

Enumeration of Primary, Secondary, and Tertiary Monosubstituted Alkanes as Stereoisomers

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Monosubstituted alkanes are counted as stereoisomers by means of Fujita's proligand method (Fujita S (2005) *Theor. Chem. Acc.* 113:73-79, 113:80-86, Fujita S (2006) *Theor. Chem. Acc.* 115:37-53), where the numbers of primary, secondary, and tertiary ones are calculated after deriving respective functional equations. The procedures of counting are programmed by means of the Maple programming language. They are executed and the results collected up to carbon content 100 in a tabular form. By omitting the sphericities of the recursive functions $a(x)$, $c(x^2)$, and $b(x)$ so as to give a single dummy variable $r(x)$, such functional equations with sphericity are transformed into Pólya's functional equations without sphericity, which are applied to the enumeration of primary, secondary, and tertiary monosubstituted alkanes as graphs (chemically, constitutional isomers). The results of Fujita's proligand method are compared with those based on Pólya's theorem in connection with several cases of pseudoasymmetry.

Keywords: Monosubstituted alkane, Primary, Secondary, Tertiary, Stereoisomer, Enumeration, Sphericity

1 Introduction

Henze and Blair [1] have obtained the numbers of aliphatic alcohols of given carbon contents, where the numbers were itemized with respect to their degrees of branching, i.e., primary, secondary, and tertiary alcohols. Their enumeration based on recursive equations was concerned with constitutional isomers (or mathematically graphs), but not with stereoisomers as three-dimensional (3D) objects.

The situation has not been restricted to such specific enumeration by Henze and Blair [1]. From the beginning when Cayley [2, 3] started the combinatorial enumeration of monosubstituted alkanes (or mathematically rooted or planted trees), calculated numbers have been concerned with constitutional isomers (graphs), but not with stereoisomers (3D-objects) in most cases with or without such itemization due to the degrees of branching.

These situations have not been so dramatically changed even after the development of a more systematic method based on Pólya's theorem [4, 5], because stereoisomers were not treated properly. Thus, by using symmetric groups, enumeration results based on Pólya's theorem [4, 5] were concerned with graphs. By using

alternating groups, on the other hand, achiral isomers, chiral isomers, and their enantiomers were counted independently, where pairwise recognition between a chiral isomer and its enantiomer was not been accomplished by Pólya's theorem. Moreover, Pólya's theorem did not take account of stereochemical problems on pseudoasymmetry and *meso*-compounds.

Among many contributions based on Pólya's theorem [4, 5] to chemistry [6–11], only Robinson et al. [12] to our best knowledge reported the enumeration of monosubstituted alkanes as stereoisomers by modifying Pólya's cycle indices (CIs). Even their treatment, however, did not take account of the classical stereochemical problems described above.

The disregard for pseudoasymmetry and *meso*-compounds has turned out to stem from the fact that both Pólya's theorem itself and its modification by Robinson et al. lack the concept of sphericity, which has been recently formulated by us [13, 14] in solving stereochemical problems and has been more recently modified so as to provide Fujita's proligand method [15–17]. Because the sphericity concept is a key to differentiate Fujita's proligand method from Pólya's theorem, it is important to exemplify how the sphericity concept works in various

enumeration problems.

The sphericity concept has been developed as three versions, i.e., the concept “the sphericities of orbits” [13, 14], the concept “the sphericities of orbits based on cyclic groups” [18–20], and the concept “the sphericities of cycles” [15–17]. Among them, the concept “the sphericities of cycles” gave a basis of Fujita’s proligand method [15–17], which is here adopted as a principal tool for solving the enumeration problems described in the first paragraph of the Introduction.

Because the enumeration of monosubstituted alkanes (rooted or planted 3D-trees) as 3D-objects has been recently accomplished by using the proligand method [21], remaining problems are to obtain the numbers of primary, secondary, and tertiary aliphatic alcohols which are regarded as 3D-objects. The present paper is devoted to solving these problems, where their calculation procedures implemented by Maple programming language [22] are discussed in detail.

2 Itemized Enumeration of Monosubstituted Alkanes

2.1 Recursive Functional Equations

Let $a(x)$ be a generating function in which the coefficient (α_k) of the term x^k represents the number of achiral monosubstituted alkanes (or planted 3D-trees) of carbon content k . Let $c(x^2)$ be a generating function in which the coefficient (γ_{2k}) of the term x^{2k} represents the number of achiral and chiral monosubstituted alkanes (or planted 3D-trees) of carbon content $2k$, where a diploid of enantiomers is counted just once [21]. Let $b(x)$ be a generating function in which the coefficient (β_k) of the term x^k represents the number of achiral and chiral monosubstituted alkanes (or planted 3D-trees) of carbon content k , where two enantiomers of each pair are separately counted. Thus, we can put the following ligand inventories:

$$a(x) = \sum_{k=0}^{\infty} \alpha_k x^k \quad (1)$$

$$c(x^2) = \sum_{k=0}^{\infty} \gamma_{2k} x^{2k} \quad (2)$$

$$b(x) = \sum_{k=0}^{\infty} \beta_k x^k, \quad (3)$$

where $\alpha_0 = 1$, $\gamma_0 = 1$, and $\beta_0 = 1$ to treat trivial cases of terminal vertices (or hydrogen atoms).

A C_{3v} -skeleton for enumerating such monosubstituted alkanes is characterized by the right coset representation $(C_s \setminus) C_{3v}$, i.e., $(1)(2)(3)$ for I , $(1\ 2\ 3)$ for C_3 , $(1\ 3\ 2)$ for C_3^2 , $(1)(2\ 3)$ for $\sigma_{v(1)}$, $(1\ 3)(2)$ for $\sigma_{v(2)}$, and $(1\ 2)(3)$ for $\sigma_{v(3)}$, so that the resulting cycles are transformed into the corresponding products of sphericity in-

stances, i.e., b_1^3 for I , b_3 for two threefold rotations, and $a_1 c_2$ for three reflections. The proligand method [15–17] is applied to this case, where relevant cycle indices with chirality fittingness (CI-CFs) are obtained and transformed into eqs. 4–6 by replacing a_d by $a(x^d)$, c_d by $c(x^d)$, and b_d by $b(x^d)$.

It follows that the three ligand inventories regarded as generating functions (eqs. 1 to 3) satisfy the following recursive functional equations:

$$a(x) = 1 + xa(x)c(x^2) \quad (4)$$

$$c(x^2) = 1 + \frac{x^2}{3} (c(x^2)^3 + 2c(x^6)) \quad (5)$$

$$b(x) = 1 + \frac{x}{3} (b(x)^3 + 2b(x^3)) \quad (6)$$

Let $B(x)$ be a generating function for counting achiral and chiral planted promolecules, where each pair of enantiomers is counted just once. Let $C(x)$ be a generating function for counting chiral planted promolecules only, where each pair of enantiomers is counted just once. They are represented by the following equations:

$$B(x) = \sum_{k=0}^{\infty} B_k x^k \quad (7)$$

$$C(x) = \sum_{k=0}^{\infty} C_k x^k, \quad (8)$$

where we put $B_0 = 1$ and $C_0 = 0$ to treat a trivial case of carbon content 0. Because we can place $B_k = \alpha_k + C_k$ and $\beta_k = \alpha_k + 2C_k$, eq. 4 (for $a(x)$) and eq. 6 (for $b(x)$) give the following equations:

$$B(x) = \frac{1}{2} (a(x) + b(x)) \quad (9)$$

$$C(x) = \frac{1}{2} (b(x) - a(x)). \quad (10)$$

2.2 Primary Monosubstituted Alkanes

Primary monosubstituted alkanes can be derived by placing an appropriate ligand on the vertex 1 of the C_s -skeleton (**1**). The action of symmetry operations is shown in Figure 1. The transitivity of the vertex 1 is characterized by a trivial right coset representation $(C_s \setminus) C_s = \{(1), (\bar{1})\}$, where the cycle (1) is hemispheric and the cycle $(\bar{1})$ is homospheric.

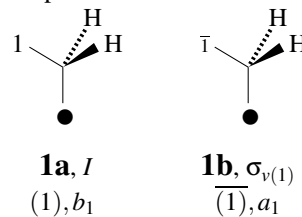


Figure 1. Symmetry operations of the C_s -skeleton for counting primary monosubstituted alkanes (**1**).

We can apply Theorem 2 of [17] to the enumeration of primary monosubstituted alkanes without any modification. Hence, by using the product of SIs collected in Figure 1, the cycle index with chirality fittingness (CI-CF) for this case is calculated as follows:

$$\text{CI-CF}(\mathbf{C}_s; a_d, b_d) = \frac{1}{2}(b_1 + a_1), \quad (11)$$

which counts achiral primary monosubstituted alkanes and enantiomeric pairs of chiral ones. Theorem 3 of [17] for the enumeration of ligands under the action of the maximum chiral subgroup is applied to this case so as to derive the following CI-CF:

$$\text{CI-CF}(\mathbf{C}_1; b_d) = b_1, \quad (12)$$

which counts achiral primary monosubstituted alkanes and chiral ones, where two enantiomers of each pair are counted separately. We apply the first proposition of Theorem 4 for the enumeration of achiral ligands [17] to this case so as to derive the following CI-CF_A:

$$\begin{aligned} \text{CI-CF}_A(\mathbf{C}_s; a_d, b_d) &= 2\text{CI-CF}(\mathbf{C}_s; a_d, b_d) - \text{CI-CF}(\mathbf{C}_1; b_d) \\ &= a_1 \end{aligned} \quad (13)$$

which counts achiral primary monosubstituted alkanes only. We use the second proposition of Theorem 4 for the enumeration of chiral ligands [17] to obtain the following CI-CF_C:

$$\begin{aligned} \text{CI-CF}_C(\mathbf{C}_s; a_d, b_d) &= \text{CI-CF}(\mathbf{C}_1; b_d) - \text{CI-CF}(\mathbf{C}_s; a_d, b_d) \\ &= \frac{1}{2}(b_1 - a_1) \end{aligned} \quad (14)$$

which counts enantiomeric pairs of chiral primary monosubstituted alkanes only, where each pair of enantiomers is counted just once.

Let P_k , $P_k^{(A)}$, and $P_k^{(C)}$ be the number of achiral primary monosubstituted alkanes plus enantiomeric pairs, the number of achiral ones, and the number of enantiomeric pairs. They are represented as the following generating functions:

$$P(x) = \sum_{k=1}^{\infty} P_k x^k \quad (15)$$

$$P(x)^{(A)} = \sum_{k=1}^{\infty} P_k^{(A)} x^k \quad (16)$$

$$P(x)^{(C)} = \sum_{k=1}^{\infty} P_k^{(C)} x^k, \quad (17)$$

where x^k corresponds to the carbon content $k \geq 1$.

By starting from eq. 11, the SIs b_1 and a_1 are replaced by $b(x)$ and $a(x)$ respectively. Thereby, we obtain the following functional equation by multiplying by x for the principal vertex:

$$P(x) = \frac{x}{2}(b(x) + a(x)). \quad (18)$$

It should be noted that the first term 1 in $b(x)$ (eq. 6) or $a(x)$ (eq. 4) is not omitted because a monosubstituted methane ($\bullet\text{—CH}_3$) should be counted as a trivial case in addition to usual primary monosubstituted alkanes. On a similar line, eq. 13 gives the following functional equation:

$$P(x)^{(A)} = xa(x) \quad (19)$$

after multiplied by x to take account of the principal vertex. Further, eq. 14 gives the following functional equation:

$$P(x)^{(C)} = \frac{x}{2}(b(x) - a(x)) \quad (20)$$

after multiplied by x .

Because $a(x)$ (by eq. 4), $c(x^2)$ (by eq. 5), and $b(x)$ (by eq. 6) have been evaluated recursively, we are able to obtain the coefficients P_k (eq. 15), $P_k^{(A)}$ (eq. 16), and $P_k^{(C)}$ (eq. 17) by expanding eqs. 18, 19, and 20. Procedures for calculating them were programmed by using Maple programming language as follows.

