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Itemized Enumeration of Quadruplets of *RS*-Stereoisomers Under the Action of *RS*-Stereoisomeric Groups

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Abstract

A quadruplet of *RS*-stereoisomers appearing in a stereoisogram is categorized into either one of five types by means of chirality, *RS*-stereogenicity, and sclerality, i.e., Type I (chiral/*RS*-stereogenic/ascleral), Type II (chiral/*RS*-astereogenic/scleral), Type III (chiral/*RS*-stereogenic/scleral), Type IV (achiral/*RS*-astereogenic/ascleral), and Type V (achiral/*RS*-stereogenic/scleral). Each quadruplet is considered to be an entity to be counted just once, where the entity can be regarded as an equivalence class under the corresponding *RS*-stereoisomeric group $\mathbf{G}$ (e.g., $\mathbf{T}_{d\tilde{\sigma}\hat{I}}$ for a quadruplet of tetrahedral promolecules). To accomplish itemized enumeration of such quadruplets, three modes of action of $\mathbf{G}$ are discussed by considering three subgroups of index 2, i.e., the maximum point subgroup $\mathbf{G}_{C\sigma}$, the maximum *RS*-permutation group $\mathbf{G}_{C\tilde{\sigma}}$, and the maximum ligand-inversion group $\mathbf{G}_{C\hat{I}}$ (e.g., $\mathbf{T}_d$, $\mathbf{T}_{\tilde{\sigma}}$, or $\mathbf{T}_{\hat{I}}$ for a quadruplet of tetrahedral promolecules). Such a quadruplet consists of two E-pairs, each of which is defined as a pair of enantiomers (chiral promolecules)

or a pair of self-enantiomers (an achiral promolecule); it consists of two D-pairs, each of which is defined as a pair of *RS*-diastereomers (*RS*-stereogenic promolecules) or a pair of self-*RS*-diastereomers (an *RS*-astereogenic promolecule); and it consists of two H-pairs, each of which is defined as a pair of holantimers (scleral promolecules) or a pair of self-holantimers (an ascleral promolecule). The two E-pairs, D-pairs, or H-pairs contained in each quadruplet are considered to construct an equivalence class of **G** and also an equivalence class of $\mathbf{G}_{C\sigma}$, $\mathbf{G}_{C\tilde{\sigma}}$, or $\mathbf{G}_{C\hat{I}}$. Thereby, such equivalence classes are enumerated under **G** and $\mathbf{G}_{C\sigma}$ (or $\mathbf{G}_{C\tilde{\sigma}}$ or $\mathbf{G}_{C\hat{I}}$) to give partially itemized generating functions, where the number of the equivalence classes can be regarded as the number of quadruplets to be counted. The results of the enumerations by means of E-pairs, D-pairs, and H-pairs are combined to accomplish itemized enumeration with respect to Types I–V. Pólya's theorem is discussed as a special case of the present approach.

1 Introduction

The dichotomy between enantiomers and "diastereomers" has been one of the fundamental concepts in stereochemistry [1, 2] . The dichotomy has been adopted in most textbooks on organic stereochemistry [3 –5] and on organic chemistry [6 –10] , although there appeared some confusion caused by a verbal transmutation of the term "diastereomers", as indicated from a chemical philological point of view [11] .

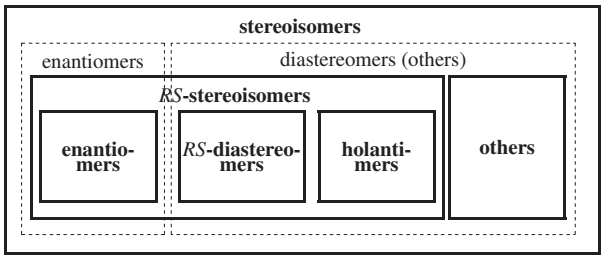

Figure 1: Conventional terminology vs. the present terminology for stereoisomerism. A broken-lined box represents a term of the conventional terminology, while a solid-lined box represents a term of the present terminology.

The term "diastereomers" connotes various kinds of stereoisomers, because it represents "others" derived from a set of stereoisomers minus pairs of enantiomers, as shown by broken-lined boxes in Fig. 1. Obviously, the term "diastereomers" suffers from diverse connotation just as the term "nonnatives" coming from the dichotomy between natives and nonnatives indefinitely refers to all people other than natives. In other words from a

mathematical point of view, such diastereomers as specified by the conventional definition cannot be categorized into an equivalence class, whereas a set of stereoisomers is an equivalence class and a pair of enantiomers is an equivalence class.

The indefiniteness of the term "diastereomers" has provided organic chemists with at least two serious confusions: a confusion over chirality and stereogenicity (Confusion 1) in the history of the CIP (Cahn, Ingold and Prelog) system [12 –14] and a confusion over prochirality and prostereogenicity (Confusion 2) in generating pro-*R*/pro-*S*-descriptors [15, 16] .

To avoid these confusions, we have developed the concept of *RS-stereoisomers* by means of newly-defined *RS*-stereoisomeric groups [17, 18] and alternatively by means of newly-defined *stereoisograms* [19 –21] . The new concept *RS-stereoisomers* is an intermediate concept to bridge the gap between stereoisomers and enantiomers, as shown by solid-lined boxes in Fig. 1. Thereby, Confusion 1 and difficulties of pseudoasymmetry associated closely with Confusion 1 have been avoided on a rational basis [20] . In addition, Confusion 2 over prochirality has also been avoided completely [22] .

One of the important features derived from the concept of *RS-stereoisomers* is the fact that a set of *RS*-stereoisomers appearing in a stereoisogram can be characterized as an equivalence class if a stereo-skeleton (e.g., a tetrahedral stereo-skeleton) is given to derive the *RS*-stereoisomers. This feature enables us to count sets of *RS*-stereoisomers one by one under the action of an *RS*-stereoisomeric group of the stereo-skeleton. This is parallel to the fact that pairs of enantiomers can be counted one by one under the action of a point group of the stereo-skeleton. Although we have reported an article entitled "Combinatorial Enumeration of *RS*-Stereoisomers Itemized by Chirality, *RS*-Stereogenicity, and Sclerality" in this journal [23] , the treatment did not directly use such equivalence classes under the action of *RS*-stereoisomeric groups but instead it employed equivalence classes under the actions of point groups, *RS*-permutation groups, and ligand-inversion groups distinctly. Hence, it is desirable to investigate the direct action of *RS*-stereoisomeric groups in order to comprehend the interaction of the groups related to *RS*-stereoisomeric groups.

As found in the preceding paragraphs, the aim of the present article is to count sets of *RS*-stereoisomers under the direct action of an *RS*-stereoisomeric group, where the direct action will be examined in comparison with the actions of its subgroups of index 2 i.e., the maximum point subgroup, the maximum *RS*-permutation subgroup, and the maximum ligand-inversion subgroup. The results are then compared with those by Pólya's theorem, which will be derived as a special case of the present approach.

2 *RS*-Stereoisomeric Groups

2.1 Quarter Cosets and Five Types of *RS*-Stereoisomers

In the previous paper reported in this journal [23] , we have defined an *RS*-stereoisomeric group (**G**) which governs a set of substitution positions of a given stereo-skeleton as follows:

$$\mathbf{G} = \mathbf{G}_C + \sigma\mathbf{G}_C + \widetilde{\sigma}\mathbf{G}_C + \widehat{I}\mathbf{G}_C. \tag{1}$$

Although the detailed formulation on **G** should not be repeated, a brief introduction of its minimum essences is desirable to keep the present paper self-contained.

The group $\mathbf{G}_C$ appearing in eq. 1 corresponds to the maximum chiral subgroup of the point group. The element σ ($\in \sigma\mathbf{G}_C$) corresponds to a rotoreflection of the point group so that the coset $\sigma\mathbf{G}_C$ contains relevant rotoreflections. The element $\widetilde{\sigma}$ ($\in \widetilde{\sigma}\mathbf{G}_C$) corresponds to a permutation σ but does not provide the reflection of ligands so that the coset $\widetilde{\sigma}\mathbf{G}_C$ contains relevant permutations. The element $\widehat{I}$ ($\in \widehat{I}\mathbf{G}_C$) represents an operation which provides the reflection of ligands, but does not the reflection of the skeleton, so that the coset $\widehat{I}\mathbf{G}_C$ contains relevant ligand-inversion operations.

The *RS*-stereoisomeric group **G** is divided into quarter cosets as shown in eq. 1. Because the group $\mathbf{G}_C$ is a normal subgroup of **G**, the set of quarter cosets, i.e.,

$$\mathbf{G}/\mathbf{G}_C = \{\mathbf{G}_C, \sigma\mathbf{G}_C, \widetilde{\sigma}\mathbf{G}_C, \widehat{I}\mathbf{G}_C\}, \tag{2}$$

can be regarded as a factor group. This remarkable feature of the group **G** has been applied to prove the existence of five types of *RS*-stereoisomers, which are characterized by means of the five subgroups of the factor group $\mathbf{G}/\mathbf{G}_C$ [18] :

$$\text{Type I:} \quad \{\mathbf{G}_C, \widehat{I}\mathbf{G}_C\} \tag{3}$$

$$\text{Type II:} \quad \{\mathbf{G}_C, \widetilde{\sigma}\mathbf{G}_C\} \tag{4}$$

$$\text{Type III:} \quad \{\mathbf{G}_C\} \tag{5}$$

$$\text{Type IV:} \quad \{\mathbf{G}_C, \sigma\mathbf{G}_C, \widetilde{\sigma}\mathbf{G}_C, \widehat{I}\mathbf{G}_C\} \tag{6}$$

$$\text{Type V:} \quad \{\mathbf{G}_C, \sigma\mathbf{G}_C\}. \tag{7}$$

The five types have been visualized by means of stereoisograms (e.g., Fig. 2) [19, 20] . Each of the stereoisograms contains four *RS*-stereoisomers corresponding to the quarter cosets, where the boldfaced letters **A** and $\overline{\mathbf{A}}$ (or **B** and $\overline{\mathbf{B}}$) represent a pair of enantiomers.

In Fig. 2, we use the following symbols for representing relationships which are contained in stereoisograms:

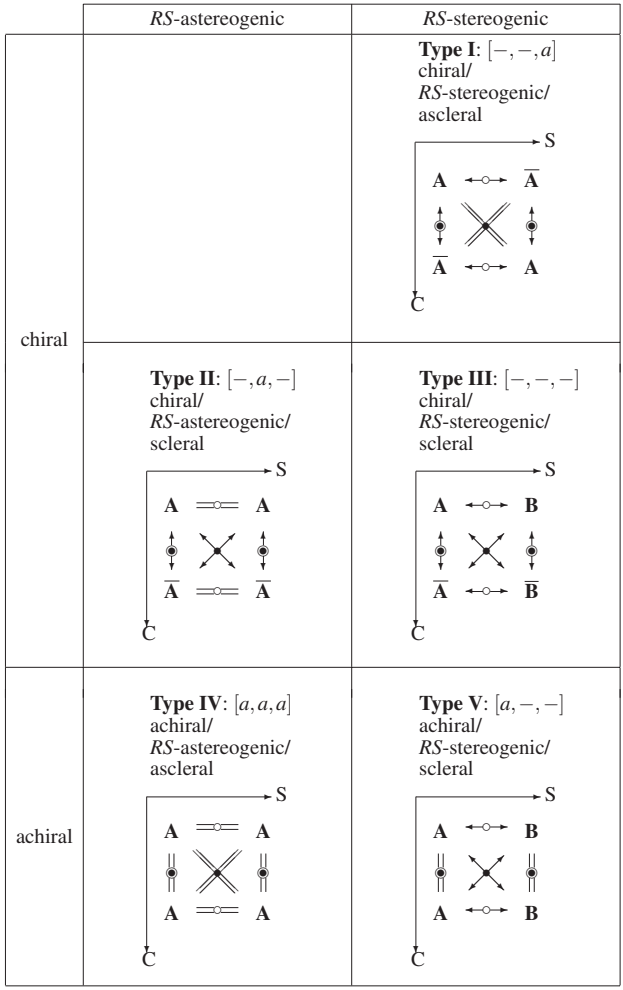

Figure 2: Stereoisograms for representing *RS*-stereoisomers of five types [20] . The symbols **A** and $\overline{\mathbf{A}}$ (or **B** and $\overline{\mathbf{B}}$) represent a pair of enantiomers. Each stereoisogram consists of a quadruplet of *RS*-stereoisomers, which may coalesce with one another according to either one of the five *RS*-stereoisomeric types. As one extreme case, the four *RS*-stereoisomers of a Type-III stereoisogram are different (i.e., **A**, $\overline{\mathbf{A}}$, **B** and $\overline{\mathbf{B}}$). The other extreme case is a Type-IV stereoisogram, which consists of a degenerate *RS*-stereoisomer (i.e., **A**).

symbol	relationship [24]	attribute [24]
	enantiomeric	chiral
	(self-enantiomeric)	achiral
	*RS*-diastereomeric	*RS*-stereogenic
	(self-*RS*-diastereomeric)	*RS*-astereogenic
	holantimeric	scleral
	(self-holantimeric)	ascleral

It should be noted that the symbol () represents a "self-enantiomeric" relationship, which is designated simply as being achiral in stereochemical convention. The symbol () in the Type-V stereoisogram shown in Fig. 2 is in agreement with the subgroup $\{\mathbf{G}_C, \sigma\mathbf{G}_C\}$ (eq. 7) for Type V. The symbol () represents a "self-*RS*-diastereomeric" relationship, which is designated as being *RS*-astereogenic if we emphasize the symmetrical nature of a relevant promolecule in the present terminology. The symbol () in the Type-II stereoisogram shown in Fig. 2 is in agreement with the subgroup $\{\mathbf{G}_C, \widetilde{\sigma}\mathbf{G}_C\}$ (eq. 4) for Type II. The symbol () representing a "self-holantimeric" relationship indicates that the Type-I stereoisogram shown in Fig. 2 is in agreement with the subgroup $\{\mathbf{G}_C, \widehat{I}\mathbf{G}_C\}$ (eq. 3) for Type I.

The set of four *RS*-stereoisomers contained in each stereoisogram (Fig. 2) is referred to as a *quadruplet*, whether the four are different or superposable according to its *RS*-stereoisomeric type (Type I, ..., or Type V). Such a quadruplet of *RS*-stereoisomers is regarded as an equivalence class under the action of the *RS*-stereoisomeric group $\mathbf{G}$, so that the quadruplet is counted just once during enumeration under $\mathbf{G}$.

Throughout the present article, a tetrahedral stereo-skeleton belonging to the point group $\mathbf{T}_d$ is adopted as a typical example to generate derivatives of Types I–V. By starting from the point group $\mathbf{T}_d$ for treating a tetrahedral skeleton, the corresponding *RS*-stereoisomeric group ($\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}$) has been discussed in previous articles [17, 19, 25] .

$$\mathbf{T}_{d\widetilde{\sigma}\widehat{I}} = \mathbf{T} + \sigma\mathbf{T} + \widetilde{\sigma}\mathbf{T} + \widehat{I}\mathbf{T} \tag{8}$$

$$\begin{aligned} = \{ & I, C_{2(1)}, C_{2(2)}, C_{2(3)}, C_{3(1)}, C_{3(3)}, C_{3(2)}, C_{3(4)}, C^2_{3(1)}, C^2_{3(4)}, C^2_{3(3)}, C^2_{3(2)}; \\ & \sigma_{d(1)}, S_{4(3)}, S^3_{4(3)}, \sigma_{d(6)}, \sigma_{d(2)}, \sigma_{d(4)}, S_{4(1)}, S^3_{4(1)}, \sigma_{d(3)}, S^3_{4(2)}, \sigma_{d(5)}, S_{4(2)}; \\ & \widetilde{\sigma}_{d(1)}, \widetilde{S}_{4(3)}, \widetilde{S}^3_{4(3)}, \widetilde{\sigma}_{d(6)}, \widetilde{\sigma}_{d(2)}, \widetilde{\sigma}_{d(4)}, \widetilde{S}_{4(1)}, \widetilde{S}^3_{4(1)}, \widetilde{\sigma}_{d(3)}, \widetilde{S}^3_{4(2)}, \widetilde{\sigma}_{d(5)}, \widetilde{S}_{4(2)}; \\ & \widehat{I}, \widehat{C}_{2(1)}, \widehat{C}_{2(2)}, \widehat{C}_{2(3)}, \widehat{C}_{3(1)}, \widehat{C}_{3(3)}, \widehat{C}_{3(2)}, \widehat{C}_{3(4)}, \widehat{C}^2_{3(1)}, \widehat{C}^2_{3(4)}, \widehat{C}^2_{3(3)}, \widehat{C}^2_{3(2)} \} \end{aligned} \tag{9}$$

$$
\begin{aligned}
= \; & \{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3), (1)(2\ 4\ 3), (1\ 2\ 3)(4), \\
& (1\ 3\ 4)(2), (1\ 4\ 2)(3), (1)(2\ 3\ 4), (1\ 2\ 4)(3), (1\ 3\ 2)(4), (1\ 4\ 3)(2); \\
& \overline{(1)(2\ 3)(4)}, \overline{(1\ 2\ 4\ 3)}, \overline{(1\ 3\ 4\ 2)}, \overline{(1\ 4)(2)(3)}, \overline{(1)(2)(3\ 4)}, \overline{(1\ 2)(3)(4)}, \\
& \overline{(1\ 3\ 2\ 4)}, \overline{(1\ 4\ 2\ 3)}, \overline{(1)(2\ 4)(3)}, \overline{(1\ 2\ 3\ 4)}, \overline{(1\ 3)(2)(4)}, \overline{(1\ 4\ 3\ 2)}; \\
& (1)(2\ 3)(4), (1\ 2\ 4\ 3), (1\ 3\ 4\ 2), (1\ 4)(2)(3), (1)(2)(3\ 4), (1\ 2)(3)(4), \\
& (1\ 3\ 2\ 4), (1\ 4\ 2\ 3), (1)(2\ 4)(3), (1\ 2\ 3\ 4), (1\ 3)(2)(4), (1\ 4\ 3\ 2); \\
& \overline{(1)(2)(3)(4)}, \overline{(1\ 2)(3\ 4)}, \overline{(1\ 3)(2\ 4)}, \overline{(1\ 4)(2\ 3)}, \overline{(1)(2\ 4\ 3)}, \overline{(1\ 2\ 3)(4)}, \\
& \overline{(1\ 3\ 4)(2)}, \overline{(1\ 4\ 2)(3)}, \overline{(1)(2\ 3\ 4)}, \overline{(1\ 2\ 4)(3)}, \overline{(1\ 3\ 2)(4)}, \overline{(1\ 4\ 3)(2)}\} \qquad (10)
\end{aligned}
$$

2.2 Action of *RS*-Stereoisomeric Groups

2.2.1 Cycle Indices of *RS*-Stereoisomeric Groups

As an extension of enumerations under point groups (e.g., Fujita's USCI (unit-subduced-cycle-index) approach [26 –29] and Fujita's proligand method [30 –32]), we shall consider cases in which a given skeleton has n substitution positions governed by an *RS*-stereoisomeric group $\mathbf{G}$.

