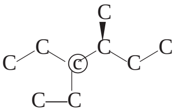
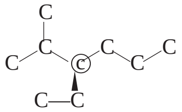
The viewpoint of continuity vs. discreteness is more clearly recognized by comparing between Table 5 and Table 14. The 3D skeleton shown in Table 5 belongs to the CR $\mathbf{K}(/\mathbf{K}')$, where $\mathbf{K}$ is a factor group of point groups (i.e., $D_{\infty h}/C_{\infty}$) and $\mathbf{K}'$ is its subgroup represented by $D_{\infty h}/C_{\infty v}$. In contrast, the graph skeleton shown in Table 14 belongs to the symmetric group of degree 2 ($\mathcal{S}^{[2]}$). Note that $\mathbf{K}(/\mathbf{K}')$ (as a group) is not isomorphic to $\mathcal{S}^{[2]}$, whereas $T_d(/C_{3v})$ (as a group) is isomorphic to $\mathcal{S}^{[4]}$. Compare eq 62 with eq 93. The additional elements $\overline{(1)(2)}$ and $\overline{(1\ 2)}$ in eq 62 are important in the integrated viewpoint of continuity and discreteness, as realized in Fujita's proligand method.

2. Internal Symmetries of Substituents: Substituents for the 3D skeletons (Table 1) are considered to have internal structures, where the chirality/achirality of ligands in isolation are taken into account. The chirality/achirality of ligands is treated in Fujita's proligand method by developing the concepts of sphericities and sphericity indices as well as the concepts of proligands and promolecules. Thereby, a pseudoasymmetric case CABp$\bar{\text{p}}$ (p and $\bar{\text{p}}$: a pair of enantiomeric ligands in isolation) is properly formulated by using a sphericity index c_2 (e.g., eq 10 in Table 1) for an enantiospheric cycle concerning p and $\bar{\text{p}}$. The pseudoasymmetric case is clearly differentiated from an asymmetric case CABXY (A, B, X, and Y: achiral ligands in isolation) by means of sphericity indices. Moreover, a meso case p–$\bar{\text{p}}$ is properly treated by using a sphericity index c_2 (e.g., eq 59 in Table 5), where the case of p–$\bar{\text{p}}$ is clearly differentiated from a simply achiral case of A–A or A–B.

In contrast, substituents for the graph skeleton (Table 12) are considered to have no internal structures. It follows that the asymmetric case CABXY is not differentiated from the pseudoasymmetric case CABp$\bar{\text{p}}$, so long as such a permutation group as $\mathcal{S}^{[4]}$ is used without considering internal structures. Moreover, the meso case p–$\bar{\text{p}}$ is not differentiated from the case A–A or A–B, so long as such a permutation group as $\mathcal{S}^{[2]}$ is used without considering internal structures.

Although the pseudoasymmetric cases and the meso cases have been differentiated at earlier stages in the history of organic stereochemistry,[44,45] they are not taken into consideration by Pólya's method.

In agreement with the two methodological differences describe above, we obtain a set of CI-CFs for characterizing 3D structures, i.e., eqs 10–21 (Table 1) and eqs 59–61 (Table 5); as well as another set of CIs for characterizing graphs, i.e. eqs 83–86 (Table 12) and eq 92 (Table 14). It should be emphasized again that the former set of CI-CFs (due to Fujita's proligand method) can be reduced into the latter set of CIs (due to Pólya's method) by considering the

CC[a]	BM[b] divergence	Centroidal Alkanes (Table 4)		Bicentroidal Alkanes (Table 8)	
		Achiral (Table 2)	Chiral (Table 3)	Achiral[c] (Table 6)	Chiral[d] (Table 7)
$k = 9$	$t^2s^3p^4$ [0,2,3,4]	 **59**  **60**  **61**	 **62**  **63**  **64**  **65**  **66**  **67**  **68**  **69**		

[a] CC: carbon content. [b] BM: branching monomial. [c] Absence of achiral bicentroidal alkanes. [d] Absence of chiral bicentroidal alkanes.

Figure 6. Alkanes of carbon content 9, which are characterized by BM $t^2s^3p^4$. Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds. The symbol © indicates a centroid.

graph-reduction condition $a_d = b_d = c_d = r_d$ (cf. eq 81).