Maple program for enumeration primary monosubstituted alkanes, "P1-100.mpl":

```
"Definition of Functional Equations";
ax := 1 + x*a1*c2;
cx := 1+ (1/3)*x^2*c2^3 + (2/3)*x^2*c6;
bx := 1 + (1/3)*x*b1^3 + (2/3)*x*b3;

"Initial Values";
a1 := 1;
c2 := 1;
b1 := 1;
b3 := 1;
c6 := 1;

"Do Loop for Calculation";
for ccntt from 1 to 100 by 1 do
ccntt:
Cbx:= coeff (bx,x^ccntt):
Cax:= coeff (ax,x^ccntt):
Ccx:= coeff (cx,x^(ccntt*2)):
a1 := a1 + Cax*x^ccntt:
c2 := c2 + Ccx*x^(ccntt*2):
b1 := b1 + Cbx*x^ccntt:
b3 := b3 + Cbx*x^(ccntt*3):
c6 := c6 + Ccx*x^(ccntt*6):
end do:

"Primary Monosubstituted Alkanes";
Px := (1/2)*x*(b1 + a1):
Pxa := x*a1:
Pxc := (1/2)*x*(b1 - a1):

"Print-Out of Results";
for ccntt from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\n",
ccntt,
coeff (Pxa,x^ccntt),
coeff (Pxc,x^ccntt),
coeff (Px,x^ccntt));
end do;
```

Table 1. Numbers of Primary Monosubstituted Alkanes as Stereoisomers^a

k	$P_k^{(A)}$ (Achiral)	$P_k^{(C)}$ (Chiral)	P_k (Achiral + Chiral)
1	1	0	1
2	1	0	1
3	1	0	1
4	2	0	2
5	3	1	4
6	5	3	8
7	8	10	18
8	14	30	44
9	23	88	111
10	41	255	296
11	69	742	811
12	122	2157	2279
13	208	6312	6520
14	370	18563	18933
15	636	54932	55568
16	1134	163479	164613
17	1963	489264	491227
18	3505	1471692	1475197
19	6099	4447896	4453995
20	10908	13500689	13511597
21	19059	41140608	41159667
22	34129	125818217	125852346
23	59836	386050543	386110379
24	107256	1188093392	1188200648
25	188576	3666547089	366735665
26	338322	11344058829	11344397151
27	596252	35180323336	35180919588
28	1070534	109339097119	109340167653
29	1890348	340508394528	340510285076
30	3396570	1062419370490	1062422767060
31	6008908	3320666310903	3320672319811
32	10801816	10395996250010	10396007051826
33	19139155	32596713516873	32596732656028
34	34422537	102354659356690	102354693779227
35	61074583	321832884381903	321832945456486
36	109894294	1013230630964436	1013230740858730
37	195217253	3193818534035050	3193818729252303
38	351404205	10078773177202180	10078773528606385
39	624913284	31840095204449021	31840095829362305
40	1125291874	100689937510048385	100689938635340259
41	2003090071	318728146981844679	318728148984934750
42	3608175239	1009849492883144730	1009849496491319969
43	6428430129	3202399570304430261	3202399576732860390
44	11582995444	10163870352469178059	10163870364052173503
45	20653101216	32284255140318002679	32284255160971103895
46	37223637886	102625414714074250195	102625414751297888081
47	66420162952	326465312628541253282	326465312694961416234
48	119740546576	1039258352830707100287	1039258352950447646863
49	213802390264	3310561173602401804486	3310561173816204194750
50	385525375648	10552597199971538944446	10552597200357064320094
51	688796847976	33657783567745352117595	33657783568434148965571
52	1242290116020	107416128908320489280104	107416128909562779396124
53	2220789746752	343005708844148436621963	343005708846369226368715
54	4006120350070	1095901875016767892361183	10959018750207740112711253
55	7165331870036	3503253701348594788382175	3503253701355760120252211
56	12928003493212	11204506183709361691881774	11204506183722289695374986
57	23134244857388	3585313432749875133777601	35853134327521885582634989
58	41746843378398	114780284499516103424710066	114780284499557850268088464
59	747385404448344	367625900577928930637205709	367625900578003669141654053
60	134890383077280	1177976917802372651276354835	1177976917802507541659432115
61	241593618271624	3776181956727075855700156889	3776181956727317449318428523
62	436099806635266	12110118510764409721547578931	12110118510764848521354214197
63	781379784134280	38852360869430891549389142546	38852360869431672929173276802
64	1410660331905744	124696551878602256306336431059	124696551878603666966683368263
65	2528481353408387	400363258120183679194030899086	400363258120186207675384307473
66	4565372792411543	1285913332058160943022006622567	1285913332058165508394799034110
67	8185868682337027	4131636451627223217905517665230	4131636451627231403774200002257
68	14782032579934260	13279472925491136452203415411282	13279472925491151234235995345542
69	26513372758159909	42695640515935232895574700033255	42695640515935259408947458193161
70	47883315932669529	137317535156294699435253007511481	137317535156294747318568940181010
71	85911079008919616	44177814668085655381196140461152	441778146680856641292275149380768
72	15517262932069894	1421721021872915186434612124418285	1421721021872915341607375056488179
73	278488395251454441	4576703637505875523107359575732692	457670363750587580159575482178133
74	503057870689711695	1473723201996662647092675667550461	14737232019966626973984627364262156
75	903086480091036027	47467941008121360276777418552412327	4746794100812136117986389864438354
76	163148280676136454	152933618235177166865457366439774884	152933618235177168496939647115911338
77	2929502464502366968	49285652690681918050106628872624509	49285652690681918343065875327491477
78	5292979792572170684	158872981012513938288615985394313591	15887298101251394358159577966484275
79	9506763767988688492	51225791804062272782893146855624013995	5122579180406227738009910623612702487
80	17177649111373079244	16520897953013100680478350495809265213	16520897953013100697655999607182344457
81	30860176979309781255	53294486738307619893870635366392366797	53294486738307619924730812345702148052
82	55765496914378281449	171961814511179425854645791758391916817	17196181451117942591041288672770198266
83	100206865580368330935	554983895358241328803983143348747181065	554983895358241328904190008929115512000
84	181091912344282520796	1791533716989490812483638575740209502702	1791533716989490812664730488084492023498
85	325479416128007866823	5784469517534031671596027732477042276730	5784469517534031671921507148605050143553
86	588244550847580438141	18680728838224735253871870332518735488272	18680728838224735254460114883366315926413
87	105747629038222641392	60341164324086142450338425947342014158465	6034116432408614245139590223724236799857
88	1911332898535080790442	194949030688973491805812076982184909280356	19494903068897349180772340988071999070798
89	3436634060302329898084	629961494518672050471790513680381903001241	6299614945186720504752271477406842328899325
90	6211963598216168485372	2036059814107841938917943348390076037599701	2036059814107841938924155311988292206085073
91	11171367303208512523636	6581862425540511747351642675384991026248219	6581862425540511747362814042688199538771855
92	20194381412648318673600	21280753827037894634102485750210174037092208	2128075382703789463412268013162282355765808
93	36323270806296768489016	68818216387594067927142141836032850951612302	68818216387594067927178465106389147720101318
94	65665395161399373233104	222585222679763459441793142423987786427153211	222585222679763459441858807819149185800386315
95	118131205680564887503088	720052435262314352511798946720114468071962449	720052435262314352511917077925795032959465537
96	213571105479833409623678	2329727991559244716140309972474067355488212719	232972799155924471614052354537547188897836397
97	384274151006716654639812	753907528518959187187622650499722022532851893	7539075285189591871876606924650728739187491705
98	694775030767874167713632	2440064056653283392478279276091469455998528189	2440064056653283392478974051122237330166241821
99	1250289517934799230260092	78986564036199958180132982278535034827084400480	78986564036199958180134232568052969626314660572
100	2260673180783432572790736	255724695264031766423233519459641127061308852807	255724695264031766423235780132821910493881643543

^aIn each value of $P_k^{(C)}$ (Chiral) or P_k (Chiral + Achiral), each enantiomeric pair is counted just once on chiral primary monosubstituted alkanes.

In this code, the abbreviated symbols for functional equations are used as follows: `a1` for $a(x)$, `c2` for $c(x^2)$, `c6` for $c(x^6)$, and so on. The first paragraph (“Definition of Functional Equations”) declares three functional equations (eqs. 4–6). In the 2nd paragraph (“Initial Values”), the initial values for the initial (trivial) planted promolecule are set as $\alpha_0 = 1$, $\gamma_0 = 1$, and $\beta_0 = 1$ by encoding `a1 := 1; c2 := 1; and so on`. The 3rd paragraph (“Do Loop for Calculation”) shows a `do` loop for calculating α_k , γ_k , and β_k recursively by using a Maple command `coeff`. After escaping from the `do` loop, the 4th paragraph (“Primary Monosubstituted Alkanes”) declares the calculation of $P(x)$ (eq. 18), $P(x)^{(A)}$ (eq. 19), and $P(x)^{(C)}$ (eq. 20). The 5th paragraph (the final `do` loop named “Print-Out of Results”) shows the print-out of the calculation results.

The code was stored in a file named “P1-100.mpl” and then executed by inputting the following command on the Maple inputting window:

```
read "P1-100.mpl";
```

Thereby, we obtained the coefficients P_k (eq. 15) for $P(x)$ (eq. 18), $P_k^{(A)}$ (eq. 16) for $P(x)^{(A)}$ (eq. 19), and $P_k^{(C)}$ (eq. 17) for $P(x)^{(C)}$ (eq. 20), as collected in Table 1. It should be noted that each enantiomeric pair is counted just once throughout the present enumeration. Hence, the value of $P_k^{(C)}$ is the number concerned with pairs of enantiomeric primary monosubstituted alkanes. On the same line, the value of P_k is the number concerned with achiral primary monosubstituted alkanes plus pairs of enantiomeric primary monosubstituted alkanes.

2.3 Secondary Monosubstituted Alkanes

Secondary monosubstituted alkanes are derived by placing two appropriate ligands on the vertices 2 and 3 of the C_s -skeleton (2). The action of symmetry operations is shown in Figure 2. The transitivity of the vertices 2 and 3 is characterized by a right coset representation $(C_1 \setminus C_s) = \{(2)(3), \overline{(2\ 3)}\}$, where the one-cycle (2) or (3) is hemispheric so as to take an SI b_1 , while the two-cycle $\overline{(2\ 3)}$ is enantiospheric so as to take an SI c_2 .

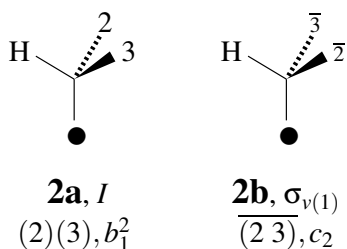


Figure 2. Symmetry operations of the C_s -skeleton for counting secondary monosubstituted alkanes (2).

We apply Theorem 2 of [17] to the enumeration of secondary monosubstituted alkanes, so that we calculate the CI-CF for this case (Figure 2) as follows:

$$\text{CI-CF}(C_s; a_d, b_d) = \frac{1}{2}(b_1^2 + c_2), \quad (21)$$

which counts achiral secondary monosubstituted alkanes and enantiomeric pairs of chiral ones. According to Theorem 3 of [17] for the enumeration of ligands under the action of the maximum chiral subgroup, we derive the following CI-CF in order to count achiral secondary monosubstituted alkanes and chiral ones:

$$\text{CI-CF}(C_1; b_d) = b_1^2, \quad (22)$$

where two enantiomers of each pair are counted separately. We apply the first proposition of Theorem 4 for the enumeration of achiral ligands [17] to this case so as to derive the following CI-CF_A:

$$\begin{aligned} \text{CI-CF}_A(C_s; a_d, b_d) &= 2\text{CI-CF}(C_s; a_d, b_d) - \text{CI-CF}(C_1; b_d) \\ &= c_2 \end{aligned} \quad (23)$$

which counts achiral secondary monosubstituted alkanes only. We adopt the second proposition of Theorem 4 for the enumeration of chiral ligands [17] to obtain the following CI-CF_C:

$$\begin{aligned} \text{CI-CF}_C(C_s; a_d, b_d) &= \text{CI-CF}(C_1; b_d) - \text{CI-CF}(C_s; a_d, b_d) \\ &= \frac{1}{2}(b_1^2 - c_2) \end{aligned} \quad (24)$$

which counts enantiomeric pairs of chiral secondary monosubstituted alkanes only, where each pair of enantiomers is counted just once.