Suppose that the action of an element P of $\mathbf{G}$ on the skeleton is represented as a product of d-cycles ($d = 1, 2, \ldots, n$), where the number of the d-cycles is equal to $\nu_d(P)$. On the same line as Fujita's proligand method [30 –32] , the number of promolecules as *RS*-stereoisomers can be counted by using the following cycle index with chirality fittingness (CI-CF):

$$
\begin{aligned}
& \text{CI-CF}(\mathbf{G}; \$_d, b_d) \\
& = \frac{1}{|\mathbf{G}|} \left\{ \sum_{P \in \mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} + \sum_{P \in \sigma\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} \right. \\
& \qquad \left. + \sum_{P \in \tilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} + \sum_{P \in \widetilde{I}\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} \right\}, \qquad (11)
\end{aligned}
$$

where the sphericity index (SI) a_d (for $\$_d$) is assigned to a d-cycle appearing in the P of $\sigma\mathbf{G}_C$ or $\widetilde{I}\mathbf{G}_C$ if d is odd; the SI c_d (for $\$_d$) is assigned to a d-cycle appearing in the P of $\sigma\mathbf{G}_C$ or $\widehat{I}\mathbf{G}_C$ if d is even; and the SI b_d is assigned to a d-cycle appearing in the P of $\mathbf{G}_C$ or $\tilde{\sigma}\mathbf{G}_C$ whether d is odd or even. Note that, during enumeration processes under eq. 11, each quadruplet which constructs a single stereoisogram is regarded as one entity which is counted just once. Thus, in one extreme case (Type IV shown in Fig. 2), a degenerate

promolecule **A** is counted just once as one quadruplet; and, in the other extreme cases (Type III shown in Fig. 2), the set of four promolecules (**A**, $\overline{\mathbf{A}}$, **B**, and $\overline{\mathbf{B}}$) is counted just once as another quadruplet.

Suppose that the n substitution positions in the skeleton of **G**-symmetry accommodate n proligands selected from the following warehouse:

$$\mathbf{X} = \{\mathrm{X}_1, \mathrm{X}_2, \ldots, \mathrm{X}_m; \mathrm{p}_1, \mathrm{p}_2, \ldots, \mathrm{p}_{m'}; \overline{\mathrm{p}}_1, \overline{\mathrm{p}}_2, \ldots \overline{\mathrm{p}}_{m'}\}, \tag{12}$$

where X_1, X_2, etc. represent achiral proligands; p_1, p_2, etc. represent chiral proligands; $\overline{\mathrm{p}}_1$, $\overline{\mathrm{p}}_2$, etc. represent chiral proligands of opposite chirality; and m and m' represent non-negative integers. The selection of such substituents produces an isomer having θ_1 of X_1, θ_2 of X_2, $\cdots$ θ_m of X_m; θ'_1 of p_1, θ'_2 of p_2, $\cdots$ $\theta'_{m'}$ of $\mathrm{p}_{m'}$; θ''_1 of $\overline{\mathrm{p}}_1$, θ''_2 of $\overline{\mathrm{p}}_2$, $\cdots$ $\theta''_{m'}$ of $\overline{\mathrm{p}}_{m'}$, where these numbers satisfy the following partition:

$$\begin{aligned} [\theta] \;\; = \;\; & \theta_1 + \theta_2 + \cdots + \theta_m \\ & + \theta'_1 + \theta'_2 + \cdots + \theta'_{m'} \\ & + \theta''_1 + \theta''_2 + \cdots + \theta''_{m'} = n. \end{aligned} \tag{13}$$

Then, each proligand is characterized by a molecular formula represented as follows:

$$W_\theta = \mathrm{X}_1^{\theta_1}\mathrm{X}_2^{\theta_2}\cdots\mathrm{X}_m^{\theta_m}\mathrm{p}_1^{\theta'_1}\mathrm{p}_2^{\theta'_2}\cdots\mathrm{p}_{m'}^{\theta'_{m'}}\overline{\mathrm{p}}_1^{\theta''_1}\overline{\mathrm{p}}_2^{\theta''_2}\cdots\overline{\mathrm{p}}_{m'}^{\theta''_{m'}}. \tag{14}$$

Let the symbol N_θ denote the number of such isomers (quadruplets) as having the molecular formula W_θ, where each quadruplet of *RS*-stereoisomers is counted just once. By using the CI-CF (eq. 11), Theorem 1 of Ref. [30] (or equivalently Theorem 2 of Ref. [32]) can be applied to this case so as to give the following theorem:

Theorem 1 Suppose that the n substitution positions in the skeleton governed by the *RS*-stereoisomeric group **G** accommodate n proligands selected from the warehouse (eq. 12) so as to give quadruplets of *RS*-stereoisomers. Then, the number N_θ of quadruplets having the formula W_θ (eq. 14) is calculated by means of the CI-CF (eq. 11) so as to give the following generating function:

$$\sum_{[\theta]} N_\theta W_\theta = \text{CI-CF}(\mathbf{G}; \$_d, b_d), \tag{15}$$

where the summation is concerned with the partitions represented by $[\theta]$ (eq. 13) and the

SIs are replaced by the following ligand inventories:

$$a_d = \mathrm{X}_1^d + \mathrm{X}_2^d + \cdots + \mathrm{X}_m^d \tag{16}$$

$$c_d = \mathrm{X}_1^d + \mathrm{X}_2^d + \cdots + \mathrm{X}_m^d + 2\mathrm{p}_1^{d/2}\overline{\mathrm{p}}_1^{d/2} + 2\mathrm{p}_2^{d/2}\overline{\mathrm{p}}_2^{d/2} + \cdots + 2\mathrm{p}_{m'}^{d/2}\overline{\mathrm{p}}_{m'}^{d/2} \tag{17}$$

$$b_d = \mathrm{X}_1^d + \mathrm{X}_2^d + \cdots + \mathrm{X}_m^d + \mathrm{p}_1^d + \mathrm{p}_2^d + \cdots + \mathrm{p}_{m'}^d + \overline{\mathrm{p}}_1^d + \overline{\mathrm{p}}_2^d + \cdots + \overline{\mathrm{p}}_{m'}^d. \tag{18}$$

It should be noted that the three modes of proligand packing due to sphericities are effective through the SIs for this case of *RS*-stereoisomeric groups on the same line as the case of point groups [30, 32] .

To exemplify the usefulness of the present approach, let us count methane derivatives by using eq. 15 and the relevant equations. The *RS*-stereoisomeric group $\mathbf{T}_{d\tilde{\sigma}\hat{I}}$ for counting methane derivatives (eq. 10) has 48 permutation operations, where the cycle structure of each operation is used by following eq. 11. Thereby, we obtain the following CI-CFs:

$$\begin{aligned}\text{CI-CF}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) = \frac{1}{48}\big\{&b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4 \\ &+ 6b_1^2b_2 + 6b_4 + a_1^4 + 3c_2^2 + 8a_1a_3\big\}.\end{aligned} \tag{19}$$

According to eq. 12, we take account of the following warehouse for methane derivatives:

$$\mathbf{X} = \{\mathrm{A}, \mathrm{B}, \mathrm{X}, \mathrm{Y};\quad \mathrm{p}, \mathrm{q}, \mathrm{r}, \mathrm{s};\quad \overline{\mathrm{p}}, \overline{\mathrm{q}}, \overline{\mathrm{r}}, \overline{\mathrm{s}}\}, \tag{20}$$

where the letters A, B, X, and Y represent achiral proligands and the pairs of p/$\overline{\mathrm{p}}$, q/$\overline{\mathrm{q}}$, r/$\overline{\mathrm{r}}$, and s/$\overline{\mathrm{s}}$ represent pairs of enantiomeric proligands. Thereby, eqs. 16–18 for counting methane derivatives are obtained as follows:

$$a_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{Y}^d \tag{21}$$

$$c_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{Y}^d + 2\mathrm{p}^{d/2}\overline{\mathrm{p}}^{d/2} + 2\mathrm{q}^{d/2}\overline{\mathrm{q}}^{d/2} + 2\mathrm{r}^{d/2}\overline{\mathrm{r}}^{d/2} + 2\mathrm{s}^{d/2}\overline{\mathrm{s}}^{d/2} \tag{22}$$

$$b_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{Y}^d + \mathrm{p}^d + \mathrm{q}^d + \mathrm{r}^d + \mathrm{s}^d + \overline{\mathrm{p}}^d + \overline{\mathrm{q}}^d + \overline{\mathrm{r}}^d + \overline{\mathrm{s}}^d. \tag{23}$$

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 19) and the resulting equation is expanded so as to give the corresponding generating function for

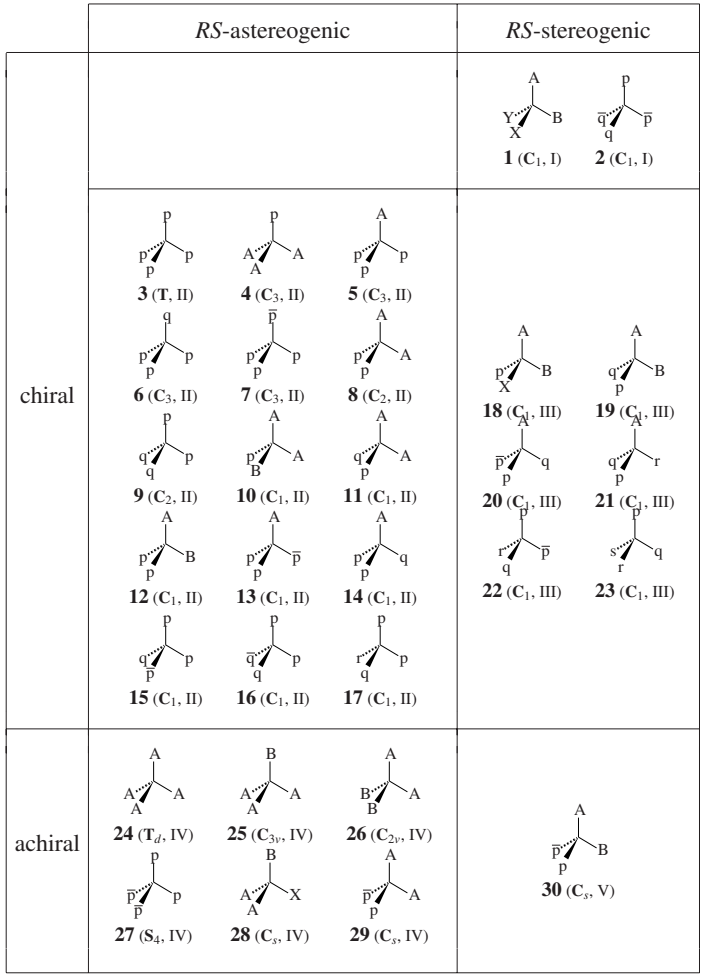

Figure 3: Quadruplets of *RS*-Stereoisomers (Types I to V) for tetrahedral molecules. The symbols A, B, C, and D represent atoms or achiral ligands. The symbols p, q, r, and s represents chiral ligands, while each symbol with an overbar represents the corresponding chiral ligand with the opposite chirality. An arbitrary promolecule is depicted as a representative of each quadruplet of *RS*-stereoisomers (e.g., **A** in Fig. 2).

counting promolecules:

$$
\begin{aligned}
f^{[\mathrm{T}]} \;=\;& \mathrm{ABXY} + [\mathrm{p\overline{p}q\overline{q}} + \cdots] \\
&+ [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] \\
&+ [\mathrm{A}^2\mathrm{BX} + \cdots] + [\mathrm{A}^2\mathrm{p\overline{p}} + \cdots] + [\mathrm{p}^2\overline{\mathrm{p}}^2 + \cdots] \\
&+ [\mathrm{ABp\overline{p}} + \cdots] \\
&+ \frac{1}{2}[(\mathrm{A}^3\mathrm{p} + \mathrm{A}^3\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{Bp} + \mathrm{A}^2\mathrm{B}\overline{\mathrm{p}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{A}^2\mathrm{p}^2 + \mathrm{A}^2\overline{\mathrm{p}}^2) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{pq} + \mathrm{A}^2\overline{\mathrm{pq}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{ABp}^2 + \mathrm{AB}\overline{\mathrm{p}}^2) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{Ap}^2\overline{\mathrm{p}} + \mathrm{A}\overline{\mathrm{p}}^2\mathrm{p}) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^3 + \mathrm{A}\overline{\mathrm{p}}^3) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^2\mathrm{q} + \mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^4 + \overline{\mathrm{p}}^4) + \cdots] + \frac{1}{2}[(\mathrm{p}^3\overline{\mathrm{p}} + \overline{\mathrm{p}}^3\mathrm{p}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^3\mathrm{q} + \overline{\mathrm{p}}^3\overline{\mathrm{q}}) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q} + \overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^2\mathrm{q}^2 + \overline{\mathrm{p}}^2\overline{\mathrm{q}}^2) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^2\mathrm{qr} + \overline{\mathrm{p}}^2\overline{\mathrm{qr}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{ABXp} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{ABpq} + \mathrm{AB}\overline{\mathrm{pq}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q} + \mathrm{Ap}\overline{\mathrm{pq}}) + \cdots] + \frac{1}{2}[(\mathrm{Apqr} + \mathrm{A}\overline{\mathrm{pqr}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{pqr}}) + \cdots] + \frac{1}{2}[(\mathrm{pqrs} + \overline{\mathrm{pqrs}}) + \cdots] \qquad (24)
\end{aligned}
$$

The results are depicted in Fig. 3, where the categorization into five types is shown for the sake of convenience, although eq. 24 itself involves no such categorization. In Fig. 3, an arbitrary representative is selected from each quadruplet of *RS*-stereoisomers. For example, an entity **18** of Type III is a representative **A** selected from **A**, $\overline{\mathbf{A}}$, **B**, and $\overline{\mathbf{B}}$, which are shown in the Type-III stereoisogram (Fig. 2). Note that the four *RS*-stereoisomers (**A**, $\overline{\mathbf{A}}$, **B**, and $\overline{\mathbf{B}}$) is conceptually recognized to become degenerate into a single entity (counted as one quadruplet) under the action of the *RS*-stereoisomeric group $\mathbf{T}_{d\bar{\sigma}\hat{I}}$. Because the present approach differentiates between a chiral proligand and its enantiomeric proligand, a quadruplet of *RS*-stereoisomers is represented by the term $\frac{1}{2}(\mathrm{ABXp}+\mathrm{ABX}\overline{\mathrm{p}})$, where the participation of two *RS*-diastereomers for ABXp (or ABX$\overline{\mathrm{p}}$) is not explicitly described. Note that the formulas of the two *RS*-diastereomers are identical with ABXp (or ABX$\overline{\mathrm{p}}$), while the formulas of the two enantiomers are different to be ABXp and ABX$\overline{\mathrm{p}}$. As a result, the number of such an entity is calculated as the

coefficient 1 appearing in the term $1\times\frac{1}{2}(\mathrm{ABXp}+\mathrm{ABX}\overline{\mathrm{p}})$, where the coefficient 1 is omitted for the sake of simplicity, as found in eq. 24.

