

# Sphericities of double cosets, double coset representations, and Fujita's proligand method for combinatorial enumeration of stereoisomers

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The concepts of *double coset representations* and *sphericities of double cosets* are proposed to characterize stereoisomerism, where double cosets are classified into three types, i.e., *homospheric* double cosets, *enantiospheric* double cosets, or *hemispheric* double cosets. They determine modes of substitutions (i.e., chirality fittingness), where homospheric double cosets permit achiral ligands only; enantiospheric ones permit achiral ligands or enantiomeric pairs; and hemispheric ones permit achiral and chiral ligands. The sphericities of double cosets are linked to the sphericities of cycles which are ascribed to right coset representations. Thus, each cycle is assigned to the corresponding sphericity index ( $a_d$ ,  $c_d$ , or  $b_d$ ) so as to construct a cycle indices with chirality fittingness (CI-CFs). The resulting CI-CFs are proved to be identical with CI-CFs introduced in Fujita's proligand method (S. Fujita, Theor. Chem. Acc. 113 (2005) 73–79 and 80–86). The versatility of the CI-CFs in combinatorial enumeration of stereoisomers is demonstrated by using methane derivatives as examples, where the numbers of achiral plus chiral stereoisomers, those of achiral stereoisomers, and those of chiral stereoisomers are calculated separately by means of respective generating functions.

**KEY WORDS:** coset representation, double coset representation, enumeration, sphericity, stereoisomer

## 1. Introduction

Pólya's theorem [1,2] has been widely applied to chemical combinatorics, as disclosed in books [3–5] and reviews [6–8]. In the applications of Pólya's theorem, permutation representations have been obtained directly by the permuting behavior of a given skeleton. Although this methodology is effective to most cases, it is insufficient when it is applied to combinatorial enumeration with taking account of both chiral and achiral ligands as substituents. For example, by following Pólya's theorem, we should use the symmetric group of degree 4 in

enumeration of molecules derived from a tetrahedral skeleton, where the two isomers (enantiomers) with the molecular formula  $ABXY$  are counted once as well as the two isomers (diastereomers) with the molecular formula  $ABp\bar{p}$  are also counted once. Note that a central carbon atom is omitted in these formulas and that  $A$ ,  $B$ ,  $X$ , and  $Y$  are achiral ligands in isolation, while  $p$  and  $\bar{p}$  are chiral and enantiomeric to each other in isolation. Because two stereoisomers with the formula  $ABp\bar{p}$  have been well-known as a pseudo-asymmetric case, they should be counted twice in order to meet the start-of-the-art stereochemistry.

To avoid the drawback of Pólya's theorem, Fujita has reported "the proligand method" [9, 10], where a new concept "sphericities of *cycles*" was proposed as a key to manipulate chiral and achiral ligands concurrently. The sphericity concept is based on the correspondence between point groups and coset representations, which gives more informative results than the simple and direct usage of permutation representations adopted by Pólya's theorem.

The original sphericity concept proposed in Fujita's unit-subduced-cycle-index (USCI) approach [11] was formulated in a slightly different context, i.e., "sphericities of *orbits*". The sphericity concept formulated in Fujita's proligand method [9, 10] was related to the original one [11] through an intermediate concept "sphericities of *orbits* for *cyclic* subgroups" [12–15], which serves as a common basis linking both of the sphericity concepts. It should be noted that the sphericity concepts of the two types and the intermediate concept are all based on the correspondence between point groups and coset representations.

On the other hand, the concept of double cosets has been used to chemical combinatorics in various contexts [16–20]. Fujita's USCI approach has been also discussed in connection with the concept of double cosets [21]. Because of the close relationship between Fujita's proligand method and Fujita's USCI approach, there should be expected the relationship between Fujita's proligand method and the concept of double cosets. Hence, the demonstration of this relationship will provide us with an additional formulation of Fujita's proligand method so as to bring out a deeper insight to stereoisomerism.

In the present paper, the concepts of *double coset representations* and *sphericities of double cosets* will be proposed to characterize stereoisomerism. The latter concept will be linked with the concept of sphericities of cycles so as to construct a cycle index with chirality fittingness (CI-CF). The CI-CF will be proved to be identical with that of Fujita's proligand method introduced in another way [9].

## 2. Double coset representations and stereoisomers

### 2.1. Right coset representations

In order to define double coset representations, we first define right coset representations, which are here distinguished from left coset representations. In

general [11], a subgroup  $\mathbf{H}$  of a given point group  $\mathbf{G}$  gives a set of right cosets as follows:

$$\mathbf{H}\backslash\mathbf{G} = \{\underbrace{\mathbf{H}g_1}_1, \underbrace{\mathbf{H}g_2}_2, \underbrace{\mathbf{H}g_3}_3, \dots, \underbrace{\mathbf{H}g_r}_r\}, \quad (1)$$

where we place  $r = |\mathbf{G}|/|\mathbf{H}|$  and  $g_1 = I$  (identity). The set is regarded as an ordered set so as to give a permutation represented by the following formula, when any operation  $g (\in \mathbf{G})$  is multiplied from the right-hand direction.

$$g \stackrel{[R]}{\sim} \begin{pmatrix} \mathbf{H}g_1 & \mathbf{H}g_2 & \mathbf{H}g_3 & \cdots & \mathbf{H}g_r \\ \mathbf{H}g_1g & \mathbf{H}g_2g & \mathbf{H}g_3g & \cdots & \mathbf{H}g_rg \end{pmatrix} \quad (2)$$

$$\sim \begin{pmatrix} 1 & 2 & 3 & \cdots & r \\ t_{g1}^{[R]} & t_{g2}^{[R]} & t_{g3}^{[R]} & \cdots & t_{gr}^{[R]} \end{pmatrix} = p_g^{[R]}, \quad (3)$$

where  $t_{gi}^{[R]}$  ( $i = 1, 2, 3, \dots, r$ ) represents a set of permuted numbers. If  $g$  is an improper rotation of  $\mathbf{G}$ , each  $t_{gi}^{[R]}$  ( $i = 1, 2, 3, \dots, r$ ) is specified by an overbar so as to show the inversion of chirality, e.g.,  $\bar{t}_{gi}^{[R]}$  ( $i = 1, 2, 3, \dots, r$ ) for an improper rotation  $g$ . When  $g$  runs over the point group  $\mathbf{G}$ , we obtain the following right coset representation:

$$(\mathbf{H}\backslash)\mathbf{G} = \{p_g^{[R]} | \forall g \in \mathbf{G}\}. \quad (4)$$

The following examples show a procedure for constructing of a right coset representation  $(\mathbf{C}_{3v}\backslash)\mathbf{T}_d$  by using a methane skeleton as examples. First, we shall demonstrate the symmetry elements and their multiplication for manipulating a methane skeleton of the  $\mathbf{T}_d$ -symmetry.

**Example 1** [Symmetry elements and multiplication table of  $\mathbf{T}_d$ ]. The notation of symmetry elements adopted here for the  $\mathbf{T}_d$ -point group (figure 1) is the same one as reported in a previous paper [22], where coset decompositions of the  $\mathbf{T}_d$ -point group have been discussed in an introductory way [22]. The detailed specification is shown in the caption of figure 1. The multiplication table of the the  $\mathbf{T}_d$ -point group is shown in figure 2, where the symmetry operations are numbered sequentially for the sake of convenience.

Although the numbering of the symmetry elements in figure 2 is selected in accord with a coset decomposition of  $\mathbf{T}_d$  by  $\mathbf{D}_2$ , i.e.,

$$\mathbf{T}_d = \mathbf{D}_2 + \mathbf{D}_2C_{3(1)} + \mathbf{D}_2C_{3(1)}^2 + \mathbf{D}_2\sigma_{d(1)} + \mathbf{D}_2\sigma_{d(2)} + \mathbf{D}_2\sigma_{d(3)} \quad (5)$$

the mode of numbering can be selected arbitrarily from the 24! ways of permutation without losing generality.

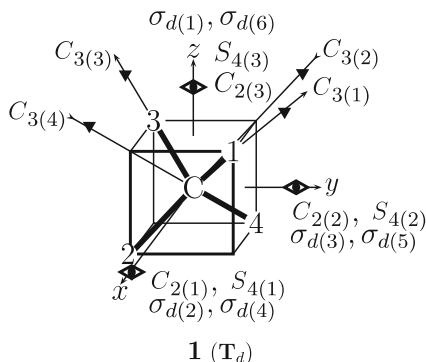


Figure 1. Methane skeleton of  $\mathbf{T}_d$ -symmetry. A pair of mirror planes ( $\sigma_{d(2)}/\sigma_{d(4)}$ ,  $\sigma_{d(3)}/\sigma_{d(5)}$ , or  $\sigma_{d(1)}/\sigma_{d(6)}$ ) located at the  $x$ -  $y$ -, or  $z$ -axis represents a perpendicular set of planes containing the respective axis. The threefold rotations  $C_{3(i)}$  ( $i = 1, 2, 3, 4$ ) represents a clockwise rotation by  $120^\circ$  around the respective threefold axes (i.e.,  $C_{3(i)}$  for  $i = 1, 2, 3, 4$ ), which run from the center to the respective positions (numbered as  $i = 1, 2, 3, 4$ ). The three twofold axes ( $C_{2(1)}$ ,  $C_{2(2)}$ , and  $C_{2(3)}$ ) and the three fourfold rotoinversion axes ( $S_{4(1)}$ ,  $S_{4(2)}$ , and  $S_{4(3)}$ ) run through  $x$ -,  $y$ -, and  $z$ -coordinate axes, respectively. The six mirror planes exhibit the following features:  $\sigma_{d(2)}$  (containing the 3-C-4 plane) and  $\sigma_{d(4)}$  (containing the 1-C-2 plane) intersect each other perpendicularly at the  $x$ -axis;  $\sigma_{d(3)}$  (containing the 2-C-3 plane) and  $\sigma_{d(5)}$  (containing the 1-C-4 plane) intersect each other perpendicularly at the  $y$ -axis; and  $\sigma_{d(1)}$  (containing the 2-C-4 plane) and  $\sigma_{d(6)}$  (containing the 1-C-3 plane) intersect each other perpendicularly at the  $z$ -axis.

**Example 2** [Right coset representation ( $\mathbf{C}_{3v} \setminus \mathbf{T}_d$ )]. One of the four threefold axes is selected to give a  $\mathbf{C}_{3v}$  point group as a subgroup of the  $\mathbf{T}_d$  point group:

$$\mathbf{C}_{3v} = \mathbf{C}_{3v(1)} = \left\{ \underbrace{I}_1, \underbrace{C_{3(1)}}_5, \underbrace{C_{3(1)}^2}_9, \underbrace{\sigma_{d(1)}}_{13}, \underbrace{\sigma_{d(2)}}_{17}, \underbrace{\sigma_{d(3)}}_{21} \right\}, \quad (6)$$

where the numbering of the symmetry operations is shown in figure 2. Thereby, we obtain the corresponding right coset decomposition as follows:

$$\begin{aligned} \mathbf{T}_d &= \mathbf{C}_{3v} + \mathbf{C}_{3v}C_{2(1)} + \mathbf{C}_{3v}C_{2(3)} + \mathbf{C}_{3v}C_{2(2)} & (7) \\ &= \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_1 + \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_2 + \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 + \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4, & (8) \end{aligned}$$

where the numbering of the symmetry operations contained in each coset is shown in figure 2. Then, the following set of right cosets is obtained:

$$\mathbf{C}_{3v} \setminus \mathbf{T}_d = \left\{ \underbrace{\mathbf{C}_{3v}}_1, \underbrace{\mathbf{C}_{3v}C_{2(1)}}_2, \underbrace{\mathbf{C}_{3v}C_{2(3)}}_3, \underbrace{\mathbf{C}_{3v}C_{2(2)}}_4 \right\}, \quad (9)$$

where these cosets are numbered sequentially from 1 to 4. Note that an arbitrary mode of numbering is selected for equation (9) from the  $4!$  ways of numbering

		first operation																							
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
second operation	1 $I$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
	2 $C_{2(1)}$	2	1	4	3	8	7	6	5	11	12	9	10	15	16	13	14	18	17	20	19	24	23	22	21
	3 $C_{2(2)}$	3	4	1	2	6	5	8	7	12	11	10	9	14	13	16	15	20	19	18	17	23	24	21	22
	4 $C_{2(3)}$	4	3	2	1	7	8	5	6	10	9	12	11	16	15	14	13	19	20	17	18	22	21	24	23
	5 $C_{3(1)}$	5	6	7	8	9	10	11	12	1	2	3	4	21	22	23	24	13	14	15	16	17	18	19	20
	6 $C_{3(3)}$	6	5	8	7	12	11	10	9	3	4	1	2	23	24	21	22	14	13	16	15	20	19	18	17
	7 $C_{3(2)}$	7	8	5	6	10	9	12	11	4	3	2	1	22	21	24	23	16	15	14	13	19	20	17	18
	8 $C_{3(4)}$	8	7	6	5	11	12	9	10	2	1	4	3	24	23	22	21	15	16	13	14	18	17	20	19
	9 $C_{3(1)}^2$	9	10	11	12	1	2	3	4	5	6	7	8	17	18	19	20	21	22	23	24	13	14	15	16
	10 $C_{3(4)}^2$	10	9	12	11	4	3	2	1	7	8	5	6	19	20	17	18	22	21	24	23	16	15	14	13
	11 $C_{3(3)}^2$	11	12	9	10	2	1	4	3	8	7	6	5	18	17	20	19	24	23	22	21	15	16	13	14
	12 $C_{3(2)}^2$	12	11	10	9	3	4	1	2	6	5	8	7	20	19	18	17	23	24	21	22	14	13	16	15
	13 $\sigma_{d(1)}$	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5	6	7	8	9	10	11	12
	14 $S_{4(3)}$	14	13	16	15	20	19	18	17	23	24	21	22	3	4	1	2	6	5	8	7	12	11	10	9
	15 $S_{4(3)}^3$	15	16	13	14	18	17	20	19	24	23	22	21	2	1	4	3	8	7	6	5	11	12	9	10
	16 $\sigma_{d(6)}$	16	15	14	13	19	20	17	18	22	21	24	23	4	3	2	1	7	8	5	6	10	9	12	11
	17 $\sigma_{d(2)}$	17	18	19	20	21	22	23	24	13	14	15	16	9	10	11	12	1	2	3	4	5	6	7	8
	18 $\sigma_{d(4)}$	18	17	20	19	24	23	22	21	15	16	13	14	11	12	9	10	2	1	4	3	8	7	6	5
	19 $S_{4(1)}$	19	20	17	18	22	21	24	23	16	15	14	13	10	9	12	11	4	3	2	1	7	8	5	6
	20 $S_{4(1)}^3$	20	19	18	17	23	24	21	22	14	13	16	15	12	11	10	9	3	4	1	2	6	5	8	7
	21 $\sigma_{d(3)}$	21	22	23	24	13	14	15	16	17	18	19	20	5	6	7	8	9	10	11	12	1	2	3	4
	22 $S_{4(2)}^3$	22	21	24	23	16	15	14	13	19	20	17	18	7	8	5	6	10	9	12	11	4	3	2	1
	23 $\sigma_{d(5)}$	23	24	21	22	14	13	16	15	20	19	18	17	6	5	8	7	12	11	10	9	3	4	1	2
	24 $S_{4(2)}$	24	23	22	21	15	16	13	14	18	17	20	19	8	7	6	5	11	12	9	10	2	1	4	3

Figure 2. Multiplication table of  $\mathbf{T}_d$ .

without losing generality. When each coset is multiplied by  $g (\in \mathbf{G})$ , the following permutation is obtained:

$$g \overset{[R]}{\sim} \begin{pmatrix} \mathbf{C}_{3v} & \mathbf{C}_{3v}\mathbf{C}_{2(1)} & \mathbf{C}_{3v}\mathbf{C}_{2(3)} & \mathbf{C}_{3v}\mathbf{C}_{2(2)} \\ \mathbf{C}_{3v}g & \mathbf{C}_{3v}\mathbf{C}_{2(1)}g & \mathbf{C}_{3v}\mathbf{C}_{2(3)}g & \mathbf{C}_{3v}\mathbf{C}_{2(2)}g \end{pmatrix} \quad (10)$$

$$\sim \begin{pmatrix} 1 & 2 & 3 & 4 \\ t_{g1}^{[R]} & t_{g2}^{[R]} & t_{g3}^{[R]} & t_{g4}^{[R]} \end{pmatrix} = p_g^{[R]}. \quad (11)$$

When  $g$  runs over  $\mathbf{G}$ , the resulting permutations generate a right coset representation as follows:

$$(\mathbf{C}_{3v} \setminus) \mathbf{T}_d = \{p_g^{[R]} \mid \forall g \in \mathbf{T}_d\}, \quad (12)$$

which is transitive under  $\mathbf{T}_d$ . For the sake of convenience, each  $p_g^{[R]}$  is expressed as a product of cycles, e.g.,

$$C_{2(1)} \stackrel{[R]}{\sim} \begin{pmatrix} \mathbf{C}_{3v}I & \mathbf{C}_{3v}C_{2(1)} & \mathbf{C}_{3v}C_{2(3)} & \mathbf{C}_{3v}C_{2(2)} \\ \mathbf{C}_{3v}C_{2(1)} & \mathbf{C}_{3v}I & \mathbf{C}_{3v}C_{2(2)} & \mathbf{C}_{3v}C_{2(3)} \end{pmatrix} \quad (13)$$

$$\sim p_{C_{2(1)}}^{[R]} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 2 & 1 & 4 & 3 \end{pmatrix} = (1 \ 2)(3 \ 4), \quad (14)$$

where (1 2) and (3 4) represent cycles to show the transformations of the relevant right cosets. The concrete form of the right coset representation  $(\mathbf{C}_{3v} \setminus) \mathbf{T}_d$  is shown in figure 3 along with other data which will be discussed later.

Each coset shown in equation (9) corresponds to a hydrogen of methane (**2**), as shown in figure 4. When the symmetry operations of  $\mathbf{T}_d$  act on the methane **2**, 24 formulas are generated as shown in figure 4, where the four hydrogen atoms of methane are governed by the right coset representation  $(\mathbf{C}_{3v} \setminus) \mathbf{T}_d$  shown in equation 12 and figure 3.

All of the 24 formulas appearing in figure 4 are identical with each other if the numbering of the positions is omitted.