In addition, the graph-reduction condition (eq 81) in the level of functional equations reveals that the divergence represented by BMs is invariant during the reduction from 3D structures to graphs. It is a reason why the concept of "divergence" serves as a common clue for characterizing 3D structures and graphs.

Pseudoasymmetry and Related Cases. The 3D structures of alkanes characterized by carbon content 10 and BM $t^3s^2p^5$ are depicted in Figure 7, where achiral alkanes of bicentroidal type are absent in agreement with Table 6.

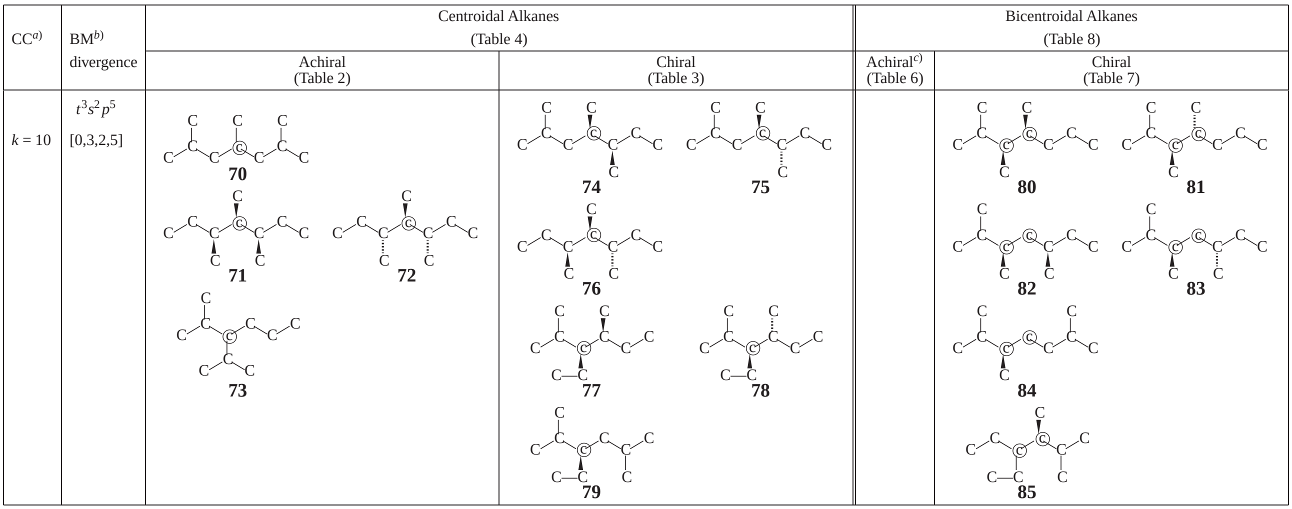
The four 3D structures depicted in the "centroidal achiral" column of Figure 7 correspond to the coefficient 4 of the term $4t^3s^2p^5$ which appears in the ($k = 10$)-row of Table 2. Among them, the alkanes **71** and **72** have a pseudoasymmetric carbon which is superposed onto a centroid. The two chiral ligands of opposite chiralities, i.e., *R*- and *S*-1-methylpropyl ligands (suppose that the R or S descriptor in each alkane is maintained even in isolation), are accommodated in **71** (or **72**) so as to exhibit the compensation of chirality. On the other hand, a relevant pair of chiral alkanes (**76** and its enantiomer) is present among the six 3D structures collected in the "centroidal chiral" column of Figure 7. Note that a pair of enantiomers is counted once in the present enumeration. The three alkanes **71**, **72**, and **76** coalesce to give a single graph, where the decrease by 2 (=3 − 1) should be taken into consideration during the reduction of 3D structures into graphs. A diastereomeric pair of **74** and **75** and another diastereomeric pair of **77** and **78**, respectively, exhibit the decrease by 1 (=2 − 1). Hence, there emerges the decrease by 4 (=2 + 1 + 1) during the reduction of the 3D structures into the graphs. The decrease by 4 is consistent with the difference between the coefficient 10 of the term $10\,t^3s^2p^5$ appearing in the ($k = 10$)-row of Table 4 (centroidal 3D structures) and the coefficient 6 of the term $6\,t^3s^2p^5$ appearing in the ($k = 10$)-row of Table 13 (centroidal graphs).