Let S_k , $S_k^{(A)}$, and $S_k^{(C)}$ be the number of achiral secondary monosubstituted alkanes plus enantiomeric pairs, the number of achiral ones, and the number of enantiomeric pairs. Then, we obtain the corresponding generating functions as follows:

$$S(x) = \sum_{k=1}^{\infty} S_k x^k \quad (25)$$

$$S(x)^{(A)} = \sum_{k=1}^{\infty} S_k^{(A)} x^k \quad (26)$$

$$S(x)^{(C)} = \sum_{k=1}^{\infty} S_k^{(C)} x^k, \quad (27)$$

where x^k corresponds to the carbon content $k \geq 1$.

To evaluate the generating function $S(x)$ (eq. 25), we replace the SIs b_1 and c_2 in eq. 21 by $b(x) - 1$ and $c(x^2) - 1$, respectively. The resulting equation is multiplied by x for the principal vertex to give the following functional equation:

Table 2. Numbers of Secondary Monosubstituted Alkanes as Stereoisomers^a

k	$S_k^{(A)}$ (Achiral)	$S_k^{(C)}$ (Chiral)	S_k (Achiral + Chiral)
1	0	0	0
2	0	0	0
3	1	0	1
4	0	1	1
5	1	2	3
6	0	7	7
7	2	17	19
8	0	49	49
9	5	134	139
10	0	384	384
11	11	1093	1104
12	0	3180	3180
13	28	9278	9306
14	0	27390	27390
15	74	81299	81373
16	0	243077	243077
17	199	730499	730698
18	0	2206994	2206994
19	551	6696652	6697203
20	0	20403645	20403645
21	1553	62391058	62392611
22	0	191421009	191421009
23	4436	589067922	589072358
24	0	1817813340	1817813340
25	12832	5623914196	5623927028
26	0	17440173420	17440173420
27	37496	54201047524	54201085020
28	0	168788248960	168788248960
29	110500	526614623876	526614734376
30	0	1645906860146	1645906860146
31	328092	5152637471574	5152637799666
32	0	16155528847513	16155528847513
33	980491	50727010152213	50727011132704
34	0	159494889064424	159494889064424
35	2946889	502122609897769	502122612844658
36	0	1582695009952591	1582695009952591
37	8901891	4994368768585840	499436877487731
38	0	15777334641762973	15777334641762973
39	27012286	49892135649565631	49892135676577917
40	0	157925978317166885	157925978317166885
41	82300275	500353942926314587	500353943008614862
42	0	1586660763132559248	1586660763132559248
43	251670563	503565450260327639	5035654550511998202
44	0	15994703113957238928	15994703113957238928
45	772160922	50842778476404854195	5084277847717701517
46	0	161733751563950248680	161733751563950248680
47	2376294040	514845264848952958540	514845264851329252580
48	0	1640003231433119619060	1640003231433119619060
49	7333282754	5227483001871491788767	5227483001878825071521
50	0	16672827119632343388008	16672827119632343388008
51	22688455980	5320886185779497727088	53208861857802186183068
52	0	169905259439122314194228	169905259439122314194228
53	70361242924	542835698052189089638074	542835698052259450880998
54	0	1735241075943454322734212	1735241075943454322734212
55	218679264772	554974062034243462149162	5549740620342653141413934
56	0	17758204594179355830374348	17758204594179355830374348
57	681018679604	56850122366848604475089608	56850122366849285493769212
58	0	182080148335269421715726704	182080148335269421715726704
59	2124842137550	583426122439603014698357555	58342612243960513954049515
60	0	1870229014730571430145667576	1870229014730571430145667576
61	6641338630714	5997679391743169227236373959	5997679391743175868575004673
62	0	19241787960120790868844440744	19241787960120790868844440744
63	20792003301836	6175552058208693355647310718	61755520582086954347650612554
64	0	198275501916867969158416084337	198275501916867969158416084337
65	65193446172901	636825148056284740390842535860	6368251480562848055842887861
66	0	2046088557545982654839652746868	2046088557545982654839652746868
67	204709353135917	6576232144372013812043670024649	6576232144372014016753023160566
68	0	21143357287075148551106264209103	21143357287075148551106264209103
69	643665829838389	6800027572758654195789738794623	68000275727586542601563213633012
70	0	218767749256017151523001852812175	218767749256017151523001852812175
71	2026461371823166	704024838909121166271756179810955	704024838909121168298217551634121
72	0	2266319012243909584326047161014871	2266319012243909584326047161014871
73	6387637263287353	7297581433775704585897911535340551	7297581433775704592285548798627904
74	0	23504895227052167507661883323913160	23504895227052167507661883323913160
75	20157546705808565	75727897833344183889185455394074673	7572789783334418390934300299883238
76	0	244044246512988647239886320675632396	244044246512988647239886320675632396
77	63680191033811326	786671355665327491330603281239464193	786671355665327491394283472273275519
78	0	253645585596616874558496053438754842	253645585596616874558496053438754842
79	201379876145388644	8180271421631120823612164236249300966	8180271421631120823813544112394689610
80	0	26388328642265172813438151385010288753	26388328642265172813438151385010288753
81	637456295966779429	85144627376163351855903064347443766622	8514462737616335185654052064310546051
82	0	274790258732300678104236015966009973324	274790258732300678104236015966009973324
83	2019698989374464699	887037028653135270174559457913663705854	887037028653135270176579156903038170553
84	0	286402099945021724096328072207813457293	286402099945021724096328072207813457293
85	6404799147037290651	9249163559612714680335121269404144728163	9249163559612714680341526068551182018814
86	0	29875720803464503094655711577970202548413	29875720803464503094655711577970202548413
87	20327740716521351562	96521025780852576095630432225312188305219	965210257808525760956028709656781
88	0	3118969100979141366772522730181845848972	3118969100979141366772522730181845848972
89	64568510301289106574	1008054223548171476688766672635446492724311	1008054223548171476688831241145747781830885
90	0	32586560834700598050188276738236745878426	32586560834700598050188276738236745878426
91	205250829465372138276	10535937157194688312231790612504288595574838	105359371571946883122319958633375396771314
92	0	34071094172842713073663584467595261589610016	34071094172842713073663584467595261589610016
93	652930625323502669516	1101984707957318052190455190159053627710086	110198470795731805219046171946530359780367702
94	0	356483964374708088112146021189221811803662100	356483964374708088112146021189221811803662100
95	2078516705781154747150	115339427567322753652172652832015678025177985	1153394275673227536521728606836862561411925135
96	0	3732393408876054896346820382302454758144286668	3732393408876054896346820382302454758144286668
97	6621122347418605999236	12080012408450562786881919983193640783859970148	12080012408450562786881926604315988202645969384
98	0	3910355899933158051561898489526653291592657022	3910355899933158051561898489526653291592657022
99	21105194400328603264540	126599687272566233668768116305546887367673690648	126599687272566233668768137410721287696276955188
100	0	409935160255998483530763106223151187530904561384	409935160255998483530763106223151187530904561384

^aIn each value of $S_k^{(C)}$ (Chiral) or S_k (Chiral + Achiral), each enantiomeric pair is counted just once for chiral secondary monosubstituted alkanes.

$$S(x) = \frac{x}{2} ((b(x) - 1)^2 + (c(x^2) - 1)). \quad (28)$$

It should be noted that the first term 1 in $b(x)$ or $c(x^2)$ is omitted; otherwise, a monosubstituted methane ($\bullet\text{—CH}_3$) and primary monosubstituted alkanes (e.g., $\bullet\text{—CH}_2\text{—R}$) would be erroneously counted in.

On a similar line, eq. 23 when modified and multiplied by x gives the following functional equation:

$$S(x)^{(A)} = x(c(x^2) - 1). \quad (29)$$

Further, the modification of eq. 24 and the subsequent multiplication by x give the following functional equation:

$$S(x)^{(C)} = \frac{x}{2} ((b(x) - 1)^2 - (c(x^2) - 1)). \quad (30)$$

Procedures for calculating S_k (eq. 25) by $S(x)$ (eq. 28), $S_k^{(A)}$ (eq. 26) by $S(x)^{(A)}$ (eq. 29), and $S_k^{(C)}$ (eq. 27) by $S(x)^{(C)}$ (eq. 30) were programmed by using Maple programming language as follows (the omitted paragraphs are the same as those of "P1-100.mpl").

Maple program for enumeration primary monosubstituted alkanes: "S1-100.mpl":

```
"Definition of Functional Equations";
(omitted)
"Initial Values";
(omitted)
"Do Loop for Calculation";
(omitted)

"Secondary Monosubstituted Alkanes";
Sx := (1/2)*x*((b1-1)^2 + c2-1):
Sxa := x*(c2-1):
Sxc := (1/2)*x*((b1-1)^2 - (c2-1)):

"Print-Out of Results";
for cntt from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\ \ \ \ \n",
cntt,
coeff(Sxa, x^cntt),
coeff(Sxc, x^cntt),
coeff(Sx, x^cntt));
end do;
```

The execution of the program gave the results collected in Table 2.

2.4 Tertiary Monosubstituted Alkanes

Tertiary monosubstituted alkanes are derived from the same skeleton (**3**) as discussed for monosubstituted alkanes without itemization due to branching (Figure 3). A different point is that all of the three substituents in a tertiary monosubstituted alkane must be alkyl ligands, but not hydrogens.

We apply Theorem 2, Theorem 3, and the two propositions of Theorem 4 of [17] to the enumeration of tertiary monosubstituted alkanes. To count achiral planted promolecules and enantiomeric pairs of chiral planted promolecules, we employ the following CI-CF:

$$\text{CI-CF}(\mathbf{C}_{3v}; a_d, c_d, b_d) = \frac{1}{6}(b_1^3 + 2b_3 + 3a_1c_2). \quad (31)$$

We use the following CI-CF:

$$\text{CI-CF}(\mathbf{C}_3; b_d) = \frac{1}{3}(b_1^3 + 2b_3) \quad (32)$$

in order to count achiral and chiral planted promolecules. For the purpose of counting achiral planted promolecules only, we start from the following CI-CF_A:

$$\begin{aligned} \text{CI-CF}_A(\mathbf{C}_{3v}; a_d, c_d, b_d) \\ &= 2\text{CI-CF}(\mathbf{C}_{3v}; a_d, c_d, b_d) - \text{CI-CF}(\mathbf{C}_3; b_d) \\ &= a_1c_2. \end{aligned} \quad (33)$$

To count chiral planted promolecules only, we use the following CI-CF_C:

$$\begin{aligned} \text{CI-CF}_C(\mathbf{C}_{3v}; a_d, c_d, b_d) \\ &= \text{CI-CF}(\mathbf{C}_3; b_d) - \text{CI-CF}(\mathbf{C}_{3v}; a_d, c_d, b_d) \\ &= \frac{1}{6}(b_1^3 + 2b_3 - 3a_1c_2). \end{aligned} \quad (34)$$

We have already used these equations to obtain the functional equations for recursive calculations, i.e., $a(x)$ (eq. 4), $c(x^2)$ (eq. 5), and $b(x)$ (eq. 6). But, we here use them in a slightly different manner in order to treat tertiary monosubstituted alkanes.

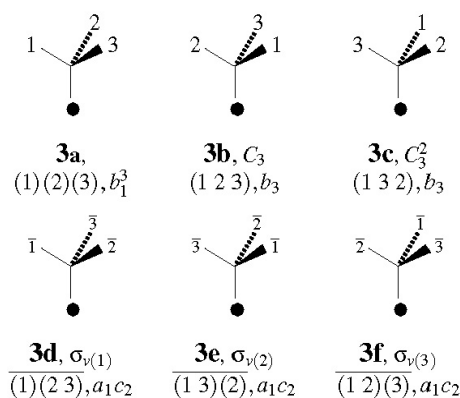


Figure 3. Symmetry operations for a \mathbf{C}_{3v} -skeleton (**3**). The identity operation (I) converts **3** into itself, where the resulting skeleton is denoted as **3a**.