## 2.2. Double coset representations

Let  $\mathbf{K}$  be another subgroup of  $\mathbf{G}$ . By starting from the set of cosets shown in equation (1), the following set of double cosets are obtained:

$$\mathbf{H} \setminus \mathbf{G} / \mathbf{K} = \{ \underbrace{\mathbf{H}g_1\mathbf{K}}_{f(1)}, \underbrace{\mathbf{H}g_2\mathbf{K}}_{f(2)}, \dots, \underbrace{\mathbf{H}g_i\mathbf{K}}_{f(i)}, \dots, \underbrace{\mathbf{H}g_r\mathbf{K}}_{f(r)} \}, \quad (15)$$

where  $f$  ( $f(i)$  for  $i = 1, 2, \dots, r$ ) is a function for numbering or labeling the resulting double cosets. If two or more double cosets are identical, they are numbered or labeled by the same value of the function but they are distinguished in accord with the numbering of the original right cosets. Because the function  $f$  corresponds to a stereoisomer as described below, the product of the components  $f(i)$  represents the molecular formula ( $M_f$ ) of the stereoisomer as follows:

$$M_f = \prod_{i=1}^r f(i). \quad (16)$$

	symmetry operation	right CR ( $C_{3v} \setminus$ ) $T_d$ as product of cycles	product of sphericity indices	product of dummy variables
$T$	$I$	$\sim (1)(2)(3)(4)$	$b_1^4$	$s_1^4$
	$C_{2(1)}$	$\sim (1\ 2)(3\ 4)$	$b_2^2$	$s_2^2$
	$C_{2(2)}$	$\sim (1\ 4)(2\ 3)$	$b_2^2$	$s_2^2$
	$C_{2(3)}$	$\sim (1\ 3)(2\ 4)$	$b_2^2$	$s_2^2$
	$C_{3(1)}$	$\sim (1)(2\ 3\ 4)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(3)}$	$\sim (1\ 2\ 4)(3)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(2)}$	$\sim (1\ 4\ 3)(2)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(4)}$	$\sim (1\ 3\ 2)(4)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(1)}^2$	$\sim (1)(2\ 4\ 3)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(4)}^2$	$\sim (1\ 2\ 3)(4)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(3)}^2$	$\sim (1\ 4\ 2)(3)$	$b_1 b_3$	$s_1 s_3$
	$C_{3(2)}^2$	$\sim (1\ 3\ 4)(2)$	$b_1 b_3$	$s_1 s_3$
$T\sigma_d(1)$	$\sigma_{d(1)}$	$\sim \overline{(1)(2\ 4)(3)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$S_{4(3)}$	$\sim \overline{(1\ 2\ 3\ 4)}$	$c_4$	$s_4$
	$S_{4(3)}^3$	$\sim \overline{(1\ 4\ 3\ 2)}$	$c_4$	$s_4$
	$\sigma_{d(6)}$	$\sim \overline{(1\ 3)(2)(4)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$\sigma_{d(2)}$	$\sim \overline{(1)(2)(3\ 4)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$\sigma_{d(4)}$	$\sim \overline{(1\ 2)(3)(4)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$S_{4(1)}$	$\sim \overline{(1\ 4\ 2\ 3)}$	$c_4$	$s_4$
	$S_{4(1)}^3$	$\sim \overline{(1\ 3\ 2\ 4)}$	$c_4$	$s_4$
	$\sigma_{d(3)}$	$\sim \overline{(1)(2\ 3)(4)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$S_{4(2)}$	$\sim \overline{(1\ 2\ 4\ 3)}$	$c_4$	$s_4$
	$\sigma_{d(5)}$	$\sim \overline{(1\ 4)(2)(3)}$	$a_1^2 c_2$	$s_1^2 s_2$
	$S_{4(2)}$	$\sim \overline{(1\ 3\ 4\ 2)}$	$c_4$	$s_4$

Figure 3. Right coset representation ( $C_{3v} \setminus$ ) $T_d$  and products of sphericity indices. Each cycle appearing in an improper rotation is designated by an overbar, which represents the inversion of ligand chirality.

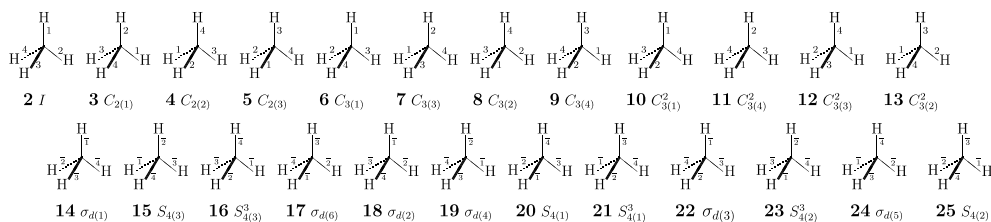


Figure 4. Four hydrogen atoms of methane, which are governed by the right coset representation ( $C_{3v} \setminus$ ) $T_d$  shown in equation (12) (and figure 3).

By starting from the right coset representation shown in equation (4) (i.e.,  $(\mathbf{H} \setminus) \mathbf{G}$ ), the following permutation is obtained:

$$g \overset{[R]}{\sim} \begin{pmatrix} \mathbf{H}g_1\mathbf{K} & \mathbf{H}g_2\mathbf{K} & \cdots & \mathbf{H}g_i\mathbf{K} & \cdots & \mathbf{H}g_r\mathbf{K} \\ \mathbf{H}g_1g\mathbf{K} & \mathbf{H}g_2g\mathbf{K} & \cdots & \mathbf{H}g_i g\mathbf{K} & \cdots & \mathbf{H}g_r g\mathbf{K} \end{pmatrix} \quad (17)$$

$$\sim \begin{pmatrix} f(1) & f(2) & \cdots & f(i) & \cdots & f(r) \\ f(t_{g1}^{[R]}) & f(t_{g2}^{[R]}) & \cdots & f(t_{gi}^{[R]}) & \cdots & f(t_{gr}^{[R]}) \end{pmatrix} = q_g^{[R]}. \quad (18)$$

If  $\mathbf{H}g_i g$  is identical with  $\mathbf{H}g_j$ , the corresponding double coset  $\mathbf{H}g_i g\mathbf{K}$  is identical with  $\mathbf{H}g_j\mathbf{K}$  so that the  $\mathbf{H}g_i g\mathbf{K}$  is specified by the same number or label as  $\mathbf{H}g_j\mathbf{K}$ . This means that each double coset appearing in equation (17) corresponds to one of the right cosets in one-to-one fashion. When  $g$  runs over the point group  $\mathbf{G}$ , we obtain the following representation of the group  $\mathbf{G}$ :

$$(\mathbf{H} \setminus) \mathbf{G} / \mathbf{K} = \{q_g^{[R]} | \forall g \in \mathbf{G}\}, \quad (19)$$

which is transitive and homomorphic to the right coset representation shown in equation (4), i.e.,  $(\mathbf{H} \setminus) \mathbf{G}$ . When the function shown in equation (15) is selected as an ordered set for reference, i.e.,

$$f_I = \{f(1), f(2), f(3), \dots, f(r)\}, \quad (20)$$

the permutation  $q_g^{[R]}$  (equation 19) generates another function represented by the following equation:

$$f_g = \left\{ f(t_{g1}^{[R]}), f(t_{g2}^{[R]}), f(t_{g3}^{[R]}), \dots, f(t_{gr}^{[R]}) \right\}. \quad (21)$$

The functions shown in equation (21) ( $g \in \mathbf{G}$ ) correspond to formulas appearing in stereoisomer enumeration. The following example shows a double coset representation, which is related to a stereoisomer derived from a methane skeleton of  $\mathbf{T}_d$ -symmetry.

**Example 3** [Double coset representation for  $\mathbf{T}_d$ ]. By starting from the set of right cosets  $\mathbf{C}_{3v} \setminus \mathbf{T}_d$  shown in equation (8) and a subgroup  $\mathbf{C}_{2v}$ :

$$\mathbf{C}_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{\sigma_{d(2)}}_{17}, \underbrace{\sigma_{d(4)}}_{18} \right\} \quad (22)$$



let us consider a set of double cosets according to equation (15) as follows:

$$\begin{aligned}
 & \mathbf{C}_{3v} \backslash \mathbf{T}_d / \mathbf{C}_{2v} \\
 & = \{ \mathbf{C}_{3v} I \mathbf{C}_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(1)} \mathbf{C}_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(3)} \mathbf{C}_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(2)} \mathbf{C}_{2v} \} \tag{23} \\
 & = \left[ \begin{array}{cccc}
 \left\{ \begin{array}{c} \{ 1 \ 5 \ 9 \} \\ \{ 13 \ 17 \ 21 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 2 \ 6 \ 10 \} \\ \{ 14 \ 18 \ 22 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 4 \ 8 \ 12 \} \\ \{ 16 \ 20 \ 24 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 3 \ 7 \ 11 \} \\ \{ 15 \ 19 \ 23 \} \end{array} \right\} \\
 \left\{ \begin{array}{c} \{ 2 \ 6 \ 10 \} \\ \{ 14 \ 18 \ 22 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 1 \ 5 \ 9 \} \\ \{ 13 \ 17 \ 21 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 3 \ 7 \ 11 \} \\ \{ 15 \ 19 \ 23 \} \end{array} \right\} & \left\{ \begin{array}{c} \{ 4 \ 8 \ 12 \} \\ \{ 16 \ 20 \ 24 \} \end{array} \right\} \\
 \underbrace{\hspace{1.5cm}}_1 & \underbrace{\hspace{1.5cm}}_2 & \underbrace{\hspace{1.5cm}}_3 & \underbrace{\hspace{1.5cm}}_4 \\
 \underbrace{\hspace{1.5cm}}_2 & \underbrace{\hspace{1.5cm}}_1 & \underbrace{\hspace{1.5cm}}_4 & \underbrace{\hspace{1.5cm}}_3 \\
 f(1) = \mathbf{A} & f(2) = \mathbf{A} & f(3) = \mathbf{B} & f(4) = \mathbf{B}
 \end{array} \right], \tag{24}
 \end{aligned}$$

where the two right cosets contained in each double coset are shown separately and put in braces for the sake of convenience. It should be noted that the numbering of the double cosets (or of the functions  $f$ ) in equation (24) is in accord with that of the right cosets shown in equation (9). Because the double cosets,  $\mathbf{C}_{3v} I \mathbf{C}_{2v}$  and  $\mathbf{C}_{3v} \mathbf{C}_{2(1)} \mathbf{C}_{2v}$ , are identical, they are labeled by the letter A so that we place  $f(1) = f(2) = \mathbf{A}$ . On the other hand, because the double cosets,  $\mathbf{C}_{3v} \mathbf{C}_{2(3)} \mathbf{C}_{2v}$  and  $\mathbf{C}_{3v} \mathbf{C}_{2(2)} \mathbf{C}_{2v}$ , are identical, they are labeled by the letter B so that we place  $f(3) = f(4) = \mathbf{B}$ . By considering  $f(1)$ ,  $f(2)$ ,  $f(3)$ , and  $f(4)$  as components, we define a function  $f = \{f(1), f(2), f(3), f(4)\}$  as a reference function. According to equation (18), the following permutation is obtained:

$$g \sim \begin{pmatrix} \mathbf{C}_{3v} I \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(1)} \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(3)} \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(2)} \mathbf{C}_{2v} \\ \mathbf{C}_{3v} I g \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(1)} g \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(3)} g \mathbf{C}_{2v} & \mathbf{C}_{3v} \mathbf{C}_{2(2)} g \mathbf{C}_{2v} \end{pmatrix} \tag{25}$$

$$\sim \begin{pmatrix} f(1) & f(2) & f(3) & f(4) \\ f(t_{g1}) & f(t_{g2}) & f(t_{g3}) & f(t_{g4}) \end{pmatrix} = \begin{pmatrix} \mathbf{A} & \mathbf{A} & \mathbf{B} & \mathbf{B} \\ T_1 & T_2 & T_3 & T_4 \end{pmatrix} = q_g, \tag{26}$$

where the alignment  $\{T_1, T_2, T_3, T_4\}$  represents a permuted alignment of  $\{\mathbf{A}, \mathbf{A}, \mathbf{B}, \mathbf{B}\}$ . By moving  $g$  over  $\mathbf{G}$ , the permutation  $q_g$  (equation (11)) generates a double coset representation according to equation (19) as follows:

$$(\mathbf{C}_{3v} \backslash) \mathbf{T}_d / (\mathbf{C}_{2v}) = \{q_g | \forall g \in \mathbf{T}_d\}. \tag{27}$$

The reference function  $f = f_I = \{f(1), f(2), f(3), f(4)\}$  corresponds to the formula 26 shown in figure 5. Each permutation  $q_g$  (equation (27)) generates a formula corresponding to the function  $f_g$ , i.e.,

$$f_g = \{f(t_{g1}), f(t_{g2}), f(t_{g3}), f(t_{g4})\}.$$

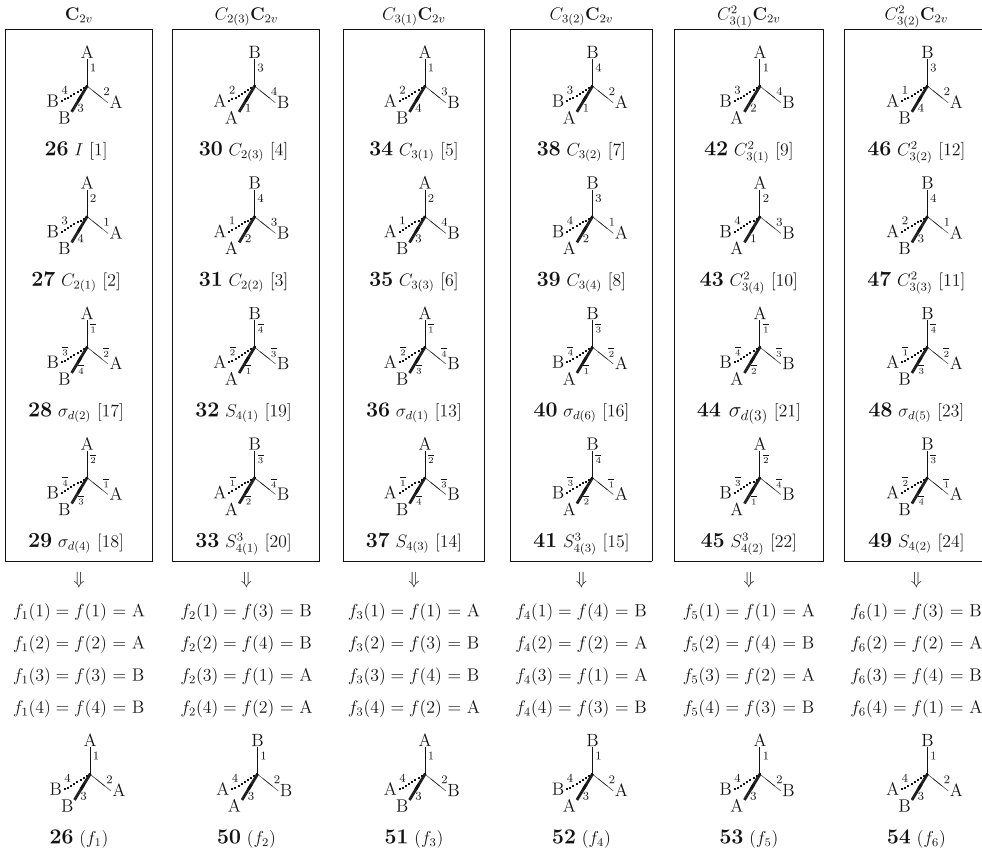


Figure 5. Tetrahedral formulas generated in accord with the double coset representation  $(C_{3v})\mathbf{T}_d/(C_{2v})$ . Each formula is accompanied by a derivative ID number, a symmetry operation, and the ID of the symmetry operation in a pair of brackets (cf. figure 2).

Each function represents a formula shown in figure 5, where the positions of each formula are numbered in the same way as those of the corresponding formula shown in figure 4. For example, the permutation (1)(2 3 4) for the threefold rotation  $C_{3(1)}$  (figure 3) generates **6** shown in figure 4 as well as **34** shown in figure 5.

By the inspection of the double coset representation (equation (17)), the term  $g\mathbf{K}$  generates left cosets when  $g$  runs over  $\mathbf{G}$ . Thereby, we obtain the corresponding set of left cosets as follows:

$$\mathbf{G}/\mathbf{K} = \{ \underbrace{\tilde{g}_1\mathbf{K}}_1, \underbrace{\tilde{g}_2\mathbf{K}}_2, \underbrace{\tilde{g}_3\mathbf{K}}_3, \dots, \underbrace{\tilde{g}_s\mathbf{K}}_s \}, \quad (28)$$

where we place  $\tilde{g}_1 = I$  (identity). The set is regarded as an ordered set so as to give a permutation represented by the following formula, when any operation  $g(\in \mathbf{G})$  is multiplied from the left-hand direction.

$$g \stackrel{[L]}{\sim} \begin{pmatrix} \tilde{g}_1\mathbf{K} & \tilde{g}_2\mathbf{K} & \tilde{g}_3\mathbf{K} & \cdots & \tilde{g}_s\mathbf{K} \\ g\tilde{g}_1\mathbf{K} & g\tilde{g}_2\mathbf{K} & g\tilde{g}_3\mathbf{K} & \cdots & g\tilde{g}_s\mathbf{K} \end{pmatrix} \quad (29)$$

$$\sim \begin{pmatrix} 1 & 2 & 3 & \cdots & s \\ t_{g1}^{[L]} & t_{g2}^{[L]} & t_{g3}^{[L]} & \cdots & t_{gs}^{[L]} \end{pmatrix} = p_g^{[L]}, \quad (30)$$

where  $t_{gj}^{[L]}$  ( $j = 1, 2, 3, \dots, s$ ) represents a set of permuted numbers and we place  $s = |\mathbf{G}|/|\mathbf{K}|$ . When  $g$  runs over the point group  $\mathbf{G}$ , we obtain the following left coset representation:

$$\mathbf{G}/(\mathbf{K}) = \{p_g^{[L]} \mid \forall g \in \mathbf{G}\}. \quad (31)$$

By the inspection of equations (17) and (29), we obtain the following theorem:

**Theorem 1. 1.** The permutations which are contained in the double coset representation  $(\mathbf{H})\mathbf{G}/(\mathbf{K})$  (equation (19)) are partitioned into  $|\mathbf{G}|/|\mathbf{K}|$  sets of permutations, where each set is represented by  $\{q_g^{[R]} \mid g \in \tilde{g}_j\mathbf{K}\}$  for  $\tilde{g}_j$  ( $j = 1, 2, \dots, s$ ) appearing in equation (28).

- Each set  $\{q_g^{[R]} \mid g \in \tilde{g}_j\mathbf{K}\}$  is fixed by the action of  $\mathbf{K}$  from the right-hand direction.  $\square$

*Proof.* 1. In equation (17), each double coset  $\mathbf{H}g_i\mathbf{K}$  is identical with  $\mathbf{H}g_i g\mathbf{K}$  ( $i = 1, 2, \dots, r$ ), if  $g \in \mathbf{K}$ . This means that  $q_g^{[R]}$  (equation (18)) is an identity permutation if  $g$  runs over  $\mathbf{K}$ .

- If  $g$  and  $k$  are selected from the coset  $\tilde{g}_j\mathbf{K}$  (i.e.,  $g \in \tilde{g}_j\mathbf{K}$  and  $k \in \tilde{g}_j\mathbf{K}$ , where  $j$  is fixed), each of them can be regarded as a representative of the coset  $\tilde{g}_j\mathbf{K}$ . Thereby, we obtain  $g\mathbf{K} = k\mathbf{K} = \tilde{g}_j\mathbf{K}$  so as to show  $\mathbf{H}g_i g\mathbf{K} = \mathbf{H}g_i k\mathbf{K} = \mathbf{H}g_i \tilde{g}_j\mathbf{K}$ . This means that  $q_g^{[R]}$  (equation (18)) represents the same permutation, if  $g$  runs over the left coset  $\tilde{g}_j\mathbf{K}$  ( $j = 1, 2, \dots, s$ ).