3 Effects of Subgroups of Index 2

The *RS*-stereoisomeric group (**G**) contains three subgroups of index 2, which correspond to the three subgroups of the factor group $\mathbf{G}/\mathbf{G}_C$ (eqs. 3, 4, and 7). This section is devoted to discuss effects of such subgroups of index 2.

3.1 Simultaneous Action of an *RS*-Stereoisomeric Group and its Maximum Point Subgroup

One of the three subgroups of index 2 contained in the *RS*-stereoisomeric group (**G**) is the maximum point-subgroup represented as follows:

$$\mathbf{G}_{C\sigma} = \mathbf{G}_C + \sigma\mathbf{G}_C, \tag{25}$$

which is concerned with chirality/achirality. The index 2 of the group $\mathbf{G}_{C\sigma}$ is represented by the following coset decomposition:

$$\mathbf{G} = \mathbf{G}_{C\sigma} + \widetilde{\sigma}\mathbf{G}_{C\sigma}, \tag{26}$$

where we have $|\mathbf{G}|/|\mathbf{G}_{C\sigma}| = 2$.

Under the the action of the point group $\mathbf{G}_{C\sigma}$, each pair of enantiomeric promolecules or each achiral promolecule is counted just once. In agreement of this feature, let us encircle the two promolecules of each enantiomeric or self-enantiomeric pair appearing in Fig. 2. Thereby, we obtain Fig. 4, where each enantiomeric pair (e.g., $\mathbf{A}$–◉–$\overline{\mathbf{A}}$) or each self-enantiomeric pair (e.g., $\mathbf{A}$=◉=$\mathbf{A}$) in a stereoisogram is regarded as an entity to be taken into consideration. It should be noted that such a self-enantiomeric pair as $\mathbf{A}$=◉=$\mathbf{A}$ is conceptually derived by putting $\mathbf{A} = \overline{\mathbf{A}}$ in the enantiomeric pair $\mathbf{A}$–◉–$\overline{\mathbf{A}}$. In order to clarify our standpoint of enumeration (cf. Fig. 4), let us refer to the entity (i.e., the pair of two enantiomeric or self-enantiomeric promolecules) as an *E-pair*. In this treatment, an E-pair for a pair two enantiomeric promolecules is regarded as being chiral, while an E-pair for a pair of self-enantiomeric promolecules (a hypothetical pair) is regarded as being achiral.

Our present target is to count inequivalent E-pairs under the action of the point group $\mathbf{G}_{C\sigma}$ and of the *RS*-stereoisomeric group **G**:

Self-*RS*-diastereomeric and/or Self-Holantimeric E-Pairs—Types I, II, and IV

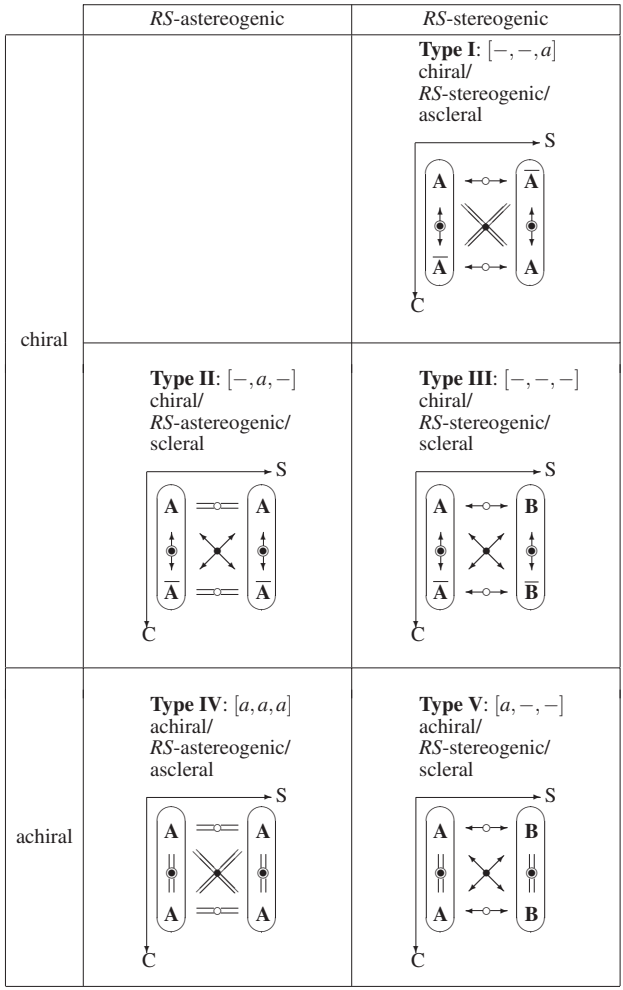

Figure 4: Stereoisograms of five types, each of which contains two chiral or achiral E-pairs encircled by oval boxes. Two E-pairs contained in a stereoisogram of Type I, II, or IV are self-*RS*-diastereomeric and/or self-holantimeric, while two E-pairs contained in a stereoisogram of Type III or V are *RS*-diastereomeric and holantimeric.

The two chiral E-pairs of the Type-I stereoisogram (Fig. 4) are identical with each other in isolation [33] . After incorporated in the Type I stereoisogram, they are superposable under the action of $\mathbf{G}$, although they are not superposable under the action of $\mathbf{G}_{C\sigma}$. Because the two E-pairs coincide with each other by the operations of $\mathbf{G}_{C\hat{I}}$, the set of the two chiral E-pairs (as an entity) can be referred to as being self-holantimeric. As a result, the two chiral E-pairs become degenerate to give a single entity which is counted just once under $\mathbf{G}_{C\sigma}$ as well as under $\mathbf{G}$ [34] .

The two chiral E-pairs of the Type-II stereoisogram (Fig. 4) are also identical with each other in isolation [33] . They are superposable under the action of $\mathbf{G}$, although they are not superposable under the action of $\mathbf{G}_{C\sigma}$. The set of the two chiral E-pairs can be referred to as being self-RS-diastereomeric. As a result, the two chiral E-pairs construct an entity to be counted just once under $\mathbf{G}_{C\sigma}$ as well as under $\mathbf{G}$.

The two achiral E-pairs of the Type-IV stereoisogram (Fig. 4) are also identical with each other in isolation [33] . They are superposable under the action of $\mathbf{G}$, just as they are superposable under the action of $\mathbf{G}_{C\sigma}$. The set of the two achiral E-pairs can be referred to as being self-RS-diastereomeric and self-holantimeric. As a result, the two achiral E-pairs become degenerate to give an entity to be counted just once under $\mathbf{G}_{C\sigma}$ as well as under $\mathbf{G}$.

RS-Diastereomeric and Holantimeric E-Pairs—Types III and V The two chiral E-pairs of the Type-III stereoisogram (Fig. 4) are not superposable under the action of $\mathbf{G}_{C\sigma}$. The two achiral E-pairs of the Type-V stereoisogram (Fig. 4) are not superposable under the action of $\mathbf{G}_{C\sigma}$. Both the set of the two chiral E-pairs (Type III) and the set of the two achiral E-pairs (Type V) can be referred to as being RS-diastereomeric and holantimeric. Because the two E-pairs of Type III (or of Type V) exhibit no degeneration, they give two entities to be counted separately under $\mathbf{G}_{C\sigma}$. Under the action of $\mathbf{G}$, on the other hand, they are regarded as constructing a quadruplet which is counted just once .

According to the behavior shown in Fig. 4, the number of the E-pairs under $\mathbf{G}_{C\sigma}$ is obtained by means of the following CI-CF:

$$\begin{aligned}&\text{CI-CF}(\mathbf{G}_{C\sigma};\$_d,b_d)\\ &\quad=\ \frac{1}{|\mathbf{G}_{C\sigma}|}\left\{\sum_{P\in\mathbf{G}_C} b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}+\sum_{P\in\sigma\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\},\end{aligned}\tag{27}$$

where each E-pair is counted just once. This means that a quadruplet of a Type-I, -II, or -IV stereoisogram contributes the number of E-pairs by one, while a quadruplet of a

Type-III or -V stereoisogram contributes the number of E-pairs by two.

By an analogy of $\mathbf{G}_C$ vs. $\mathbf{G}_{C\sigma}$ (index 2), the index 2 for $\mathbf{G}_{C\sigma}$ vs. $\mathbf{G}$ indicates that the number of self-*RS*-diastereomeric and/or self-holantimeric E-pairs (i.e., the number of quadruplets of Type-I, -II, and -IV) can be calculated by means of following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{I/II/IV}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ 2\text{CI-CF}(\mathbf{G};\$_d,b_d)-\text{CI-CF}(\mathbf{G}_{C\sigma};\$_d,b_d)\\
&\quad=\ \frac{2}{|\mathbf{G}|}\left\{\sum_{P\in\widetilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}+\sum_{P\in\widehat{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\},
\end{aligned}\tag{28}$$

which is obtained by collecting the SIs for the elements contained in the coset $\widetilde{\sigma}\mathbf{G}_{C\sigma}$ of eq. 26. The derivation of eq. 28 is alternatively rationalized as follows: The CI-CF($\mathbf{G};\$_d,b_d$) (eq. 11) counts each quadruplet just once, so that the resulting number is the sum of the number (N_E) of self-*RS*-diastereomeric and/or self-holantimeric E-pairs (i.e., the number of quadruplets of Type I, II, and IV) plus the number (N'_E) of *RS*-diastereomeric and holantimeric E-pairs (i.e., the number of quadruplets of Type III and V). On the other hand, the CI-CF($\mathbf{G}_{C\sigma};\$_d,b_d$) (eq. 27) counts each self-*RS*-diastereomeric and/or self-holantimeric E-pair (i.e., each quadruplet of Type I, II, and IV) just once (N_E), while it counts two E-pairs separately for a quadruplet of Type III and V ($2N'_E$). It follows that we can put $2(N_E+N'_E)-(N_E+2N'_E)=N_E$, which is the number to be obtained (eq. 28).

The number (N'_E) of *RS*-diastereomeric and holantimeric E-pairs (i.e., the number of quadruplets of Type III and V) is calculated by the following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{III/V}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}(\mathbf{G}_{C\sigma};\$_d,b_d)-\text{CI-CF}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \frac{1}{|\mathbf{G}|}\left\{\sum_{P\in\mathbf{G}_C} b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}+\sum_{P\in\sigma\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right.\\
&\qquad\left.-\sum_{P\in\widetilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}-\sum_{P\in\widehat{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\},
\end{aligned}\tag{29}$$

because we can put $(N_E+2N'_E)-(N_E+N'_E)=N'_E$. Obviously, eq. 29 is obtained by changing the signs of the elements corresponding to the coset $\widetilde{\sigma}\mathbf{G}_{C\sigma}$ (eq. 26, i.e., $\widetilde{\sigma}\mathbf{G}_C+\widehat{I}\mathbf{G}_C$) which appears in eq. 11.

Let us use the warehouse (eq. 12), the partition (eq. 13), and the molecular formula (eq. 14). Let the symbol $N_\theta^{[\tau]}$ (τ = I, II, ..., V or their combination) denote the number of

such isomers as having the molecular formula W_θ, where each quadruplet contained in a stereoisomer is counted just once. By using one of the CI-CFs (eqs. 28 and 29), Theorem 1 of Ref. [30] (or equivalently Theorem 2 of Ref. [32]) can be applied to this case so as to give the following generating function:

$$\sum_{[\theta]} N_\theta^{[\tau]} W_\theta = \text{CI-CF}^{[\tau]}(\mathbf{G}; \$_d, b_d), \tag{30}$$

where τ = I/II/IV or III/V; the summation is concerned with the partitions represented by $[\theta]$ (eq. 13); and the SIs are replaced by the ligand inventories shown in eqs. 16–18. It should be noted that three modes of proligand packing are effective for this case of *RS*-stereoisomeric groups on the same line as the case of point groups [30, 32] .

The maximum point group ($\mathbf{T}_d$) of the *RS*-stereoisomeric group $\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}$ (eq. 10) has the following 24 permutation operations:

$$\begin{aligned}
\mathbf{T}_d &= \mathbf{T} + \sigma\mathbf{T} && (31)\\
&= \{I, C_{2(1)}, C_{2(2)}, C_{2(3)}, C_{3(1)}, C_{3(3)}, C_{3(2)}, C_{3(4)}, C_{3(1)}^2, C_{3(4)}^2, C_{3(3)}^2, C_{3(2)}^2;\\
&\quad \sigma_{d(1)}, S_{4(3)}, S_{4(3)}^3, \sigma_{d(6)}, \sigma_{d(2)}, \sigma_{d(4)}, S_{4(1)}, S_{4(1)}^3, \sigma_{d(3)}, S_{4(2)}^3, \sigma_{d(5)}, S_{4(2)}\} && (32)\\
&= \{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3), (1)(2\ 4\ 3), (1\ 2\ 3)(4),\\
&\quad (1\ 3\ 4)(2), (1\ 4\ 2)(3), (1)(2\ 3\ 4), (1\ 2\ 4)(3), (1\ 3\ 2)(4), (1\ 4\ 3)(2);\\
&\quad \overline{(1)(2\ 3)(4)}, \overline{(1\ 2\ 4\ 3)}, \overline{(1\ 3\ 4\ 2)}, \overline{(1\ 4)(2)(3)}, \overline{(1)(2)(3\ 4)}, \overline{(1\ 2)(3)(4)},\\
&\quad \overline{(1\ 3\ 2\ 4)}, \overline{(1\ 4\ 2\ 3)}, \overline{(1)(2\ 4)(3)}, \overline{(1\ 2\ 3\ 4)}, \overline{(1\ 3)(2)(4)}, \overline{(1\ 4\ 3\ 2)}\}. && (33)
\end{aligned}$$

According to eq. 26, we obtain the following coset decomposition:

$$\mathbf{T}_{d\widetilde{\sigma}\widehat{I}} = \mathbf{T}_d + \widetilde{\sigma}\mathbf{T}_d, \tag{34}$$

where we have $|\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}|/|\mathbf{T}_d| = 2$.

By collecting the SIs for the elements contained in the coset $\widetilde{\sigma}\mathbf{T}_d$ of eq. 34, eq. 28 for this case gives the following CI-CF:

$$\text{CI-CF}^{[\text{I/II/IV}]}(\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}; \$_d, b_d) = \frac{1}{24}\left(a_1^4 + 3c_2^2 + 8a_1a_3 + 6b_1^2b_2 + 6b_4\right). \tag{35}$$

We change the signs of the elements corresponding to the coset $\widetilde{\sigma}\mathbf{T}_d$ (eq. 34, i.e., $\widetilde{\sigma}\mathbf{T} + \widehat{I}\mathbf{T}$) which appears in eq. 19. Thereby, eq. 29 for this case gives the following CI-CF:

$$\begin{aligned}
\text{CI-CF}^{[\text{III/V}]}(\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}; \$_d, b_d) &= \frac{1}{48}\left(b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4\right.\\
&\quad \left. - 6b_1^2b_2 - 6b_4 - a_1^4 - 3c_2^2 - 8a_1a_3\right). && (36)
\end{aligned}$$

Let us use the warehouse for methane derivatives (eq. 20) and the ligand inventories (eqs. 21–23). Suppose that the right-hand side of eq. 30 is replaced by eq. 35 or eq. 36 and that the left-hand side is regarded as $N_\theta^{[\mathrm{I/II/IV}]}$ or $N_\theta^{(\mathrm{III/V})}$.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 35). The expansion of the resulting equation gives the corresponding generating function for counting quadruplets:

$$
\begin{aligned}
f^{[\mathrm{I/II/IV}]} \;=\;& \mathrm{ABXY} + [\mathrm{p\overline{p}q\overline{q}} + \cdots] \\
&+ [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] \\
&+ [\mathrm{A}^2\mathrm{BX} + \cdots] + [\mathrm{A}^2\mathrm{p\overline{p}} + \cdots] + [\mathrm{p}^2\overline{\mathrm{p}}^2 + \cdots] \\
&+ \frac{1}{2}[(\mathrm{A}^3\mathrm{p} + \mathrm{A}^3\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{Bp} + \mathrm{A}^2\mathrm{B}\overline{\mathrm{p}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{A}^2\mathrm{p}^2 + \mathrm{A}^2\overline{\mathrm{p}}^2) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{pq} + \mathrm{A}^2\overline{\mathrm{pq}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{ABp}^2 + \mathrm{AB}\overline{\mathrm{p}}^2) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{Ap}^2\overline{\mathrm{p}} + \mathrm{A}\overline{\mathrm{p}}^2\mathrm{p}) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^3 + \mathrm{A}\overline{\mathrm{p}}^3) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^2\mathrm{q} + \mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^4 + \overline{\mathrm{p}}^4) + \cdots] + \frac{1}{2}[(\mathrm{p}^3\overline{\mathrm{p}} + \overline{\mathrm{p}}^3\mathrm{p}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^3\mathrm{q} + \overline{\mathrm{p}}^3\overline{\mathrm{q}}) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q} + \overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^2\mathrm{q}^2 + \overline{\mathrm{p}}^2\overline{\mathrm{q}}^2) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}^2\mathrm{qr} + \overline{\mathrm{p}}^2\overline{\mathrm{qr}}) + \cdots]
\end{aligned}
\tag{37}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{I/II/IV}]}$, to which each quadruplet corresponding to a stereoisogram contributes by one.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 36) and the resulting equation is expanded so as to give the corresponding generating function for counting quadruplets:

$$
\begin{aligned}
f^{[\mathrm{III/V}]} \;=\;& [\mathrm{ABp\overline{p}} + \cdots] \\
&+ \frac{1}{2}[(\mathrm{ABXp} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{ABpq} + \mathrm{AB}\overline{\mathrm{pq}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q} + \mathrm{Ap}\overline{\mathrm{pq}}) + \cdots] + \frac{1}{2}[(\mathrm{Apqr} + \mathrm{A}\overline{\mathrm{pqr}}) + \cdots] \\
&+ \frac{1}{2}[(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{pqr}}) + \cdots] + \frac{1}{2}[(\mathrm{pqrs} + \overline{\mathrm{pqrs}}) + \cdots]
\end{aligned}
\tag{38}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{III/V}]}$, to which each quadruplet corre-

sponding to a stereoisogram contributes by one. The categorization according to eqs. 37 and 38 is in agreement with Fig. 3.