Table 3. Numbers of Tertiary Monosubstituted Alkanes as Stereoisomers^a

k	$T_k^{(A)}$ (Achiral)	$T_k^{(C)}$ (Chiral)	T_k (Achiral + Chiral)
1	0	0	0
2	0	0	0
3	0	0	0
4	1	0	1
5	1	0	1
6	3	0	3
7	4	3	7
8	9	9	18
9	13	33	46
10	28	103	131
11	42	322	364
12	86	975	1061
13	134	2973	3107
14	266	8979	9245
15	424	27248	27672
16	829	82708	83537
17	1343	251929	253272
18	2594	769210	771804
19	4258	2356141	2360399
20	8151	7236274	7244425
21	13517	22286551	22300068
22	25707	68811317	68837024
23	42984	212974927	213017911
24	81320	660640357	660721677
25	136914	2053597544	2053734458
26	257930	6396091087	6396349017
27	436786	19957726259	19958163045
28	820014	62381048449	62381868463
29	1395522	195296352086	195297747608
30	2612338	612340080267	612342692605
31	4464816	1922692467533	1922696932349
32	8337339	6045188419350	6045196756689
33	14302891	19030935687604	19030949990495
34	26652046	59983335960789	59983362612835
35	45872822	189275136684764	189275182557586
36	85322959	597892893118023	597892978440982
37	147285061	1890585874581290	1890586021866351
38	273509079	5983987385483868	5983987658992947
39	473366304	18957706656033733	18957707129400037
40	877798197	60112231154629409	60112232032427606
41	1522784893	190767402974985464	190767404497770357
42	2820254890	605889314288726283	605889317108981173
43	4902894752	1925816231904420159	1925816236807314911
44	9070105772	6125681673891585692	6125681682961691464
45	15798375748	19498381097351393321	19498381113149769069
46	29196525066	62106146350516754407	62106146379713279473
47	50944089584	197947775353212888465	197947775404156978049
48	94061843688	631299589338575085139	631299589432636928827
49	164389702630	2014553024497645351193	2014553024662035053823
50	303271472328	6432359248141469785141	6432359248444741257469
51	530804812064	20549483482795639435421	20549483483326444247885
52	978499630732	65684320496705633147631	65684320497684132778363
53	1714969360394	210060468120430366101146	210060468122145335461540
54	3159211519966	672110750388372573286780	672110750391531784806746
55	5543992358404	2151511862018332441350437	2151511862023876433708841
56	10206241364176	6890423549610033815521479	689042354962040056885655
57	17931579841406	22077027805168747611842857	22077027805186679191684263
58	32991661069946	70765467743143405496768939	70765467743176397157838885
59	58027036491386	226924894784840705940791571	226924894784898732977282957
60	106703235194344	727976024194131774278134488	727976024194238477513328832
61	187864849732928	2336257162294164638611048073	2336257162294352503460781001
62	345279977499014	7500454398545690958997122871	7500454398546036238974621885
63	608488544469628	24088670427084431201299977795	2408867042708503969844447423
64	1117821021502643	77391204324713453729278383690	77391204324714571550299886333
65	197169792830255	248724925881692523437133187621	248724925881694495135126017876
66	3620495889925484	799634562023079620043858295795	799634562023083240539748221279
67	6391454544461316	2571604329491899422254227721403	2571604329491905813708772182719
68	11731340178225649	827281030368947892265020412870	82728103036895962360198638519
69	20726277344671231	26621618912772924581780923683603	2662161891277294530805826834834
70	38027763076250087	85692862268544704422941280137496	85692862268544742450704356387583
71	67235222551327112	275918036282937464781659804146178	275918036282937532016882355473290
72	12331562319384547	8886636033890507523467002099536	888663603389050875662332609684033
73	218181838174969901	2862946948685046361921485563477218	2862946948685046580103323738447119
74	400028609401324332	9225813761102566298188778553948706	9225813761102566698217387955273038
75	708238253879291862	29737779393711622699494492493287884	29737779393711623407732746372579746
76	1298110183826230514	95878662158653366395722601657217229	95878662158653367693832785483447743
77	2299707137035992390	309201927540367266456946415382224889	309201927540367268756653552418217279
78	4213783975416517808	997393514697096915746034816790945562	997393514697096919958918792207463370
79	7469505467239002108	3218047350975752128273039403935950252	3218047350975752135742544871174952360
80	13682527867936702011	10385260143029346399954133485572812831	10385260143029346413636661353509514842
81	24267863639101720765	33522700396708454104872092044555783398	33522700396708454129139956683657504163
82	44441368665990049486	108231822114761224845101335624345290924	108231822114761224889542704290335340410
83	78865347774539725162	349512792978114213505095974477798615783	349512792978114213583961322252338340945
84	144387503783725346027	1128914800599519135016061084529019316735	1128914800599519135160448588312744662672
85	2563603557253280667	3647095761077988901940721330637548483379	3647095761077988902197081666210083764046
86	469231739534642203251	11784714682396904101810844036853076121780	1178471468239690410228007577638718325031
87	833528867436336797488	38086840584034773259843218809530706816672	38086840584034773260676747676967043614160
88	1525301161767249107642	123115553731784421988253209396378535261913	123115553731784421989778510558145784369555
89	2710761027612549480714	398044096040998411757386162072427641874149	398044096040998411760096923101860191354863
90	4959403704992344038264	1287146527961969210383511050256678242770092	1287146527961969210388470453961670586808336
91	8817763279974434011688	4162954244302694574519052462320894415269151	416295424430269457452780225600868849280839
92	1612888939364849815416	13466368387713460219376071618227415324910078	1346636838771346021939220050762106377425494
93	2868919372979102074572	43568535496437586295605481572049899197830823	4356853549643758629563417065779678299905395
94	52465810519165514269984	140983248207842804957859783106904869841147138	140983248207842804957912248917424035554471722
95	93361383093487367373440	456281280623702827106784497433796107159072285	45628128062370282710687785881688959425645725
96	170703045526883245016134	14769538847542922593890229572319908900352506	1476953884754292259389269987687292145368640
97	303879757413738907074584	4781552872893128733720136642398106649605706148	478155287289312873372044052215520388512780732
98	555514487166925062546460	15482367569733516736092804513186912079493215269	15482367569733516736093360027674079004555761729
99	98927846848304739266104	5013844395526557457433242087559204866550761679	5013844395526557457433341015402765331712990027783
100	1808153272044227049489940	162393303186002227859827929458851823386547984868	162393303186002227859829737612123867613597474808

^aIn each value of $T_k^{(C)}$ (Chiral) or T_k (Chiral + Achiral), each enantiomeric pair is counted just once for chiral tertiary monosubstituted alkanes.

Let T_k , $T_k^{(A)}$, and $T_k^{(C)}$ be the number of achiral tertiary monosubstituted alkanes plus enantiomeric pairs, the number of achiral ones, and the number of enantiomeric pairs. They satisfy the following generating functions:

$$T(x) = \sum_{k=1}^{\infty} T_k x^k \quad (35)$$

$$T(x)^{(A)} = \sum_{k=1}^{\infty} T_k^{(A)} x^k \quad (36)$$

$$T(x)^{(C)} = \sum_{k=1}^{\infty} T_k^{(C)} x^k, \quad (37)$$

where x^k corresponds to the carbon content $k \geq 1$.

The SIs a_d , c_d , and b_d in eq. 31 are replaced by $a(x^d) - 1$, $c(x^d) - 1$ and $b(x^d) - 1$ respectively. The resulting equation is multiplied by x to take the principal vertex into consideration. Thereby, we obtain the following functional equation:

$$T(x) = \frac{x}{6} ((b(x) - 1)^3 + 2(b(x) - 1) + 3(a(x) - 1)(c(x^2) - 1)). \quad (38)$$

It should be noted that the first term 1 in $b(x)$, $a(x)$, or $c(x^2)$ is omitted in order to exclude monosubstituted methane ($\bullet\text{---CH}_3$), primary (e.g., $\bullet\text{---CH}_2\text{---R}$), and secondary monosubstituted alkanes (e.g., $\bullet\text{---CH---RR}$). On a similar line, eq. 33 gives the following functional equation:

$$T(x)^{(A)} = x(a(x) - 1)(c(x^2) - 1). \quad (39)$$

Further, eq. 34 gives the following functional equation:

$$T(x)^{(C)} = \frac{x}{6} ((b(x) - 1)^3 + 2(b(x) - 1) - 3(a(x) - 1)(c(x^2) - 1)). \quad (40)$$

Procedures for calculating T_k (eq. 35) by $T(x)$ (eq. 38), $T_k^{(A)}$ (eq. 36) by $T(x)^{(A)}$ (eq. 39), and $T_k^{(C)}$ (eq. 37) by $T(x)^{(C)}$ (eq. 40) were programmed by using the Maple programming language as follows (the omitted paragraphs are the same as those of "P1-100.mpl").

Maple program for enumeration primary monosubstituted alkanes: "T1-100.mpl":

```
"Definition of Functional Equations";
(omitted)
"Initial Values";
(omitted)
"Do Loop for Calculation";
(omitted)

"Tertiary Monosubstituted Alkanes";
Tx := (1/6)*x*((b1-1)^3 + 2*(b3-1)
+ 3*(a1-1)*(c2-1)):
Txa := x*(a1-1)*(c2-1):
```

```
Txc := (1/6)*x*((b1-1)^3 + 2*(b3-1)
- 3*(a1-1)*(c2-1)):
```

```
"Print-Out of Results";
for ccntt from 1 to 100 by 1 do
printf("%d & %d & %d & %d \\\ \n",
ccntt,
coeff(Txa,x^ccntt),
coeff(Txc,x^ccntt),
coeff(Tx,x^ccntt));
end do;
```

The execution of the program gave the results collected in Table 3.

2.5 Total Numbers

The total numbers of achiral stereoisomers of primary, secondary, and tertiary monosubstituted alkanes are calculated by adding the coefficients of the term x^k appearing in eqs. 19, 29, and 39. The results should be identical with the values α_k alternatively calculated by using eq. 4. In fact, we can obtain the following relationship:

$$P(x)^{(A)} + S(x)^{(A)} + T(x)^{(A)} = xa(x)c(x^2), \quad (41)$$

where the coefficient of each term is identical with that of eq. 4 except x^0 .

The total numbers of achiral enantiomeric pairs of primary, secondary, and tertiary monosubstituted alkanes are calculated by adding the coefficients of the term x^k appearing in eqs. 20, 30, and 40. The results should be identical with the values C_k alternatively calculated by using $C(x)$ (eq. 10). In fact, we can obtain the following relationship:

$$P(x)^{(C)} + S(x)^{(C)} + T(x)^{(C)} = \frac{x}{6}(b(x)^3 + 2b(x^3) - 3a(x)c(x^2)), \quad (42)$$

which is identical with the expanded equation derived from $C(x)$ (eq. 10).

The total numbers of achiral plus enantiomeric pairs of primary, secondary, and tertiary monosubstituted alkanes are calculated by adding the coefficients of the term x^k appearing in eqs. 18, 28, and 38. The results should be identical with the values B_k alternatively obtained by $B(x)$ (eq. 9). In fact, we can obtain

$$P(x) + S(x) + T(x) = \frac{x}{6}(b(x)^3 + 2b(x^3) + 3a(x)c(x^2)), \quad (43)$$

which is identical with the expanded equation derived from $B(x)$ (eq. 9) except the term x^0 .

We are able to verify these facts numerically by the following Maple program "Test1-100.mpl", where we put: AA for eq. 41, CC for eq. 42, BB for eq. 43, BBx for eq. 9, CCx for eq. 10.