- Because  $\mathbf{H}g_i g\mathbf{K} = \mathbf{H}g_i \tilde{g}_j\mathbf{K}$  for  $g \in \tilde{g}_j\mathbf{K}$  when  $j$  is fixed, we obtain  $\mathbf{H}g_i g\mathbf{K}k = \mathbf{H}g_i \tilde{g}_j\mathbf{K}k = \mathbf{H}g_i \tilde{g}_j\mathbf{K}$  if  $k \in \mathbf{K}$ . It follows that each set  $\{q_g^{[R]} \mid g \in \tilde{g}_j\mathbf{K}\}$  is fixed by the action of  $\mathbf{K}$ .  $\square$

In terms of theorem 1(2), the formulas contained in respective sets  $\{q_g^{[R]} \mid g \in \tilde{g}_j\mathbf{K}\}$  express different modes of permutation, representing a single stereoisomer of  $\mathbf{K}$ -symmetry (strictly speaking, a single achiral stereoisomer or a single enantiomeric pair of chiral stereoisomers). The relationship between the formulas contained in each set is referred to as being *identical*, while the relationship among such sets is referred to as being *homomeric*.

As a continuation of example 3, the following example shows the partition of  $A_2B_2$ -formulas into equivalence classes (orbits).

**Example 4** [Homomeric formulas]. Each permutation  $q_g$  (equation (11) for  $g \in \mathbf{T}_d$ ) transforms  $f_I$  (26) into one of the 24 formulas shown in figure 5, which are in accord with the double coset representation  $(\mathbf{C}_{3v} \setminus) \mathbf{T}_d / (\mathbf{C}_{2v})$  (equation (27)).

Theorem 1 indicates that the 24 formulas are partitioned into six ( $= |\mathbf{T}_d|/|\mathbf{C}_{2v}| = 24/4$ ) sets, each of which is surrounded with a box (figure 5). This is confirmed by the following procedure. Because the left coset decomposition of  $\mathbf{T}_d$  by  $\mathbf{C}_{2v}$  is expressed by

$$\mathbf{T}_d = I\mathbf{C}_{2v} + C_{2(3)}\mathbf{C}_{2v} + C_{3(1)}\mathbf{C}_{2v} + C_{3(2)}\mathbf{C}_{2v} + C_{3(1)}^2\mathbf{C}_{2v} + C_{3(2)}^2\mathbf{C}_{2v} \quad (32)$$

its representative (i.e.,  $\{I, C_{2(3)}, C_{3(1)}, C_{3(2)}, C_{3(1)}^2, C_{3(2)}^2\} = \{1, 4, 5, 7, 9, 12\}$ ) are selected to partition the functions  $f_g$  ( $g \in \mathbf{T}_d$ ). Because the operations  $I$ ,  $C_{2(1)}$ ,  $\sigma_{d(2)}$ , and  $\sigma_{d(4)}$  are contained in  $\mathbf{C}_{2v}$ , we obtain  $C_{3v}g_i I\mathbf{C}_{2v} = C_{3v}g_i C_{2(1)}\mathbf{C}_{2v} = C_{3v}g_i \sigma_{d(2)}\mathbf{C}_{2v} = C_{3v}g_i \sigma_{d(4)}\mathbf{C}_{2v} = C_{3v}\mathbf{C}_{2v}$ . This means that  $f_I = f_{C_{2(1)}} = f_{\sigma_{d(2)}} = f_{\sigma_{d(4)}}$ , so that the four formulas listed in the first box of figure 5 are identical with each other when the numbering is omitted.

Let us next consider the action of  $C_{2(3)}$ . Equations (10) and (11) for  $g = C_{2(3)}$  are calculated as follows:

$$\begin{aligned} C_{2(3)} &\sim \begin{pmatrix} C_{3v}IC_{2v} & C_{3v}C_{2(1)}\mathbf{C}_{2v} & C_{3v}C_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(2)}\mathbf{C}_{2v} \\ C_{3v}IC_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(1)}C_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(3)}C_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(2)}C_{2(3)}\mathbf{C}_{2v} \end{pmatrix} \\ &= \begin{pmatrix} C_{3v}IC_{2v} & C_{3v}C_{2(1)}\mathbf{C}_{2v} & C_{3v}C_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(2)}\mathbf{C}_{2v} \\ C_{3v}C_{2(3)}\mathbf{C}_{2v} & C_{3v}C_{2(2)}\mathbf{C}_{2v} & C_{3v}IC_{2v} & C_{3v}C_{2(1)}\mathbf{C}_{2v} \end{pmatrix} \end{aligned} \quad (33)$$

$$\sim \begin{pmatrix} f(1) & f(2) & f(3) & f(4) \\ f(3) & f(4) & f(1) & f(2) \end{pmatrix} = \begin{pmatrix} A & A & B & B \\ B & B & A & A \end{pmatrix} = q_{C_{2(3)}}, \quad (34)$$

which generates the function  $f_{C_{2(3)}} = \{B, B, A, A\}$ , corresponding to the formula 30. Because the operations  $C_{2(3)}$ ,  $C_{2(2)}$ ,  $S_{4(1)}$ , and  $S_{4(1)}^3$  are contained in  $C_{2(3)}\mathbf{C}_{2v}$ , we obtain  $C_{3v}g_i C_{2(3)}\mathbf{C}_{2v} = C_{3v}g_i C_{2(2)}\mathbf{C}_{2v} = C_{3v}g_i S_{4(1)}\mathbf{C}_{2v} = C_{3v}g_i S_{4(1)}^3\mathbf{C}_{2v}$ . Hence, the same function  $\{B, B, A, A\}$  is obtained, i.e.,  $f_{C_{2(3)}} = f_{C_{2(2)}} = f_{S_{4(1)}} = f_{S_{4(1)}^3}$ . It follows that the four formulas listed in the second box of figure 5 are identical with each other when the numbering is omitted.

In a similar way, each representative shown in equation (32) generates the formula at the top of the corresponding box shown in figure 5 (i.e., **26**, **30**, **34**, **38**, **42**, and **46**) so that each box represents an orbit of four formulas. The six representatives (i.e., **26**, **30**, **34**, **38**, **42**, and **46**) express homomeric formulas, which are regarded as expressing a single achiral stereoisomers having a molecular formula  $A^2B^2$ .  $\square$

The formulas collected in figure 5 can be related directly to a multiplication table (figure 6), which is obtained by reordering the elements of figure 2. The following example demonstrates the construction of the reordered multiplication table for  $(\mathbf{C}_{3v} \setminus) \mathbf{T}_d / (\mathbf{C}_{2v})$  (equation (27)).

		$IC_{2v}$	$C_{2(3)}C_{2v}$	$C_{3(1)}C_{2v}$	$C_{3(2)}C_{2v}$	$C_{3(1)}^2C_{2v}$	$C_{3(2)}^2C_{2v}$
		first operation					
		1 2 17 18	4 3 19 20	5 6 13 14	7 8 16 15	9 10 21 22	12 11 23 24
$C_{3v}I$		A	B	A	B	A	B
	1 $I$	1 2 17 18	4 3 19 20	5 6 13 14	7 8 16 15	9 10 21 22	12 11 23 24
	5 $C_{3(1)}$	5 6 13 14	8 7 15 16	9 10 21 22	11 12 24 23	1 2 17 18	4 3 19 20
	9 $C_{3(1)}^2$	9 10 21 22	12 11 23 24	1 2 17 18	3 4 20 19	5 6 13 14	8 7 15 16
	13 $\sigma_{d(1)}$	13 14 5 6	16 15 7 8	17 18 1 2	19 20 4 3	21 22 9 10	24 23 11 12
	17 $\sigma_{d(2)}$	17 18 1 2	20 19 3 4	21 22 9 10	23 24 12 11	13 14 5 6	16 15 7 8
21 $\sigma_{d(3)}$	21 22 9 10	24 23 11 12	13 14 5 6	15 16 8 7	17 18 1 2	20 19 3 4	
$C_{3v}C_{2(1)}$		A	B	B	A	B	A
	2 $C_{2(1)}$	2 1 18 17	3 4 20 19	8 7 15 16	6 5 14 13	11 12 24 23	10 9 22 21
	6 $C_{3(3)}$	6 5 14 13	7 8 16 15	12 11 23 24	10 9 22 21	3 4 20 19	2 1 18 17
	10 $C_{3(4)}^2$	10 9 22 21	11 12 24 23	4 3 19 20	2 1 18 17	7 8 16 15	6 5 14 13
	14 $S_{4(3)}$	14 13 6 5	15 16 8 7	20 19 3 4	18 17 2 1	23 24 12 11	22 21 10 9
	18 $\sigma_{d(4)}$	18 17 2 1	19 20 4 3	24 23 11 12	22 21 10 9	15 16 8 7	14 13 6 5
22 $S_{4(2)}^3$	22 21 10 9	23 24 12 11	16 15 7 8	14 13 6 5	19 20 4 3	18 17 2 1	
$C_{3v}C_{2(3)}$		B	A	B	A	A	B
	4 $C_{2(3)}$	4 3 19 20	1 2 17 18	7 8 16 15	5 6 13 14	10 9 22 21	11 12 24 23
	8 $C_{3(4)}$	8 7 15 16	5 6 13 14	11 12 24 23	9 10 21 22	2 1 18 17	3 4 20 19
	12 $C_{3(2)}^2$	12 11 23 24	9 10 21 22	3 4 20 19	1 2 17 18	6 5 14 13	7 8 16 15
	16 $\sigma_{d(6)}$	16 15 7 8	13 14 5 6	19 20 4 3	17 18 1 2	22 21 10 9	23 24 12 11
	20 $S_{4(1)}^3$	20 19 3 4	17 18 1 2	23 24 12 11	21 22 9 10	14 13 6 5	15 16 8 7
24 $S_{4(2)}$	24 23 11 12	21 22 9 10	15 16 8 7	13 14 5 6	18 17 2 1	19 20 4 3	
$C_{3v}C_{2(2)}$		B	A	A	B	B	A
	3 $C_{2(2)}$	3 4 20 19	2 1 18 17	6 5 14 13	8 7 15 16	12 11 23 24	9 10 21 22
	7 $C_{3(2)}$	7 8 16 15	6 5 14 13	10 9 22 21	12 11 23 24	4 3 19 20	1 2 17 18
	11 $C_{3(3)}^2$	11 12 24 23	10 9 22 21	2 1 18 17	4 3 19 20	8 7 15 16	5 6 13 14
	15 $S_{4(3)}^3$	15 16 8 7	14 13 6 5	18 17 2 1	20 19 3 4	24 23 11 12	21 22 9 10
	19 $S_{4(1)}$	19 20 4 3	18 17 2 1	22 21 10 9	24 23 11 12	16 15 7 8	13 14 5 6
23 $\sigma_{d(5)}$	23 24 12 11	22 21 10 9	14 13 6 5	16 15 7 8	20 19 3 4	17 18 1 2	
cf. Fig. 5		<b>26 27 28 29</b>	<b>30 31 32 33</b>	<b>34 35 36 37</b>	<b>38 39 40 41</b>	<b>42 43 44 45</b>	<b>46 47 48 49</b>

Figure 6. Reordered multiplication table for the double coset representation  $(C_{3v})\backslash T_d(/C_{2v})$ .

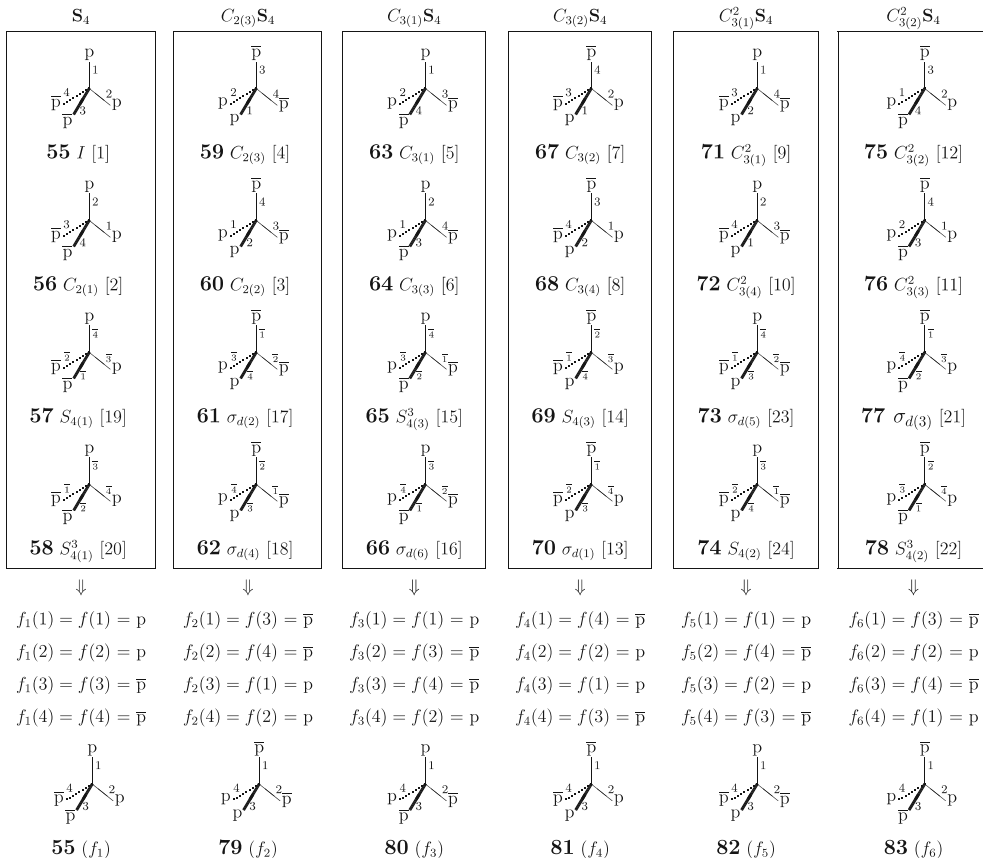


Figure 7. Tetrahedral formulas generated in accord with the double coset representation  $(C_{3v} \setminus) T_d / (S_4)_{[R]}$ .

**Example 5** [Reordered multiplication table for  $(C_{3v} \setminus) T_d / (C_{2v})$ ]. The construction of the double coset representation  $(C_{3v} \setminus) T_d / (C_{2v})$  (equation (27)) can be regarded as the reordering of the multiplication table shown in figure 2. By reordering the rows of figure 2 in accord with the right coset decomposition of  $T_d$  by  $C_{3v}$  (equation (8)) and by reordering the columns of figure 2 in accord with the left coset decomposition of  $T_d$  by  $C_{2v}$  (equation (32)), we can obtain a reordered multiplication table, as shown in Figure 6.

The four blocks of each column represent the corresponding right cosets, each of which contains a half part of the corresponding double coset (equation (24)) so as to be specified by the symbol A or B, as shown at the top of each block. Thereby, the corresponding function  $f_g$  (via a set of double cosets) is obtained by collecting a permuted set of symbols A, A, B, and B from the tops of the blocks. As a result, each column corresponds to one of the 24 formulas (26–49), as shown in the bottom of figure 6. For example, the column #4 (i.e.,

$C_{2(3)}$ ), which corresponds to equations (33) and (34), is specified by the function  $f_{C_{2(3)}} = \{B, B, A, A\}$  so that the column is linked to the formula 30, as shown in the bottom of the column.  $\square$

2.3. Conjugate subgroups for homomers of stereoisomers

According to theorem 1, a permutation  $q_{\tilde{g}_j}^{[R]}$  can be selected as a representative selected from each of the sets  $\{q_g^{[R]} | g \in \tilde{g}_j \mathbf{K}\}$  ( $j = 1, 2, \dots, s$ ). The permutations ( $q_{\tilde{g}_j}^{[R]}$ ) correspond to  $s$  functions, i.e.,  $f_{\tilde{g}_1}, f_{\tilde{g}_2}, \dots, f_{\tilde{g}_j}, \dots, f_{\tilde{g}_s}$ , where  $\tilde{g}_j$  represents the representatives appearing in equation (28). Note that the functions  $f_{\tilde{g}_j}$  ( $i = 1, 2, \dots, s$ ) indicate homomers, which represent a single stereoisomer (an achiral stereoisomer or an enantiomeric pair of chiral stereoisomers). Because of equation (21), each function is represented by  $r$  ( $= |\mathbf{G}|/|\mathbf{H}|$ ) components, i.e.,  $f_{\tilde{g}_j} = \{f(t_{g_1}^{[R]}), f(t_{g_2}^{[R]}), \dots, f(t_{g_r}^{[R]})\}$  for  $g = \tilde{g}_j$  ( $j = 1, 2, \dots, s(= |\mathbf{G}|/|\mathbf{K}|)$ ) appearing in equation (28). The numbering of the components is changed so as to give a renumbered function  $f_j$ , the components of which are represented by  $f_j(1) = f(t_{g_1}^{[R]})$ ,  $f_j(2) = f(t_{g_2}^{[R]})$ ,  $\dots$ ,  $f_j(r) = f(t_{g_r}^{[R]})$ . Thereby, we obtain

$$f_j = \{f_j(1), f_j(2), \dots, f_j(r)\} = \{f(t_{g_1}^{[R]}), f(t_{g_2}^{[R]}), \dots, f(t_{g_r}^{[R]})\} \tag{35}$$

for  $g = \tilde{g}_j$  ( $j = 1, 2, \dots, s(= |\mathbf{G}|/|\mathbf{K}|)$ ) appearing in equation (28).

The procedure of renumbering (equation (35)) is ascribed to  $(\mathbf{H}g_i \tilde{g}_j \mathbf{K})\tilde{g}_j^{-1}$ , which is equal to  $\mathbf{H}g_i(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  because of the associative law. As a result, the renumbering means that the group  $\mathbf{K}$  in the double coset  $\mathbf{H}g_i \mathbf{K}$  is replaced by a conjugate subgroup  $\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$  so as to select another double coset  $\mathbf{H}g_i(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  for each  $j$  ( $= 1, 2, \dots, s(= |\mathbf{G}|/|\mathbf{K}|)$ ). Hence, we obtain a set of double cosets as follows:

$$\mathbf{H} \backslash \mathbf{G} / \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1} = \underbrace{\{\mathbf{H}g_1(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})\}}_{f_j(1)}, \underbrace{\{\mathbf{H}g_2(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})\}}_{f_j(2)}, \dots, \underbrace{\{\mathbf{H}g_r(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})\}}_{f_j(r)}, \tag{36}$$

where  $\mathbf{H}g_i(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  in equation (36) and  $\mathbf{H}g_i g_j \mathbf{K}$  (cf. equations (15) and (17)) are equalized to be renumbered as designated in equation (35). On the same line as equation (18), we obtain the following permutation:

$$\begin{aligned} g &\sim \begin{pmatrix} \mathbf{H}g_1(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) & \mathbf{H}g_2(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) & \dots & \mathbf{H}g_r(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) \\ \mathbf{H}g_{1g}(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) & \mathbf{H}g_{2g}(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) & \dots & \mathbf{H}g_{rg}(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) \end{pmatrix} \\ &= \begin{pmatrix} f_j(1) & f_j(2) & \dots & f_j(r) \\ f_j(t_{g_1}^{[R]}) & f_j(t_{g_2}^{[R]}) & \dots & f_j(t_{g_r}^{[R]}) \end{pmatrix} = q_g^{(j)[R]}, \end{aligned} \tag{37}$$

where  $g$  runs over  $\mathbf{G}$ . Each double coset appearing in equation (37) corresponds to one of the right cosets in one-to-one fashion. When  $g$  runs over the point group  $\mathbf{G}$ , we obtain the following representation of the group  $\mathbf{G}$ :

$$(\mathbf{H} \setminus) \mathbf{G} / (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) = \{q_g^{(j)[R]} \mid \forall g \in \mathbf{G}\}, \tag{38}$$

which is transitive and homomorphic to the right coset representation shown in equation (4), i.e.,  $(\mathbf{H} \setminus) \mathbf{G}$ .