3.2 Simultaneous Action of an *RS*-Stereoisomeric Group and its Maximum *RS*-Permutation Subgroup

As another subgroup of index 2 contained in the *RS*-stereoisomeric group ($\mathbf{G}$), we then examine the maximum *RS*-permutation subgroup:

$$\mathbf{G}_{C\widetilde{\sigma}} = \mathbf{G}_C + \widetilde{\sigma}\mathbf{G}_C \tag{39}$$

for representing *RS*-stereogenic/*RS*-astereogenic. The index 2 of the group $\mathbf{G}_{C\widetilde{\sigma}}$ is represented by the following coset decomposition:

$$\mathbf{G} = \mathbf{G}_{C\widetilde{\sigma}} + \sigma\mathbf{G}_{C\widetilde{\sigma}}, \tag{40}$$

where we have $|\mathbf{G}|/|\mathbf{G}_{C\widetilde{\sigma}}| = 2$. Under the the action of the maximum *RS*-permutation subgroup $\mathbf{G}_{C\widetilde{\sigma}}$, each pair of *RS*-diastereomeric promolecules or each *RS*-astereogenic promolecule is counted just once.

Let us encircle each *RS*-diastereomeric or self-*RS*-diastereomeric pair appearing in Fig. 2. Thereby, we obtain Fig. 5, where each *RS*-diastereomeric (e.g., $\mathbf{A}\!-\!\circ\!-\!\overline{\mathbf{A}}$ or $\mathbf{A}\!-\!\circ\!-\!\overline{\mathbf{B}}$) or self-*RS*-diastereomeric pair (e.g., $\mathbf{A}\!=\!\circ\!=\!\mathbf{A}$) is explicitly indicated. Note that each *RS*-diastereomeric pair or each self-*RS*-diastereomeric one is an entity which belongs to the maximum *RS*-permutation subgroup $\mathbf{G}_{C\widetilde{\sigma}}$ or its subgroup. As an analogy to the term *E-pair*, let us refer to a pair of two *RS*-diastereomeric promolecules and a self-*RS*-diastereomeric promolecule under the names of an *RS*-stereogenic *D-pair* and an *RS*-astereogenic *D-pair*, respectively.

Our target is to count inequivalent D-pairs under the action of the *RS*-permutation group $\mathbf{G}_{C\widetilde{\sigma}}$ and of the *RS*-stereoisomeric group $\mathbf{G}$:

Self-Enantiomeric and/or Self-Holantimeric D-Pairs—Types I, IV, and V The two D-pairs of the Type-I stereoisogram (Fig. 5) are identical with each other in isolation. After the two D-pairs are incorporated into a stereoisogram, they are superposable under the action of $\mathbf{G}$, while they are not superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. The set of the two D-pairs can be referred to as being self-holantimeric. As a result, the two D-pairs become degenerate to construct an entity to be counted just once under $\mathbf{G}_{C\widetilde{\sigma}}$ as well as under $\mathbf{G}$.

The two *RS*-astereogenic D-pairs of the Type-IV stereoisogram (Fig. 5) are also identical with each other in isolation. After incorporation in a stereoisogram, they

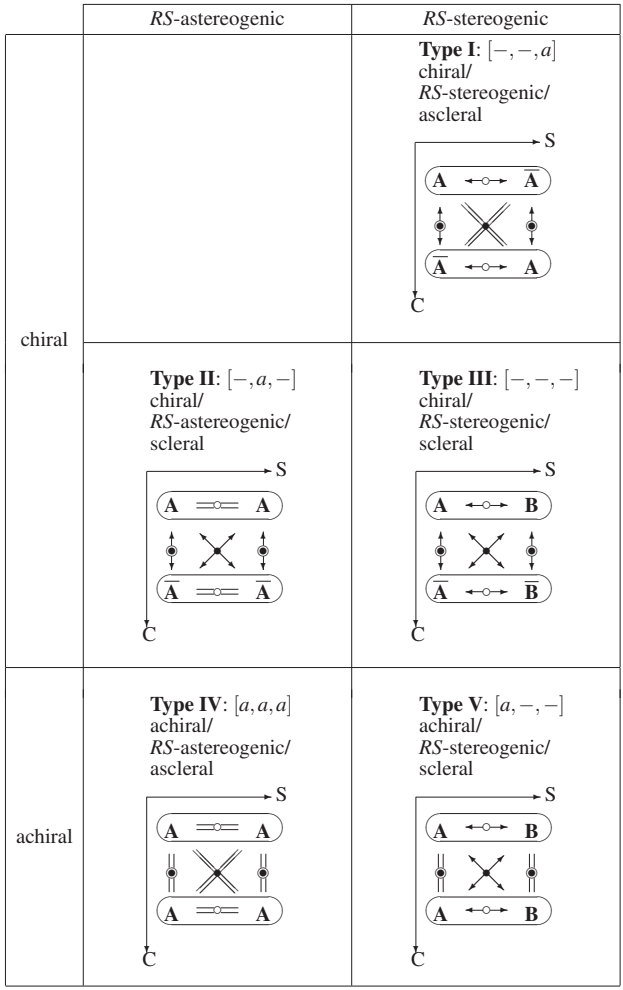

Figure 5: Stereoisograms of five types, each of which contains two *RS*-stereogenic or *RS*-astereogenic D-pairs encircled by oval boxes. Two D-pairs contained in a stereoisogram of Type I, IV, or V are self-enantiomeric and/or self-holantimeric, while two D-pairs contained in a stereoisogram of Type II or III are enantiomeric and holantimeric.

are superposable under the action of $\mathbf{G}$, just as they are superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. The set of the *RS*-astereogenic D-pairs can be referred to as being self-enantiomeric and self-holantimeric. It follows that the two *RS*-astereogenic D-pairs construct an entity to be counted just once under $\mathbf{G}_{C\widetilde{\sigma}}$ as well as under $\mathbf{G}$.

The two *RS*-stereogenic D-pairs of the Type-V stereoisogram (Fig. 5) are identical with each other in isolation. They are superposable under the action of $\mathbf{G}$, although they are not superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. Hence, the set of the two D-pairs can be referred to as being self-enantiomeric. The two D-pairs construct an entity to be counted just once under $\mathbf{G}_{C\widetilde{\sigma}}$ as well as under $\mathbf{G}$.

Enantiomeric and Holantimeric D-Pairs—Types II and III The two *RS*-stereogenic D-pairs of the Type-III stereoisogram (Fig. 5) are not superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. The two *RS*-astereogenic D-pairs of the Type-II stereoisogram (Fig. 5) are not superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. Both the set of the two *RS*-stereogenic D-pairs (Type III) and the set of the two *RS*-astereogenic D-pairs (Type II) can be referred to as being enantiomeric and holantimeric. Because the two D-pairs of Type III (or of Type II) exhibit no degeneration, they give two entities to be counted separately under $\mathbf{G}_{C\widetilde{\sigma}}$. Under the action of $\mathbf{G}$, on the other hand, they are regarded as constructing a quadruplet which is counted just once .

According to the behavior shown in Fig. 5, the number of the D-pairs under $\mathbf{G}_{C\widetilde{\sigma}}$ is obtained by means of the following CI-CF:

$$\begin{aligned} &\text{CI-CF}(\mathbf{G}_{C\widetilde{\sigma}}; b_d) \\ &= \frac{1}{|\mathbf{G}_{C\widetilde{\sigma}}|} \left\{ \sum_{P \in \mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} + \sum_{P \in \widetilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} \right\}, \end{aligned} \tag{41}$$

where each D-pair is counted just once. This means that a quadruplet of a Type-I, -IV, or -V stereoisogram contributes the number of D-pairs by one, while a quadruplet of a Type-II or -III stereoisogram contributes the number of D-pairs by two.

By an analogy of $\mathbf{G}_C$ vs. $\mathbf{G}_{C\sigma}$ (index 2) and $\mathbf{G}_{C\sigma}$ vs. $\mathbf{G}$ (index 2), the index 2 for $\mathbf{G}_{C\widetilde{\sigma}}$ vs. $\mathbf{G}$ indicates that the number of self-enantiomeric and/or self-holantimeric D-pairs (i.e., the number of quadruplets of Type-I, -IV, and -V) can be calculated by means of

following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ 2\text{CI-CF}(\mathbf{G};\$_d,b_d)-\text{CI-CF}(\mathbf{G}_{C\widetilde{\sigma}};b_d)\\
&\quad=\ \frac{2}{|\mathbf{G}|}\left\{\sum_{P\in\sigma\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}+\sum_{P\in\widehat{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\},
\end{aligned}\tag{42}$$

which is obtained by collecting the SIs for the elements contained in the coset $\sigma\mathbf{G}_{C\widetilde{\sigma}}$ of eq. 26.

In an analogous way to the derivation of eq. 28, the derivation of eq. 42 is rationalized as follows: The CI-CF$(\mathbf{G};\$_d,b_d)$ (eq. 11) counts each quadruplet just once, so that the resulting number is the sum of the number (N_D) of self-enantiomeric and/or self-holantimeric D-pairs (i.e., the number of quadruplets of Type I, IV, and V) plus the number (N'_D) of enantiomeric and holantimeric D-pairs (i.e., the number of quadruplets of Type II and III). On the other hand, the CI-CF$(\mathbf{G}_{C\widetilde{\sigma}};\$_d,b_d)$ (eq. 41) counts each self-enantiomeric and/or self-holantimeric D-pair (i.e., each quadruplet of Type I, IV, and V) just once (N_D), while it counts two D-pairs separately for a quadruplet of Type II and III $(2N'_D)$. It follows that we can put $2(N_D+N'_D)-(N_D+2N'_D)=N_D$, which is the number to be obtained (eq. 42).

The number (N'_D) of enantiomeric and holantimeric D-pairs (i.e., the number of quadruplets of Type II and III) is calculated by the following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{II/III}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}(\mathbf{G}_{C\widetilde{\sigma}};b_d)-\text{CI-CF}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \frac{1}{|\mathbf{G}|}\left\{\sum_{P\in\mathbf{G}_C}b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}-\sum_{P\in\sigma\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right.\\
&\qquad\left.+\sum_{P\in\widetilde{\sigma}\mathbf{G}_C}b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}-\sum_{P\in\widehat{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\},
\end{aligned}\tag{43}$$

because we can put $(N_D+2N'_D)-(N_D+N'_D)=N'_D$. Obviously, eq. 43 is obtained by changing the signs of the elements corresponding to the coset $\sigma\mathbf{G}_{C\widetilde{\sigma}}$ (eq. 26, i.e., $\sigma\mathbf{G}_C+\widehat{I}\mathbf{G}_C$) which appears in eq. 11.

Let us use the warehouse (eq. 12), the partition (eq. 13), and the molecular formula (eq. 14). eq. 30 is effective for the simultaneous action of the *RS*-stereoisomeric group and its maximum *RS*-permutation subgroup, where we put $\tau=$ I/IV/V or II/III and the CI-CF in the right-hand side is replaced by eq. 42 or eq. 43.

The maximum *RS*-permutation subgroup ($\mathbf{T}_{\tilde{\sigma}}$) of the *RS*-stereoisomeric group $\mathbf{T}_{d\tilde{\sigma}\hat{I}}$ (eq. 10) has the following 24 permutation operations:

$$\begin{aligned}
\mathbf{T}_{\tilde{\sigma}} &= \mathbf{T} + \tilde{\sigma}\mathbf{T} && (44)\\
&= \{I, C_{2(1)}, C_{2(2)}, C_{2(3)}, C_{3(1)}, C_{3(3)}, C_{3(2)}, C_{3(4)}, C^2_{3(1)}, C^2_{3(4)}, C^2_{3(3)}, C^2_{3(2)};\\
&\quad \tilde{\sigma}_{d(1)}, \widetilde{S}_{4(3)}, \widetilde{S}^3_{4(3)}, \tilde{\sigma}_{d(6)}, \tilde{\sigma}_{d(2)}, \tilde{\sigma}_{d(4)}, \widetilde{S}_{4(1)}, \widetilde{S}^3_{4(1)}, \tilde{\sigma}_{d(3)}, \widetilde{S}^3_{4(2)}, \tilde{\sigma}_{d(5)}, \widetilde{S}_{4(2)}\} && (45)\\
&= \{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3), (1)(2\ 4\ 3), (1\ 2\ 3)(4),\\
&\quad (1\ 3\ 4)(2), (1\ 4\ 2)(3), (1)(2\ 3\ 4), (1\ 2\ 4)(3), (1\ 3\ 2)(4), (1\ 4\ 3)(2);\\
&\quad (1)(2\ 3)(4), (1\ 2\ 4\ 3), (1\ 3\ 4\ 2), (1\ 4)(2)(3), (1)(2)(3\ 4), (1\ 2)(3)(4),\\
&\quad (1\ 3\ 2\ 4), (1\ 4\ 2\ 3), (1)(2\ 4)(3), (1\ 2\ 3\ 4), (1\ 3)(2)(4), (1\ 4\ 3\ 2)\}. && (46)
\end{aligned}$$

According to eq. 40, we obtain the following coset decomposition:

$$\mathbf{T}_{d\tilde{\sigma}\hat{I}} = \mathbf{T}_{\tilde{\sigma}} + \sigma\mathbf{T}_{\tilde{\sigma}}, \tag{47}$$

where we have $|\mathbf{T}_{d\tilde{\sigma}\hat{I}}|/|\mathbf{T}_{\tilde{\sigma}}| = 2$.