The six 3D structures depicted in the "bicentroidal chiral" column of Figure 7 correspond to the coefficient 6 of the term $6t^3s^2p^5$ which appears in the ($k = 10$)-row of Table 7 as well as in the ($k = 10$)-row of Table 8. This value is compared with the coefficient 4 of the term $4t^3s^2p^5$ which appears in the ($k = 10$)-row of Table 15. The difference 2 (=6 − 4) stems from the fact that a diastereomeric pair of **80** and **81** coalesces into a single graph and at the same time another diastereomeric pair of **82** and **83** coalesces into another single graph.

Without Branching Indicators. Centroidal Alkanes without Introducing Branching indicators: Let the symbol $\widehat{A}_k$ be the summation of $\widehat{A}_{kn_qn_tn_sn_p}$ at a given carbon content k; the symbol $\widehat{C}_k$ be the summation of $\widehat{C}_{kn_qn_tn_sn_p}$ at a given carbon content k; and the symbol $\widehat{B}_k$ be the summation of $\widehat{B}_{kn_qn_tn_sn_p}$ at a given carbon content k ($k = n_q + n_t + n_s + n_p$). By putting $q = t = s = p = 1$ in eqs 7–9 and by selecting the coefficient of each x^k, we obtain:

$$\widehat{A}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{A}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{99}$$

$$\widehat{C}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{C}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{100}$$



[a)] CC: carbon content. [b)] BM: branching monomial. [c)] Absence of achiral bicentroidal alkanes.

Figure 7. Alkanes of carbon content 10, which are characterized by BM $t^3s^2p^5$. Either one of two enantiomers is depicted as a representative. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds. The symbol © indicates a centroid, while the symbol ©–© indicates a bicentroid.

$$\widehat{B}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widehat{B}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{101}$$

where we can put:

$$\widehat{B}_k = \widehat{A}_k + \widehat{C}_k \tag{102}$$

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

$$\widehat{A}(x) = \sum_{k=0}^{\infty}\widehat{A}_k x^k = \widehat{A}(x,1,1,1,1) \tag{103}$$

$$\widehat{C}(x) = \sum_{k=0}^{\infty}\widehat{C}_k x^k = \widehat{C}(x,1,1,1,1) \tag{104}$$

$$\widehat{B}(x) = \sum_{k=0}^{\infty}\widehat{B}_k x^k = \widehat{B}(x,1,1,1,1) \tag{105}$$

which can be obtained by putting $q = t = s = p = 1$ in eqs 7–9.

The generating functions $\widehat{A}(x,q,t,s,p)$, $\widehat{C}(x,q,t,s,p)$, and $\widehat{B}(x,q,t,s,p)$ have been already calculated by the above-mentioned program "AlkaneBI02.mpl" and stored respectively in the form of the series denoted by `Abi`, `Cbi`, and `Bbi`. Hence, the following code for evaluating eqs 103–105 are added to the program "AlkaneBI02.mpl:"

```
"Without branching indicators";
CeAchiral := sort(subs({p=1,s=1,t=1,q=1}, Abi),[x],ascending);
CeChiral := sort(subs({p=1,s=1,t=1,q=1}, Cbi),[x],ascending);
CeTotal := sort(subs({p=1,s=1,t=1,q=1}, Bbi),[x],ascending);
```

Thereby, we obtain the following generating functions:

$$\begin{aligned}\widehat{A}(x) &= x + x^3 + x^4 + 3x^5 + 2x^6 + 7x^7 + 7x^8\\ &\quad + 21x^9 + 22x^{10} + 61x^{11}\\ &\quad + 72x^{12} + 186x^{13} + 220x^{14}\\ &\quad + 567x^{15} + \ldots + 7149x^{20} + \ldots\end{aligned} \tag{106}$$

$$\begin{aligned}\widehat{C}(x) &= 2x^7 + x^8 + 17x^9 + 24x^{10} + 142x^{11}\\ &\quad + 211x^{12} + 1113x^{13} + 1784x^{14}\\ &\quad + 8780x^{15} + \ldots + 1091507x^{20} + \ldots\end{aligned} \tag{107}$$

$$\begin{aligned}\widehat{B}(x) &= x + x^3 + x^4 + 3x^5 + 2x^6 + 9x^7 + 8x^8\\ &\quad + 38x^9 + 46x^{10} + 203x^{11}\\ &\quad + 283x^{12} + 1299x^{13} + 2004x^{14}\\ &\quad + 9347x^{15} + \ldots + 1098656x^{20} + \ldots\end{aligned} \tag{108}$$

These values are identical to those reported previously (Table 2 of Ref. 20 (up to carbon content 20) and Table 1 of Ref. 34 (up to carbon content 100)). Hence, the previous results can be regarded as special cases of the present enumeration, where branching indicators are disregarded.