Maple program for enumeration monosubstituted alkanes: "Test1-100.mpl":

```
"Definition of Functional Equations";
(omitted)
"Initial Values";
(omitted)
"Do Loop for Calculation";
(omitted)

"Sum of Achiral Isomers";
Pxa := x*a1;
Sxa := x*(c2-1);
Txa := x*(a1-1)*(c2-1);
AA := Pxa + Sxa + Txa;

"Sum of Chiral Isomers";
Pxc := (1/2)*x*(b1 - a1);
Sxc := (1/2)*x*((b1-1)^2 - (c2-1));
Txc := (1/6)*x*((b1-1)^3 + 2*(b3-1) - 3*(a1-1)*(c2-1));
CC := Pxc + Sxc + Txc;
CCx := (1/2)*(b1-a1);

"Sum of Achiral and Chiral Isomers";
Px := (1/2)*x*(b1 + a1);
Sx := (1/2)*x*((b1-1)^2 + c2-1);
```

```
Tx := (1/6)*x*((b1-1)^3 + 2*(b3-1) + 3*(a1-1)*(c2-1));
BB := Px + Sx + Tx;
BBx := (1/2)*(a1 + b1);

"Print-Out of Results";
for ccntt from 1 to 100 by 1 do
printf("%d & %d & %d & %d & %d & %d & %d \\ \\ \\ \n",
ccntt,
coeff(AA,x^ccntt),
coeff(a1,x^ccntt),
coeff(CC,x^ccntt),
coeff(CCx,x^ccntt),
coeff(BB,x^ccntt),
coeff(BBx,x^ccntt));
end do;
```

The results are summarized in Table 4, where the coefficients appearing in AA, CC, and BB are listed in the $B_k^{(A)}$ -, $B_k^{(C)}$ -, and B_k -columns, respectively. For comparison, Table 4 also collects the values of α_k (eq. 4), C_k (eq. 10), and B_k (eq. 9). Obviously, we can find equality between $B_k^{(A)}$ and α_k , between $B_k^{(C)}$ and C_k , as well as between $B_k^{(A)}$ and B_k .

Table 4. Total Numbers of Monosubstituted Alkanes as Stereoisomers^a

k	Achiral		Chiral		Achiral + Chiral	
	$B_k^{(A)}$	α_k	$B_k^{(C)}$	C_k	$B_k^{(A)}$	B_k
1	1	1	0	0	1	1
2	1	1	0	0	1	1
3	2	2	0	0	2	2
4	3	3	1	1	4	4
5	5	5	3	3	8	8
6	8	8	10	10	18	18
7	14	14	30	30	44	44
8	23	23	88	88	111	111
9	41	41	255	255	296	296
10	69	69	742	742	811	811
11	122	122	2157	2157	2279	2279
12	208	208	6312	6312	6520	6520
13	370	370	18563	18563	18933	18933
14	636	636	54932	54932	55568	55568
15	1134	1134	163479	163479	164613	164613
16	1963	1963	489264	489264	491227	491227
17	3505	3505	1471692	1471692	1475197	1475197
18	6099	6099	4447896	4447896	4453995	4453995
19	10908	10908	13500689	13500689	13511597	13511597
20	19059	19059	41140608	41140608	41159667	41159667
21	34129	34129	125818217	125818217	125852346	125852346
22	59836	59836	386050543	386050543	386110379	386110379
23	107256	107256	1188093392	1188093392	1188200648	1188200648
24	188576	188576	3666547089	3666547089	3666735665	3666735665
25	338322	338322	11344058829	11344058829	11344397151	11344397151
26	596252	596252	35180323336	35180323336	35180919588	35180919588
27	1070534	1070534	109339097119	109339097119	109340167653	109340167653
28	1890548	1890548	340508394528	340508394528	340510285076	340510285076
29	3396570	3396570	1062419370490	1062419370490	1062422767060	1062422767060
30	6008908	6008908	3320666310903	3320666310903	3320672319811	3320672319811
31	10801816	10801816	10395996250010	10395996250010	10396007051826	10396007051826
32	19139155	19139155	32596713516873	32596713516873	32596732656028	32596732656028
33	34422537	34422537	102354659356690	102354659356690	10235469379227	10235469379227
34	61074583	61074583	321832884381903	321832884381903	321832945456486	321832945456486
35	109894294	109894294	1013230630964436	1013230630964436	1013230740858730	1013230740858730
36	195217253	195217253	3193818534035050	3193818534035050	3193818729252303	3193818729252303
37	351404205	351404205	10078773177202180	10078773177202180	10078773528606385	10078773528606385
38	624913284	624913284	31840095204449021	31840095204449021	31840095829362305	31840095829362305
39	1125291874	1125291874	100689937510048385	100689937510048385	100689938635340259	100689938635340259
40	2003090071	2003090071	318728146981844679	318728146981844679	318728148984934750	318728148984934750
41	3608175239	3608175239	1009849492883144730	1009849492883144730	1009849496491319969	1009849496491319969
42	6428430129	6428430129	3202399570304430261	3202399570304430261	3202399576732860390	3202399576732860390
43	11582995444	11582995444	10163870352469178059	10163870352469178059	10163870364052173503	10163870364052173503
44	20653101216	20653101216	32284255140318002679	32284255140318002679	32284255160971103895	32284255160971103895
45	37223637886	37223637886	102625414714074250195	102625414714074250195	102625414751297888081	102625414751297888081
46	66420162952	66420162952	326465312628541253282	326465312628541253282	326465312694961416234	326465312694961416234
47	119740546576	119740546576	1039258352830707100287	1039258352830707100287	1039258352950447646863	1039258352950447646863
48	213802390264	213802390264	3310561173602401804486	3310561173602401804486	3310561173816204194750	3310561173816204194750
49	385525375648	385525375648	10552597199971538944446	10552597199971538944446	10552597200357064320094	10552597200357064320094
50	688796847976	688796847976	33657783567745352117595	33657783567745352117595	33657783568434148965571	33657783568434148965571

^aIn each value of $B_k^{(C)}$, C_k , B_k , and C_k , each enantiomeric pair is counted just once for chiral monosubstituted alkanes.

By comparing eq. 9 and eq. 18, we obtain the following relationship:

$$P(x) = xB(x). \quad (44)$$

This equation results in the equality between the coefficients of eq. 9 (P_{k+1}) and those of eq. 18 (B_k), i.e.,

$$P_{k+1} = B_k. \quad (45)$$

In fact, this relationship can be verified by comparing the P_k -column of Table 1 with the B_k -column of Table 4.

Because eq. 19 for achiral primary monosubstituted alkanes is akin to eq. 44, we are able to obtain the following equation:

$$P_{k+1}^{(A)} = \alpha_k. \quad (46)$$

This relationship can be verified by comparing the $P_k^{(A)}$ -column of Table 1 with the α_k -column of Table 4.

On the same line as eq. 44, we obtain the following relationship by comparing eq. 10 and eq. 20:

$$P(x)^{(C)} = xC(x). \quad (47)$$

This equation results in the equality between the coefficients of eq. 9 (P_{k+1}) and those of eq. 20 (C_k), i.e.,

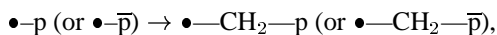
$$P_{k+1}^{(C)} = C_k. \quad (48)$$

This relationship can be verified by comparing the $P_k^{(C)}$ -column of Table 1 with the C_k -column of Table 4.

Chemically speaking, eq. 46 reflects the exclusive derivation of achiral primary monosubstituted alkanes from lower achiral alkyl ligands, e.g.,



On the other hand, eq. 47 reflects the exclusive derivation of chiral primary monosubstituted alkanes from lower chiral alkyl ligands, e.g.,



where each enantiomeric pair is counted just once. It follows that eq. 45 reflects the total derivation of primary monosubstituted alkanes from lower alkyl ligands.

3 Enumeration of Monosubstituted Alkanes as Graphs

To emphasize the difference between stereoisomers and graphs (constitutional isomers), let us count monosubstituted alkanes as graphs by using Pólya's theorem. Note that any CIs based on Pólya's theorem [4, 5] can be derived from the CI-CFs of Fujita's proligand method [15–17] by omitting sphericities. In other words, Pólya's theorem lacks the sphericity concept. Although Pólya put it, "The cycle index knows many things." [10](page 67), the cycle index (CI) does not know the sphericities of cycles.

In connection with the present viewpoint of stereoisomer enumeration, it is important to know how Pólya's theorem lacks the sphericity concept.

Suppose that the number (R_k) of monosubstituted alkanes of carbon content k is itemized into those of primary ($P_k^{(G)}$), secondary ($S_k^{(G)}$), and tertiary ones ($T_k^{(G)}$), as shown in the following generating functions:

$$r(x) = \sum_{k=0}^{\infty} R_k x^k \quad (49)$$

$$P(x)^{(G)} = \sum_{k=0}^{\infty} P_k^{(G)} x^k \quad (50)$$

$$S(x)^{(G)} = \sum_{k=1}^{\infty} S_k^{(G)} x^k \quad (51)$$

$$T(x)^{(G)} = \sum_{k=1}^{\infty} T_k^{(G)} x^k \quad (52)$$

where x^k corresponds to the carbon content k and we put $R_0 = 1$, $P_{(G)} = 1$, $S_0^{(G)} = 0$ (omitted), and $T_0^{(G)} = 0$ (omitted).

Because any Pólya's CI can be regarded as a special case of the CI-CF of Fujita's proligand method with putting $r_d = a_d = c_d = b_d$, eq. 43 can be converted to the following functional equation by putting $r(x) = P(x) + S(x) + T(x)$ in the left-hand side and $r(x) = b(x) = a(x) = c(x)$ in the right-hand side and by adding 1 to assure recursive character:

$$r(x) = 1 + \frac{x}{6} (r(x)^3 + 2r(x^3) + 3r(x)r(x^2)). \quad (53)$$

Note that this equation gains recursive nature at the expense of the sphericity concept in contrast to eq. 43.

Enumeration of primary monosubstituted alkanes as graphs is regarded as a special case of eq. 18. Hence, by putting $r(x) = a(x) = b(x)$, we obtain:

$$P(x)^{(G)} = xr(x). \quad (54)$$

Similarly, enumeration of secondary monosubstituted alkanes as graphs can be conducted as a special case of eq. 28, where we put $r(x) = b(x) = c(x)$ as follows:

$$S(x)^{(G)} = \frac{x}{2} ((r(x) - 1)^2 + (r(x^2) - 1)). \quad (55)$$

On a similar line, enumeration of tertiary monosubstituted alkanes as graphs is regarded as a special case of eq. 38. Hence, we obtain the following functional equation by putting $r(x) = a(x) = b(x) = c(x)$:

$$T(x)^{(G)} = \frac{x}{6} ((r(x) - 1)^3 + 2(r(x) - 1) + 3(r(x) - 1)(r(x^2) - 1)). \quad (56)$$

These generating functions were programmed by means of Maple programming language and the code stores in a file named "Graph1-100.mpl" tentatively.