By collecting the SIs for the elements contained in the coset $\sigma\mathbf{T}_{\tilde{\sigma}}$ of eq. 47, eq. 42 for this case gives the following CI-CF:

$$\text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) = \frac{1}{24}\left(6a_1^2c_2 + 6c_4 + a_1^4 + 3c_2^2 + 8a_1a_3\right). \tag{48}$$

We change the signs of the elements corresponding to the coset $\sigma\mathbf{T}_{\tilde{\sigma}}$ (eq. 47, i.e., $\sigma\mathbf{T} + \widehat{I}\mathbf{T}$) which appears in eq. 19. Thereby, eq. 43 for this case gives the following CI-CF:

$$\begin{aligned}
\text{CI-CF}^{[\text{II/III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) &= \frac{1}{48}\left(b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 - 6c_4\right.\\
&\quad \left. + 6b_1^2b_2 + 6b_4 - a_1^4 - 3c_2^2 - 8a_1a_3\right). && (49)
\end{aligned}$$

Let us use the warehouse for methane derivatives (eq. 20) and the ligand inventories (eqs. 21–23). Suppose that the right-hand side of eq. 30 is replaced by eq. 48 or eq. 49 and that the left-hand side is regarded as $N_\theta^{[\text{I/IV/V}]}$ or $N_\theta^{[\text{II/III}]}$.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 48). The expansion of the resulting equation gives the corresponding generating function for counting

promolecules:

$$
\begin{aligned}
f^{[\mathrm{I/IV/V}]} \;=\; & \mathrm{ABXY} + [\mathrm{p\overline{p}q\overline{q}} + \cdots] \\
& + [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] \\
& + [\mathrm{A}^2\mathrm{BX} + \cdots] + [\mathrm{A}^2\mathrm{p\overline{p}} + \cdots] + [\mathrm{p}^2\overline{\mathrm{p}}^2 + \cdots] \\
& + [\mathrm{ABp\overline{p}} + \cdots], \qquad (50)
\end{aligned}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{I/IV/V}]}$, to which each quadruplet corresponding to a stereoisogram contributes by one.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 49) and the resulting equation is expanded so as to give the corresponding generating function for counting promolecules:

$$
\begin{aligned}
f^{[\mathrm{II/III}]} \;=\; & \frac{1}{2}[(\mathrm{A}^3\mathrm{p} + \mathrm{A}^3\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{Bp} + \mathrm{A}^2\mathrm{B}\overline{\mathrm{p}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{A}^2\mathrm{p}^2 + \mathrm{A}^2\overline{\mathrm{p}}^2) + \cdots] + \frac{1}{2}[(\mathrm{A}^2\mathrm{pq} + \mathrm{A}^2\overline{\mathrm{pq}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{ABp}^2 + \mathrm{AB}\overline{\mathrm{p}}^2) + \cdots] \\
& + \frac{1}{2}[(\mathrm{Ap}^2\overline{\mathrm{p}} + \mathrm{A}\overline{\mathrm{p}}^2\mathrm{p}) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^3 + \mathrm{A}\overline{\mathrm{p}}^3) + \cdots] + \frac{1}{2}[(\mathrm{Ap}^2\mathrm{q} + \mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{p}^4 + \overline{\mathrm{p}}^4) + \cdots] + \frac{1}{2}[(\mathrm{p}^3\overline{\mathrm{p}} + \overline{\mathrm{p}}^3\mathrm{p}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{p}^3\mathrm{q} + \overline{\mathrm{p}}^3\overline{\mathrm{q}}) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q} + \overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{p}^2\mathrm{q}^2 + \overline{\mathrm{p}}^2\overline{\mathrm{q}}^2) + \cdots] + \frac{1}{2}[(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{p}^2\mathrm{qr} + \overline{\mathrm{p}}^2\overline{\mathrm{qr}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{ABXp} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots] + \frac{1}{2}[(\mathrm{ABpq} + \mathrm{AB}\overline{\mathrm{pq}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q} + \mathrm{Ap}\overline{\mathrm{pq}}) + \cdots] + \frac{1}{2}[(\mathrm{Apqr} + \mathrm{A}\overline{\mathrm{pqr}}) + \cdots] \\
& + \frac{1}{2}[(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{pqr}}) + \cdots] + \frac{1}{2}[(\mathrm{pqrs} + \overline{\mathrm{pqrs}}) + \cdots], \qquad (51)
\end{aligned}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{II/III}]}$, to which each quadruplet corresponding to a stereoisogram contributes by one. The categorization according to eqs. 50 and 51 is in agreement with Fig. 3.

3.3 Simultaneous Action of an *RS*-Stereoisomeric Group and its Maximum Ligand-Inversion Subgroup

As a further subgroup of index 2 contained in the *RS*-stereoisomeric group ($\mathbf{G}$), we examine the maximum ligand-inversion subgroup:

$$\mathbf{G}_{C\hat{I}} = \mathbf{G}_C + \widehat{I}\mathbf{G}_C \tag{52}$$

for representing sclerality/asclerality. The index 2 of the group $\mathbf{G}_{C\hat{I}}$ is represented by the following coset decomposition:

$$\mathbf{G} = \mathbf{G}_{C\hat{I}} + \widetilde{\sigma}\mathbf{G}_{C\hat{I}} \tag{53}$$

where we have $|\mathbf{G}|/|\mathbf{G}_{C\hat{I}}| = 2$.

Under the the action of the maximum ligand-inversion subgroup $\mathbf{G}_{C\hat{I}}$, each pair of holantimeric promolecules or each ascleral promolecule is counted just once. Let us encircle each holantimeric or self-holantimeric pair appearing in Fig. 2. Thereby, we obtain Fig. 6, where each holantimeric (e.g., $\mathbf{A}\text{-}\bullet\text{-}\overline{\mathbf{B}}$ or $\mathbf{A}\text{-}\bullet\text{-}\mathbf{B}$) or self-holantimeric pair (e.g., $\mathbf{A}\text{=}\bullet\text{=}\mathbf{A}$ or $\overline{\mathbf{A}}\text{=}\bullet\text{=}\overline{\mathbf{A}}$) is explicitly indicated so that it is regarded as equivalent so as to be counted just once under the action of the maximum inversion subgroup $\mathbf{G}_{C\hat{I}}$.

As an analogy to the terms *E-pair* and *D-pair*, let us refer to such a pair of two holantimeric or self-holantimeric promolecules as an *H-pair*. Thereby, such H-pairs can be treated in an analogous way to E-pairs and D-pairs.

Self-Enantiomeric and/or Self-*RS*-diastereomeric H-Pairs—Types II, IV, and V

If the two scleral H-pairs of the Type-II stereoisogram (Fig. 6) are examined in isolation, they are identical with each other. When incorporated in the stereoisogram, they are superposable under the action of $\mathbf{G}$, although they are not superposable under the action of $\mathbf{G}_{C\hat{I}}$. The set of the two scleral H-pairs can be referred to as being self-*RS*-diastereomeric. Hence, the two scleral H-pairs become degenerate to give a single entity, which is counted just once under $\mathbf{G}_{C\hat{I}}$ as well as under $\mathbf{G}$.

The two ascleral H-pairs of the Type-IV stereoisogram (Fig. 6) are also identical with each other in isolation. They are superposable under the action of $\mathbf{G}$, just as they are superposable under the action of $\mathbf{G}_{C\widetilde{\sigma}}$. The set of the two scleral H-pairs can be referred to as being self-enantiomeric and self-*RS*-diastereomeric. The two ascleral H-pairs construct an entity to be counted just once under $\mathbf{G}_{C\hat{I}}$ as well as under $\mathbf{G}$.

The two scleral H-pairs of the Type-V stereoisogram (Fig. 6) are identical with each other in isolation. They are superposable under the action of $\mathbf{G}$, although they are not superposable under the action of $\mathbf{G}_{C\hat{I}}$. The set of the two scleral H-pairs can

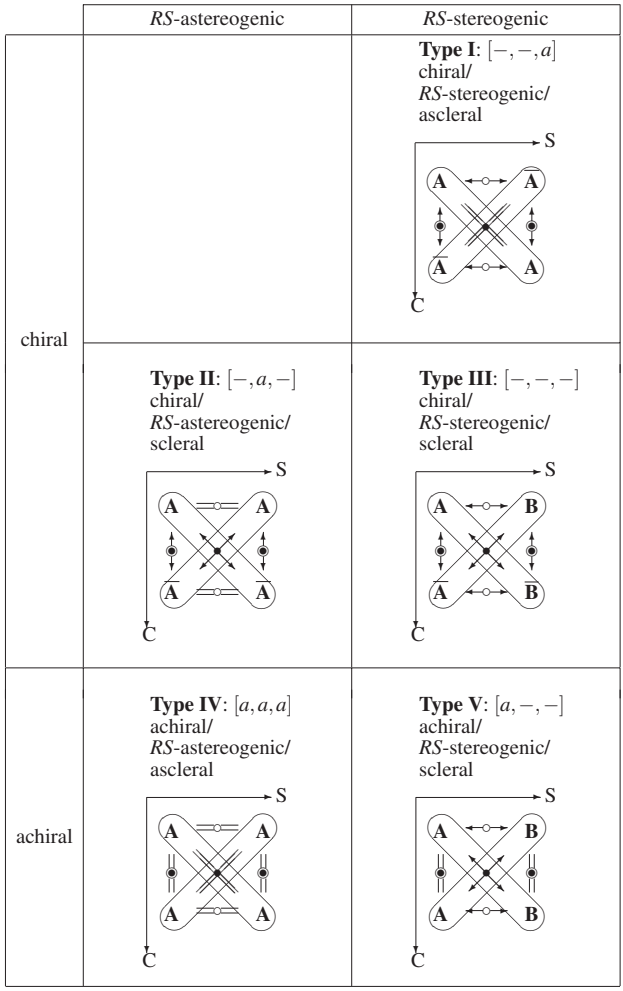

Figure 6: Stereoisograms of five types, each of which contains two scleral or ascleral H-pairs encircled by oval boxes. Two H-pairs contained in a stereoisogram of Type II, IV, or V are self-enantiomeric and/or self-RS-diastereomeric, while two H-pairs contained in a stereoisogram of Type I or III are enantiomeric and RS-diastereomeric.

be referred to as being self-enantiomeric. The two identical H-pairs are regarded as an entity to be counted just once under $\mathbf{G}_{C\hat{I}}$ as well as under $\mathbf{G}$.

Enantiomeric and *RS*-Diastereomeric H-Pairs—Types I and III The two scleral H-pairs of the Type-III stereoisogram (Fig. 6) are not superposable under the action of $\mathbf{G}_{C\hat{I}}$. The two ascleral H-pairs of the Type-I stereoisogram (Fig. 6) are not superposable under the action of $\mathbf{G}_{C\hat{I}}$. Both the set of the two scleral H-pairs (Type III) and the set of the two ascleral H-pairs (Type I) can be referred to as being enantiomeric and *RS*-diastereomeric. Because the two H-pairs of Type III (or of Type I) exhibit no degeneration, they give two entities to be counted separately under $\mathbf{G}_{C\hat{I}}$. Under the action of $\mathbf{G}$, on the other hand, they are regarded as constructing a quadruplet which is counted just once.

According to the behavior shown in Fig. 6, the number of the H-pairs under $\mathbf{G}_{C\hat{I}}$ is obtained by means of the following CI-CF:

$$\begin{aligned}
&\text{CI-CF}(\mathbf{G}_{C\tilde{I}}; \$_d, b_d) \\
&\quad = \frac{1}{|\mathbf{G}_{C\tilde{I}}|} \left\{ \sum_{P\in\mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} + \sum_{P\in\tilde{I}\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} \right\}. \qquad (54)
\end{aligned}$$

where each H-pair is counted just once. This means that a quadruplet of a Type-II, -IV, or -V stereoisogram contributes to the number of H-pairs by one, while a quadruplet of a Type-I or -III stereoisogram contributes to the number of H-pairs by two.

By an analogy of $\mathbf{G}_C$ vs. $\mathbf{G}_{C\sigma}$ (index 2), $\mathbf{G}_{C\sigma}$ vs. $\mathbf{G}$ (index 2), and $\mathbf{G}_{C\tilde{\sigma}}$ vs. $\mathbf{G}$ (index 2), the index 2 for $\mathbf{G}_{C\hat{I}}$ vs. $\mathbf{G}$ indicates that the number of self-enantiomeric and/or self-*RS*-diastereomeric H-pairs (i.e., the number of quadruplets of Type-II, -IV, and -V) can be calculated by means of following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{G}; \$_d, b_d) \\
&\quad = 2\text{CI-CF}(\mathbf{G}; \$_d, b_d) - \text{CI-CF}(\mathbf{G}_{C\tilde{I}}; \$_d, b_d) \\
&\quad = \frac{2}{|\mathbf{G}|} \left\{ \sum_{P\in\sigma\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} + \sum_{P\in\tilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} \right\}, \qquad (55)
\end{aligned}$$

which is obtained by collecting the SIs for the elements contained in the coset $\tilde{\sigma}\mathbf{G}_{C\hat{I}}$ of eq. 26.

In an analogous way to the derivation of eqs. 28 and 42, the derivation of eq. 55 is rationalized as follows: The CI-CF$(\mathbf{G}; \$_d, b_d)$ (eq. 11) counts each quadruplet just once, so that the resulting number is the sum of the number (N_H) of self-enantiomeric and/or self-*RS*-diastereomeric H-pairs (i.e., the number of quadruplets of Type II, IV, and V)

plus the number (N'_H) of enantiomeric and *RS*-diastereomeric H-pairs (i.e., the number of quadruplets of Type I and III). On the other hand, the CI-CF($\mathbf{G}_{C\widehat{I}}$; $\$_d, b_d$) (eq. 54) counts each self-enantiomeric and/or self-*RS*-diastereomeric H-pair (i.e., each quadruplet of Type II, IV, and V) just once (N_H), while it counts two H-pairs separately for a quadruplet of Type I and III ($2N'_H$). It follows that we can put $2(N_H + N'_H) - (N_H + 2N'_H) = N_H$, which is the number to be obtained (eq. 55).

The number (N'_H) of enantiomeric and *RS*-diastereomeric H-pairs (i.e., the number of quadruplets of Type I and III) is calculated by the following CI-CF:

$$
\begin{aligned}
&\text{CI-CF}^{[\text{I/III}]}(\mathbf{G}; \$_d, b_d) \\
&\quad = \text{CI-CF}(\mathbf{G}_{C\widetilde{I}}; \$_d, b_d) - \text{CI-CF}(\mathbf{G}; \$_d, b_d) \\
&\quad = \frac{1}{|\mathbf{G}|} \left\{ \sum_{P \in \mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} - \sum_{P \in \sigma\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} \right. \\
&\qquad \left. - \sum_{P \in \widetilde{\sigma}\mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} + \sum_{P \in \widehat{I}\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} \right\}, \qquad (56)
\end{aligned}
$$

because we can put $(N_H + 2N'_H) - (N_H + N'_H) = N'_H$. Obviously, eq. 56 is obtained by changing the signs of the elements corresponding to the coset $\sigma\mathbf{G}_{C\widehat{I}}$ (eq. 53, i.e., $\sigma\mathbf{G}_C + \widetilde{\sigma}\mathbf{G}_C$) which appears in eq. 11.

Let us use the warehouse (eq. 12), the partition (eq. 13), and the molecular formula (eq. 14). eq. 30 is effective for the simultaneous action of the *RS*-stereoisomeric group and its maximum ligand-inversion subgroup, where we put τ = II/IV/V or I/III and the CI-CF in the right-hand side is replaced by eq. 55 or eq. 56.

The maximum ligand-inversion subgroup ($\mathbf{T}_{\widehat{I}}$) of the *RS*-stereoisomeric group $\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}$ (eq. 10) has the following 24 permutation operations:

$$
\begin{aligned}
\mathbf{T}_{\widehat{I}} &= \mathbf{T} + \widehat{I}\mathbf{T} \qquad (57) \\
&= \{I, C_{2(1)}, C_{2(2)}, C_{2(3)}, C_{3(1)}, C_{3(3)}, C_{3(2)}, C_{3(4)}, C^2_{3(1)}, C^2_{3(4)}, C^2_{3(3)}, C^2_{3(2)}; \\
&\quad \widehat{I}, \widehat{C}_{2(1)}, \widehat{C}_{2(2)}, \widehat{C}_{2(3)}, \widehat{C}_{3(1)}, \widehat{C}_{3(3)}, \widehat{C}_{3(2)}, \widehat{C}_{3(4)}, \widehat{C}^2_{3(1)}, \widehat{C}^2_{3(4)}, \widehat{C}^2_{3(3)}, \widehat{C}^2_{3(2)}\} \qquad (58) \\
&= \{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3), (1)(2\ 4\ 3), (1\ 2\ 3)(4), \\
&\quad (1\ 3\ 4)(2), (1\ 4\ 2)(3), (1)(2\ 3\ 4), (1\ 2\ 4)(3), (1\ 3\ 2)(4), (1\ 4\ 3)(2); \\
&\quad \overline{(1)(2)(3)(4)}, \overline{(1\ 2)(3\ 4)}, \overline{(1\ 3)(2\ 4)}, \overline{(1\ 4)(2\ 3)}, \overline{(1)(2\ 4\ 3)}, \overline{(1\ 2\ 3)(4)}, \\
&\quad \overline{(1\ 3\ 4)(2)}, \overline{(1\ 4\ 2)(3)}, \overline{(1)(2\ 3\ 4)}, \overline{(1\ 2\ 4)(3)}, \overline{(1\ 3\ 2)(4)}, \overline{(1\ 4\ 3)(2)}\}. \qquad (59)
\end{aligned}
$$

According to eq. 53, we obtain the following coset decomposition:

$$\mathbf{T}_{d\widetilde{\sigma}\widehat{I}} = \mathbf{T}_{\widehat{I}} + \sigma\mathbf{T}_{\widehat{I}}, \tag{60}$$

where we have $|\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}|/|\mathbf{T}_{\widehat{I}}| = 2$.