The generating functions described in the preceding paragraph (eqs 106–108) can be verified more systematically in the level of functional equations. By put $q = t = s = p = 1$ in eqs 34 and 36, we are able to obtain the following functional equations corresponding to eqs 103–105:

$$\begin{aligned}\widehat{A}(x) &= \widehat{A}(x,1,1,1,1)\\ &= \frac{x}{2}\{a(x)^2c(x^2) + c(x^4)\}\end{aligned} \tag{109}$$

$$\begin{aligned}\widehat{C}(x) &= \widehat{C}(x,1,1,1,1)\\ &= \frac{x}{24}\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3)\\ &\quad - 6a(x)^2c(x^2) - 6c(x^4)\}\end{aligned} \tag{110}$$

$$\begin{aligned}\widehat{B}(x) &= \widehat{B}(x,1,1,1,1)\\ &= \frac{x}{24}\{b(x)^4 + 3b(x^2)^2 + 8b(x)b(x^3)\\ &\quad + 6a(x)^2c(x^2) + 6c(x^4)\}\end{aligned} \tag{111}$$

which disregard the effect of branching. These functional equations without branching indicators (eqs. 109–111) are identical to those which have been alternatively derived in previous papers, eq 38 of Ref. 20 (eq 19 of Ref. 34), eq 40 of Ref. 20 (eq 20 of Ref. 34), and eq 29 of Ref. 20 (eq 18 of Ref. 34). The previous functional equations (without BIs) were used to provide the generating functions (eqs 106–108).

A parallel discussion allows us to obtain the total number $\widehat{R}_k$ of graphs which is the summation of $\widehat{R}_{kn_qn_tn_sn_p}$ at a given carbon content k ($k = n_q + n_t + n_s + n_p$). By putting $q = t = s = p = 1$ in eq 82, we obtain the following generating function:

$$\widehat{R}(x) = \sum_{k=0}^{\infty} \widehat{R}_k x^k = \widehat{R}(x, 1, 1, 1, 1) \tag{112}$$

where the coefficient of each x^k is represented as follows:

$$\widehat{R}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} \widehat{R}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{113}$$

Because the evaluated $\widehat{R}(x, q, t, s, p)$ is stored in the series represented by `Rbi` of the program "GraphCAlkane1.mpl," we are able to obtain $\widehat{R}(x) = \widehat{R}(x, 1, 1, 1, 1)$ by putting $q = t = s = p = 1$. Thereby, we obtain the following series:

$$\begin{aligned}\widehat{R}(x) = {} & x + x^3 + x^4 + 3x^5 + 2x^6 + 9x^7 + 8x^8 \\ & + 35x^9 + 39x^{10} + 159x^{11} \\ & + 202x^{12} + 802x^{13} + 1078x^{14} \\ & + 4347x^{15} + \ldots + 237541x^{20} + \ldots\end{aligned} \tag{114}$$

This generating function has been implicitly calculated in a previous report (the program named "Graph1-100.mpl"),[34] where the following functional equation (eq 77 of Ref. 34) was used in the calculation:

$$\begin{aligned}\widehat{R}(x) = \frac{x}{24}\{ & r(x)^4 + 3r(x^2)^2 + 8r(x)r(x^3) \\ & + 6r(x)^2 r(x^2) + 6r(x^4)\}\end{aligned} \tag{115}$$

It should be noted that eq 115 has been first noted by Pólya (eq 2.50 of Refs. 8 and 12) on the basis of Pólya's theorem. The same equation as eq 115 can be obtain by starting from eq 36 for counting 3D structures, where we put $q = t = s = p = 1$ and $a(x, 1, 1, 1, 1,) = a(x)$ etc. and then we employ the graph-reduction condition represented by

$$a(x^d) = b(x^d) = c(x^d) = r(x^d) \tag{116}$$

which is a modified form of eq 81. This is also derived from eq 111 by using the graph-reduction condition (eq 81). It should be emphasized again that the graph-reduction condition (eq 81) reveals the relationship between Pólya's method and Fujita's proligand method on which the present method relies.