Table 5. Numbers of Monosubstituted Alkanes as Graphs

k	$P_k^{(G)}$ (Primary)	$S_k^{(G)}$ (Secondary)	$T_k^{(G)}$ (Tertiary)	R_k (Total)	V_k
1	1	0	0	1	1
2	1	0	0	1	1
3	1	0	0	1	2
4	2	0	0	2	4
5	4	0	0	4	8
6	8	0	0	8	17
7	17	0	0	17	39
8	39	0	0	39	89
9	89	0	0	89	211
10	211	0	0	211	507
11	507	0	0	507	1238
12	1238	0	0	1238	3057
13	3057	0	0	3057	7639
14	7639	0	0	7639	19241
15	19241	0	0	19241	48965
16	48965	0	0	48965	124906
17	124906	0	0	124906	321198
18	321198	0	0	321198	830219
19	830219	0	0	830219	2156010
20	2156010	0	0	2156010	5622109
21	5622109	0	0	5622109	14715813
22	14715813	0	0	14715813	38649152
23	38649152	0	0	38649152	101821927
24	101821927	0	0	101821927	269010485
25	269010485	0	0	269010485	712566567
26	712566567	0	0	712566567	1891993344
27	1891993344	0	0	1891993344	5034704828
28	5034704828	0	0	5034704828	1342517806
29	1342517806	0	0	1342517806	3586655089
30	3586655089	0	0	3586655089	95991365288
31	95991365288	0	0	95991365288	25732864506
32	25732864506	0	0	25732864506	690928354105
33	690928354105	0	0	690928354105	1857821351559
34	1857821351559	0	0	1857821351559	500235607153
35	500235607153	0	0	500235607153	13486440075669
36	13486440075669	0	0	13486440075669	36404382430278
37	36404382430278	0	0	36404382430278	9838079170283
38	9838079170283	0	0	9838079170283	26615892500477
39	26615892500477	0	0	26615892500477	720807976831447
40	720807976831447	0	0	720807976831447	195402030661819
41	195402030661819	0	0	195402030661819	530195062017063
42	530195062017063	0	0	530195062017063	14398991611139217
43	14398991611139217	0	0	14398991611139217	3913776875465752
44	3913776875465752	0	0	3913776875465752	1064659546531465
45	1064659546531465	0	0	1064659546531465	289841389106439413
46	289841389106439413	0	0	289841389106439413	789624117549095761
47	789624117549095761	0	0	789624117549095761	215281494597162856
48	215281494597162856	0	0	215281494597162856	587252808361531054
49	587252808361531054	0	0	587252808361531054	1603349524757039074
50	1603349524757039074	0	0	1603349524757039074	4379755494193757760
51	4379755494193757760	0	0	4379755494193757760	1197105380642883814
52	1197105380642883814	0	0	1197105380642883814	32738706144038739008
53	32738706144038739008	0	0	32738706144038739008	895843085951178143691
54	895843085951178143691	0	0	895843085951178143691	2452673338705855184
55	2452673338705855184	0	0	2452673338705855184	67182627892985973622
56	67182627892985973622	0	0	67182627892985973622	1841171398697833823000
57	1841171398697833823000	0	0	1841171398697833823000	5048249780995534038577
58	5048249780995534038577	0	0	5048249780995534038577	13847960282822198112039
59	13847960282822198112039	0	0	13847960282822198112039	380035071896680874765695
60	380035071896680874765695	0	0	380035071896680874765695	104339311165230873060544
61	104339311165230873060544	0	0	104339311165230873060544	2865843809192062819497928
62	2865843809192062819497928	0	0	2865843809192062819497928	787465397974760120343666
63	787465397974760120343666	0	0	787465397974760120343666	216460809440022057892722
64	216460809440022057892722	0	0	216460809440022057892722	5952393603181888124081873
65	5952393603181888124081873	0	0	5952393603181888124081873	163742112144282534714835522
66	163742112144282534714835522	0	0	163742112144282534714835522	45059233945898249869218319
67	45059233945898249869218319	0	0	45059233945898249869218319	1240384226853579484504152814
68	1240384226853579484504152814	0	0	1240384226853579484504152814	3415642888456985955252130
69	3415642888456985955252130	0	0	3415642888456985955252130	940872333877528298214212
70	940872333877528298214212	0	0	940872333877528298214212	2592534110456284276604383001
71	2592534110456284276604383001	0	0	2592534110456284276604383001	7145798269164383844917552096
72	7145798269164383844917552096	0	0	7145798269164383844917552096	197017958333002225561436794
73	19701795833300225561436794	0	0	19701795833300225561436794	5433806698116791491048793218
74	5433806698116791491048793218	0	0	5433806698116791491048793218	149895349616752566890201439
75	149895349616752566890201439	0	0	149895349616752566890201439	4136270918924366555319895187994
76	413627091892436655319895187994	0	0	413627091892436655319895187994	11416819269749659903244393933095
77	11416819269749659903244393933095	0	0	11416819269749659903244393933095	31520543697567184300586727635
78	31520543697567184300586727635	0	0	31520543697567184300586727635	87046595346326327991021865784
79	87046595346326327991021865784	0	0	87046595346326327991021865784	2404458126402111648189057815169
80	2404458126402111648189057815169	0	0	2404458126402111648189057815169	6643320729647167736372953010226
81	6643320729647167736372953010226	0	0	6643320729647167736372953010226	1835920910504187020289976469861
82	1835920910504187020289976469861	0	0	1835920910504187020289976469861	507487328645475180423389761634
83	507487328645475180423389761634	0	0	507487328645475180423389761634	140310810663022772814029017828712
84	140310810663022772814029017828712	0	0	140310810663022772814029017828712	3880175247739183194852898941088
85	3880175247739183194852898941088	0	0	3880175247739183194852898941088	1073256622668141408907129890499717
86	1073256622668141408907129890499717	0	0	1073256622668141408907129890499717	2969243115703216548467456351866990
87	2969243115703216548467456351866990	0	0	2969243115703216548467456351866990	8216289590106652460677197152568
88	8216289590106652460677197152568	0	0	8216289590106652460677197152568	227400562877047052134466050233781
89	227400562877047052134466050233781	0	0	227400562877047052134466050233781	629403446864037356808196702637899337
90	629403446864037356808196702637899337	0	0	629403446864037356808196702637899337	174290172523175523202391776963723417
91	174290172523175523202391776963723417	0	0	174290172523175523202391776963723417	482625749301875060233977354369433592
92	482625749301875060233977354369433592	0	0	482625749301875060233977354369433592	1336826716063011168192583116008336852
93	1336826716063011168192583116008336852	0	0	1336826716063011168192583116008336852	370328190471825264663855048541321953
94	370328190471825264663855048541321953	0	0	370328190471825264663855048541321953	102608705221182542559706310289069618
95	102608705221182542559706310289069618	0	0	102608705221182542559706310289069618	2843796375661093061594575695504922758
96	2843796375661093061594575695504922758	0	0	2843796375661093061594575695504922758	788111805790330406879598021785239267924
97	788111805790330406879598021785239267924	0	0	788111805790330406879598021785239267924	218472128982852735129113460976162456395
98	218472128982852735129113460976162456395	0	0	218472128982852735129113460976162456395	60572193491813719514851889145800693998935
99	60572193491813719514851889145800693998935	0	0	60572193491813719514851889145800693998935	16796477524064167296692581041530933570844
100	16796477524064167296692581041530933570844	0	0	16796477524064167296692581041530933570844	46583210746366514387591208851597457674802

Maple program for enumeration monosubstituted alkanes, "Graph1-100.mpl":

"Definition of Functional Equation";

rx := 1 + (1/6)*x*(r1^3+2*r1^3+3*r1^2*r2);

"Initial Values";

r1 := 1;

r2 := 1;

r3 := 1;

"Do Loop fo Calculation";

for cntnt from 1 to 100 by 1 do

ccntt :=

Rx:= coeff(rx,x^ccntt);

r1 := r1 + Rx*x^ccntt;

r2 := r2 + Rx*x^(ccntt+2);

r3 := r3 + Rx*x^(ccntt+3);

end do;

"Itemized Planted Trees";

Pg := x*r1;

Sg := (1/2)*x*(r1-1)^2 + (r2-1);

Tg := (1/6)*x*(r1-1)^3 + 2*(r3-1) + 3*(r1-1)*(r2-1);

RR := Pg + Sg + Tg;

"Validity Test";

V := rx - RR;

"Print-Out of Results";

for cntnt from 1 to 100 by 1 do

printf("%d & %d & %d & %d

& %d & %d \\\ \n",

cntnt,

coeff(Pg,x^ccntt),

coeff(Sg,x^ccntt),

coeff(Tg,x^ccntt),

coeff(rx,x^ccntt),

coeff(V,x^ccntt);

end do;

In this code, we use the following symbols: $r(x)$ (eq. 53), $P(x)^{(G)}$ (eq. 54), $S(x)^{(G)}$ (eq. 55, and $T(x)^{(G)}$ (eq. 56); as well as $r1$ for $r(x)$, $r2$ for $r(x^2)$, and $r3$ for $r(x^3)$. The paragraph “Validity Test” confirms that the values by the recursive calculation ($r(x)$ for $r(x)$) are equal to the sum of the itemized values (RR or $P(x)^{(G)}+S(x)^{(G)}+T(x)^{(G)}$). This is directly confirmed by summing up the functional equations:

$$P(x)^{(G)} + S(x)^{(G)} + T(x)^{(G)} = \frac{x}{6}(r(x)^3 + 2r(x^3) + 3r(x)r(x^2)), \quad (57)$$

which is identical with $r(x)$ (eq. 53) except for the initial value 1 added for recursion.

The results are summarized in Table 5, where the coefficients appear in the $P_k^{(G)}$ - (primary), the $S_k^{(G)}$ - (secondary), the $T_k^{(G)}$ - (tertiary), and the R_k -columns, respectively. The last column V_k contains zero values for indicating the validity of the present calculation.

The results up to 20 shown in Table 5 are identical with those of Henze and Blair [1], the results from carbon content 21 to 30 are identical with those of Perry [23], and the results from carbon content up to 50 are identical with those collected in Trinajstić’s book [24](pages 153-154 of Vol. II).

According to eq. 54, we obtain the following relationship:

$$P_{k+1}^{(G)} = R_k. \quad (58)$$

The relationship can be verified by comparing the $P_k^{(G)}$ -column of Table 5 with the R_k -column of the same table. Obviously, this is a graph-counting counterpart of eq. 45. Chemically speaking, eq. 58 reflects the exclusive derivation of primary monosubstituted alkanes (as graphs) from lower alkyl ligands (as graphs).

4 Discussions

4.1 Pseudoasymmetric Cases

Among the enumeration results collected in Tables 1–3, the $S_k^{(A)}$ -column in Table 2 exhibits a special feature to be pointed out. Thus, we can find that each value of $S_k^{(A)}$ (Table 2) vanishes to zero when the carbon content k is even. This feature holds true in general. In order to be achiral, a secondary monosubstituted alkane should have a formula represented by $X-CHR_2$ or $X-CHp\bar{p}$ where the R is an achiral ligand or the pair $p\bar{p}$ represents a pair of enantiomeric ligands. As a result, the total carbon content (k) is calculated to be odd because the number represented by $2\ell + 1 (=k)$ means an odd number whether the carbon content (ℓ) of the R (or p) is odd or even. Hence,

there exists no achiral secondary monosubstituted alkane with an even k (i.e., $S_k^{(A)} = 0$ if k is even). In other words, all of the secondary monosubstituted alkanes characterized by even carbon contents (k) are chiral and contribute to $S_k^{(C)}$ (k : even).

Achiral secondary monosubstituted alkanes having the general formula $X-CHp\bar{p}$ are recognized as pseudoasymmetric cases. The two diastereomers corresponding to each formula $X-CHp\bar{p}$ with carbon content k contribute by two to the value of $S_k^{(A)}$ (Table 2).

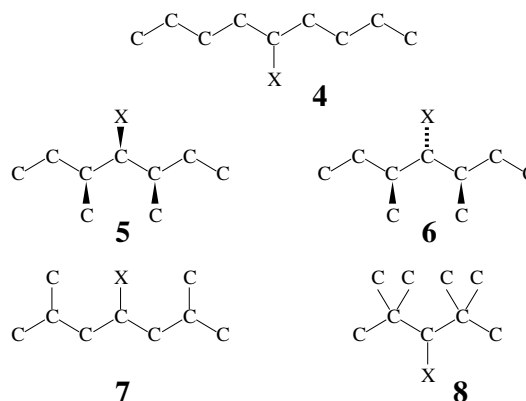


Figure 4. Achiral secondary monosubstituted alkanes of carbon content 9. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

For example, let us examine the case of $S_9^{(A)} = 5$ in Table 2. The five achiral monosubstituted alkanes are listed in Figure 4. Among them, **5** and **6** are diastereomeric and show pseudoasymmetric nature. The remaining monosubstituted alkanes **4**, **7**, and **8** are obviously represented by the general formula $X-CHR_2$, where the R represents an achiral butyl ligand. It should be noted that Figure 4 contains all types of butyl substituents, i.e., *n*-butyl (for **4**), *sec*-butyl (for **5** and **6**), *iso*-butyl (for **7**), and *t*-butyl (for **8**). These butyls in turn are enumerated as $P_4^{(A)} = 2$ (Table 1), $S_4^{(C)} = 1$ (Table 2), and $T_4^{(A)} = 1$ (Table 3). Note that the numbers of such alkyl ligands are equal to the numbers of the corresponding monosubstituted alkanes.