The component  $\mathbf{H}g_i \tilde{g}_j \mathbf{K}$ , which is generated from  $\mathbf{H}g_i \mathbf{K}$  by the action of  $\tilde{g}_j$  (equation (19)), is further transformed into  $\mathbf{H}g_i \tilde{g}_j (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$ , where the  $\mathbf{K}$  of the  $\mathbf{H}g_i \tilde{g}_j \mathbf{K}$  is replaced by the conjugate subgroup  $\tilde{g}_j^{-1} \mathbf{K} \tilde{g}_j$ . On the other hand, the component  $\mathbf{H}g_i (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$ , which is generated from  $\mathbf{H}g_i \mathbf{K}$  by the process  $\mathbf{K} \rightarrow \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$ , is transformed by the action of  $\tilde{g}_j$  (equation (38)) into the same  $\mathbf{H}g_i \tilde{g}_j (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  as above. The two routes are summarized so as to generate the following scheme:

$$\begin{array}{ccc}
 \mathbf{K}g_i \mathbf{K} & \xrightarrow[\text{equation (19)}]{\tilde{g}_j} & \mathbf{H}g_i \tilde{g}_j \mathbf{K} \\
 \mathbf{K} \rightarrow \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1} \downarrow & & \downarrow \mathbf{K} \rightarrow \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1} \\
 \mathbf{H}g_i (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}) & \xrightarrow[\text{equation (38)}]{\tilde{g}_j} & \mathbf{H}g_i \tilde{g}_j (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})
 \end{array} \tag{39}$$

This scheme means that  $s$  ( $= |\mathbf{G}|/|\mathbf{K}|$ ) double coset representations ( $j = 1, 2, \dots, s$  in equation (37)) move concurrently in agreement with the same right coset representation  $(\mathbf{H} \setminus) \mathbf{G}$  (equation (4)), as summarized in the following theorem.

**Theorem 2. 1.** The  $s$  ( $= |\mathbf{G}|/|\mathbf{K}|$ ) homomers specified by  $\{q_g^{[R]} \mid g \in \tilde{g}_j \mathbf{K}\}$  ( $j = 1, 2, \dots, s$ ) in theorem 1 are alternatively expressed as  $s$  sets of double cosets, i.e.,  $\mathbf{H} \setminus \mathbf{G} / \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$  ( $j = 1, 2, \dots, s$  in equation (36)), which is based on the subgroups  $\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$  conjugate to  $\mathbf{K}$ .

2. Each set of double cosets  $\mathbf{H} \setminus \mathbf{G} / \tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$  ( $g_j$  is tentatively fixed) is permuted in terms of the double coset representation (equation (37)), which is in accord with the same right coset representation  $(\mathbf{H} \setminus) \mathbf{G}$  (equation (4)). □

Theorem 1(2) indicates that the function  $f_1$  is transformed into  $|\mathbf{G}|$  functions but fixed under the action of  $\mathbf{K}$ , where the number of fixed functions is equal to  $|\mathbf{K}|$ . On the same line, the function  $f_j$  is transformed into  $|\mathbf{G}|$  functions but fixed under the action of  $\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$ , because the component  $\mathbf{H}g_i g (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  is equal to the original one  $\mathbf{H}g_i (\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  if  $g$  is contained in the subgroup  $\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}$ . It follows that the number of fixed functions is equal to  $|\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1}| = |\mathbf{K}|$  for each  $j$ . When  $j$  runs from 1 to  $s$  ( $= |\mathbf{G}|/|\mathbf{K}|$ ), the total number of fixed functions for  $f_j$  is calculated to be  $|\mathbf{K}| \times s = |\mathbf{G}|$ . It should be noted that the functions  $f_j$  ( $j = 1, 2, \dots, s$ ) are so equivalent as to represent a derivative of  $\mathbf{K}$ -symmetry on



the basis of the skeleton governed by  $(\mathbf{H} \setminus) \mathbf{G}$ . In other words, theorem 2 indicates that the set  $(\mathbf{F})$  represented by

$$\mathbf{F} = \{f_1, f_2, \dots, f_s\}, \quad (40)$$

where the functions  $f_j$  are shown in equation (35) ( $j = 1, 2, \dots, s$ ) and  $s = |\mathbf{G}|/|\mathbf{K}|$ , represents a equivalence class (orbit). The orbit  $\mathbf{F}$  is regarded as a homomer set indicating a single achiral derivative of  $\mathbf{K}$ -symmetry or a single enantiomeric pair of chiral derivatives of  $\mathbf{K}$ -symmetry on the basis of the skeleton governed by  $(\mathbf{H} \setminus) \mathbf{G}$ . This is summarized to give a theorem:

**Theorem 3.** When the set  $\mathbf{F}$  of functions shown in equation (40) represent a derivative of  $\mathbf{K}$ -symmetry on the basis of the skeleton governed by  $(\mathbf{H} \setminus) \mathbf{G}$ , the total number of fixed functions under the action of  $\mathbf{G}$  is equal to  $|\mathbf{G}|$ .  $\square$

It should be noted that a derivative of  $\mathbf{K}$ -symmetry means a single achiral derivative if  $\mathbf{K}$  is an achiral group, or a single pair of enantiomers if  $\mathbf{K}$  is a chiral group.

**Example 6** [Renumbered formulas]. As shown in the bottom part of figure 5, the positions of the formulas **26** (reference), **30**, **34**, **38**, **42**, and **46** are renumbered by following equation (35) so that we obtain the corresponding renumbered formulas **26** (reference), **50–54**.

In accord with the representative due to equation (32), the subgroups conjugate to  $\mathbf{C}_{2v}$  are calculated as follows.

$$\mathbf{C}_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{\sigma_{d(2)}}_{17}, \underbrace{\sigma_{d(4)}}_{18} \right\}, \quad (41)$$

$$C_{2(3)} \mathbf{C}_{2v} C_{2(3)}^{-1} = \mathbf{C}_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{\sigma_{d(2)}}_{17}, \underbrace{\sigma_{d(4)}}_{18} \right\}, \quad (42)$$

$$C_{3(1)} \mathbf{C}_{2v} C_{3(1)}^{-1} = \mathbf{C}'_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(2)}}_3, \underbrace{\sigma_{d(1)}}_{21}, \underbrace{\sigma_{d(3)}}_{23} \right\}, \quad (43)$$

$$C_{3(2)} \mathbf{C}_{2v} C_{3(2)}^{-1} = \mathbf{C}'_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(2)}}_3, \underbrace{\sigma_{d(1)}}_{21}, \underbrace{\sigma_{d(3)}}_{23} \right\}, \quad (44)$$

$$C_{3(1)}^2 \mathbf{C}_{2v} C_{3(1)}^{-2} = \mathbf{C}''_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(3)}}_4, \underbrace{\sigma_{d(1)}}_{13}, \underbrace{\sigma_{d(3)}}_{16} \right\}, \quad (45)$$

$$C_{3(2)}^2 \mathbf{C}_{2v} C_{3(2)}^{-2} = \mathbf{C}''_{2v} = \left\{ \underbrace{I}_1, \underbrace{C_{2(3)}}_4, \underbrace{\sigma_{d(1)}}_{13}, \underbrace{\sigma_{d(3)}}_{16} \right\}. \quad (46)$$

The reference function  $f$  obtained by using the set of double cosets  $\mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}_{2v}$  (equation (23)) is adopted as  $f_1$ , i.e.,  $f_1(1) = \mathbf{A}$ ,  $f_1(2) = \mathbf{A}$ ,  $f_1(3) = \mathbf{B}$ , and  $f_1(4) = \mathbf{B}$ , which corresponds to **26**. The function  $f_1$  generates 24 (=

$|\mathbf{T}_d|/|\mathbf{C}_{2v}|$ ) formulas shown in figure 5 on the action of the permutations contained in the coset representation  $(\mathbf{C}_{3v} \setminus) \mathbf{T}_d$  (Figure 3).

The same set of double cosets  $\mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}_{2v}$  is regarded as  $\mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}_{2(3)} \mathbf{C}_{2v} \mathbf{C}_{2(3)}^{-1}$ , which gives the function  $f_2$  corresponding to **50**, i.e.,  $f_2(1) = \mathbf{B}$ ,  $f_2(2) = \mathbf{B}$ ,  $f_2(3) = \mathbf{A}$ , and  $f_2(4) = \mathbf{A}$ .

By combining  $\mathbf{C}_{3v} \setminus \mathbf{T}_d$  (equation (9)) with  $\mathbf{C}_{3(1)} \mathbf{C}_{2v} \mathbf{C}_{3(1)}^{-1}$  ( $= \mathbf{C}'_{2v}$  shown in equation (43)), we obtain another set of double cosets  $\mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}'_{2v}$ , i.e.,

$$\begin{aligned} \mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}_{3(1)} \mathbf{C}_{2v} \mathbf{C}_{3(1)}^{-1} &= \mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}'_{2v} \\ &= \{ \mathbf{C}_{3v} \mathbf{I} \mathbf{C}'_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(1)} \mathbf{C}'_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(3)} \mathbf{C}'_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(2)} \mathbf{C}'_{2v} \} \end{aligned} \tag{47}$$

$$= \left\{ \begin{array}{c} \left[ \begin{array}{c} \left\{ \begin{array}{c} 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \end{array} \right\} \\ 1 \\ \left\{ \begin{array}{c} 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \end{array} \right\} \\ 4 \\ f_3(1) = \mathbf{A} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \end{array} \right\} \\ 2 \\ \left\{ \begin{array}{c} 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \end{array} \right\} \\ 3 \\ f_3(2) = \mathbf{B} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \end{array} \right\} \\ 3 \\ \left\{ \begin{array}{c} 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \end{array} \right\} \\ 2 \\ f_3(3) = \mathbf{B} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \end{array} \right\} \\ 4 \\ \left\{ \begin{array}{c} 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \end{array} \right\} \\ 1 \\ f_3(4) = \mathbf{A} \end{array} \right] \end{array} \right\} . \tag{48}$$

This set gives the function  $f_3$  corresponding to **51**, i.e.,  $f_3(1) = \mathbf{A}$ ,  $f_3(2) = \mathbf{B}$ ,  $f_3(3) = \mathbf{B}$ , and  $f_3(4) = \mathbf{A}$ . By taking equation (44) into consideration, the same set of double cosets  $\mathbf{C}_{3v} \setminus \mathbf{T} / \mathbf{C}'_{2v}$  (equation (48)) is regarded as  $\mathbf{C}_{3v} \setminus \mathbf{T} / \mathbf{C}_{3(2)} \mathbf{C}_{2v} \mathbf{C}_{3(2)}^{-1}$ , which gives the function  $f_4$  corresponding to **52**, i.e.,  $f_4(1) = \mathbf{B}$ ,  $f_4(2) = \mathbf{B}$ ,  $f_4(3) = \mathbf{A}$ , and  $f_4(4) = \mathbf{A}$ .

By combining  $\mathbf{C}_{3v} \setminus \mathbf{T}_d$  (equation (9)) with  $\mathbf{C}_{3(1)}^2 \mathbf{C}_{2v} \mathbf{C}_{3(1)}^{-2}$  ( $= \mathbf{C}''_{2v}$  shown in equation (45)), we obtain an additional set of double cosets  $\mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}''_{2v}$ , i.e.,

$$\begin{aligned} \mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}_{3(1)}^2 \mathbf{C}_{2v} \mathbf{C}_{3(1)}^{-2} &= \mathbf{C}_{3v} \setminus \mathbf{T}_d / \mathbf{C}''_{2v} \\ &= \{ \mathbf{C}_{3v} \mathbf{I} \mathbf{C}''_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(1)} \mathbf{C}''_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(3)} \mathbf{C}''_{2v}, \mathbf{C}_{3v} \mathbf{C}_{2(2)} \mathbf{C}''_{2v} \} \end{aligned} \tag{49}$$

$$= \left\{ \begin{array}{c} \left[ \begin{array}{c} \left\{ \begin{array}{c} 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \end{array} \right\} \\ 1 \\ \left\{ \begin{array}{c} 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \end{array} \right\} \\ 3 \\ f_5(1) = \mathbf{A} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \end{array} \right\} \\ 2 \\ \left\{ \begin{array}{c} 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \end{array} \right\} \\ 4 \\ f_5(2) = \mathbf{B} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \end{array} \right\} \\ 3 \\ \left\{ \begin{array}{c} 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \end{array} \right\} \\ 2 \\ f_5(3) = \mathbf{A} \end{array} \right] , \left[ \begin{array}{c} \left\{ \begin{array}{c} 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \end{array} \right\} \\ 4 \\ \left\{ \begin{array}{c} 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \end{array} \right\} \\ 2 \\ f_5(4) = \mathbf{B} \end{array} \right] \end{array} \right\} . \tag{50}$$

This set gives the function  $f_5$  corresponding to **53**, i.e.,  $f_5(1) = \mathbf{A}$ ,  $f_5(2) = \mathbf{B}$ ,  $f_5(3) = \mathbf{A}$ , and  $f_5(4) = \mathbf{B}$ . By taking equation (46) into consideration, the same set of double cosets  $\mathbf{C}_{3v} \backslash \mathbf{T} / \mathbf{C}_{2v}''$  (equation (48)) is regarded as  $\mathbf{C}_{3v} \backslash \mathbf{T} / \mathbf{C}_{3(2)}^2 \mathbf{C}_{2v} \mathbf{C}_{3(2)}^{-2}$ , which gives the function  $f_6$  corresponding to **54**, i.e.,  $f_6(1) = \mathbf{B}$ ,  $f_6(2) = \mathbf{A}$ ,  $f_6(3) = \mathbf{B}$ , and  $f_6(4) = \mathbf{A}$ .

As found in the preceding paragraphs, each function  $f_j$  ( $j = 1, 2, \dots, 6 = |\mathbf{T}_d|/|\mathbf{C}_{2v}|$ ) generates 24 ( $= |\mathbf{T}_d|$ ) formulas (cf. figure 5 for  $f_1$ ), among which four ( $= |\mathbf{C}_{2v}|$ ) formulas are fixed under the action of  $\tilde{g}_j \mathbf{C}_{2v} \tilde{g}_j^{-1}$ , where  $\tilde{g}_j$  is selected from the representative appearing in equation (32), i.e.,  $\{I, C_{2(3)}, C_{3(1)}, C_{3(2)}, C_{3(1)}^2, C_{3(2)}^2\}$ . Hence, total number of fixed formulas is determined to be  $|\mathbf{C}_{2v}| \times |\mathbf{T}_d|/|\mathbf{C}_{2v}| = 4 \times (24/4) = 24$ , which is in agreement with theorem 3. Note that  $|\tilde{g}_j \mathbf{C}_{2v} \tilde{g}_j^{-1}| = |\mathbf{C}_{2v}| = 4$ .  $\square$

### 3. Sphericities

#### 3.1. Sphericities of double cosets

When  $\mathbf{K}$  is achiral, there exists the maximum chiral subgroup  $\mathbf{K}'$ , which contains all of the proper rotations of  $\mathbf{K}$ , satisfying  $|\mathbf{K}| = 2|\mathbf{K}'|$ . The subgroup  $\mathbf{K}'$  generates a coset decomposition as follows:

$$\mathbf{K} = \mathbf{K}' + \sigma \mathbf{K}', \quad (51)$$

where the  $\sigma$  operation is an improper rotation which satisfies  $\sigma\sigma \in \mathbf{K}'$ . Then, each double coset  $\mathbf{H}g_i\mathbf{K}$  shown in equation (15) is partitioned into two parts at most as follows:

$$\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_i\mathbf{K}' \cup \mathbf{H}g_i\sigma\mathbf{K}', \quad (52)$$

where  $\mathbf{H}g_i\mathbf{K}'$  may be equal or not equal to  $\mathbf{H}g_i\sigma\mathbf{K}'$ . On the same line as equation (15), the following set of double cosets are obtained:

$$\mathbf{H} \backslash \mathbf{G} / \mathbf{K}' = \underbrace{\{\mathbf{H}g_1\mathbf{K}'\}}_{f'(1)}, \underbrace{\{\mathbf{H}g_2\mathbf{K}'\}}_{f'(2)}, \dots, \underbrace{\{\mathbf{H}g_i\mathbf{K}'\}}_{f'(i)}, \dots, \underbrace{\{\mathbf{H}g_r\mathbf{K}'\}}_{f'(r)}, \quad (53)$$

where  $f'$  ( $f'(i)$  for  $i = 1, 2, \dots, r$ ) is a function for numbering or labeling the resulting double cosets. If two or more double cosets are identical, they are numbered or labeled by the same value of the function but they are distinguished in accord with the numbering of the original right cosets.

By starting from the right coset representation shown in equation (4) (i.e.,  $(\mathbf{H} \backslash) \mathbf{G}$ ), the following permutation is obtained:

$$g \stackrel{[R]}{\sim} \left( \mathbf{H}g_1\mathbf{K}' \ \mathbf{H}g_2\mathbf{K}' \ \cdots \ \mathbf{H}g_i\mathbf{K}' \ \cdots \ \mathbf{H}g_r\mathbf{K}' \right) \quad (54)$$

$$\sim \left( f'(1) \ f'(2) \ \cdots \ f'(i) \ \cdots \ f'(r) \right) \\ \sim \left( f'(t_{g1}^{[R]}) \ f'(t_{g2}^{[R]}) \ \cdots \ f'(t_{gi}^{[R]}) \ \cdots \ f'(t_{gr}^{[R]}) \right) = q_g^{[R]}. \quad (55)$$

When  $g$  runs over the point group  $\mathbf{G}$ , we obtain the following representation of the group  $\mathbf{G}$ :

$$(\mathbf{H} \setminus) \mathbf{G} (/ \mathbf{K}') = \{q_g^{[R]} | \forall g \in \mathbf{G}\}, \quad (56)$$

which is transitive and homomorphic to the right coset representation shown in equation (4), i.e.,  $(\mathbf{H} \setminus) \mathbf{G}$ .

When  $\mathbf{K}$  is achiral or chiral and the supergroup  $\mathbf{G}$  is achiral, there exist three cases in terms of equation (52):

1. Homospheric case: The double coset  $\mathbf{H}g_i\mathbf{K}$  is defined to be *homospheric* if  $\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_i\mathbf{K}'$  for an achiral group  $\mathbf{K}$  and its maximum chiral subgroup  $\mathbf{K}'$ .
2. Enantiospheric case: The double coset  $\mathbf{H}g_i\mathbf{K}$  is defined to be *enantiospheric* if  $\mathbf{H}g_i\mathbf{K} \neq \mathbf{H}g_i\mathbf{K}'$  for an achiral group  $\mathbf{K}$  and its maximum chiral subgroup  $\mathbf{K}'$ .
3. Hemispheric case: The double coset  $\mathbf{H}g_i\mathbf{K}$  is defined to be *hemispheric* if  $\mathbf{K}$  represents a chiral subgroup.

The target of the present paper is to find functions  $f$  suitable to the sphericities of double cosets. As for homospheric and enantiospheric cases, in particular, our target is to find a common function to the two sets of double cosets, i.e.,  $\mathbf{H} \setminus \mathbf{G} / \mathbf{K}$  (equation (15)) and  $\mathbf{H} \setminus \mathbf{G} / \mathbf{K}'$  (equation (53)). In other words, we shall find a way to equalize the function  $f$  for  $\mathbf{H} \setminus \mathbf{G} / \mathbf{K}$  (equation (15)) and the function  $f'$  for  $\mathbf{H} \setminus \mathbf{G} / \mathbf{K}'$  (equation (53)).