By collecting the SIs for the elements contained in the coset $\sigma\mathbf{T}_{\widehat{I}}$ of eq. 60, we apply eq. 55 to this case, obtaining the following CI-CF:

$$\begin{aligned} \text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}; \$_d, b_d) &= \frac{1}{24}\left(6b_1^2b_2 + 6b_4 + 6a_1^2c_2 + 6c_4\right) \\ &= \frac{1}{4}\left(b_1^2b_2 + b_4 + a_1^2c_2 + c_4\right). \end{aligned} \tag{61}$$

In eq. 19, the signs of the terms which correspond to the elements contained in the coset $\sigma\mathbf{T}_{\widehat{I}}$ (eq. 60, i.e., $\sigma\mathbf{T} + \widetilde{\sigma}\mathbf{T}$) are changed from plus to minus. Thereby, eq. 56 for this case gives the following CI-CF:

$$\begin{aligned} \text{CI-CF}^{[\text{I/III}]}(\mathbf{T}_{d\widetilde{\sigma}\widehat{I}}; \$_d, b_d) &= \frac{1}{48}\left(b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 - 6c_4\right. \\ &\quad \left. - 6b_1^2b_2 - 6b_4 + a_1^4 + 3c_2^2 + 8a_1a_3\right). \end{aligned} \tag{62}$$

Let us use the warehouse for methane derivatives (eq. 20) and the ligand inventories (eqs. 21–23). Suppose that the right-hand side of eq. 30 is replaced by eq. 61 or eq. 62 and that the left-hand side is regarded as $N_\theta^{[\text{II/IV/V}]}$ or $N_\theta^{[\text{I/III}]}$.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 61). The expansion of the resulting equation gives the corresponding generating function for counting

quadruplets:

$$
\begin{aligned}
f^{[\mathrm{II/IV/V}]} \;=\;& [\mathrm{A}^4+\cdots]+[\mathrm{A}^3\mathrm{B}+\cdots]+[\mathrm{A}^2\mathrm{B}^2+\cdots] \\
&+[\mathrm{A}^2\mathrm{BX}+\cdots]+[\mathrm{A}^2\mathrm{p}\overline{\mathrm{p}}+\cdots]+[\mathrm{p}^2\overline{\mathrm{p}}^2+\cdots] \\
&+[\mathrm{ABp}\overline{\mathrm{p}}+\cdots] \\
&+\frac{1}{2}[(\mathrm{A}^3\mathrm{p}+\mathrm{A}^3\overline{\mathrm{p}})+\cdots]+\frac{1}{2}[(\mathrm{A}^2\mathrm{Bp}+\mathrm{A}^2\mathrm{B}\overline{\mathrm{p}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{A}^2\mathrm{p}^2+\mathrm{A}^2\overline{\mathrm{p}}^2)+\cdots]+\frac{1}{2}[(\mathrm{A}^2\mathrm{pq}+\mathrm{A}^2\overline{\mathrm{pq}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{ABp}^2+\mathrm{AB}\overline{\mathrm{p}}^2)+\cdots] \\
&+\frac{1}{2}[(\mathrm{Ap}^2\overline{\mathrm{p}}+\mathrm{A}\overline{\mathrm{p}}^2\mathrm{p})+\cdots]+\frac{1}{2}[(\mathrm{Ap}^3+\mathrm{A}\overline{\mathrm{p}}^3)+\cdots]+\frac{1}{2}[(\mathrm{Ap}^2\mathrm{q}+\mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{p}^4+\overline{\mathrm{p}}^4)+\cdots]+\frac{1}{2}[(\mathrm{p}^3\overline{\mathrm{p}}+\overline{\mathrm{p}}^3\mathrm{p})+\cdots] \\
&+\frac{1}{2}[(\mathrm{p}^3\mathrm{q}+\overline{\mathrm{p}}^3\overline{\mathrm{q}})+\cdots]+\frac{1}{2}[(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q}+\overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{p}^2\mathrm{q}^2+\overline{\mathrm{p}}^2\overline{\mathrm{q}}^2)+\cdots]+\frac{1}{2}[(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}}+\overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{p}^2\mathrm{qr}+\overline{\mathrm{p}}^2\overline{\mathrm{qr}})+\cdots],
\end{aligned}
\tag{63}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{II/IV/V}]}$, to which each quadruplet corresponding to a stereoisogram contributes by one.

The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 62) and the resulting equation is expanded so as to give the corresponding generating function for counting quadruplets:

$$
\begin{aligned}
f^{[\mathrm{I/III}]} \;=\;& \mathrm{ABXY}+[\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}}+\cdots] \\
&+\frac{1}{2}[(\mathrm{ABXp}+\mathrm{ABX}\overline{\mathrm{p}})+\cdots]+\frac{1}{2}[(\mathrm{ABpq}+\mathrm{AB}\overline{\mathrm{pq}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q}+\mathrm{Ap}\overline{\mathrm{pq}})+\cdots]+\frac{1}{2}[(\mathrm{Apqr}+\mathrm{A}\overline{\mathrm{pqr}})+\cdots] \\
&+\frac{1}{2}[(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr}+\mathrm{p}\overline{\mathrm{pqr}})+\cdots]+\frac{1}{2}[(\mathrm{pqrs}+\overline{\mathrm{pqrs}})+\cdots]
\end{aligned}
\tag{64}
$$

where each coefficient represents the number $N_\theta^{[\mathrm{I/III}]}$, to which each quadruplet corresponding to a stereoisogram contributes by one. The categorization according to eqs. 63 and 64 is consistent to Fig. 3.

4 Itemized Enumerations

4.1 Usage of Several Differences

A general method to categorize into each of the five types (Types I to V) is not always available. However, there are several cases which can be itemized to the five types.

Let us consider the difference between eq. 42 and eq. 55. Because Types IV and V are commonly contained in both of the CI-CFs, they are cancelled out to give the following CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{I}-\text{II}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{G};\$_d,b_d)-\text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}(\mathbf{G}_{C\tilde{I}};\$_d,b_d)-\text{CI-CF}(\mathbf{G}_{C\tilde{\sigma}};b_d)\\
&\quad=\ \frac{2}{|\mathbf{G}|}\left\{\sum_{P\in\tilde{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}-\sum_{P\in\tilde{\sigma}\mathbf{G}_C}b_1^{\nu_1(P)}b_2^{\nu_2(P)}\cdots b_n^{\nu_n(P)}\right\},
\end{aligned}\tag{65}$$

where the symbol [I−II] designates the difference between Type I and Type II. If the formulas of Type-I promolecules and those of Type II have no overlap, the terms for Type-I promolecules have plus signs while the terms for Type-II promolecules have minus signs. This condition holds true for the present enumeration based on a tetrahedral skeleton.

As for tetrahedral promolecules of the present enumeration, the difference between eq. 48 and eq. 61 gives the following CI-CF:

$$\begin{aligned}
\text{CI-CF}^{[\text{I}-\text{II}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}};\$_d,b_d)\ &=\ \text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}};\$_d,b_d)-\text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}};\$_d,b_d)\\
&=\ \frac{1}{24}\left(a_1^4+3c_2^2+8a_1a_3-6b_1^2b_2-6b_4\right).
\end{aligned}\tag{66}$$

It should be noted that, so long as we use the warehouse for methane derivatives (eq. 20), the formulas of Type-I promolecules and those of Type II have no overlap. The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 66). The expansion of the

resulting equation gives the corresponding generating function for counting quadruplets:

$$
\begin{aligned}
f^{[\mathrm{I-II}]} &= \mathrm{ABXY} + [\mathrm{p\overline{p}q\overline{q}} + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{A^3p} + \mathrm{A^3\overline{p}}) + \cdots] - \frac{1}{2}[(\mathrm{A^2Bp} + \mathrm{A^2B\overline{p}}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{A^2p^2} + \mathrm{A^2\overline{p}^2}) + \cdots] - \frac{1}{2}[(\mathrm{A^2pq} + \mathrm{A^2\overline{pq}}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{ABp^2} + \mathrm{AB\overline{p}^2}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{Ap^2\overline{p}} + \mathrm{A\overline{p}^2p}) + \cdots] - \frac{1}{2}[(\mathrm{Ap^3} + \mathrm{A\overline{p}^3}) + \cdots] - \frac{1}{2}[(\mathrm{Ap^2q} + \mathrm{A\overline{p}^2\overline{q}}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{p^4} + \mathrm{\overline{p}^4}) + \cdots] - \frac{1}{2}[(\mathrm{p^3\overline{p}} + \mathrm{\overline{p}^3p}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{p^3q} + \mathrm{\overline{p}^3\overline{q}}) + \cdots] - \frac{1}{2}[(\mathrm{p^2\overline{p}q} + \mathrm{\overline{p}^2p\overline{q}}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{p^2q^2} + \mathrm{\overline{p}^2\overline{q}^2}) + \cdots] - \frac{1}{2}[(\mathrm{p^2q\overline{q}} + \mathrm{\overline{p}^2q\overline{q}}) + \cdots] \\
&\quad - \frac{1}{2}[(\mathrm{p^2qr} + \mathrm{\overline{p}^2\overline{qr}}) + \cdots]. \qquad (67)
\end{aligned}
$$

By collecting terms having a plus sign from eq. 67, we obtain the following generating function for counting quadruplets of Type I:

$$
f^{[\mathrm{I}]} = \mathrm{ABXY} + [\mathrm{p\overline{p}q\overline{q}} + \cdots]. \qquad (68)
$$

Obviously, the remaining terms having a minus sign correspond to promolecules of Type II.

Let us consider the difference between eq. 42 and eq. 28 Because Types I and IV are commonly contained in both of the CI-CFs, they are cancelled out to give the following CI-CF:

$$
\begin{aligned}
&\text{CI-CF}^{[\mathrm{V-II}]}(\mathbf{G}; \$_d, b_d) \\
&= \text{CI-CF}^{[\mathrm{I/IV/V}]}(\mathbf{G}; \$_d, b_d) - \text{CI-CF}^{[\mathrm{I/II/IV}]}(\mathbf{G}; \$_d, b_d) \\
&= \text{CI-CF}(\mathbf{G}_{C\sigma}; \$_d, b_d) - \text{CI-CF}(\mathbf{G}_{C\bar{\sigma}}; b_d) \\
&= \frac{2}{|\mathbf{G}|}\left\{ \sum_{P \in \sigma \mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)} - \sum_{P \in \bar{\sigma} \mathbf{G}_C} b_1^{\nu_1(P)} b_2^{\nu_2(P)} \cdots b_n^{\nu_n(P)} \right\}. \qquad (69)
\end{aligned}
$$

As for tetrahedral promolecules of the present enumeration, the difference between eq.

48 and eq. 35 gives the following CI-CF:

$$\begin{aligned}\text{CI-CF}^{[\text{V}-\text{II}]}(\mathbf{T}_{d\bar{\sigma}\widehat{I}};\$_d,b_d) &= \text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{T}_{d\bar{\sigma}\widehat{I}};\$_d,b_d)-\text{CI-CF}^{[\text{I/II/IV}]}(\mathbf{T}_{d\bar{\sigma}\widehat{I}};\$_d,b_d)\\ &= \frac{1}{24}\left(6a_1^2c_2+6c_4-6b_1^2b_2-6b_4\right)\\ &= \frac{1}{4}\left(a_1^2c_2+c_4-b_1^2b_2-b_4\right). \qquad (70)\end{aligned}$$

So long as we use the warehouse for methane derivatives (eq. 20), the formulas of Type-V promolecules and those of Type II have no overlap also. The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 70). The expansion of the resulting equation gives the corresponding generating function for counting quadruplets:

$$\begin{aligned}f^{[\text{V}-\text{II}]} &= [\text{ABp}\overline{\text{p}}+\cdots]\\ &\quad-\frac{1}{2}[(\text{A}^3\text{p}+\text{A}^3\overline{\text{p}})+\cdots]-\frac{1}{2}[(\text{A}^2\text{Bp}+\text{A}^2\text{B}\overline{\text{p}})+\cdots]\\ &\quad-\frac{1}{2}[(\text{A}^2\text{p}^2+\text{A}^2\overline{\text{p}}^2)+\cdots]-\frac{1}{2}[(\text{A}^2\text{pq}+\text{A}^2\overline{\text{pq}})+\cdots]\\ &\quad-\frac{1}{2}[(\text{ABp}^2+\text{AB}\overline{\text{p}}^2)+\cdots]\\ &\quad-\frac{1}{2}[(\text{Ap}^2\overline{\text{p}}+\text{A}\overline{\text{p}}^2\text{p})+\cdots]-\frac{1}{2}[(\text{Ap}^3+\text{A}\overline{\text{p}}^3)+\cdots]-\frac{1}{2}[(\text{Ap}^2\text{q}+\text{A}\overline{\text{p}}^2\overline{\text{q}})+\cdots]\\ &\quad-\frac{1}{2}[(\text{p}^4+\overline{\text{p}}^4)+\cdots]-\frac{1}{2}[(\text{p}^3\overline{\text{p}}+\overline{\text{p}}^3\text{p})+\cdots]\\ &\quad-\frac{1}{2}[(\text{p}^3\text{q}+\overline{\text{p}}^3\overline{\text{q}})+\cdots]-\frac{1}{2}[(\text{p}^2\overline{\text{p}}\text{q}+\overline{\text{p}}^2\text{p}\overline{\text{q}})+\cdots]\\ &\quad-\frac{1}{2}[(\text{p}^2\text{q}^2+\overline{\text{p}}^2\overline{\text{q}}^2)+\cdots]-\frac{1}{2}[(\text{p}^2\text{q}\overline{\text{q}}+\overline{\text{p}}^2\text{q}\overline{\text{q}})+\cdots]\\ &\quad-\frac{1}{2}[(\text{p}^2\text{qr}+\overline{\text{p}}^2\overline{\text{qr}})+\cdots]. \qquad (71)\end{aligned}$$

By collecting terms having a plus sign from eq. 71, we obtain the following generating function for counting quadruplets of Type V:

$$f^{[\text{V}]}=[\text{ABp}\overline{\text{p}}+\cdots]. \qquad (72)$$

Obviously, the remaining terms having a minus sign correspond to quadruplets of Type II.

Let us consider the difference between eq. 28 and eq. 55. Because Types II and IV are commonly contained in both of the CI-CFs, they are cancelled out to give the following

CI-CF:

$$\begin{aligned}
&\text{CI-CF}^{[\text{I}-\text{V}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}^{[\text{I/II/IV}]}(\mathbf{G};\$_d,b_d)-\text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{G};\$_d,b_d)\\
&\quad=\ \text{CI-CF}(\mathbf{G}_{C\widehat{I}};\$_d,b_d)-\text{CI-CF}(\mathbf{G}_{C\sigma};\$_d,b_d)\\
&\quad=\ \frac{2}{|\mathbf{G}|}\left\{\sum_{P\in\widehat{I}\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}-\sum_{P\in\sigma\mathbf{G}_C}\$_1^{\nu_1(P)}\$_2^{\nu_2(P)}\cdots\$_n^{\nu_n(P)}\right\}. \qquad (73)
\end{aligned}$$

As for tetrahedral promolecules of the present enumeration, the difference between eq. 35 and eq. 61 gives the following CI-CF:

$$\begin{aligned}
\text{CI-CF}^{[\text{I}-\text{V}]}(\mathbf{T}_{d\widehat{\sigma}\widehat{I}};\$_d,b_d)&=\text{CI-CF}^{[\text{I/II/IV}]}(\mathbf{T}_{d\widehat{\sigma}\widehat{I}};\$_d,b_d)-\text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{T}_{d\widehat{\sigma}\widehat{I}};\$_d,b_d)\\
&=\frac{1}{24}\left(a_1^4+3c_2^2+8a_1a_3-6a_1^2c_2-6c_4\right). \qquad (74)
\end{aligned}$$

So long as we use the warehouse for methane derivatives (eq. 20), the formulas of Type-I promolecules and those of Type V have no overlap also. The ligand inventories (eqs. 21–23) are introduced into the CI-CF (eq. 74). The expansion of the resulting equation gives the corresponding generating function for counting quadruplets:

$$f^{[\text{I}-\text{V}]}\ =\ \text{ABXY}+[\text{p}\overline{\text{p}}\text{q}\overline{\text{q}}+\cdots]-[\text{AB}\text{p}\overline{\text{p}}+\cdots]. \qquad (75)$$

The terms having a plus sign in eq. 75 correspond to eq. 68, while the terms having a minus sign in eq. 75 is in agreement with eq. 72.

By applying eqs. 68 and 72 to eq. 50, we are able to obtain the following generating function for counting tetrahedral quadruplets of Type IV:

$$\begin{aligned}
f^{[\text{IV}]}&=f^{[\text{I/IV/V}]}-f^{[\text{I}]}-f^{[\text{V}]}\\
&=[\text{A}^4+\cdots]+[\text{A}^3\text{B}+\cdots]+[\text{A}^2\text{B}^2+\cdots]\\
&\quad+[\text{A}^2\text{BX}+\cdots]+[\text{A}^2\text{p}\overline{\text{p}}+\cdots]+[\text{p}^2\overline{\text{p}}^2+\cdots]. \qquad (76)
\end{aligned}$$

Obviously, the generating functions for counting quadruplets of all of Types I–V can be obtained by combining the above-mentioned generating functions.

It should be noted, however, that eq. 76 has not been derived by introducing the ligand inventories (eqs. 21–23) into a single CI-CF. Such a single CI-CF is not so easy to be obtained in general, unless we have more detailed data of the group-subgroup lattice of an *RS*-stereoisomeric group.