The last finding in the preceding paragraph can be extended into general cases. When achiral secondary monosubstituted alkanes of carbon content k are represented by the formula $X-CHR_2$ or $X-CHp\bar{p}$, they are composed of two R 's of carbon content $(k - 1)/2$ or of a pair of p and \bar{p} of carbon content $(k - 1)/2$. The two R 's and the pair of p and \bar{p} cover all of alkyl ligands of carbon content $(k - 1)/2$.

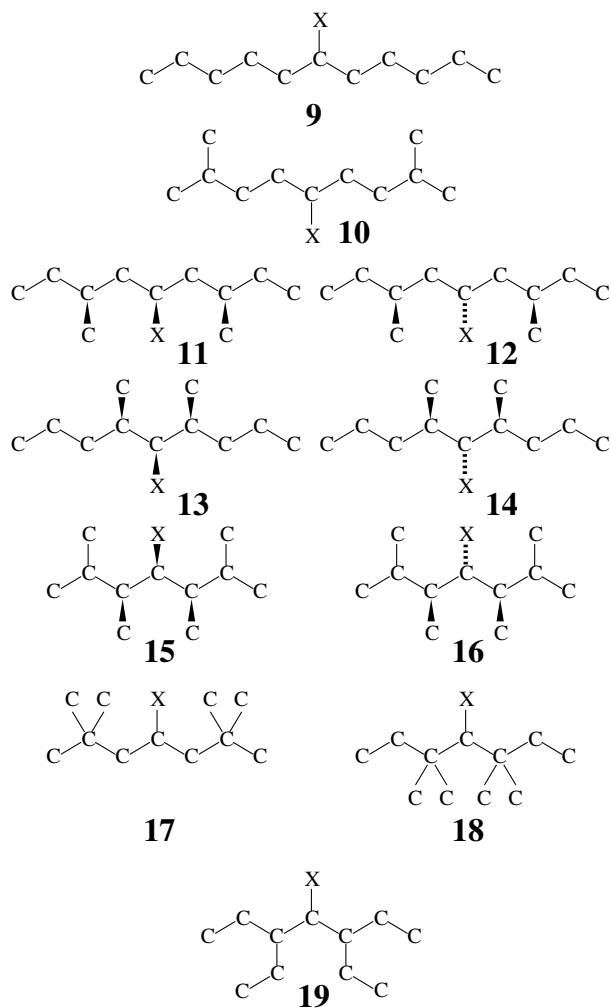


Figure 5. Achiral secondary monosubstituted alkanes of carbon content 11. If necessary, configurations are shown by wedged bonds and/or hashed dash bonds.

To exemplify a more complicated case, let us examine the case of $S_{11}^{(A)} = 11$ in Table 2. Because of the relationship $(11 - 1)/2 = 5$, we should take alkyl ligands of carbon content 5 into account. Thus, there are 8 alkyl ligands of carbon content 5, where we find $P_5^{(A)} = 3$ (for pentyl, 3-methylbut-1-yl, and 2,2-dimethylprop-1-yl) and $P_5^{(C)} = 1$ (for 2-methylbut-1-yl) in Table 1; $S_5^{(A)} = 1$ (for pent-3-yl) and $S_5^{(C)} = 2$ (for 1-methylbut-1-yl and 3-methylbut-2-yl) in Table 2; as well as $T_5^{(A)} = 1$ (for *t*-pentyl) and $T_5^{(C)} = 0$ in Table 3. Because each enantiomeric pair of chiral ligands ($P_5^{(C)}$, $S_5^{(C)}$, and $T_5^{(C)}$) generates two diastereomers of pseudoasymmetric nature, there should appear 11 achiral secondary monosubstituted alkanes, where we calculate $P_5^{(A)} + 2P_5^{(C)} + S_5^{(A)} + 2S_5^{(C)} + T_5^{(A)} + 2T_5^{(C)} = 3 + 1 \times 2 + 1 + 2 \times 2 + 1 + 0 = 11$.

The 11 achiral monosubstituted alkanes of carbon content 11 are listed in Figure 5. Among them, three pairs, i.e., **11/12** (from 2-methylbut-1-yl), **13/14** (from 1-

methylbut-1-yl), and **15/16** (from 3-methylbut-2-yl) are produced from pairs of chiral pentyl ligands according to the general formula $X-CHp\bar{p}$, where the two stereoisomers of each pair are diastereomeric and show pseudoasymmetric nature. The remaining 5 monosubstituted alkanes are obviously represented by the general formula $X-CHR_2$, where the R represents an achiral pentyl ligand.

4.2 Stereoisomers vs. Graphs

To show the effect of itemization due to the degree of branching, let us depict monosubstituted alkanes of carbon content 7.

The $k = 7$ row of Table 1 shows that there are 8 achiral primary monosubstituted alkanes and 10 enantiomeric pairs of chiral ones. They are listed in Figure 6, where either one enantiomer is depicted as a representative of each pair of enantiomers.

Because the 8 achiral primary monosubstituted alkanes (**20–27**) are different from each other as graphs, they are constitutional isomers, which are counted so as to be 8 constitutional isomers (graphs).

As found easily, they are represented by $X-CH_2-R$, where the R covers all of the achiral hexyl ligands. In agreement with eq. 46, the presence of the 8 achiral primary monosubstituted alkanes of carbon content 7 (i.e., **20–27**) is related to the value $\alpha_6 = 8$ in Table 4.

In agreement with eq. 48, the presence of 10 chiral primary monosubstituted alkanes of carbon content 7 ($P_7^{(C)} = 10$ in Table 1) is related to the value $C_6 = 10$ in Table 4. Note that they are represented by $X-CH_2-p$ (or $X-CH_2-\bar{p}$), where the p (or \bar{p}) covers all the chiral hexyl ligands.

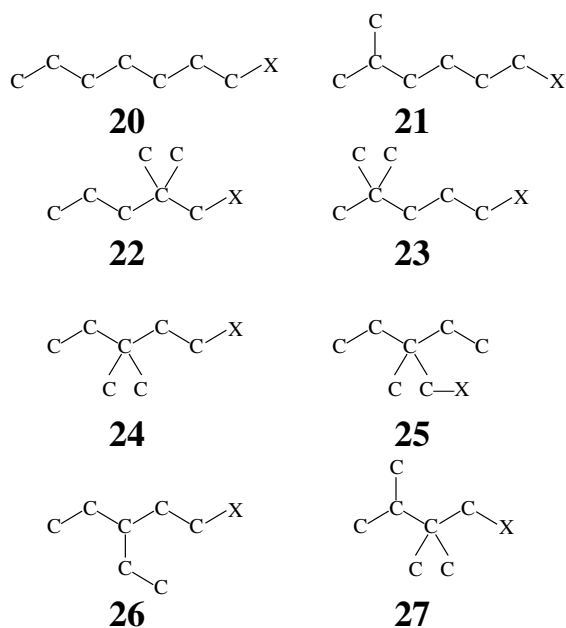
Among the 10 chiral primary monosubstituted alkanes (**28–37**), there appears one diastereomeric case, i.e., **32** and **33**, which are identical with each other as graphs. The set of **32** and **33** is regarded as a single constitutional isomer, which is counted just once, if we rely on Pólya's theorem. It follows that the 10 primary monosubstituted alkanes (**28–37**) are counted so as to be 9 constitutional isomers (graphs).

As a result, there are 17 constitutional isomers for primary monosubstituted alkanes ($8 + 9 = 17$). The number appears as $P_7^{(G)}$ in Table 5, which is obtained by means of the enumeration based on Pólya's theorem.

Because of eq. 58, the number of hexyl ligands as graphs is evaluated to be $R_6 = 17$, as shown in Table 5. Hence we can confirm the relationship, $P_7^{(G)} = R_6 = 17$, in agreement with eq. 58.

The $k = 7$ row of Table 3 shows that there are 2 achiral secondary monosubstituted alkanes and 17 enantiomeric pairs of chiral ones. They are listed in Figure 7, where either one enantiomer is depicted as a representative of each pair of enantiomers.

Achiral primary monosubstituted alkanes



Chiral primary monosubstituted alkanes

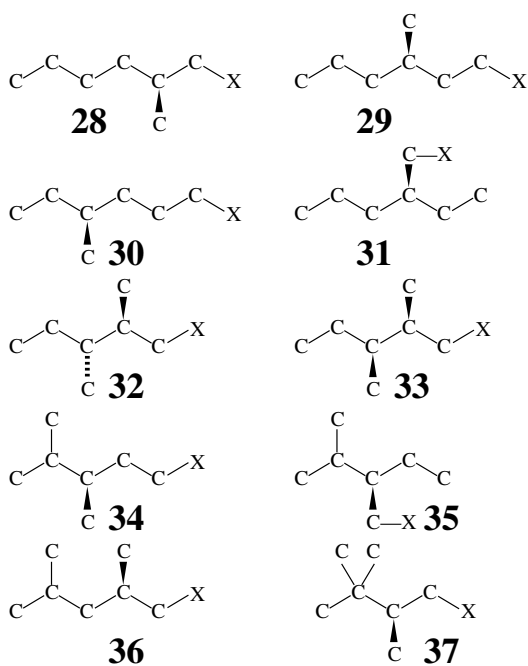
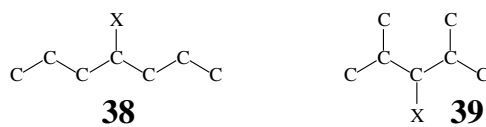


Figure 6. Primary monosubstituted alkanes of carbon content 7. Configurations are shown by wedged bonds and/or hashed dash bonds, if necessary. An arbitrary enantiomer is depicted for a representative of each pair of enantiomers.

Achiral secondary monosubstituted alkanes



Chiral secondary monosubstituted alkanes

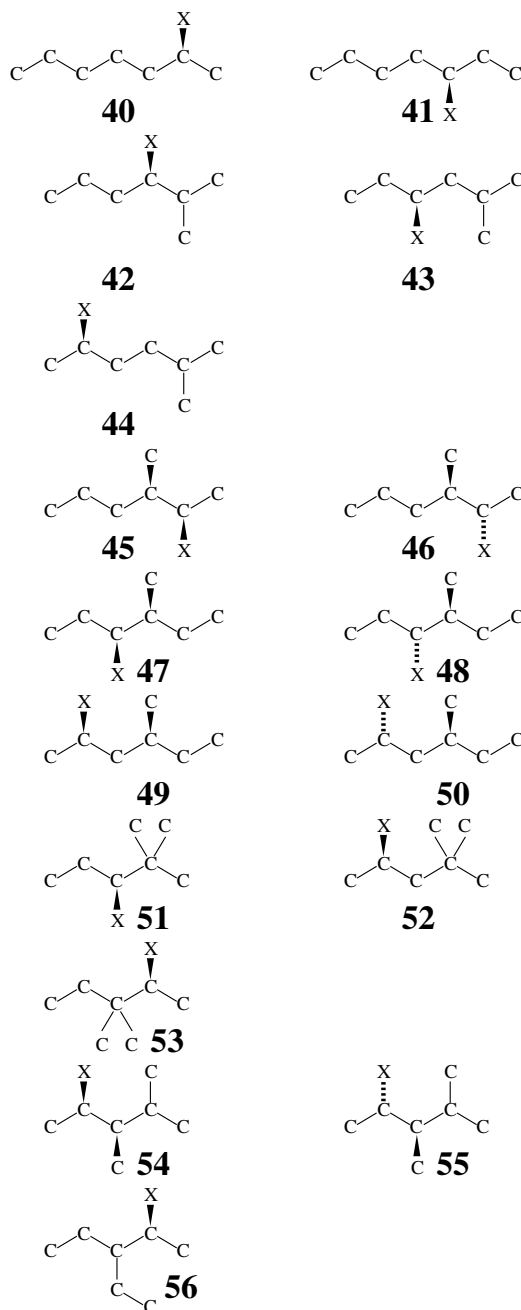


Figure 7. Secondary monosubstituted alkanes of carbon content 7. Configurations are shown by wedged bonds and/or hashed dash bonds, if necessary. An arbitrary enantiomer is depicted for a representative of each pair of enantiomers.