### 3.1.1. Homospheric double cosets

When the relationship  $\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_i\mathbf{K}'$  holds true for the homospheric double coset  $\mathbf{H}g_i\mathbf{K}$ , equation (51) shows that  $\mathbf{H}g_i\mathbf{K}' \cup \mathbf{H}g_i\sigma\mathbf{K}' = \mathbf{H}g_i\mathbf{K}'$ . This means that  $\mathbf{H}g_i\mathbf{K}' = \mathbf{H}g_i\sigma\mathbf{K}'$ , because  $\mathbf{H}g_i\sigma\mathbf{K}'$  is not vacant. Because of  $\mathbf{H}g_i\mathbf{K}' = \mathbf{H}g_i\sigma\mathbf{K}'$ , the two double cosets due to the achiral  $\mathbf{K}$  are equal to each other, i.e.,  $\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_i\sigma\mathbf{K}$ . It follows that  $f(i)$  and  $f(\bar{t}_{\sigma_i})$  shown in equation (18) are equal to each other and, at the same time,  $f'(i)$  and  $f'(\bar{t}_{\sigma_i})$  shown in equation (55) are equal to each other. Because the pairs  $f(i)/f(\bar{t}_{\sigma_i})$  and  $f'(i)/f'(\bar{t}_{\sigma_i})$  indicate enantiomeric pairs, respectively, the present case is regarded as a self-enantiomeric one. Hence, in order that the functions  $f(i)$  and  $f'(i)$  are labeled commonly, they should allow the occupation of an achiral object (chemically speaking, an

achiral ligand) and by no means the occupation of a chiral object (a chiral ligand). This mode of occupation is called “chirality fittingness (CF)”, which has been discussed in different contexts such as “chirality fittingness of a homospheric orbit” [11] and “chirality fittingness of a homospheric cycle” [9]. In the present case, the CFs is concerned with a homospheric double coset so that a homospheric double coset exhibits CFs in which only an achiral ligand is allowed.

Obviously, the same conclusion holds true if the homospheric double cosets  $\mathbf{H}g_i(g_j\mathbf{K}g_j^{-1})$  are considered in place of the homospheric double coset  $\mathbf{H}g_i\mathbf{K}$  described above.

**Example 7** [Homospheric double coset for  $(\mathbf{C}_{3v}\backslash)\mathbf{T}_d(/C_{2v})$ ]. This is a continuation of example 3. The homosphericities of double cosets contained in  $(\mathbf{C}_{3v}\backslash)\mathbf{T}_d(/C_{2v})$  are tested here. By starting from  $\mathbf{C}_{3v}\backslash\mathbf{T}_d$  shown in equation (9) and a subgroup  $\mathbf{C}_2$ :

$$\mathbf{C}_2 = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2 \right\} \quad (57)$$

let us consider a set of double cosets according to equation (15) as follows:

$$\begin{aligned} \mathbf{C}_{3v}\backslash\mathbf{T}_d/C_2 &= \{ \mathbf{C}_{3v}I\mathbf{C}_2, \mathbf{C}_{3v}C_{2(1)}\mathbf{C}_2, \mathbf{C}_{3v}C_{2(3)}\mathbf{C}_2, \mathbf{C}_{3v}C_{2(2)}\mathbf{C}_2 \} \quad (58) \\ &= \left[ \begin{array}{cccc} \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_1 \\ \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_2 \end{array} \right\}, & \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_2 \\ \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_1 \end{array} \right\}, & \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \\ \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \end{array} \right\}, & \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \\ \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \end{array} \right\} \\ \underbrace{f'(1) = A, \bar{A}} & \underbrace{f'(2) = A, \bar{A}} & \underbrace{f'(3) = B, \bar{B}} & \underbrace{f'(4) = B, \bar{B}} \end{array} \right] \quad (59) \end{aligned}$$

This is identical with equation (24) so that we obtain  $\mathbf{C}_{3v}\mathbf{C}_{2v} = \mathbf{C}_{3v}\mathbf{C}_2$ ,  $\mathbf{C}_{3v}C_{2(1)}\mathbf{C}_{2v} = \mathbf{C}_{3v}C_{2(1)}\mathbf{C}_2\mathbf{C}_{3v}C_{2(3)}\mathbf{C}_{2v} = \mathbf{C}_{3v}C_{2(3)}\mathbf{C}_2$ , and  $\mathbf{C}_{3v}C_{2(2)}\mathbf{C}_{2v} = \mathbf{C}_{3v}C_{2(2)}\mathbf{C}_2$ . Hence, the double cosets  $\mathbf{C}_{3v}\mathbf{C}_{2v}$ ,  $\mathbf{C}_{3v}C_{2(1)}\mathbf{C}_{2v}$ ,  $\mathbf{C}_{3v}C_{2(3)}\mathbf{C}_{2v}$ , and  $\mathbf{C}_{3v}C_{2(2)}\mathbf{C}_{2v}$  are homospheric. The functions such as  $f'(1) = A$  (or  $\bar{A}$ ) represent self-enantiomeric ligands. Thus, an achiral ligand  $A$  and its hypothetical mirror image  $\bar{A}$  are superposable, i.e.,  $A = \bar{A}$ .  $\square$

### 3.1.2. Enantiospheric double cosets

When the relationship  $\mathbf{H}g_i\mathbf{K} \neq \mathbf{H}g_i\mathbf{K}'$  holds true for the enantiospheric double coset  $\mathbf{H}g_i\mathbf{K}$ , equation (51) shows that  $\mathbf{H}g_i\mathbf{K}' \neq \mathbf{H}g_i\sigma\mathbf{K}'$ . In other words, equation (52) can be rewritten as follows:

$$\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_i\mathbf{K}' + \mathbf{H}g_i\sigma\mathbf{K}'. \quad (60)$$

Because  $\mathbf{H}g_i\mathbf{K}'$  and  $\mathbf{H}g_i\sigma\mathbf{K}'$  are different, the set of double coset represented by equation (53) contains  $\mathbf{H}g_i\mathbf{K}'$  and  $\mathbf{H}g_{i'}\mathbf{K}'$  as distinct double cosets, where we place  $g_{i'} = g_i\sigma$ . It should be noted that the pair  $\mathbf{H}g_i\mathbf{K}'$  and  $\mathbf{H}g_i\sigma\mathbf{K}'$  is considered to show mirror images of each other.

Let us consider  $\mathbf{H}g_i\sigma\mathbf{K}$  that corresponds to  $\mathbf{H}g_i\sigma\mathbf{K}'$  as the  $\mathbf{H}g_i\mathbf{K}$  corresponds to  $\mathbf{H}g_i\mathbf{K}'$ . Then, equation (60) gives:

$$\mathbf{H}g_i\sigma\mathbf{K} = \mathbf{H}g_i\sigma\mathbf{K}' + \mathbf{H}g_i\sigma\sigma\mathbf{K}' = \mathbf{H}g_i\sigma\mathbf{K}' + \mathbf{H}g_i\mathbf{K}' = \mathbf{H}g_i\mathbf{K}. \quad (61)$$

Because we place  $g_{i'} = g_i\sigma$ , equation (61) shows that  $\mathbf{H}g_i\mathbf{K} = \mathbf{H}g_{i'}\mathbf{K}$ . In accord with the pairwise appearance of  $\mathbf{H}g_i\mathbf{K}'$  and  $\mathbf{H}g_{i'}\mathbf{K}'$  as distinct double cosets ( $f'(i) \neq f'(i')$ ), the double cosets  $\mathbf{H}g_i\mathbf{K}$  and  $\mathbf{H}g_{i'}\mathbf{K}$  appear *pairwise*, although their labels become degenerate so as to be equal to each other (i.e.,  $f(i) = f(i')$ ) under  $\mathbf{K}$ . These results can be summarized as the following scheme:

Scheme I

$$\begin{array}{ccc} \mathbf{H}g_i\mathbf{K} = \mathbf{H}g_{i'}\mathbf{K}(= \mathbf{H}g_i\sigma\mathbf{K}) \cdots \mathbf{H}\backslash\mathbf{G}/\mathbf{K} & \text{(equation (15))} \\ f(i) & f(i') \\ \Downarrow & \Downarrow \\ \mathbf{H}g_i\mathbf{K}' \neq \mathbf{H}g_{i'}\mathbf{K}'(= \mathbf{H}g_i\sigma\mathbf{K}') \cdots \mathbf{H}\backslash\mathbf{G}/\mathbf{K}' & \text{(equation (53))} \\ f'(i) & f'(i') \end{array}$$

It should be emphasized again that the set of double cosets  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}$  (equation (15)) contains the pair of  $\mathbf{H}g_i\mathbf{K}$  and  $\mathbf{H}g_{i'}\mathbf{K}(= \mathbf{H}g_i\sigma\mathbf{K})$ , which are equal to each other, i.e.,  $f(i) = f(i')$ . However, the corresponding pair of  $\mathbf{H}g_i\mathbf{K}'$  and  $\mathbf{H}g_{i'}\mathbf{K}'$  contained in the set of double coset  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}'$  (equation (53)) indicates different double cosets so as to exhibit  $f'(i) \neq f'(i')$ . In other words, the  $i$ th double coset  $\mathbf{H}g_i\mathbf{K}$  and the  $i'$ th double coset  $\mathbf{H}g_{i'}\mathbf{K}$ , although they are equal under  $\mathbf{K}$ , correspond to  $\mathbf{H}g_i\mathbf{K}'$  ( $f'(i)$ ) and  $\mathbf{H}g_{i'}\mathbf{K}'$  ( $f'(i')$ ), respectively.

By operating a proper rotation  $g$  on the whole of scheme I, the scheme is converted into the following scheme:

Scheme II

$$\begin{array}{ccc} \mathbf{H}g_i g\mathbf{K} = \mathbf{H}g_{i'} g\mathbf{K}(= \mathbf{H}g_i\sigma g\mathbf{K}) \cdots \mathbf{H}\backslash\mathbf{G}/\mathbf{K} & \text{(equation (15))} \\ f(t_{gi}) & f(t_{gi'}) \\ \Downarrow & \Downarrow \\ \mathbf{H}g_i g\mathbf{K}' \neq \mathbf{H}g_{i'} g\mathbf{K}'(= \mathbf{H}g_i\sigma g\mathbf{K}') \cdots \mathbf{H}\backslash\mathbf{G}/\mathbf{K}'. & \text{(equation (53)).} \\ f'(t_{gi}) & f'(t_{gi'}) \end{array}$$

Because  $\sigma g$  is an improper rotation, we obtain  $\mathbf{H}g_i g\mathbf{K}' \neq \mathbf{H}g_i\sigma g\mathbf{K}' = \mathbf{H}g_{i'} g\mathbf{K}'$ . The comparison between schemes I and II shows that the nature of the pair

$g_i/g_{i'}$  (i.e., proper/improper or improper/proper) for scheme I remain unchanged on the action of  $g$  so as to be equal to the nature of the pair  $g_i g/g_{i'} g$  (i.e., proper/improper or improper/proper) for scheme II. In particular, when we select  $g (\in \mathbf{K}')$ , the double cosets contained in scheme II are calculated as follows:  $\mathbf{H}g_i g \mathbf{K}' = \mathbf{H}g_i \mathbf{K}'$  and  $\mathbf{H}g_{i'} g \mathbf{K}' = \mathbf{H}g_{i'} \mathbf{K}' (= \mathbf{H}g_i \sigma \mathbf{K}')$ . It follows that the double coset  $\mathbf{H}g_i \mathbf{K}'$  contained in  $\mathbf{H}g_i \mathbf{K}$  is not mixed with the double coset  $\mathbf{H}g_{i'} \mathbf{K}'$  contained in  $\mathbf{H}g_{i'} \mathbf{K}$  on the action of a proper rotation  $g$ .

On the other hand, by operating an improper rotation  $\sigma g$  on the whole of scheme I, the scheme is converted into the following scheme:

$$\begin{array}{ccc} \mathbf{H}g_i \sigma g \mathbf{K} = \mathbf{H}g_{i'} \sigma g \mathbf{K} (= \mathbf{H}g_i \sigma \sigma g \mathbf{K}) \cdots \mathbf{H} \setminus \mathbf{G} / \mathbf{K} & \text{(equation (15))} \\ f(\bar{t}_{\sigma g_i}) & f(\bar{t}_{\sigma g_{i'}}) \\ \Downarrow & \Downarrow \\ \mathbf{H}g_i \sigma g \mathbf{K}' \neq \mathbf{H}g_{i'} \sigma g \mathbf{K}' (= \mathbf{H}g_i \sigma \sigma g \mathbf{K}') \cdots \mathbf{H} \setminus \mathbf{G} / \mathbf{K}' & \text{(equation (53)),} \\ f'(\bar{t}_{\sigma g_i}) & f'(\bar{t}_{\sigma g_{i'}}) \end{array}$$

which means:

$$\begin{array}{ccc} \text{Scheme III} \\ \mathbf{H}g_{i'} g \mathbf{K} = \mathbf{H}g_i (\sigma \sigma g) \mathbf{K} \cdots \mathbf{H} \setminus \mathbf{G} / \mathbf{K} & \text{(equation (15)),} \\ f(\bar{t}_{\sigma g_i}) & f(\bar{t}_{\sigma g_{i'}}) \\ \Downarrow & \Downarrow \\ \mathbf{H}g_{i'} g \mathbf{K}' \neq \mathbf{H}g_i (\sigma \sigma g) \mathbf{K}' \cdots \mathbf{H} \setminus \mathbf{G} / \mathbf{K}' & \text{(equation (53)).} \\ f'(\bar{t}_{\sigma g_i}) & f'(\bar{t}_{\sigma g_{i'}}) \end{array}$$

Note that  $\sigma \sigma g$  is a proper rotation because both the  $\sigma \sigma (\in \mathbf{K}')$  and the  $g$  are proper rotations. The comparison between schemes I and III shows that the nature of the pair  $g_i/g_{i'}$  (i.e., proper/improper or improper/proper) for scheme I suffers from inversion of chirality on the action of the improper rotation  $\sigma g$  so as to be opposite to the nature of the resulting pair  $g_{i'} g/g_i (\sigma \sigma g)$  (i.e., improper/proper or proper/improper) for scheme III. It follows that the operation of  $\sigma g$  results in the exchange between  $\mathbf{H}g_i \mathbf{K}$  and  $\mathbf{H}g_{i'} \mathbf{K}$  as well as the exchange between  $\mathbf{H}g_i \mathbf{K}'$  and  $\mathbf{H}g_{i'} \mathbf{K}'$ .

The discussions in the preceding paragraphs, the pair  $f(i)/f(i')$  in scheme I represents the occupation of an enantiomeric pair of chiral objects (or ligands). Even if achiral objects are used, the pair  $f(i)/f(i')$  means that their symmetries are restricted to be chiral locally. The pair  $f(\bar{t}_{g_i})/f(\bar{t}_{g_{i'}})$  generated on the action of a proper rotation  $g$  in scheme II represents the maintenance of the local chirality, while the pair  $f(\bar{t}_{\sigma g_i})/f(\bar{t}_{\sigma g_{i'}})$  generated on the action of an improper rotation  $\sigma g$  in scheme III represents the inversion of the local chirality. It follows that  $f(i)$  and  $f(i')$  should be occupied (1) by achiral ligands of the same kind or (2) by an enantiomeric set of chiral ligands. In agreement with “chirality fittingness of an enantiospheric orbit” [11] and “chirality fittingness of an enantiospheric cycle” [9], the present case shows CF of an enantiospheric double coset, in which two

achiral ligands or an enantiomeric pair of chiral ligands are allowed. Thereby, the two functions, i.e.,  $f$  for  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}$  (equation (15)) and  $f'$  for  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}'$  (equation (53)), are occupied commonly in agreement with the chirality fittingness.

Obviously, the same conclusion holds true if the enantiospheric double cosets  $\mathbf{H}g_i(g_j\mathbf{K}g_j^{-1})$  are considered in place of the enantiospheric double coset  $\mathbf{H}g_i\mathbf{K}$  described above.

**Example 8** [Enantiospheric double cosets for  $(\mathbf{C}_{3v}\backslash)\mathbf{T}_d(/)\mathbf{S}_4$ ]. By starting from  $\mathbf{C}_{3v}\backslash\mathbf{T}_d$  (equation (9)) and a subgroup  $\mathbf{S}_4$ :

$$\mathbf{S}_4 = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{S_{4(1)}}_{19}, \underbrace{S_{4(1)}^3}_{20} \right\} \quad (62)$$

let us consider a set of double cosets according to equation (15) as follows:

$$\mathbf{C}_{3v}\backslash\mathbf{T}_d/\mathbf{S}_4 = \{ \mathbf{C}_{3v}I\mathbf{S}_4, \mathbf{C}_{3v}C_{2(1)}\mathbf{S}_4, \mathbf{C}_{3v}C_{2(3)}\mathbf{S}_4, \mathbf{C}_{3v}C_{2(2)}\mathbf{S}_4 \}. \quad (63)$$

$$= \left[ \begin{array}{c} \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_1 \\ \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_2 \\ \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \\ \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \\ f(1) = p \end{array} \right\}, \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_2 \\ \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_1 \\ \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \\ \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \\ f(2) = p \end{array} \right\}, \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \\ \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \\ \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_2 \\ \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_1 \\ f(3) = \bar{p} \end{array} \right\}, \left\{ \begin{array}{c} \underbrace{\begin{Bmatrix} 3 & 7 & 11 \\ 15 & 19 & 23 \end{Bmatrix}}_4 \\ \underbrace{\begin{Bmatrix} 4 & 8 & 12 \\ 16 & 20 & 24 \end{Bmatrix}}_3 \\ \underbrace{\begin{Bmatrix} 1 & 5 & 9 \\ 13 & 17 & 21 \end{Bmatrix}}_2 \\ \underbrace{\begin{Bmatrix} 2 & 6 & 10 \\ 14 & 18 & 22 \end{Bmatrix}}_1 \\ f(4) = \bar{p} \end{array} \right\} \end{array} \right]. \quad (64)$$

Hence, we obtain a set of double cosets of the same kind, i.e.,  $\mathbf{C}_{3v}I\mathbf{S}_4 = \mathbf{C}_{3v}C_{2(1)}\mathbf{S}_4 = \mathbf{C}_{3v}C_{2(3)}\mathbf{S}_4 = \mathbf{C}_{3v}C_{2(2)}\mathbf{S}_4$ , each of which contains all of the operations of  $\mathbf{T}_d$ .



The maximum chiral subgroup of the group  $S_4$  is the group  $C_2$  shown in equation (57), which gives the same set of double cosets shown in equation (59):

$$\begin{aligned} C_{3v} \backslash T_d / C_2 &= \{C_{3v} I C_2, C_{3v} C_{2(1)} C_2, C_{3v} C_{2(3)} C_2, C_{3v} C_{2(2)} C_2\}. \quad (65) \\ &= \left[ \begin{array}{cccc} \left\{ \begin{array}{c} \{ 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \} \\ \overline{1} \\ \{ 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \} \\ \underline{2} \\ f'(1) = p, \bar{p} \end{array} \right\}, & \left\{ \begin{array}{c} \{ 2 \ 6 \ 10 \\ 14 \ 18 \ 22 \} \\ \overline{2} \\ \{ 1 \ 5 \ 9 \\ 13 \ 17 \ 21 \} \\ \underline{1} \\ f'(2) = p, \bar{p} \end{array} \right\}, & \left\{ \begin{array}{c} \{ 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \} \\ \overline{3} \\ \{ 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \} \\ \underline{4} \\ f'(3) = \bar{p}, p \end{array} \right\}, & \left\{ \begin{array}{c} \{ 3 \ 7 \ 11 \\ 15 \ 19 \ 23 \} \\ \overline{4} \\ \{ 4 \ 8 \ 12 \\ 16 \ 20 \ 24 \} \\ \underline{3} \\ f'(4) = \bar{p}, p \end{array} \right\} \end{array} \right]. \quad (66) \end{aligned}$$

The set  $C_{3v} \backslash T_d / C_2$  (equation (66)) is not equal to the set  $C_{3v} \backslash T_d / S_4$  (equation (64)) so that the latter set is concluded to be enantiospheric.