Bicentroidal Alkanes without Introducing Branching indicators: We use the symbols $\widetilde{A}_k$, $\widetilde{C}_k$, and $\widetilde{B}_k$ to denote the respective summations of $\widetilde{A}_{kn_qn_tn_sn_p}$, $\widetilde{C}_{kn_qn_tn_sn_p}$, and $\widetilde{B}_{kn_qn_tn_sn_p}$, where n_q, n_t, n_s, and n_p run to satisfy $k = n_q + n_t + n_s + n_p$ at a given carbon content k.

By putting $q = t = s = p = 1$ in eqs 54–56 and by selecting the coefficient of each x^k, we obtain:

$$\widetilde{A}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} \widetilde{A}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{117}$$

$$\widetilde{C}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} \widetilde{C}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{118}$$

$$\widetilde{B}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty} \widetilde{B}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{119}$$

where we can put:

$$\widetilde{B}_k = \widetilde{A}_k + \widetilde{C}_k \tag{120}$$

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

$$\widetilde{A}(x) = \sum_{k=0}^{\infty} \widetilde{A}_k x^k = \widetilde{A}(x, 1, 1, 1, 1) \tag{121}$$

$$\widetilde{C}(x) = \sum_{k=0}^{\infty} \widetilde{C}_k x^k = \widetilde{C}(x, 1, 1, 1, 1) \tag{122}$$

$$\widetilde{B}(x) = \sum_{k=0}^{\infty} \widetilde{B}_k x^k = \widetilde{B}(x, 1, 1, 1, 1) \tag{123}$$

which can be obtained by putting $q = t = s = p = 1$ in eqs 54–56.

The generating functions $\widetilde{A}(x, q, t, s, p)$, $\widetilde{C}(x, q, t, s, p)$, and $\widetilde{B}(x, q, t, s, p)$ have been already calculated in the above-mentioned program for bicentroidal 3D structures (as shown below eqs 66–68) and stored respectively in the form of the series denoted by `Abbi`, `Cbbi`, and `Bbbi`. Hence, the following code for evaluating eqs 121–123 are added to the program as follows:

```
"Without branching indicators";
BiAchiral := sort(subs({p=1,s=1,t=1,q=1}, Abbi),[x],ascending);
BiChiral := sort(subs({p=1,s=1,t=1,q=1}, Cbbi),[x],ascending);
BiTotal := sort(subs({p=1,s=1,t=1,q=1}, Bbbi),[x],ascending);
```

Thereby, we obtain the following generating functions:

$$\begin{aligned}\widetilde{A}(x) = {} & x^2 + x^4 + 3x^6 + 7x^8 + 18x^{10} + 46x^{12} \\ & + 135x^{14} + 364x^{16} + 1116x^{18} + 3157x^{20} + \ldots\end{aligned} \tag{124}$$

$$\begin{aligned}\widetilde{C}(x) = {} & 4x^8 + 24x^{10} + 180x^{12} \\ & + 1320x^{14} + 9768x^{16} + 75480x^{18} + 601762x^{20} + \ldots\end{aligned} \tag{125}$$

$$\begin{aligned}\widetilde{B}(x) = {} & x^2 + x^4 + 3x^6 + 11x^8 + 42x^{10} + 226x^{12} \\ & + 1455x^{14} + 10132x^{16} + 76596x^{18} + 604919x^{20} + \ldots\end{aligned} \tag{126}$$

These values are identical to those reported previously (Table 3 of Ref. 20 (up to carbon content 20) and Table 2 of Ref. 34 (up to carbon content 100)). Hence, the previous results can be regarded as special cases of the present enumeration, where branching indicators are disregarded.