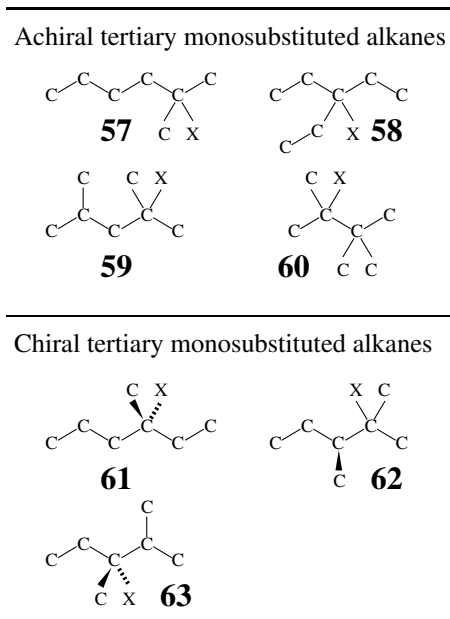


Figure 8. Tertiary monosubstituted alkanes of carbon content 7. Configurations are shown by wedged bonds and/or hashed dash bonds, if necessary. An arbitrary enantiomer is depicted for a representative of each pair of enantiomers.

The 2 achiral secondary monosubstituted alkanes (**38** and **39**) are different from each other as graphs so that there are 2 constitutional isomers.

Among the 17 chiral secondary monosubstituted alkanes (**40–56**), there appear four sets of diastereomers, i.e., **45/46**, **47/48**, **49/50**, and **54/55**, each of which is regarded as a single constitutional isomer. Hence, the 17 chiral secondary monosubstituted alkanes (**40–56**) are counted so as to be 13 constitutional isomers.

It follows that there are 15 constitutional isomers for secondary monosubstituted alkanes ($2 + 13 = 15$). The number appears as $S_7^{(G)}$ in Table 5, which is obtained by means of the enumeration based on Pólya's theorem.

According to the $k = 7$ row of Table 3, there are 4 achiral tertiary monosubstituted alkanes and 3 enantiomeric pairs of chiral ones. They are listed in Figure 8, where either one enantiomer is depicted as a representative of each pair of enantiomers.

The 4 achiral tertiary monosubstituted alkanes (**57–60**) are constitutional isomers and the 3 chiral tertiary monosubstituted alkanes (**61–63**) are constitutional isomers. Hence, there are 7 constitutional isomers for tertiary monosubstituted alkanes. The number appears as $T_7^{(G)}$ in Table 3, which is obtained by means of the enumeration based on Pólya's theorem.

Consequently, we obtain $17 + 15 + 7 = 39$ for the total number of constitutional isomers of monosubstituted alkanes, which appears as R_7 in Table 5.

	The present enumeration under C_s	Stereochemical convention under $\mathcal{A}^{[1]}$
<p>5</p>	1 achiral (self-enantiomeric pair)	1 (not specified)
<p>6</p>	1 achiral (self-enantiomeric pair)	1 (not specified)
<p>64</p>	1 chiral (enantiomeric pair)	1 (not specified)
<p>$\overline{\mathbf{64}}$</p>		1 (not specified)
total	3	4

Figure 9. Equivalence classes for secondary monosubstituted alkanes of carbon content 9. Pseudoasymmetric cases and a related pair of enantiomers.

4.3 Selection of Equivalence Classes

According to a stereochemical convention, two enantiomers of each pair are counted separately so as to contribute enumeration values by 2. In contrast, the present methodology adopts the criterion that each pair of enantiomers is counted just once so as to contribute enumeration values by 1. It is worthwhile to discuss the effect of the present criterion in comparison with the former criterion of the stereochemical convention.

The difference between the two criteria stems from the selection of equivalence classes, which depends on the selection of groups as bases of respective enumeration procedures. The difference is exemplified by using pseudoasymmetric and related cases, as shown in Figure 9.

The stereochemical convention counts **5**, **6**, **64**, and $\overline{\mathbf{64}}$ separately so as to give isomer number 4, as shown in Figure 9. This enumeration result implies the use of the alternating group of degree 1 ($\mathcal{A}^{[1]}$), which is isomorphic to C_1 in the present approach. To illustrate what happens under the stereochemical convention, let us adopt the CI-CF for C_1 (eq. 22), where we use the following ligand inventory:

$$b_d = p^d + \overline{p}^d = x^{4d} + \overline{x}^{4d} = 2x^{4d} \quad (59)$$

in accord with the substitution of enantiomeric *sec*-butyl ligands $p = x^4$ and $\overline{p} = \overline{x}^4 = x^4$). Note that the symbol \overline{x} represents the enantiomer of x , but is equal to x if carbon content is considered. By introducing eq. 59 into

the right-hand side of eq. 22 and by multiplying x for the central carbon atom, we obtain the following generating functions:

$$xb_1^2 = x(p + \bar{p})^2 = x(x^4 + \bar{x}^4)^2 = 4x^9, \quad (60)$$

where the coefficient 4 of the term x^9 indicates the presence of 4 isomers of carbon content 9 under the criterion provided by C_1 (or equivalently $\mathcal{A}^{[1]}$). This result is in agreement with the stereochemical convention, where the four compounds **5**, **6**, **64**, and **64** are counted separately. In other words, each of the compounds counted (i.e., **5**, **6**, **64**, and **64**) is independently regarded as an equivalence class due to C_1 ($\mathcal{A}^{[1]}$).

The enumeration result described in the preceding paragraph reveals implications concealed in the stereochemical convention:

1. The independent behavior under the action of C_1 ($\mathcal{A}^{[1]}$) means that each compound is recognized to be “chiral” in spite of its realistic chirality/achirality, because the action of C_1 ($\mathcal{A}^{[1]}$) contains no reflection operations. If the expression “chiral” used in characterizing the achiral compounds (**5** and **6**) seems to be rather strange, we can safely say that the compounds have no information on their chirality/achirality, as shown by the note “not specified” in Figure 9. Hence, the recognition of chirality/achirality is left afterward in the hands of stereochemists, who subsequently apply reflection operations to each compound for the purpose of symmetry characterization.
2. Moreover, the enumeration under the action of C_1 (or equivalently $\mathcal{A}^{[1]}$) specifies no relationships among the four compounds, **5**, **6**, **64**, and **64**. In particular, the enantiomeric relationship between **64** and **64** cannot be specified under the action of C_1 (or equivalently $\mathcal{A}^{[1]}$), because the C_1 contains no reflection operations. Hence, the specification of enantiomeric relationships is regarded as a subsequent and distinct step using reflection operations. This step of symmetry characterization requires a manual examination by intelligence of stereochemists.

The implications itemized above reveal that the number 4 for counting **5**, **6**, **64**, and **64** has been obtained at the expense of symmetry characterizations, i.e., the recognition of chirality/achirality and the specification of enantiomeric relationships. In other words, there is a logical gap between the first step using C_1 or $\mathcal{A}^{[1]}$ (the enumeration step) and the second step using reflection operations (the step of symmetry characterization). The logical gap has been frequently overlooked by organic stereochemists, because they can easily and unconsciously skip the logical gap by their intuition.

In contrast, the present approach has attempted to fill the logical gap explicitly by using the point group C_s , as shown in Figure 2. It should be emphasized that an equivalence class under the action of C_s is composed of an achiral compound (as a self-enantiomeric pair) or of a pair of enantiomers. Thus, chiral compounds are counted once per pair of enantiomers.

By following Fujita’s proligand method [15–17], we use the following ligand inventories:

$$b_d = p^d + \bar{p}^d = x^{4d} + \bar{x}^{4d} = 2x^{4d} \quad (61)$$

$$c_d = 2p^{d/2}\bar{p}^{d/2} = 2x^{2d}\bar{x}^{2d} = 2x^{4d}, \quad (62)$$

where we select enantiomeric *sec*-butyl ligands as substituents ($p = x^4$ and $\bar{p} = \bar{x}^4$). These inventories are introduced into the CI-CF shown in eq. 21 and multiplied by x to give the following generating function:

$$\begin{aligned} & \frac{x}{2}(b_1^2 + c_2) \\ &= \frac{x}{2}\{(p + \bar{p})^2 + 2p\bar{p}\} \\ &= \frac{x}{2}\{(x^4 + \bar{x}^4)^2 + 2x^4\bar{x}^4\} = 3x^9. \end{aligned} \quad (63)$$

The coefficient 3 of the term x^9 indicates the presence of three compounds counted per pair of enantiomers, which are **5** (an achiral compound as a self-enantiomeric pair), **6** (an achiral compound as a self-enantiomeric pair), and **64/64** (an enantiomeric pair of two chiral compounds), as shown in Figure 6.

To count achiral compounds, the inventory (eq. 62) is introduced into the CI-CF_A shown in eq. 23 and multiplied by x to give the following generating function:

$$xc_2 = x(2x^4\bar{x}^4) = 2x^9. \quad (64)$$

The coefficient 2 of the term x^9 indicates the presence of two achiral compounds counted per pair of enantiomers. They are **5** and **6**, each of which is an achiral compound regarded as being a self-enantiomeric pair (Figure 6).

After the inventories (eqs. 61 and 62) are introduced into the CI-CF_C shown in eq. 24 and x is multiplied, the resulting equation is expanded to give the following generating function:

$$\begin{aligned} & \frac{x}{2}(b_1^2 - c_2) \\ &= \frac{x}{2}\{(p + \bar{p})^2 - 2p\bar{p}\} \\ &= \frac{x}{2}\{(x^4 + \bar{x}^4)^2 - 2x^4\bar{x}^4\} = x^9. \end{aligned} \quad (65)$$

The coefficient 1 of the term x^9 indicates the presence of one pair of enantiomers, which is represented by the pair **64/64**, as shown in Figure 6.

Moreover, eq. 22, which has been used to obtain eq. 60 is also involved in the present approach because the C_1 is a subgroup of the C_s . Obviously, the combination of eqs. 63–65 together with eq. 60 is more informative than the stereochemical convention using eq. 60 only.

From the viewpoint of the present approach, the values collected in the $P_k^{(A)}$ -, $P_k^{(C)}$ -, and P_k -columns of Table 1 are concerned with equivalence classes due to C_s , because they are based on the C_s -skeleton shown in Figure 1. The three columns contain consistent values under the action of C_s . This situation holds true for the columns contained in Tables 2 and 3.

In place of the present column constitutions of Tables 1–3, we can select, for example, a column listing the values of $P_k^{(A)}$, a column listing the values of $2P_k^{(C)}$, and a column listing the values of $P_k^{(A)} + 2P_k^{(C)}$ in agreement with the stereochemical convention. As a result of this type of column constitution, we find that the column listing the values of $P_k^{(A)}$ is based on C_s , while the column listing the values of $2P_k^{(C)}$ and the column listing the values of $P_k^{(A)} + 2P_k^{(C)}$ are based on C_1 . Hence, this type of column constitution is inconsistent from the viewpoint of point-group theory.

5 Conclusions

Primary, secondary, and tertiary monosubstituted alkanes are counted as stereoisomers by means of Fujita's prolignand method [15–17]. According to cycle indices with chirality fittingness (CI-CFs), three kinds of sphericity indices (SIs), i.e., a_d for homospheric cycles, c_d for enantiospheric cycles, and b_d for hemispheric cycles, are replaced by $a(x^d)$, $c(x^d)$, and $b(x^d)$ so as to produce functional equations for recursive calculation. After the derivation of respective functional equations for counting primary, secondary, and tertiary monosubstituted alkanes, they are programmed by means of the Maple programming language and executed to obtain values up to carbon content 100. The respective results are collected in a tabular form, where the numbers of stereoisomers are further itemized into achiral and chiral ones. By omitting the sphericity concept, such CI-CFs are transformed into Pólya's cycle indices (CIs), which are applied to the enumeration of primary, secondary, and tertiary monosubstituted alkanes as graphs (chemically, constitutional isomers). The results of Fujita's prolignand method are compared with those based on Pólya's theorem in connection with several cases of pseudoasymmetry.

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