In accord with the enantiospheric nature of  $C_{3v} \backslash T_d / S_4$  (equation (64)), a common function  $f = f'$  is allowed by selecting components such as  $\{f(1) = f'(1) = p, f(2) = f'(2) = p, f(3) = f'(3) = \bar{p}, f(4) = f'(4) = \bar{p}\}$  or  $\{f(1) = f'(1) = \bar{p}, f(2) = f'(2) = \bar{p}, f(3) = f'(3) = p, f(4) = f'(4) = p\}$  if chiral ligands are taken into consideration. Moreover a function having achiral ligands  $A (= \bar{A})$  is also allowed as components, i.e.,  $\{f(1) = f'(1) = A, f(2) = f'(2) = A, f(3) = f'(3) = \bar{A}, f(4) = f'(4) = \bar{A}\}$ .

When a methane skeleton is considered, the function  $f$  (i.e.,  $\{f(1) = f'(1) = p, f(2) = f'(2) = p, f(3) = f'(3) = \bar{p}, f(4) = f'(4) = \bar{p}\}$ ) for  $C_{3v} \backslash T_d / S_4$  (equation (64)) corresponds to the formula **55** shown in figure 7. According to equation (18), the following permutation is obtained:

$$g \sim \begin{pmatrix} C_{3v} I S_4 & C_{3v} C_{2(1)} S_4 & C_{3v} C_{2(3)} S_4 & C_{3v} C_{2(2)} S_4 \\ C_{3v} I g S_4 & C_{3v} C_{2(1)} g S_4 & C_{3v} C_{2(3)} g S_4 & C_{3v} C_{2(2)} g S_4 \end{pmatrix} \quad (67)$$

$$\sim \begin{pmatrix} f(1) & f(2) & f(3) & f(4) \\ f(t_{g1}) & f(t_{g2}) & f(t_{g3}) & f(t_{g4}) \end{pmatrix} = \begin{pmatrix} p & p & \bar{p} & \bar{p} \\ T_1 & T_2 & T_3 & T_4 \end{pmatrix} = q_g, \quad (68)$$

where the alignment  $\{T_1, T_2, T_3, T_4\}$  represents a permuted alignment of  $\{p, p, \bar{p}, \bar{p}\}$ . By moving  $g$  over  $G$ , the permutation  $q_g$  (equation (68)) generates a double coset representation according to equation (19) as follows:

$$(C_{3v} \backslash) T_d (/ S_4) = \{q_g | \forall g \in T_d\}. \quad (69)$$

Each permutation of equation (69) generates the corresponding formula shown in figure 7.

		$IS_4$	$C_{2(3)}S_4$	$C_{3(1)}S_4$	$C_{3(2)}S_4$	$C_{3(1)}^2S_4$	$C_{3(2)}^2S_4$
		first operation					
		1 2 19 20	4 3 17 18	5 6 15 16	7 8 14 13	9 10 23 24	12 11 21 22
$C_{3v}I$	1 $I$	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )
	5 $C_{3(1)}$	1 2 19 20	4 3 17 18	5 6 15 16	7 8 14 13	9 10 23 24	12 11 21 22
	9 $C_{3(1)}^2$	5 6 15 16	8 7 13 14	9 10 23 24	11 12 22 21	1 2 19 20	4 3 17 18
	13 $\sigma_{d(1)}$	9 10 23 24	12 11 21 22	1 2 19 20	3 4 18 17	5 6 15 16	8 7 13 14
	17 $\sigma_{d(2)}$	13 14 7 8	16 15 5 6	17 18 3 4	19 20 2 1	21 22 11 12	24 23 9 10
	21 $\sigma_{d(3)}$	17 18 3 4	20 19 1 2	21 22 11 12	23 24 10 9	13 14 7 8	16 15 5 6
$C_{3v}C_{2(1)}$	2 $C_{2(1)}$	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )
	6 $C_{3(3)}$	2 1 20 19	3 4 18 17	8 7 13 14	6 5 16 15	11 12 22 21	10 9 24 23
	10 $C_{3(4)}^2$	6 5 16 15	7 8 14 13	12 11 21 22	10 9 24 23	3 4 18 17	2 1 20 19
	14 $S_{4(3)}$	10 9 24 23	11 12 22 21	4 3 17 18	2 1 20 19	7 8 14 13	6 5 16 15
	18 $\sigma_{d(4)}$	14 13 8 7	15 16 6 5	20 19 1 2	18 17 4 3	23 24 10 9	22 21 12 11
	22 $S_{4(2)}^3$	18 17 4 3	19 20 2 1	24 23 9 10	22 21 12 11	15 16 6 5	14 13 8 7
$C_{3v}C_{2(3)}$	4 $C_{2(3)}$	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )
	8 $C_{3(4)}$	4 3 17 18	1 2 19 20	7 8 14 13	5 6 15 16	10 9 24 23	11 12 22 21
	12 $C_{3(2)}^2$	8 7 13 14	5 6 15 16	11 12 22 21	9 10 23 24	2 1 20 19	3 4 18 17
	16 $\sigma_{d(6)}$	12 11 21 22	9 10 23 24	3 4 18 17	1 2 19 20	6 5 16 15	7 8 14 13
	20 $S_{4(1)}^3$	16 15 5 6	13 14 7 8	19 20 2 1	17 18 3 4	22 21 12 11	23 24 10 9
	24 $S_{4(2)}$	20 19 1 2	17 18 3 4	23 24 10 9	21 22 11 12	14 13 8 7	15 16 6 5
$C_{3v}C_{2(2)}$	3 $C_{2(2)}$	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )	p ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	$\bar{p}$ ( $\bar{p}$ )	p ( $\bar{p}$ )
	7 $C_{3(2)}$	3 4 18 17	2 1 20 19	6 5 16 15	8 7 13 14	12 11 21 22	9 10 23 24
	11 $C_{3(3)}^2$	7 8 14 13	6 5 16 15	10 9 24 23	12 11 21 22	4 3 17 18	1 2 19 20
	15 $S_{4(3)}^3$	11 12 22 21	10 9 24 23	2 1 20 19	4 3 17 18	8 7 13 14	5 6 15 16
	19 $S_{4(1)}$	15 16 6 5	14 13 8 7	18 17 4 3	20 19 1 2	24 23 9 10	21 22 11 12
	23 $\sigma_{d(5)}$	19 20 2 1	18 17 4 3	22 21 12 11	24 23 9 10	16 15 5 6	13 14 7 8
cf. Fig. 7		<b>55 56 57 58</b>	<b>59 60 61 62</b>	<b>63 64 65 66</b>	<b>67 68 69 70</b>	<b>71 72 73 74</b>	<b>75 76 77 78</b>

Figure 8. Reordered multiplication table of  $T_d$ .

Because the left coset decomposition of  $\mathbf{T}_d$  by  $\mathbf{S}_4$  is expressed by

$$\mathbf{T}_d = I\mathbf{S}_4 + C_{2(3)}\mathbf{S}_4 + C_{3(1)}\mathbf{S}_4 + C_{3(2)}\mathbf{S}_4 + C_{3(1)}^2\mathbf{S}_4 + C_{3(2)}^2\mathbf{S}_4 \quad (70)$$

its representative (i.e.,  $\{I, C_{2(3)}, C_{3(1)}, C_{3(2)}, C_{3(1)}^2, C_{3(2)}^2\} = \{1, 4, 5, 7, 9, 12\}$ ) are selected to partition the functions  $f_g$  ( $g \in \mathbf{T}_d$ ). Theorem 1 indicates that the 24 formulas are partitioned into six ( $= |\mathbf{T}_d|/|\mathbf{S}_4| = 24/4$ ) sets, each of which is surrounded with a box (figure 7). The top formulas of respective boxes, i.e., **55**, **59**, **63**, **67**, **71**, and **75**, are renumbered to the formulas shown at the respective bottoms, i.e., **55**, **79–83**. □

**Example 9** [Reordered multiplication table for  $(C_{3v} \setminus) \mathbf{T}_d (/ \mathbf{S}_4)$ ]. The construction of the double coset representation  $(C_{3v} \setminus) \mathbf{T}_d (/ \mathbf{S}_4)$  (equation (69)) can be regarded as the reordering of the multiplication table shown in figure 2. By reordering the rows of figure 2 in accord with the right coset decomposition of  $\mathbf{T}_d$  by  $C_{3v}$  (equation (8)) and by reordering the columns of figure 2 in accord with the left coset decomposition of  $\mathbf{T}_d$  by  $\mathbf{S}_4$  (equation (70)), we can obtain a reordered multiplication table, as shown in figure 8.

The four blocks of each column represent the corresponding right cosets, each of which contains a half-part of the corresponding double coset (equation (66)) so as to be specified by the symbol  $p$  ( $= \bar{p}$ ) or  $\bar{p}$ , as shown at the top of each block. Thereby, the corresponding function  $f_g$  (via a set of double cosets) is obtained by collecting a permuted set of symbols  $p$ ,  $\bar{p}$ ,  $\bar{p}$ , and  $\bar{p}$  from the tops of the blocks. As a result, each column corresponds to one of the 24 formulas (**55–78**), as shown in the bottom of figure 8. □

**Example 10** [Renumbered formulas]. Let us consider the renumbered formulas shown in the bottom part of figure 7 (i.e., **55–83**). In accord with the representative due to equation (70), the subgroups conjugate to  $\mathbf{S}_4$  are calculated as follows.

$$\mathbf{S}_4 = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{S_{4(1)}}_{19}, \underbrace{S_{4(1)}^3}_{20} \right\} \quad \cdots \mathbf{55}(f_1), \quad (71)$$

$$C_{2(3)}\mathbf{S}_4 C_{2(3)}^{-1} = \mathbf{S}_4 = \left\{ \underbrace{I}_1, \underbrace{C_{2(1)}}_2, \underbrace{S_{4(1)}}_{19}, \underbrace{S_{4(1)}^3}_{20} \right\} \quad \cdots \mathbf{79}(f_2), \quad (72)$$

$$C_{3(1)}\mathbf{S}_4 C_{3(1)}^{-1} = \mathbf{S}'_4 = \left\{ \underbrace{I}_1, \underbrace{C_{2(2)}}_3, \underbrace{S_{4(2)}}_{24}, \underbrace{S_{4(2)}^3}_{22} \right\} \quad \cdots \mathbf{80}(f_3), \quad (73)$$

$$C_{3(2)}\mathbf{S}_4 C_{3(2)}^{-1} = \mathbf{S}'_4 = \left\{ \underbrace{I}_1, \underbrace{C_{2(2)}}_3, \underbrace{S_{4(2)}}_{24}, \underbrace{S_{4(2)}^3}_{22} \right\} \quad \cdots \mathbf{81}(f_4), \quad (74)$$

$$C_{3(1)}^2 S_4 C_{3(1)}^{-2} = S_4'' = \left\{ \underbrace{I}_1, \underbrace{C_{2(3)}}_4, \underbrace{S_{4(3)}}_{14}, \underbrace{S_{4(3)}^3}_{15} \right\} \quad \dots \mathbf{82}(f_5), \tag{75}$$

$$C_{3(2)}^2 S_4 C_{3(2)}^{-2} = S_4'' = \left\{ \underbrace{I}_1, \underbrace{C_{2(3)}}_4, \underbrace{S_{4(3)}}_{14}, \underbrace{S_{4(3)}^3}_{15} \right\} \quad \dots \mathbf{83}(f_6). \tag{76}$$

The reference function  $f$  obtained by using the set of double cosets  $C_{3v} \setminus T_d / S_4$  (equation (23)) is adopted as  $f_1$ , i.e.,  $f_1(1) = p$ ,  $f_1(2) = p$ ,  $f_1(3) = \bar{p}$ , and  $f_1(4) = \bar{p}$ , which corresponds to **55**. Other functions are collected in figure 7. Each function  $f_j$  ( $j = 1, 2, \dots, 6$ ) generates four ( $= |S_4|$ ) formulas which are fixed under the corresponding stabilizer ( $S_4, S_4'$ , or  $S_4''$ ) conjugate to  $S_4$ . According to theorem 3, the total number of fixed formulas is equal to 24 ( $= |S_4| \times |T_d| / |S_4| = 4 \times (24/4) = 24$ ).  $\square$

**Example 11** [Enantiospheric double cosets for  $(C_{3v} \setminus) T_d (/C_s)$ ]. This example demonstrates so-called pseudoasymmetry. By starting from  $C_{3v} \setminus T_d$  shown in equation (9) and a subgroup:

$$C_s = \left\{ \underbrace{I}_1, \underbrace{\sigma_{d(2)}}_{17} \right\} \tag{77}$$

let us consider a set of double cosets according to equation (15) as follows:

$$C_{3v} \setminus T_d / C_s = \{C_{3v} I C_s, C_{3v} C_{2(1)} C_s, C_{3v} C_{2(3)} C_s, C_{3v} C_{2(2)} C_s\}. \tag{78}$$

$$= \left[ \left[ \begin{array}{c} \left\{ \begin{array}{ccc} 1 & 5 & 9 \\ 13 & 17 & 21 \end{array} \right\} \\ \underbrace{1} \\ \left\{ \begin{array}{ccc} 1 & 5 & 9 \\ 13 & 17 & 21 \end{array} \right\} \\ \underbrace{1} \end{array} \right], \left[ \begin{array}{c} \left\{ \begin{array}{ccc} 2 & 6 & 10 \\ 14 & 18 & 22 \end{array} \right\} \\ \underbrace{2} \\ \left\{ \begin{array}{ccc} 2 & 6 & 10 \\ 14 & 18 & 22 \end{array} \right\} \\ \underbrace{2} \end{array} \right], \left[ \begin{array}{c} \left\{ \begin{array}{ccc} 4 & 8 & 12 \\ 16 & 20 & 24 \end{array} \right\} \\ \underbrace{3} \\ \left\{ \begin{array}{ccc} 3 & 7 & 11 \\ 15 & 19 & 23 \end{array} \right\} \\ \underbrace{4} \end{array} \right], \left[ \begin{array}{c} \left\{ \begin{array}{ccc} 3 & 7 & 11 \\ 15 & 19 & 23 \end{array} \right\} \\ \underbrace{4} \\ \left\{ \begin{array}{ccc} 4 & 8 & 12 \\ 16 & 20 & 24 \end{array} \right\} \\ \underbrace{3} \end{array} \right] \right]. \tag{79}$$

The first double coset  $C_{3v} I C_s$  contains one coset, i.e.,  $C_{3v} I C_s (= C_{3v})$ ; and the second double coset  $C_{3v} C_{2(1)} C_s$  contains one coset, i.e.,  $C_{3v} C_{2(1)} C_s (= C_{3v} C_{2(1)})$ . On the other hand, the third and fourth double cosets represent the same double coset, i.e.,  $C_{3v} C_{2(3)} C_s = C_{3v} C_{2(2)} C_s$ .

In accord with the homospheric or enantiospheric nature of the double cosets appearing in  $C_{3v} \setminus T_d / C_s$ , a function ( $f$ ) is allowed by selecting components such as  $\{f(1) = A, f(2) = B, f(3) = p, f(4) = \bar{p}\}$ , where A and B correspond to distinct homospheric double cosets, while a pair of p and  $\bar{p}$  corresponds to an enantiospheric double cosets (equation (79)).

When a methane skeleton is considered, the function  $f$  (i.e.,  $\{f(1) = A, f(2) = B, f(3) = p, f(4) = \bar{p}\}$ ) for  $C_{3v} \backslash T_d / C_s$  (equation (79)) corresponds to the formula **84** shown in figure 9. According to equation (18), the following permutation is obtained:

$$g \sim \begin{pmatrix} C_{3v} I C_s & C_{3v} C_{2(1)} C_s & C_{3v} C_{2(3)} C_s & C_{3v} C_{2(2)} C_s \\ C_{3v} I g C_2 & C_{3v} C_{2(1)} g C_s & C_{3v} C_{2(3)} g C_s & C_{3v} C_{2(2)} g C_s \end{pmatrix} \quad (80)$$

$$\sim \begin{pmatrix} f(1) & f(2) & f(3) & f(4) \\ f(t_{g1}) & f(t_{g2}) & f(t_{g3}) & f(t_{g4}) \end{pmatrix} = \begin{pmatrix} A & B & p & \bar{p} \\ T_1 & T_2 & T_3 & T_4 \end{pmatrix} = q_g, \quad (81)$$

where the alignment  $\{T_1, T_2, T_3, T_4\}$  represents a permuted alignment of  $\{A, B, p, \bar{p}\}$ . By moving  $g$  over  $G$ , the permutation  $q_g$  (equation (81)) generates a double coset representation according to equation (19) as follows:

$$(C_{3v} \backslash) T_d (/ C_s) = \{q_g | \forall g \in T_d\}. \quad (82)$$

Each permutation of equation (82) generates the corresponding formula shown in figure 9. Because the left coset decomposition of  $T_d$  by  $C_s$  is expressed by

$$T_d = I C_s + C_{2(1)} C_s + C_{2(2)} C_s + C_{2(3)} C_s + C_{3(1)} C_s + C_{3(3)} C_s \\ + C_{3(2)} C_s + C_{3(4)} C_s + C_{3(1)}^2 C_s + C_{3(4)}^2 C_s + C_{3(3)}^2 C_s + C_{3(2)}^2 C_s \quad (83)$$

its representative (i.e.,  $\{I, C_{2(1)}, C_{2(2)}, C_{2(3)}, C_{3(1)}, C_{3(3)}; C_{3(2)}, C_{3(4)}, C_{3(1)}^2, C_{3(4)}^2, C_{3(3)}^2, C_{3(2)}^2\} = \{1, 2, 3, 4, 5, 6; 7, 8, 9, 10, 11, 12\}$ ) are selected to partition the functions  $f_g$  ( $g \in T_d$ ). Theorem 1 indicates that the 24 formulas are partitioned into 12 ( $= |T_d| / |C_s| = 24/2$ ) sets, each of which is surrounded with a box (figure 9).

It should be noted that another distinct function  $f$  having components,  $\{f(1) = A, f(2) = B, f(3) = \bar{p}, f(4) = p\}$ , is allowed in place of the set of components described above, i.e.,  $\{f(1) = A, f(2) = B, f(3) = p, f(4) = \bar{p}\}$ . The distinct function indicates the diastereomer of **84** so that it generates 24 formulas, each of which is diastereomeric to the corresponding formula shown in figure 9. The 24 formulas generated newly are also partitioned into 12 ( $= |T_d| / |C_s| = 24/2$ ) in agreement with theorem 1. Thus, the two functions  $\{f(1) = A, f(2) = B, f(3) = p, f(4) = \bar{p}\}$  and  $\{f(1) = A, f(2) = B, f(3) = \bar{p}, f(4) = p\}$  represent so-called ‘‘pseudo-asymmetry’’.  $\square$

**Example 12** [Reordered formulas]. The top formulas of respective boxes in figure 9, i.e., **84, 86, 88, 90, 92, 94, 101, 103, 105, 107, 109**, and **111**, are renumbered by the functions  $f_1$  to  $f_{12}$  (for their components, see figure 9) so as to generated the formulas shown at the respective bottoms, i.e., **84, 96–100, 113–118**.