Although eqs 63–65 do not explicitly contain such branching indicators, the component $a(x, q, t, s, p)$ etc. contain the branching indicators. By putting $q = t = s = p = 1$ according to eqs 121–123 and replacing the resulting $a(x, 1, 1, 1, 1)$ etc.

by $a(x)$ etc., eqs 63–65 are converted into the following functional equations:

$$\begin{aligned}\widetilde{A}(x) &= \widetilde{A}(x,1,1,1,1)\\ &= \frac{1}{2}\{[a(x)-1]^2 + [c(x^2)-1]\}\end{aligned} \tag{127}$$

$$\begin{aligned}\widetilde{C}(x) &= \widetilde{C}(x,1,1,1,1)\\ &= \frac{1}{4}\{[b(x)-1]^2 + [b(x^2)-1]\\ &\quad - [a(x)-1]^2 - [c(x^2)-1]\}\end{aligned} \tag{128}$$

$$\begin{aligned}\widetilde{B}(x) &= \widetilde{B}(x,1,1,1,1)\\ &= \frac{1}{4}\{[b(x)-1]^2 + [b(x^2)-1]\\ &\quad + [a(x)-1]^2 + [c(x^2)-1]\}\end{aligned} \tag{129}$$

The present set of the functional equations without branching indicators (eqs. 127–129) are essentially equivalent to the previous set which have been alternatively derived, i.e., eq 56 of Ref. 20 (eq 37 of Ref. 34), eq 58 of Ref. 20 (eq 38 of Ref. 34), and eq 52 of Ref. 20 (eq 36 of Ref. 34), except that the subtraction by 1 in each pair of brackets is different between the present set and the previous one. Note that we are able to the same results whether we select either one from the sets of equations.

To discuss the total number of bicentroidal alkanes as graphs, let the symbol $\widetilde{R}_k$ be represented as follows:

$$\widetilde{R}_k = \sum_{n_q=0}^{\infty}\left(\sum_{n_t=0}^{\infty}\left(\sum_{n_s=0}^{\infty}\left(\sum_{n_p=0}^{\infty}\widetilde{R}_{kn_qn_tn_sn_p}\right)\right)\right) \tag{130}$$

Then, we obtain the following generating function:

$$\widetilde{R}(x) = \sum_{k=0}^{\infty}\widetilde{R}_k x^k = \widetilde{R}(x,1,1,1,1) \tag{131}$$

This equation is obtained by putting $q = t = s = p = 1$ in eq 94.

Because the evaluated $\widetilde{R}(x,q,t,s,p)$ is stored in the series represented by `Rbi` of the program "GraphCAlkane1.mpl," we are able to obtain $\widetilde{R}(x) = \widetilde{R}(x,1,1,1,1)$ by putting $q = t = s = p = 1$. Thereby, we obtain the following series:

$$\begin{aligned}\widetilde{R}(x) &= x^2 + x^4 + 3x^6 + 10x^8 + 36x^{10}\\ &\quad + 153x^{12} + 780x^{14} + 4005x^{16}\\ &\quad + 22366x^{18} + 128778x^{20} + \ldots\end{aligned} \tag{132}$$

The functional equation (eq 94) for counting bicentroidal alkanes as graphs is obtained by applying the graph-reduction condition (eq 81) to eq 65 for counting bicentroidal alkanes as 3D structures. By putting $r(x) = r(x,1,1,1,1)$, eq 94 is further converted into following functional equation:

$$\widetilde{R}(x) = \widetilde{R}(x,1,1,1,1) = \frac{1}{2}\left\{[r(x)-1]^2 + [r(x^2)-1]\right\} \tag{133}$$

This equation is alternatively obtained by applying the graph-reduction (eq 116) to eq 129. The reduced functional equation (eq 133) is essentially equivalent to the previous equation, i.e. eq 83 of Ref. 34, except that the subtraction by 1 in each pair of brackets is different between the present equation and the previous one. Note that the criterion for characterizing bicentroidal alkanes (eq 58) does not allow the substitution of one or two hydrogens even if the subtraction by 1 is not involved, as found in eq 83 of Ref. 34.

"Per Divergence" vs. "Per Constitution." Throughout the history of organic chemistry, alkanes have been categorized by carbon contents (molecular formulas), or at most they have roughly characterized as being straight-chain or branched-chain.[40,41] For example, the 19 alkanes listed in Figure 5 are categorized by carbon content 8, where **48** is a straight-chain alkane and the other 18 alkanes are regarded as branched-chain alkanes. Thus, categorization by branching in conventional organic chemistry has a limited capability so that the criterion "per constitution" (per carbon content) has been substantially an only clue for categorizing alkanes as 3D structures and as graphs.