4.2 Itemization with Respect to Types I–V

4.2.1 Action of the Maximum Point Subgroup and its Maximum Chiral Subgroup

Although such a single CI-CF for counting Type-IV quadruplets is not so easy to be obtained in general, the one for counting tetrahedral Type-IV quadruplets can be obtained without full data of the group-subgroup lattice of the *RS*-stereoisomeric group $\mathbf{T}_{d\tilde{\sigma}\hat{I}}$.

The action of the maximum point subgroup ($\mathbf{G}_{C\sigma}$) and its maximum chiral subgroup ($\mathbf{G}_C$) has been reported in our previous paper [23] , which showed that achiral promolecules (Types IV and V) are counted by means of the following CI-CF (eq. 20 of [23]):

$$\begin{aligned} \text{CI-CF}^{(\text{IV/V})}(\mathbf{G}_{C\sigma}; \$_d) &= 2\text{CI-CF}(\mathbf{G}_{C\sigma}; \$_d, b_d) - \text{CI-CF}(\mathbf{G}_C; b_d) && (77) \\ &= \frac{1}{|\mathbf{G}_C|} \sum_{P \in \sigma\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)}, && (78) \end{aligned}$$

where we use the relationship $|\mathbf{G}_{C\sigma}| = 2|\mathbf{G}_C|$. The action of the $\mathbf{G}_{C\sigma}$ in the left-hand side of eq. 78 (eq. 20 of [23]) is concerned with each promolecule, not with each E-pair. However, eq. 78 can be considered to be concerned with E-pairs, because the formal description of the CI-CF($\mathbf{G}_{C\sigma}; \$_d, b_d$) in eq. 77 is equal to eq. 27. Because the two E-pairs of each Type-V stereoisogram coalesce with each other to give a quadruplet under $\mathbf{G}$, the results of eq. 78 contain twice the number of such quadruplets of Type V. Let use the superscript [IV/2V] in place of the one (IV/V) of the original notation [23] so as to emphasize that the two *RS*-diastereomers (or E-pairs) of a Type-V stereoisogram are counted separately. Thereby, we obtain:

$$\begin{aligned} \text{CI-CF}^{[\text{IV/2V}]}(\mathbf{G}; \$_d) &= \text{CI-CF}^{(\text{IV/V})}(\mathbf{G}_{C\sigma}; \$_d) \\ &= \frac{1}{|\mathbf{G}_C|} \sum_{P \in \sigma\mathbf{G}_C} \$_1^{\nu_1(P)} \$_2^{\nu_2(P)} \cdots \$_n^{\nu_n(P)}. && (79) \end{aligned}$$

As for the maximum point subgroup $\mathbf{T}_d$, the cycle structures appearing in the coset $\sigma\mathbf{T}$ are collected according to eq. 79 so as to give the following CI-CF:

$$\begin{aligned} \text{CI-CF}^{[\text{IV/2V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d) &= \text{CI-CF}^{(\text{IV/V})}(\mathbf{T}_d; \$_d) \\ &= \frac{1}{12}(6a_1^2c_2 + 6c_4) \\ &= \frac{1}{2}(a_1^2c_2 + c_4). && (80) \end{aligned}$$

One of the products of SIs ($a_1^2c_2$) in eq. 80 is related to pseudoasymmetric promolecules

(Type V, e.g., **30** as well as to other achiral promolecules (Type IV). Hence, we should select $a_1^2a_2$ and a_2c_2 for counting Type IV-promolecules other than the Type-V promolecules. The terms $a_1^2a_2$ and a_2c_2 contain a duplicated component represented by a_2^2 so that the product $a_1^2c_2$ is replaced by the combined term $a_1^2a_2 + a_2c_2 - a_2^2$ in order to to exclude contamination by pseudoasymmetry (Type-V promolecules). The other product of SIs (c_4) is not related to pseudoasymmetry. Hence, eq. 80 for this case takes the following form:

$$\text{CI-CF}^{[\text{IV}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d) = \text{CI-CF}^{(\text{IV})}(\mathbf{T}_d; \$_d) = \frac{1}{2}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4). \tag{81}$$

This is the single CI-CF for counting Type-IV promolecules, which is the present target to be pursued. Note that the number of Type-IV promolecules is equal to the number of Type-IV quadruplets to be counted.

The subtraction of eq. 81 from eq. 80 gives the CI-CF for counting quadruplets of Type V as follows:

$$\begin{aligned}
\text{CI-CF}^{[\text{V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d) &= \frac{1}{2}\left\{\text{CI-CF}^{[\text{IV/2V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d) - \text{CI-CF}^{[\text{IV}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d)\right\} \\
&= \frac{1}{4}(a_1^2c_2 + c_4) - \frac{1}{4}(a_1^2a_2 + a_2c_2 - a_2^2 + c_4) \\
&= \frac{1}{4}(a_1^2c_2 - a_1^2a_2 - a_2c_2 + a_2^2).
\end{aligned} \tag{82}$$

Note that the number of Type-V promolecules is twice the number of Type-V quadruplets to be counted.

4.2.2 CI-CFs of Other Types

By means of eqs. 48, 81 and 82, we obtain the CI-CF for counting quadruplets of Type I as follows:

$$\begin{aligned}
&\text{CI-CF}^{[\text{I}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) \\
&= \text{CI-CF}^{[\text{I/IV/V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) - \text{CI-CF}^{[\text{IV}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) - \text{CI-CF}^{[\text{V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) \\
&= \frac{1}{24}\left(a_1^4 + 3c_2^2 + 8a_1a_3 - 6a_1^2a_2 - 6a_2c_2 + 6a_2^2 - 6c_4\right).
\end{aligned} \tag{83}$$

The CI-CF for counting quadruplets of Type II is obtained by means of eqs. 61, 81 and 82 as follows:

$$\begin{aligned}
&\text{CI-CF}^{[\text{II}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) \\
&= \text{CI-CF}^{[\text{II/IV/V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) - \text{CI-CF}^{[\text{IV}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) - \text{CI-CF}^{[\text{V}]}(\mathbf{T}_{d\tilde{\sigma}\widehat{I}}; \$_d, b_d) \\
&= \frac{1}{4}\left(b_1^2b_2 + b_4 - a_1^2a_2 - a_2c_2 + a_2^2 - c_4\right).
\end{aligned} \tag{84}$$

Finally, the subtraction of eq. 84 from eq. 49 gives the CI-CF for counting quadruplets of Type III as follows:

$$\begin{aligned}
&\text{CI-CF}^{[\text{III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) \\
&= \text{CI-CF}^{[\text{II/III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) - \text{CI-CF}^{[\text{II}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d) \\
&= \frac{1}{48}\left(b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 + 6c_4\right. \\
&\quad \left. - a_1^4 - 3c_2^2 - 8a_1a_3 - 6b_1^2b_2 - 6b_4 + 12a_1^2a_2 + 12a_2c_2 - 12a_2^2\right). \qquad (85)
\end{aligned}$$

4.2.3 Generating Functions for Types I–V

The ligand inventories (eqs. 21–23) are introduced into the CI-CFs (eqs. 81–85). The expansion of the resulting equations gives the corresponding generating functions for counting quadruplets:

$$\begin{aligned}
f^{[\text{I}]} &= \text{ABXY} + [\text{p}\overline{\text{p}}\text{q}\overline{\text{q}} + \cdots] \qquad (86) \\
f^{[\text{II}]} &= \frac{1}{2}[(\text{A}^3\text{p} + \text{A}^3\overline{\text{p}}) + \cdots] + \frac{1}{2}[(\text{A}^2\text{Bp} + \text{A}^2\text{B}\overline{\text{p}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{A}^2\text{p}^2 + \text{A}^2\overline{\text{p}}^2) + \cdots] + \frac{1}{2}[(\text{A}^2\text{pq} + \text{A}^2\overline{\text{pq}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{ABp}^2 + \text{AB}\overline{\text{p}}^2) + \cdots] \\
&\quad + \frac{1}{2}[(\text{Ap}^2\overline{\text{p}} + \text{A}\overline{\text{p}}^2\text{p}) + \cdots] + \frac{1}{2}[(\text{Ap}^3 + \text{A}\overline{\text{p}}^3) + \cdots] + \frac{1}{2}[(\text{Ap}^2\text{q} + \text{A}\overline{\text{p}}^2\overline{\text{q}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{p}^4 + \overline{\text{p}}^4) + \cdots] + \frac{1}{2}[(\text{p}^3\overline{\text{p}} + \overline{\text{p}}^3\text{p}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{p}^3\text{q} + \overline{\text{p}}^3\overline{\text{q}}) + \cdots] + \frac{1}{2}[(\text{p}^2\overline{\text{p}}\text{q} + \overline{\text{p}}^2\text{p}\overline{\text{q}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{p}^2\text{q}^2 + \overline{\text{p}}^2\overline{\text{q}}^2) + \cdots] + \frac{1}{2}[(\text{p}^2\text{q}\overline{\text{q}} + \overline{\text{p}}^2\text{q}\overline{\text{q}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{p}^2\text{qr} + \overline{\text{p}}^2\overline{\text{qr}}) + \cdots] \qquad (87) \\
f^{[\text{III}]} &= \frac{1}{2}[(\text{ABXp} + \text{ABX}\overline{\text{p}}) + \cdots] + \frac{1}{2}[(\text{ABpq} + \text{AB}\overline{\text{pq}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{Ap}\overline{\text{p}}\text{q} + \text{Ap}\overline{\text{pq}}) + \cdots] + \frac{1}{2}[(\text{Apqr} + \text{A}\overline{\text{pqr}}) + \cdots] \\
&\quad + \frac{1}{2}[(\text{p}\overline{\text{p}}\text{qr} + \text{p}\overline{\text{pqr}}) + \cdots] + \frac{1}{2}[(\text{pqrs} + \overline{\text{pqrs}}) + \cdots], \qquad (88) \\
f^{[\text{IV}]} &= [\text{A}^4 + \cdots] + [\text{A}^3\text{B} + \cdots] + [\text{A}^2\text{B}^2 + \cdots] \\
&\quad + [\text{A}^2\text{BX} + \cdots] + [\text{A}^2\text{p}\overline{\text{p}} + \cdots] + [\text{p}^2\overline{\text{p}}^2 + \cdots]. \qquad (89) \\
f^{[\text{V}]} &= [\text{AB}\text{p}\overline{\text{p}} + \cdots]. \qquad (90)
\end{aligned}$$

As we found easily, eqs. 86, 89, and 90 are identical with eqs. 68, 76, and 72, respectively. Similarly, eqs. 87 and 88 can be examined to be identical with those derived by the method described in the preceding subsection.

5 Discussions

It is worthwhile to show that cycle indices (CIs) based on Pólya's Theorem can be derived as special cases of the present approach. This approach also reveals an implicit basis of the CIP-system.

5.1 Symmetries of the Tetrahedral Skeleton

In the present approach, the tetrahedral skeleton is considered to be governed by an *RS*-stereoisomeric group $\mathbf{T}_{d\tilde{\sigma}\hat{I}}$. On the other hand, Pólya's theorem [35, 36] has adopted the symmetric group of degree 4 ($\mathcal{S}^{[4]}$) in order to describe the symmetric nature of the tetrahedral skeleton.

By putting $r_d = a_d = b_d = c_d$, the CI-CF($\mathbf{T}_{d\tilde{\sigma}\hat{I}}; \$_d, b_d$) (eq. 19) is converted into the following CI:

$$\text{CI-CF}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) \;=\; \frac{1}{24}\left(r_1^4 + 3r_2^2 + 8r_1r_3 + 6r_1^2r_2 + 6r_4\right). \tag{91}$$

This type of equation was first noted by Pólya [36, page 21] , where the direct action of the symmetric group of degree 4 ($\mathcal{S}^{[4]}$) was used without taking account of the sphericity concept. This means that Pólya's theorem [35, 36] did not take chiral proligands into consideration.

According to the warehouse for methane derivatives (eq. 20) which contains achiral proligands as well as chiral ones, we adopt the following ligand inventory:

$$r_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{Y}^d + \mathrm{p}^d + \mathrm{q}^d + \mathrm{r}^d + \mathrm{s}^d + \overline{\mathrm{p}}^d + \overline{\mathrm{q}}^d + \overline{\mathrm{r}}^d + \overline{\mathrm{s}}^d, \tag{92}$$

where two proligands of an enantiomeric pair are presumed to participate separately. The ligand inventory (eq. 92) is introduced into the CI (eq. 91) to give the following generating

function:

$$
\begin{aligned}
g^{[\mathrm{T}]} \;=\;& \mathrm{ABXY} + [\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}} + \cdots] \\
&+ [\mathrm{AB}\mathrm{p}\overline{\mathrm{p}} + \cdots] \\
&+ [(\mathrm{ABXp} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots] + [(\mathrm{ABpq} + \mathrm{AB}\overline{\mathrm{pq}}) + \cdots] \\
&+ [(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q} + \mathrm{Ap}\overline{\mathrm{pq}}) + \cdots] + [(\mathrm{Apqr} + \mathrm{A}\overline{\mathrm{pqr}}) + \cdots] \\
&+ [(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{pqr}}) + \cdots] + [(\mathrm{pqrs} + \overline{\mathrm{pqrs}}) + \cdots] \\
&+ [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] \\
&+ [\mathrm{A}^2\mathrm{BX} + \cdots] + [\mathrm{A}^2\mathrm{p}\overline{\mathrm{p}} + \cdots] + [\mathrm{p}^2\overline{\mathrm{p}}^2 + \cdots]. \\
&+ [(\mathrm{A}^3\mathrm{p} + \mathrm{A}^3\overline{\mathrm{p}}) + \cdots] + [(\mathrm{A}^2\mathrm{Bp} + \mathrm{A}^2\mathrm{B}\overline{\mathrm{p}}) + \cdots] \\
&+ [(\mathrm{A}^2\mathrm{p}^2 + \mathrm{A}^2\overline{\mathrm{p}}^2) + \cdots] + [(\mathrm{A}^2\mathrm{pq} + \mathrm{A}^2\overline{\mathrm{pq}}) + \cdots] \\
&+ [(\mathrm{ABp}^2 + \mathrm{AB}\overline{\mathrm{p}}^2) + \cdots] \\
&+ [(\mathrm{Ap}^2\overline{\mathrm{p}} + \mathrm{A}\overline{\mathrm{p}}^2\mathrm{p}) + \cdots] + [(\mathrm{Ap}^3 + \mathrm{A}\overline{\mathrm{p}}^3) + \cdots] + [(\mathrm{Ap}^2\mathrm{q} + \mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^4 + \overline{\mathrm{p}}^4) + \cdots] + [(\mathrm{p}^3\overline{\mathrm{p}} + \overline{\mathrm{p}}^3\mathrm{p}) + \cdots] \\
&+ [(\mathrm{p}^3\mathrm{q} + \overline{\mathrm{p}}^3\overline{\mathrm{q}}) + \cdots] + [(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q} + \overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^2\mathrm{q}^2 + \overline{\mathrm{p}}^2\overline{\mathrm{q}}^2) + \cdots] + [(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^2\mathrm{qr} + \overline{\mathrm{p}}^2\overline{\mathrm{qr}}) + \cdots]. \qquad (93)
\end{aligned}
$$

In eq. 93, such a term as (ABXp and ABX$\overline{\mathrm{p}}$) represents a quadruplet of a stereoisogram. This result can be sophisticated by considering the itemization represented by eqs. 81–85, as shown in the next subsection.

5.2 Implication of the CIP-System

By putting $r_d = a_d = b_d = c_d$, the CI-CFs (eqs. 81–85) for the present itemized enumeration are converted into the following CIs:

$$
\begin{aligned}
\text{CI-CF}^{[\mathrm{I}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) &= \frac{1}{24}\left(r_1^4 + 3r_2^2 + 8r_1r_3 - 6r_1^2r_2 - 6r_4\right) && (94)\\
\text{CI-CF}^{[\mathrm{II}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) &= 0 && (95)\\
\text{CI-CF}^{[\mathrm{III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) &= 0 && (96)\\
\text{CI-CF}^{[\mathrm{IV}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) &= \frac{1}{2}(r_1^2r_2 + r_4) && (97)\\
\text{CI-CF}^{[\mathrm{V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d) &= 0 && (98)
\end{aligned}
$$

Among them, CI-CF$^{[\mathrm{II}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$, CI-CF$^{[\mathrm{III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$, and CI-CF$^{[\mathrm{V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$ vanish to zero. The non-zero equations were first noted by Pólya [36] , although he took an alter-

native approach. Thus, eq. 94 corresponds to the CI derived by Pólya [36, page 24] , who used the symmetric group of degree 4 ($\mathcal{S}^{[4]}$) and the alternating group of degree 4 ($\mathcal{A}^{[4]}$) in the form of $\mathcal{A}^{[4]} - \mathcal{S}^{[4]}$; and eq. 97 corresponds to the CI which he derived by putting $2\mathcal{S}^{[4]} - \mathcal{A}^{[4]}$ [36, page 24] .