In accord with the representative due to equation (83), the subgroups conjugate to  $C_s$  are calculated as follows.

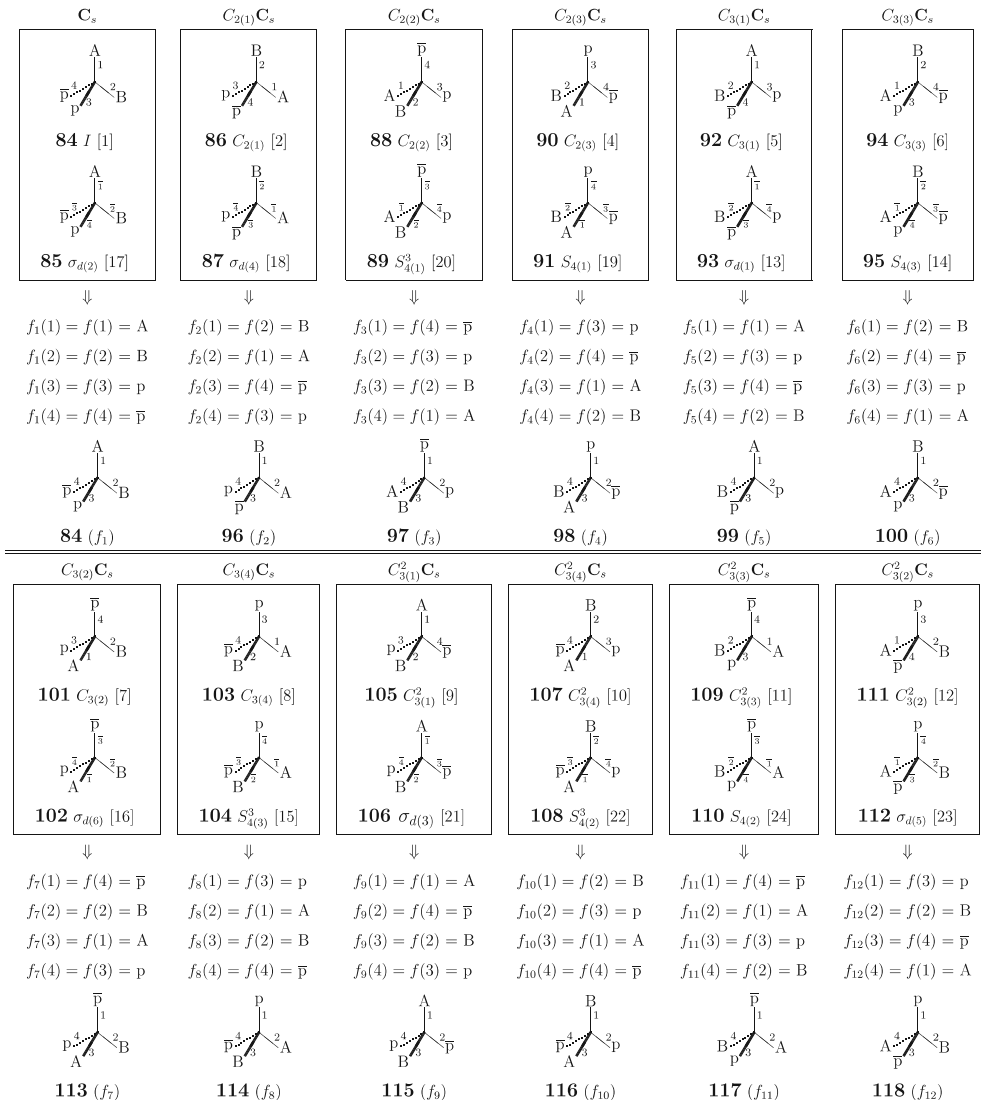


Figure 9. Tetrahedral formulas generated in accord with the double coset representation  $(C_{3v} \backslash) \Gamma_d / (C_s)_{[R]}$ .

$$C_s = C_{2(1)}C_sC_{2(1)}^{-1} = \underbrace{\{I\}}_1, \underbrace{\{\sigma_{d(2)}\}}_{17}, \quad (84)$$

$$C'_s = C_{2(2)}C_sC_{2(2)}^{-1} = C_{2(3)}C_sC_{2(3)}^{-1} = \underbrace{\{I\}}_1, \underbrace{\{\sigma_{d(4)}\}}_{18}, \quad (85)$$

$$C_s^* = C_{3(1)}C_sC_{3(1)}^{-1} = C_{3(1)}C_sC_{3(1)}^{-1} = \underbrace{\{I\}}_1, \underbrace{\{\sigma_{d(3)}\}}_{21}, \quad (86)$$

$$\mathbf{C}_s^{*'} = C_{3(2)} \mathbf{C}_s C_{3(2)}^{-1} = C_{3(4)} \mathbf{C}_s C_{3(4)}^{-1} = \left\{ \underbrace{I}_1, \underbrace{\sigma_{d(5)}}_{23} \right\}, \quad (87)$$

$$\mathbf{C}_s^{\dagger} = C_{3(1)}^2 \mathbf{C}_s C_{3(1)}^{-2} = C_{3(4)}^2 \mathbf{C}_s C_{3(4)}^{-2} = \left\{ \underbrace{I}_1, \underbrace{\sigma_{d(1)}}_{13} \right\}, \quad (88)$$

$$\mathbf{C}_s^{\dagger'} = C_{3(3)}^2 \mathbf{C}_s C_{3(3)}^{-2} = C_{3(2)}^2 \mathbf{C}_s C_{3(2)}^{-2} = \left\{ \underbrace{I}_1, \underbrace{\sigma_{d(6)}}_{16} \right\}. \quad (89)$$

Among the 24 operations of the right coset representation  $(C_{3v} \setminus) T_d$  (figure 9), the operations of  $\mathbf{C}_s$  fix the formulas **84** and **96** so that the number of fixed formulas of each case is equal to 2. The numbers of fixed formulas by the operations of  $\mathbf{C}_s'$  are determined as indicated in the following pairs of parentheses: **97** (2) and **98** (2). The numbers of fixed formulas by the operations of  $\mathbf{C}_s^*$  are determined as follows: **99** (2) and **100** (2). The numbers of fixed formulas by the operations of  $\mathbf{C}_s^{*'}$  are determined as follows: **113** (2) and **114** (2). The numbers of fixed formulas by the operations of  $\mathbf{C}_s^{\dagger}$  are determined as follows: **115** (2) and **116** (2). The numbers of fixed formulas by the operations of  $\mathbf{C}_s^{\dagger'}$  are determined as follows: **117** (2) and **118** (2). The remaining operations among the 24 operations of the right coset representation  $(C_{3v} \setminus) T_d$  move the above formulas so as to give no fixed formulas. Hence, the total number of fixed formulas for  $ABp\bar{p}$  is concluded to be equal to 24. Obviously, the diastereomer of **26** exhibits another series of fixation, the total number of which is equal to 24, although the generated formulas have the same molecular formula  $ABp\bar{p}$ .  $\square$

### 3.1.3. Hemispheric case

When  $\mathbf{K}$  is a chiral subgroup of the achiral group  $\mathbf{G}$ , a supergroup  $\widehat{\mathbf{K}}$  can be selected so as to satisfy the following left coset decomposition:

$$\widehat{\mathbf{K}} = \mathbf{K} + \sigma \mathbf{K}, \quad (90)$$

where the  $\sigma$  is an improper rotation, satisfying  $\sigma\sigma \in \mathbf{K}$ . Consider the double cosets  $\mathbf{H}g_i\mathbf{K}$  and  $\mathbf{H}g_i\sigma\mathbf{K}$ . They are contained in the set of double cosets  $\mathbf{H} \setminus \mathbf{G} / \widehat{\mathbf{K}}$  (cf. equation (15)) as distinct double cosets, i.e.,

$$\mathbf{H}g_i\mathbf{K} \neq \mathbf{H}g_i\sigma\mathbf{K} \quad (= \mathbf{H}g_{i'}\mathbf{K}). \quad (91)$$

Although the double cosets  $\mathbf{H}g_i\mathbf{K}$  and  $\mathbf{H}g_{i'}\mathbf{K}$  ( $= \mathbf{H}g_i\sigma\mathbf{K}$ ) (equation (91)) appear in the set of double cosets  $\mathbf{H} \setminus \mathbf{G} / \mathbf{K}$  as distinct double cosets, they are not equivalent under the chiral  $\mathbf{K}$ , as shown in the following equation:

$$\mathbf{H} \setminus \mathbf{G} / \mathbf{K} = \{ \dots, \underbrace{\mathbf{H}g_i\mathbf{K}}_{f(i)}, \dots; \dots, \underbrace{\mathbf{H}g_{i'}\mathbf{K}}_{f(i')}, \dots \}. \quad (92)$$

It follows that  $\mathbf{H}g_i\mathbf{K}$  and  $\mathbf{H}g_{i'}\mathbf{K}$  correspond to components of different values, i.e.,  $f(i) \neq f(i')$ .

Let  $g_i$  be a proper rotation. Then  $g_i' (= g_i\sigma)$  is an improper rotation. The action of a proper rotation  $g$  converts  $\mathbf{H}g_i\mathbf{K}$  into  $\mathbf{H}g_i g\mathbf{K}$ , but they correspond to components of the same value, i.e.,  $f(t_{g_i}) = f(i)$ , because the  $g_i g$  is a proper rotation. On the other hand, the action of an improper rotation  $\sigma g$  converts  $\mathbf{H}g_i\mathbf{K}$  into  $\mathbf{H}g_i\sigma g\mathbf{K} (= \mathbf{H}g_i' g\mathbf{K})$ . Because the operation  $g_i' g (= g_i\sigma g)$  is improper, the latter (i.e.,  $\mathbf{H}g_i\sigma g\mathbf{K} (= \mathbf{H}g_i' g\mathbf{K})$ ) corresponds to a component of  $f(\bar{t}_{g_i'})$ , which represents the chirality opposite to the  $f(i)$ . The opposite chirality is designated by an overbar. Thus, any improper rotation results in the alternation of chirality.

A similar discussion is available to the double coset  $\mathbf{H}g_i'\mathbf{K}$ . The action of a proper rotation  $g$  converts  $\mathbf{H}g_i'\mathbf{K}$  into  $\mathbf{H}g_i' g\mathbf{K}$ , but they correspond to components of the same value, i.e.,  $f(t_{g_i'}) = f(i')$ . Thus no alternation of chirality occurs because the  $g_i'$  and the  $g_i' g$  are both improper rotations. On the other hand, the action of an improper rotation  $\sigma g$  converts  $\mathbf{H}g_i'\mathbf{K}$  into  $\mathbf{H}g_i'\sigma g\mathbf{K} (= \mathbf{H}(g_i\sigma\sigma)g\mathbf{K})$ , where the alternation of chirality occurs because the  $g_i'$  is improper while the  $g_i\sigma\sigma g$  is proper (cf.  $\sigma\sigma \in \mathbf{K}$ ).

Because the chiral group  $\mathbf{K}$  is taken into primary consideration, the CF<sub>s</sub> of a hemispheric double coset can be summarized as follows:

1. A function  $f$  (equation (92)) for satisfying the  $\mathbf{K}$ -symmetry has its components, i.e.,  $f(i) = p$  and  $f(i') = q$ , where  $p$  and  $q$  represent chiral ligands. The inverse accommodation is also permissible, i.e.,  $f(i) = q$  and  $f(i') = p$ .
2. Another type of functions  $f$  for satisfying the  $\mathbf{K}$ -symmetry is possible, where its components are represented by  $f(i) = p$  and  $f(i') = A$  or  $f(i) = A$  and  $f(i') = p$ .
3. If the  $\mathbf{K}$  symmetry is determined by the remaining parts of  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}$ , such functions as  $f(i) = A$  and  $f(i') = B$  are also permissible, where  $A$  and  $B$  represent achiral ligands.

Obviously, the same conclusion holds true if the hemispheric double cosets  $\mathbf{H}g_i(g_j\mathbf{K}g_j^{-1})$  are considered in place of the hemispheric double coset  $\mathbf{H}g_i\mathbf{K}$  described above.

When  $\mathbf{G}$  is chiral, all of the subgroups of  $\mathbf{G}$  are chiral. By considering  $\widehat{\mathbf{G}}$  as a supergroup of the  $\mathbf{G}$ , where the  $\widehat{\mathbf{G}}$  contains the  $\mathbf{G}$  as the maximum chiral subgroup. Thereby, the present cases of  $\mathbf{H}\backslash\mathbf{G}/\mathbf{K}$  can be regarded as another type of hemispheric ones so that the discussions for the hemispheric double cosets described above are applicable to the present cases.

**Example 13** [Hemispheric double cosets]. The chiral subgroup  $\mathbf{C}_2$  shown in equation (57), which gives the same set of double cosets  $\mathbf{C}_{3v}\backslash\mathbf{T}_d/\mathbf{C}_2$  shown in equation (59) and (66). In accord with the hemispheric nature of  $\mathbf{C}_{3v}\backslash\mathbf{T}_d/\mathbf{C}_2$ , a function ( $f$ ) is allowed by selecting components such as  $\{f(1) = p, f(2) = p,$



$f(3) = q, f(4) = q\}$  or  $\{f(1) = q, f(2) = q, f(3) = p, f(4) = p\}$  if chiral ligands are taken into consideration. Moreover a function having achiral ligands  $A (= \bar{A})$  is also allowed as components, i.e.,  $\{f(1) = A, f(2) = A, f(3) = p, f(4) = p\}$ , and so on.

When a methane skeleton is considered, the function  $f$  (i.e.,  $\{f(1) = A, f(2) = A, f(3) = p, f(4) = p\}$ ) for  $C_{3v} \setminus T_d / C_2$  (equations (59) and (66)) corresponds to the formula **119** shown in figure 10. According to equation (18), the following permutation is obtained:

$$g \sim \begin{pmatrix} C_{3v}IC_2 & C_{3v}C_{2(1)}C_2 & C_{3v}C_{2(3)}C_2 & C_{3v}C_{2(2)}C_2 \\ C_{3v}IgC_2 & C_{3v}C_{2(1)}gC_2 & C_{3v}C_{2(3)}gC_2 & C_{3v}C_{2(2)}gC_2 \end{pmatrix} \quad (93)$$

$$\sim \begin{pmatrix} f(1) & f(2) & f(3) & f(4) \\ f(t_{g1}) & f(t_{g2}) & f(t_{g3}) & f(t_{g4}) \end{pmatrix} = \begin{pmatrix} A & A & p & p \\ T_1 & T_2 & T_3 & T_4 \end{pmatrix} = q_g, \quad (94)$$

where the alignment  $\{T_1, T_2, T_3, T_4\}$  represents a permuted alignment of  $\{A, A, p, p\}$ . By moving  $g$  over  $\mathbf{G}$ , the permutation  $q_g$  (equation (94)) generates a double coset representation according to equation (19) as follows:

$$(C_{3v} \setminus) T_d (/ C_2) = \{q_g | \forall g \in T_d\}. \quad (95)$$

If  $g$  is an improper rotation, the numbering in equation (94) is specified by an overbar indicating the alternation of chirality, i.e.,  $\bar{t}_{g1}, \bar{t}_{g2}, \bar{t}_{g3}$ , and  $\bar{t}_{g4}$ , so that the alignment  $\{\bar{T}_1, \bar{T}_2, \bar{T}_3, \bar{T}_4\}$ , represents a permuted alignment of  $\{A, A, \bar{p}, \bar{p}\}$ .

Each permutation of equation (95) generates the corresponding formula shown in figure 10. Because the left coset decomposition of  $T_d$  by  $C_2$  is expressed by

$$T_d = IC_2 + C_{2(3)}C_2 + C_{3(1)}C_2 + C_{3(2)}C_2 + C_{3(1)}^2C_2 + C_{3(2)}^2C_2 + \sigma_{d(2)}C_2 + S_{4(1)}C_2 + \sigma_{d(1)}C_2 + \sigma_{d(6)}C_2 + \sigma_{d(3)}C_2 + \sigma_{d(5)}C_2 \quad (96)$$

its representative (i.e.,  $\{I, C_{2(3)}, C_{3(1)}, C_{3(2)}, C_{3(1)}^2, C_{3(2)}^2; \sigma_{d(2)}, S_{4(1)}, \sigma_{d(1)}, \sigma_{d(6)}, \sigma_{d(3)}, \sigma_{d(5)}\} = \{1, 4, 5, 7, 9, 12; 17, 19, 13, 16, 21, 23\}$ ) are selected to partition the functions  $f_g$  ( $g \in T_d$ ). Theorem 1 indicates that the 24 formulas are partitioned into 12 ( $= |T_d|/|C_2| = 24/2$ ) sets, each of which is surrounded with a box (figure 10).  $\square$

**Example 14** [Reordered formulas]. The top formulas of respective boxes in the first row of boxes (figure 10), i.e., **119, 121, 123, 125, 127, and 129**, are representatives generated by proper rotations. They are renumbered to give the formulas shown at the respective bottoms, i.e., **119, 131–135**. On the other hand, the top formulas of respective boxes in the second row of boxes (figure 10), i.e., **136, 138, 140, 142, 144, and 146**, are representatives generated by improper rotations. They are renumbered to the formulas shown at the respective bottoms, i.e., **136, 148–152**, where an overbar represents the alternation of chirality. In accord with the representative due to equation (96), the subgroups conjugate to  $C_2$  are calculated as follows.