In contrast, the present method provides us with a versatile clue for categorizing alkanes as 3D structures and as graphs, i.e., "per divergence" based on branching indicators. Thus, the 19 alkanes of carbon content 8 are further categorized by means of a polynomial of BMs, i.e., $q^2p^6 + (t^3 + 3qts)p^5 + (6t^2s^2 + 3qs^3)p^4 + 4ts^4p^3 + s^6p^2$, which appears in the ($k = 8$)-row of Table 11. They are reduced into 18 graphs, which are categorized also by means of a polynomial of BMs in the ($k = 8$)-row of Table 16, i.e., $q^2p^6 + (t^3 + 3qts)p^5 + (5t^2s^2 + 3qs^3)p^4 + 4ts^4p^3 + s^6p^2$. Because the 3D structures and the graphs are categorized commonly by such polynomials of BMs, we are able to find that the reduction occurs at BM $t^2s^2p^4$ ($6t^2s^2p^4 \rightarrow 5t^2s^2p^4$). This reduction stems from the fact that the 3D structures **50** and **52** depicted in Figure 5 are reduced into a single graph. Moreover, the 19 alkanes as 3D structures are categorized into 7 achiral centroidal alkanes ($(t^3 + qts)p^5 + (2qs^3 + t^2s^2)p^4 + 2ts^4p^3$ in the ($k = 8$)-row of Table 2), one chiral centroidal alkanes ($t^2s^2p^4$ in the ($k = 8$)-row of Table 3), 7 achiral bicentroidal alkanes ($q^2p^6 + qtsp^5 + (qs^3 + 2t^2s^2)p^4 + ts^4p^3 + s^6p^2$ in the ($k = 8$)-row of Table 6), and 4 chiral bicentroidal alkanes ($qtsp^5 + 2t^2s^2p^4 + ts^4p^3$ in the ($k = 8$)-row of Table 7). Thereby, the present method is capable of accomplishing detailed categorization of the 19 alkanes of carbon content 8, as shown in Figure 5.

As found in most textbooks on organic chemistry,[40,41] there have been no systematic treatments of such "divergence" as discussed in the present article. It should be again emphasized that the concept of "divergence" serves as a common clue for characterizing 3D structures and graphs. Because "divergence" is embodied on the basis of BMs composed of branching indicators (q, t, s, and p), the concept is applicable not only to qualitative discussions but also to quantitative discussions such as combinatorial enumerations. Because we put $k = n_q + n_t + n_s + n_p$ for each carbon content k, the present clue "divergence" provides us with more detailed categorization than the conventional clue "constitution" in which the conventional concept "constitution" corresponds to carbon content k.

Conclusion

Branching indicators (BIs, i.e, q, t, s, and p) are introduced to specify an alkane of carbon content k in the form of a branching monomial (BM, i.e., i.e., $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$ or shortly $q^{n_q}t^{n_t}s^{n_s}p^{n_p}$) or in the form of a mode of divergence

$[n_q, n_t, n_s, n_p]$, where the k carbons are partitioned into n_q quaternary, n_t tertiary, n_s secondary, and n_q quaternary carbons ($k = n_q + n_t + n_s + n_p$). Thereby, the effect of internal branching is evaluated in the enumeration of alkanes as achiral and chiral 3D structures and as graphs.

To incorporate the effect of internal branching, preformed alkyl moieties (PAMs) specified by BIs are first enumerated recursively by following Fujita's proligand method.[21–23] The resulting series of counting PAMs are used to the enumeration of centroidal and bicentroidal alkanes as achiral and chiral 3D structures. Functional equations for respective cases (centroidal/bicentroidal and achiral/chiral alkanes) are derived according to Fujita's proligand method (on the basis of sphericity indices for cycles) and alternatively Fujita's USCI approach (on the basis of sphericity indices for orbits). Then the series of counting PAMs are introduced into the functional equations so as to provide respective generating functions, in which the number of alkanes of each case having n_q quaternary, n_t tertiary, n_s secondary, and n_q quaternary carbons appears as the coefficient of a BM $q^{n_q}t^{n_t}s^{n_s}p^{n_p}x^k$. The nullification of the effect of internal branching is systematically discussed so as to derive previous approaches without considering BIs.[20–35] Moreover, the reduction of 3D structures into graphs is systematically investigated so as to derive Pólya's theorem, which therefore turns out to be a special case of Fujita's proligand method. Thereby, difference between stereoisomers (3D structures) and constitutional isomers (graphs) has been discussed by common criterion due to BMs (or modes of divergence), which provides more detailed results than the previous criterion based on carbon contents (constitutions) only.

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