The zero values of CI-CF$^{[\mathrm{III}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$ (eq. 96) and CI-CF$^{[\mathrm{V}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$ (eq. 98) are interpreted well by considering that they coalesce with the non-zero CI-CF$^{[\mathrm{I}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$. On the other hand, the fact that the CI-CF$^{[\mathrm{II}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$ (eq. 95) vanishes to zero indicates that it coalesces with the non-zero CI-CF$^{[\mathrm{IV}]}(\mathbf{T}_{d\tilde{\sigma}\hat{I}}; r_d)$. It should be noted that Types I, III, and V are *RS*-stereogenic, while Types II and IV are *RS*-astereogenic (cf. Fig. 3).

These features are confirmed by introducing the ligand inventory (eq. 92) into the CI-CFs (eqs. 94 and 97). The expansion of the resulting equations give the corresponding generating functions for counting promolecules:

$$
\begin{aligned}
g^{[\mathrm{I}]} \;=\;& \mathrm{ABXY} + [\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}} + \cdots] \\
&+ [\mathrm{AB}\mathrm{p}\overline{\mathrm{p}} + \cdots] \\
&+ [(\mathrm{ABX}\mathrm{p} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots] + [(\mathrm{AB}\mathrm{pq} + \mathrm{AB}\overline{\mathrm{pq}}) + \cdots] \\
&+ [(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q} + \mathrm{Ap}\overline{\mathrm{p}}\overline{\mathrm{q}}) + \cdots] + [(\mathrm{Apqr} + \mathrm{A}\overline{\mathrm{pqr}}) + \cdots] \\
&+ [(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{p}}\overline{\mathrm{qr}}) + \cdots] + [(\mathrm{pqrs} + \overline{\mathrm{pqrs}}) + \cdots] \qquad (99) \\
g^{[\mathrm{IV}]} \;=\;& [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] \\
&+ [\mathrm{A}^2\mathrm{BX} + \cdots] + [\mathrm{A}^2\mathrm{p}\overline{\mathrm{p}} + \cdots] + [\mathrm{p}^2\overline{\mathrm{p}}^2 + \cdots]. \\
&+ [(\mathrm{A}^3\mathrm{p} + \mathrm{A}^3\overline{\mathrm{p}}) + \cdots] + [(\mathrm{A}^2\mathrm{Bp} + \mathrm{A}^2\mathrm{B}\overline{\mathrm{p}}) + \cdots] \\
&+ [(\mathrm{A}^2\mathrm{p}^2 + \mathrm{A}^2\overline{\mathrm{p}}^2) + \cdots] + [(\mathrm{A}^2\mathrm{pq} + \mathrm{A}^2\overline{\mathrm{pq}}) + \cdots] \\
&+ [(\mathrm{ABp}^2 + \mathrm{AB}\overline{\mathrm{p}}^2) + \cdots] \\
&+ [(\mathrm{Ap}^2\overline{\mathrm{p}} + \mathrm{A}\overline{\mathrm{p}}^2\mathrm{p}) + \cdots] + [(\mathrm{Ap}^3 + \mathrm{A}\overline{\mathrm{p}}^3) + \cdots] + [(\mathrm{Ap}^2\mathrm{q} + \mathrm{A}\overline{\mathrm{p}}^2\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^4 + \overline{\mathrm{p}}^4) + \cdots] + [(\mathrm{p}^3\overline{\mathrm{p}} + \overline{\mathrm{p}}^3\mathrm{p}) + \cdots] \\
&+ [(\mathrm{p}^3\mathrm{q} + \overline{\mathrm{p}}^3\overline{\mathrm{q}}) + \cdots] + [(\mathrm{p}^2\overline{\mathrm{p}}\mathrm{q} + \overline{\mathrm{p}}^2\mathrm{p}\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^2\mathrm{q}^2 + \overline{\mathrm{p}}^2\overline{\mathrm{q}}^2) + \cdots] + [(\mathrm{p}^2\mathrm{q}\overline{\mathrm{q}} + \overline{\mathrm{p}}^2\mathrm{q}\overline{\mathrm{q}}) + \cdots] \\
&+ [(\mathrm{p}^2\mathrm{qr} + \overline{\mathrm{p}}^2\overline{\mathrm{qr}}) + \cdots]. \qquad (100)
\end{aligned}
$$

It is interesting that each term contained in $g^{[\mathrm{I}]}$ (eq. 99) corresponds to an object to be assigned to an *R*- or *S*-descriptor (or *r*- or *s*-descriptor) of the CIP-system. The terms ABXY and $[\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}} + \cdots]$ correspond to Type I; the terms $[\mathrm{AB}\mathrm{p}\overline{\mathrm{p}} + \cdots]$ correspond to Type V; and the remaining terms ($[(\mathrm{ABX}\mathrm{p} + \mathrm{ABX}\overline{\mathrm{p}}) + \cdots]$ etc.) correspond to Type III. This fact suggests that the CIP-system is implicitly based on the process in which the ligand inventory (eq. 92) is introduced into the CI-CFs (eqs. 94 and 97). Because Types I, III,

and V are *RS*-stereogenic, the enumeration result (eq. 99) reinforces the conclusion that *RS*-stereogenicity (not chirality) is concerned with the CIP-system [19, 20] .

5.3 Pólya's Theorem as a Special Case

The generating functions shown in eqs. 93, 99, and 100 presume that each chiral proligand (e.g., p) is discriminated from its enantiomeric proligand (e.g., $\overline{\mathrm{p}}$). In contrast, Póya's theorem does not take account of such inner structures, where each object is regarded as a graph. Hence, in order to get access to Póya's theorem, each chiral proligand (e.g., p) is equalized to its enantiomeric proligand (e.g., $\overline{\mathrm{p}}$). By putting $\mathrm{P} = \mathrm{p} = \overline{\mathrm{p}}$, $\mathrm{Q} = \mathrm{q} = \overline{\mathrm{q}}$, $\mathrm{R} = \mathrm{r} = \overline{\mathrm{r}}$, and $\mathrm{S} = \mathrm{s} = \overline{\mathrm{s}}$ and by avoiding the resulting duplication, eq. 92 is converted into another ligand inventory:

$$r_d = \mathrm{A}^d + \mathrm{B}^d + \mathrm{X}^d + \mathrm{Y}^d + \mathrm{P}^d + \mathrm{Q}^d + \mathrm{R}^d + \mathrm{S}^d. \tag{101}$$

Strictly speaking, we put $\mathrm{P}^d = \mathrm{p}^d + \overline{\mathrm{p}}^d$ etc. in eq. 92 so as to obtain eq. 101.

The ligand inventory (eq. 101) is introduced into the CI-CFs (eqs. 94 and 97). The expansion of the resulting equations give the corresponding generating functions for counting graphs:

$$\begin{aligned} g'^{[\mathrm{I}]} &= \mathrm{ABXY} \\ &\quad + [\mathrm{ABXP} + \cdots] + [\mathrm{ABPQ} + \cdots] \\ &\quad + [\mathrm{APQR} + \cdots] + [\mathrm{PQRS} + \cdots] \qquad (102) \\ g'^{[\mathrm{IV}]} &= [\mathrm{A}^4 + \cdots] + [\mathrm{A}^3\mathrm{B} + \cdots] + [\mathrm{A}^2\mathrm{B}^2 + \cdots] + [\mathrm{A}^2\mathrm{BX} + \cdots] \\ &\quad + [\mathrm{A}^3\mathrm{P} + \cdots] + [\mathrm{A}^2\mathrm{BP} + \cdots] \\ &\quad + [\mathrm{A}^2\mathrm{P}^2 + \cdots] + [\mathrm{A}^2\mathrm{PQ} + \cdots] + [\mathrm{ABP}^2 + \cdots] \\ &\quad + [\mathrm{AP}^3 + \cdots] + [\mathrm{AP}^2\mathrm{Q} + \cdots] \\ &\quad + [\mathrm{P}^4 + \cdots] + [\mathrm{P}^3\mathrm{Q} + \cdots] \\ &\quad + [\mathrm{P}^2\mathrm{Q}^2 + \cdots] + [\mathrm{P}^2\mathrm{QR} + \cdots] \qquad (103) \end{aligned}$$

Note that the terms $[\mathrm{p}\overline{\mathrm{p}}\mathrm{q}\overline{\mathrm{q}}+\cdots]$ (Type I), $[\mathrm{ABp}\overline{\mathrm{p}}+\cdots]$ (Type V), $[(\mathrm{Ap}\overline{\mathrm{p}}\mathrm{q}+\mathrm{Ap}\overline{\mathrm{pq}})+\cdots]$ (Type III), and $[(\mathrm{p}\overline{\mathrm{p}}\mathrm{qr} + \mathrm{p}\overline{\mathrm{pqr}}) + \cdots]$ (Type III) contained in eq. 99 have disappeared in eq. 102. Among them, in particular, the term $[\mathrm{ABp}\overline{\mathrm{p}} + \cdots]$ (Type V) corresponds to pseudoasymmetry.

It should be emphasized that the ligand inventory shown in eq. 101 essentially takes account of only achiral (pro)ligands by substituting achiral counterparts (P etc.) for

chiral (pro)ligands (p/$\overline{\text{p}}$ etc.). This condition restricts Pólya's theorem within graph enumeration, where the sphericities of cycles represented by the sphericity indices (a_d, c_d and b_d) are unnecessary to be taking into consideration, as pointed out by a previous article [37] .

5.4 Historical Comments

It is worthwhile to compare the enumeration results from a historical point of view. Let us align the three sets of generating functions for itemized enumeration reversely, i.e., $g'^{[\mathrm{I}]}/g'^{[\mathrm{IV}]}$ (eq. 102/eq. 103) $\Longrightarrow$ $g^{[\mathrm{I}]}/g^{[\mathrm{IV}]}$ (eq. 99/eq. 100) $\Longrightarrow$ $f^{[\mathrm{I}]}$–$f^{[\mathrm{V}]}$ (eqs. 86–90). The difference among the three sets stems from the selection of ligand inventories, i.e., eq. 101 $\Longrightarrow$ eq. 92 $\Longrightarrow$ eqs. 21–23. The alignment corresponds to the steps of development in the history of stereochemical terminology and chemical combinatorics.

By referring to Fig. 3, we find that the quadruplets **30** (ABp$\overline{\text{p}}$, Type V) and **12** (ABp^2, Type II) coalesce to give the term ABP^2 in the generating function $g'^{[\mathrm{IV}]}$ (eq. 103); and that the quadruplets **29** (A^{2}p$\overline{\text{p}}$, Type IV) and **8** (A^{2}p^2, Type II) coalesce to give the term A^{2}P^2. In other words, the pair of *RS*-stereogenicity/*RS*-astereogenicity and the pair of chirality/achirality are both mixed up. We can safely say that this step corresponds to the era before van't Hoff in the stereochemical terminology and to Pólya's theorem in the chemical combinatorics.

Each term contained in $g^{[\mathrm{I}]}$ (eq. 99) is concerned with an *RS*-stereogenic quadruplet (Types I, III, or V) by referring to Fig. 3, while $g^{[\mathrm{IV}]}$ (eq. 100) is concerned with an *RS*-astereogenic quadruplet (Types II or IV). The quadruplets corresponding to $g^{[\mathrm{I}]}$ (eq. 99) can be assigned to *R*- or *S*-descriptors (*r*- or *s*-descriptors) of the CIP-system, although chirality was mixed up with stereogenicity. This step corresponds to the era after the CIP-system, when the difference between stereogenicity and chirality was not fully investigated.

The present results summarized by $f^{[\mathrm{I}]}$–$f^{[\mathrm{V}]}$ (eqs. 86–90) clarify the importance of the five *RS*-stereoisomeric types shown in Fig. 3. Most parts of the connotation of the conventional term "stereogenicity" are replaced by the present terms *RS*-stereogenicity/*RS*-astereogenicity.

6 Conclusions

A quadruplet of promolecules appearing in a stereoisogram is considered to be an entity to be counted just once by using the corresponding *RS*-stereoisomeric group **G** (e.g., $\mathbf{T}_{d\hat{\sigma}\hat{I}}$ for a quadruplet of tetrahedral promolecules). Such a quadruplet consists of two E-pairs, each of which is defined as a pair of enantiomers (chiral promolecules) or a pair of self-enantiomers (an achiral promolecule). The two E-pairs of each quadruplet are

considered to construct an equivalence class of $\mathbf{G}$ and also an equivalence class of the maximum point subgroup $\mathbf{G}_{C\sigma}$ (e.g., $\mathbf{T}_d$ for a quadruplet of tetrahedral promolecules). Thereby, such equivalence classes are enumerated under $\mathbf{G}$ and $\mathbf{G}_{C\sigma}$ to give partially itemized generating functions. The quadruplet is considered to consist of two D-pairs, each of which is defined as a pair of *RS*-diastereomers (*RS*-stereogenic promolecules) or a pair of self-*RS*-diastereomers (an *RS*-astereogenic promolecule). Thereby, quadruplets as equivalence classes for D-pairs are enumerated under $\mathbf{G}$ and its maximum *RS*-permutation group $\mathbf{G}_{C\tilde{\sigma}}$ (e.g., $\mathbf{T}_{\tilde{\sigma}}$ for a quadruplet of tetrahedral promolecules). The quadruplet is considered to consist of two H-pairs, each of which is defined as a pair of holantimers (scleral promolecules) or a pair of self-holantimers (an ascleral promolecule). Thereby, quadruplets as equivalence classes for H-pairs are enumerated under $\mathbf{G}$ and its maximum ligand-inversion group $\mathbf{G}_{C\hat{I}}$ (e.g., $\mathbf{T}_{\hat{I}}$ for a quadruplet of tetrahedral promolecules). The results of the enumerations concerning E-pairs, D-pairs, and H-pairs are combined to accomplish itemized enumeration with respect to Types I–V. Pólya's theorem is discussed as a special case of the present approach.

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[2] According to IUPAC Recommendations 1996 [1] , the definitions of *stereoisomers* and related terms are as follows:

1. *Stereoisomers*: "Isomers that possess identical constitution, but which differ in the arrangement of their atoms in space."
2. *Enantiomer*: "One of a pair of molecular entities which are mirror images of each other and non-superposable."
3. *Diastereomers*: "See Diastereoisomerism."
4. *Diastereoisomerism*: "Stereoisomerism other than enantiomerism. Diastereoisomers (or diastereomers) are stereoisomers not related as mirror images. Diastereomers are characterised by differences in physical properties, and by some differences in chemical behaviours towards achiral as well as chiral reagents."

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[24] In the conventional stereochemistry, such a term as *enantiomeric* or "diastereomeric" is used to specify a relationship between two 3D-objects. Although the term *enantiomeric* corresponds to the nature of being chiral or achiral (an attribute of each 3D-object), the term "diastereomeric" does not correspond to any definite nature. Even if the term "diastereomeric" is presumed to correspond to "stereogenic", it should be noted that the term "astereogenic" is absent in contrast to the presence of the pair of chirality/achirality. In other words, although an achiral object is regarded as being self-enantiomeric, a "self-diastereomeric" object does not exist according to the conventional stereochemistry. Although most textbooks on stereochemistry [3 –5] and on organic chemistry [6 –10] have adopted such a dichotomous definition as "diastereomers are stereoisomers other than enantiomers", the conceptual difference between the term *enantiomeric* and the term "diastereomeric" makes the wide-spread dichotomy more or less unconvincing. In contrast, the present approach presumes that a quadruplet of *RS*-stereoisomers has attributes shown in a stereoisogram (i.e., chiral, *RS*-stereogenic, and scleral). Terms for relationships can be correlated to these attributes.

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[33] To do the task of counting quadruplets (i.e., pairs of E-pairs), each E-pair *in isolation* (not contained in a stereoisogram) should be determined to be identical or not with its *RS*-permutated and/or ligand-inverted image. This pretreatment is parallel to the a pretreatment in enumeration of promolecules, where each proligand in isolation is determined to be identical or not with its mirror image.

[34] This conclusion is understandable on the analogy with a point group $\mathbf{G}_{C\sigma}$ and its maximum subgroup of index 2 (i.e, the maximum chiral subgroup $\mathbf{G}_C$). An achiral promolecule and its hypothetical (self-)enantiomeric promolecule (i.e., its mirror image) are not superposable with each other under the action of $\mathbf{G}_C$, while they are superposable with each other under the action of $\mathbf{G}_{C\sigma}$. In spite of this situation, the achiral promolecule is regarded as one entity under $\mathbf{G}_C$ and $\mathbf{G}_{C\sigma}$. Suppose that the set of $\mathbf{G}_C$ and $\mathbf{G}_{C\sigma}$ is replaced by the set of $\mathbf{G}_{C\sigma}$ and $\mathbf{G}$ and that the set of the achiral promolecule and its hypothetical (self-)enantiomeric promolecule (i.e., its mirror image) is replaced by the set of an ascleral E-pair and its hypothetical (self-)holantimeric E-pair, which are contained in a stereoisogram of Type I. Then an analogous discussion can be developed, as found in the text.

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