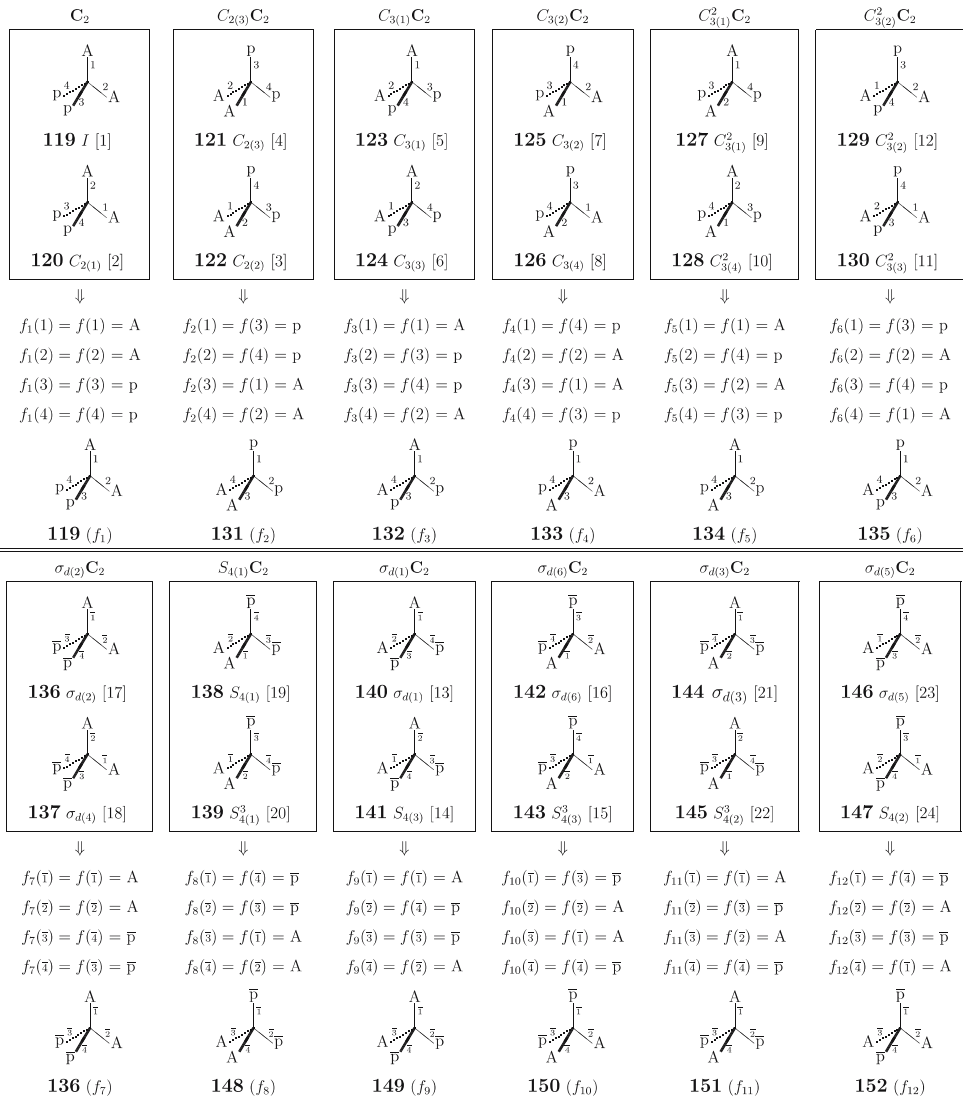


Figure 10. Tetrahedral formulas generated in accord with the double coset representation  $(C_{3v} \setminus) T_d / C_2$ .

$$C_2 = C_{2(3)}C_2C_{2(3)}^{-1} = \sigma_{d(2)}C_2\sigma_{d(2)}^{-1} = S_{4(1)}C_2S_{4(1)}^{-1} = \underbrace{\{I\}}_1, \underbrace{C_{2(1)}}_2, \quad (97)$$

$$C_2' = C_{3(1)}C_2C_{3(1)}^{-1} = C_{3(2)}C_2C_{3(2)}^{-1}\sigma_{d(1)}C_2\sigma_{d(1)}^{-1} = \sigma_{d(6)}C_2\sigma_{d(6)}^{-1} = \underbrace{\{I\}}_1, \underbrace{C_{2(2)}}_3, \quad (98)$$

$$\mathbf{C}_2'' = \mathbf{C}_{3(1)}^2 \mathbf{C}_2 \mathbf{C}_{3(1)}^{-2} = \mathbf{C}_{3(2)}^2 \mathbf{C}_2 \mathbf{C}_{3(2)}^{-2} = \sigma_{d(3)} \mathbf{C}_2 \sigma_{d(3)}^{-1} = \sigma_{d(5)} \mathbf{C}_2 \sigma_{d(5)}^{-1} = \underbrace{\{I\}}_1, \underbrace{\mathbf{C}_{2(3)}}_4 \quad (99)$$

Among the 24 operations of the right coset representation  $\mathbf{C}_{3v} \backslash \mathbf{T}_d$  (figure 3), the operations of  $\mathbf{C}_2$  fix the formula **119** so that the number of fixed formulas is equal to 2. On the same line, the numbers of fixed formulas by the operations of  $\mathbf{C}_2$  are determined as indicated in the following pairs of parentheses: **131** (2), **136** (2), and **148** (2). Note that **119** and **131** are ascribed to molecular formulas  $A^2p^2$ , while **136** and **148** are ascribed to molecular formulas  $A^2\bar{p}^2$ .

The numbers of fixed formulas by the operations of  $\mathbf{C}_2'$  are determined as follows: **132** (2) and **133** (2) for  $A^2p^2$ ; as well as **149** (2), and **150** (2) for  $A^2\bar{p}^2$ . The numbers of fixed formulas by the operations of  $\mathbf{C}_2''$  are determined as follows: **134** (2) and **135** (2) for  $A^2\bar{p}^2$ ; as well as **151** (2) and **152** (2) for  $A^2\bar{p}^2$ .

The remaining operations among the 24 operations of the right coset representation  $\mathbf{C}_{3v} \backslash \mathbf{T}_d$  move the above formulas so as to give no fixed formulas. Hence, the number of fixed formulas for  $A^2p^2$  is equal to 12 and that for  $A^2\bar{p}^2$  is also equal to 12. Totally, the number of fixed formulas is concluded to be equal to 24.  $\square$

## 4. Combinatorial enumeration

### 4.1. Number of fixed formulas per stereoisomer

To generalize the discussions described above, the symbols A, B, X, Y for achiral ligands, and p and  $\bar{p}$  for a pair of enantiomeric ligands, we use a set (**X**) of achiral and chiral ligands as follows:

$$\mathbf{X} = \{X_1, X_2, \dots, X_r; p_1, p_2, \dots, p_r; \bar{p}_1, \bar{p}_2, \dots, \bar{p}_r\}, \quad (100)$$

where  $X_i$  are achiral and a pair of  $p_i$  and  $\bar{p}_i$  represents an enantiomeric pair. Strictly speaking, the ligands contained in **X** should be regarded as *proligands*, which are hypothetical ligands which are structureless but have chirality/achirality in accord with Fujita's proligand method [9]. For the sake of convenience, we here use the term "ligands" in place of the term "proligands" because this usage would cause no confusion.

Consider  $\theta_1$  of  $X_1$ ,  $\theta_2$  of  $X_2$ , ...,  $\theta_r$  of  $X_r$ ;  $\theta'_1$  of  $p_1$ ,  $\theta'_2$  of  $p_2$ , ...,  $\theta'_r$  of  $p_r$ ;  $\theta''_1$  of  $\bar{p}_1$ ,  $\theta''_2$  of  $\bar{p}_2$ , ...,  $\theta''_r$  of  $\bar{p}_r$  for the components of the function  $f$  (equation (15)), where

$$\begin{aligned} [\theta] : & \theta_1 + \theta_2 + \dots + \theta_r \\ & + \theta'_1 + \theta'_2 + \dots + \theta'_r \\ & + \theta''_1 + \theta''_2 + \dots + \theta''_r = r. \end{aligned} \quad (101)$$

Then, the molecular formula  $M_f$  (equation (16) is represented by the following equation:

$$M_f = X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \overline{p_1^{\theta''_1} p_2^{\theta''_2} \dots p_r^{\theta''_r}} \quad (102)$$

It should be noted that a chiral stereoisomer of  $\mathbf{K}$ -symmetry corresponds to  $|\mathbf{K}|/2$  fixed formulas of one chirality and  $|\mathbf{K}|/2$  fixed formulas of the opposite chirality, as exemplified by example 14 (figure 10). Hence, a pair of such enantiomeric stereoisomers must be taken into consideration so as to have the following molecular formula:

$$M_f = \frac{1}{2} \left\{ X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \overline{p_1^{\theta''_1} p_2^{\theta''_2} \dots p_r^{\theta''_r}} \right. \\ \left. + X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta''_1} p_2^{\theta''_2} \dots p_r^{\theta''_r} \overline{p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r}} \right\} \quad (103)$$

Obviously, we can derive a molecular formula for an achiral stereoisomer by placing  $\theta'_i = \theta''_i$  ( $i = 1, 2, \dots, r$ ) in equation (102) as well as in equation (103). We have already shown examples of this case, where chiral ligands are placed in an enantiospheric environment (e.g.,  $p^2\overline{p}^2$  in figure 8 and  $ABp\overline{p}$  in figure 9).

Strictly speaking, each achiral  $X_i$  in the second term of equation (103) should be hypothetically expressed by  $\overline{X}_i$ . Because of  $X_i = \overline{\overline{X}_i}$ , the symbol  $X_i$  is used in place of  $\overline{X}_i$ . For example, in cases where only achiral ligands are taken into consideration (e.g.,  $ABXY$ ), even a chiral stereoisomer takes a molecular formula apparently represented by equation (102). Such cases as  $ABXY$  should be interpreted by considering a hypothetical term,  $\frac{1}{2}(ABXY + \overline{ABXY})$ , which is equal to  $ABXY$  because of  $ABXY = \overline{\overline{ABXY}}$ . Whether the molecular formula is represented by equation (102) or equation (103), the number of fixed formulas is concluded to be equal to  $|\mathbf{G}|$ .

The  $\mathbf{K}$ -symmetry described above moves over the subgroups of  $\mathbf{G}$  so as to result in the occurrence of one or more stereoisomers of various subsymmetries of  $\mathbf{G}$ , even though a given pattern  $[\theta]$  is taken into consideration. Let the symbol  $B_\theta$  denote the number of such stereoisomers as assigned to the partition  $[\theta]$  (equation (101)), the generating function for  $B_\theta$  is expressed as follows:

$$\sum_{[\theta]} B_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \overline{p_1^{\theta''_1} p_2^{\theta''_2} \dots p_r^{\theta''_r}}, \quad (104)$$

where the summation is concerned with all of the partitions ( $[\theta]$ ) shown in equation (101). It should be noted that, if the molecular formula  $M_f$  (equation (102)) represents a chiral stereoisomer, it is combined with the molecular formula of its

enantiomer so as to be interpreted by the following combined molecular formula:

$$B_\theta \times \frac{1}{2} \left\{ X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r} \right. \\ \left. + X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta''_1} p_2^{\theta''_2} \dots p_r^{\theta''_r} \bar{p}_1^{\theta'_1} \bar{p}_2^{\theta'_2} \dots \bar{p}_r^{\theta'_r} \right\}, \quad (105)$$

which is based on equation (103). Because each stereoisomer (or each pair of enantiomers) appearing in equation (104) has  $|\mathbf{G}|$  fixed formulas, the numbers of fixed formulas appear as the coefficients of the terms in the following generating function:

$$|\mathbf{G}| \sum_{[\theta]} B_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r}. \quad (106)$$

#### 4.2. Number of fixed formulas per permutation

##### 4.2.1. Sphericities of cycles

In the preceding discussions, the CFs has been clarified as follows: homospheric double cosets correspond to achiral ligands; enantiospheric double cosets correspond to achiral ligands as well as a enantiomeric pair of chiral ligands; and hemispheric double cosets correspond to achiral ligands and chiral ligands.

A right coset representation (equation (4) and the corresponding double coset representation (equation (19)) move concurrently through  $g$  ( $\in \mathbf{G}$ ), because the set of right cosets (equation (1)) corresponds to the set of double cosets (equation (15)) in one-to-one fashion.

Let the permutation  $p_g^{[R]}$  (equation (3)) be represented by a cycle decomposition involving the number  $v_d(p_g^{[R]})$  of  $d$ -cycles, where we place

$$\sum_{d=1}^r d v_d(p_g^{[R]}) = r. \quad (107)$$

Thus, the permutation  $p_g^{[R]}$  (equation (3)) possesses a cycle structure represented as follows:

$$1^{v_1(p_g^{[R]})} 2^{v_2(p_g^{[R]})} \dots d^{v_d(p_g^{[R]})} \dots r^{v_r(p_g^{[R]})}. \quad (108)$$

Each  $d$ -cycle appearing in equation (107) acts on the corresponding set of double cosets, which appears in equation (15). The action of the  $d$ -cycle varies in accord with the sphericities of the double cosets.

Strictly speaking, equation (108) should be multiplied in accord with right cosets to be considered. In other words, the  $\mathbf{H}$  of  $(\mathbf{H})\mathbf{G}$  moves on the set of subgroups of  $\mathbf{G}$  so as to cover the right cosets to be considered. Even such cases, however, we obtain cycle structures of the same kind as equation (108) so that we can continue our discussion by using equation (108) without losing generality.

Next, the sphericities of double cosets proposed in the present paper shall be correlated to those of cycles which have been formulated in Fujita's proligand method [9,10].

1. When  $g (\in \mathbf{G})$  is a proper rotation, a  $d$ -cycle of  $p_g^{[R]}$  (cf. equation (107) whether  $d$  is odd or even) permutes  $d$  double cosets, which are equivalent so as to construct a  $d$ -membered set of hemispheric double cosets, a  $d$ -membered set of homospheric double cosets, or a  $d$ -membered set of enantiospheric double cosets. It follows that the  $d$ -cycle is allowed to act on chiral and achiral ligands of the same kind without any restriction. The  $d$ -cycle is called a *hemispheric cycle*, which is designated by the sphericity index  $b_d$ . The action on each  $d$ -membered set can be expressed by the following equation:

$$b_d = X_1^d + X_2^d + \cdots + X_r^d + p_1^d + p_2^d + \cdots + p_r^d + \bar{p}_1^d + \bar{p}_2^d + \cdots + \bar{p}_r^d, \quad (109)$$

which is called a *ligand inventory for the hemispheric cycle*.

2. Let  $g (\in \mathbf{G})$  be an improper rotation and the integer  $d$  be odd. A  $d$ -cycle contained in  $p_g^{[R]}$  (cf. equation (107)) permutes  $d$  double cosets, which are equivalent so as to construct a  $d$ -membered set of homospheric double cosets. It follows that the  $d$ -cycle is allowed to act on achiral ligands of the same kind. The  $d$ -cycle is called a *homospheric cycle*, which is designated by the sphericity index  $a_d$ . The action on each  $d$ -membered set can be expressed by the following equation:

$$a_d = X_1^d + X_2^d + \cdots + X_r^d, \quad (110)$$

which is called a *ligand inventory for the homospheric cycle*.

3. Let  $g (\in \mathbf{G})$  be an improper rotation and the integer  $d$  be even. A  $d$ -cycle contained in  $p_g^{[R]}$  (cf. equation (107)) permutes  $d$  double cosets, which are equivalent so as to construct a  $d$ -membered set of homospheric double cosets or a  $d$ -membered set of enantiospheric double cosets. It follows that the  $d$ -cycle is allowed to act on a set of achiral ligands of the same kind or on a pairwise set, which contains  $d/2$  of chiral ligands of the same kind and  $d/2$  of their enantiomeric ligands. The  $d$ -cycle is called a *enantiospheric cycle*, which is designated by the sphericity index  $c_d$ . The action on each  $d$ -membered set can be expressed by the following equation:

$$c_d = X_1^d + X_2^d + \cdots + X_r^d + 2p_1^{d/2} \bar{p}_1^{d/2} + 2p_2^{d/2} \bar{p}_2^{d/2} + \cdots + 2p_r^{d/2} \bar{p}_r^{d/2}, \quad (111)$$

which is called a *ligand inventory for the enantiospheric cycle*.

The present ligand inventories are the same contents as defined otherwise in Fujita's proligand method [9,10].

#### 4.2.2. Products of sphericity indices

The sphericities of cycles described above allow us to assign a product of sphericity indices to each permutation  $p_g^{[R]}$  (equation (3)) in accord with equation (107), i.e.,

$$\$_1^{v_1(p_g^{[R]})} \$_2^{v_2(p_g^{[R]})} \dots \$_d^{v_d(p_g^{[R]})} \dots \$_r^{v_r(p_g^{[R]})}, \quad (112)$$

where the symbol  $\$_d$  indicates  $b_d$  for a hemispheric cycle,  $a_d$  for a homospheric cycle, or  $c_d$  for an enantiospheric cycle. After the introduction of the ligand inventories (equations (109)–(111)) into the product of sphericity indices (equation (112)), the expansion of the resulting equation produces a generating function for calculating the numbers of fixed formulas which are concerned with equation (112). When  $g$  runs over  $\mathbf{G}$  in the form of the right coset representation  $\mathbf{H} \backslash \mathbf{G}$ , the respective products (equation (112)) are summed up after the introduction of the ligand inventories so as to give the generating function:

$$\sum_{g \in \mathbf{G}} \$_1^{v_1(p_g^{[R]})} \$_2^{v_2(p_g^{[R]})} \dots \$_d^{v_d(p_g^{[R]})} \dots \$_r^{v_r(p_g^{[R]})}, \quad (113)$$

where the number of fixed formulas for each molecular formula (equation (102) or equation (103)) appears as the coefficient of the corresponding term.

### 4.3. Fujita's proligand method

#### 4.3.1. Enumeration of achiral plus chiral stereoisomers

The total number of fixed formulas calculated from the numbers of fixed formulas per stereoisomer (equation (106)) is equal to the total number of fixed formulas calculated from the numbers of fixed formulas per permutation (equation (113)), because they are simply different in the orders of summation. Hence, the equalization of equation (106) with equation (113) gives the following generating function:

$$\begin{aligned} & \sum_{[\theta]} B_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r} \\ &= \frac{1}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \$_1^{v_1(p_g^{[R]})} \$_2^{v_2(p_g^{[R]})} \dots \$_d^{v_d(p_g^{[R]})} \dots \$_r^{v_r(p_g^{[R]})}, \end{aligned} \quad (114)$$

where the sphericity indices  $\$_d$  ( $= a_d, b_d, c_d$ ) are replaced by the ligand inventories shown in equations (109)–(111).

To go on with further discussions, a CI-CFs is defined as follows:

$$\text{CI-CF}(\mathbf{G}, \mathcal{S}_d) = \frac{1}{|\mathbf{G}|} \sum_{g \in \mathbf{G}} \mathcal{S}_1^{v_1(p_g^{[R]})} \mathcal{S}_2^{v_2(p_g^{[R]})} \dots \mathcal{S}_d^{v_d(p_g^{[R]})} \dots \mathcal{S}_r^{v_r(p_g^{[R]})} \quad (115)$$

by using the right-hand side of equation (114) without introducing the ligand inventories. For cases in which  $\mathbf{H}$  of the  $(\mathbf{H})\mathbf{G}$  moves on the subgroups of  $\mathbf{G}$  so as to construct two or more orbits, the CI-CF should be expressed on the basis of  $\sum_{\mathbf{H}}, (\mathbf{H})\mathbf{G}$ . Thereby, we obtain following theorem:

**Theorem 4.** Let  $(\mathbf{H})\mathbf{G}$  be a right coset representation of a point group  $\mathbf{G}$  by its subgroup  $\mathbf{H}$ , where such a set of double cosets as represented by equations (15) or (36) is governed by the corresponding double coset representation, i.e.,  $(\mathbf{H})\mathbf{G}/(\mathbf{K})$  (equation (19)) or generally  $(\mathbf{H})\mathbf{G}/(\tilde{g}_j \mathbf{K} \tilde{g}_j^{-1})$  (equation (38)). On the action of  $g$  ( $\in \mathbf{G}$ ), the double coset representations ( $j = 1, 2, \dots, s = (|\mathbf{G}|/|\mathbf{K}|)$ ) moves concurrently with the right coset representation  $(\mathbf{H})\mathbf{G}$ .

Suppose the cycle structure of the  $(\mathbf{H})\mathbf{G}$  is represented by equation (108). Each set of double cosets corresponds to a function, i.e.,  $f_j$  ( $j = 1, 2, \dots$ , or  $s$ ) of  $\mathbf{F}$  (equation (40)), where its components,  $f_j(i)$  ( $i = 1, 2, \dots, r (= |\mathbf{G}|/|\mathbf{H}|)$ ), correspond to the double cosets of the set. Then, suppose that each component of the function  $f_j$  is ascribed to an achiral or a chiral ligand selected from such a set of ligands as represented by equation (100) so that the resulting set  $\mathbf{F}$  represents a stereoisomer having a molecular formula of the partition  $[\theta]$  (equations (102) or (103)). The  $\mathbf{F}$  is correlated to the  $\mathbf{K}$ -symmetry, which runs over the subgroups of  $\mathbf{G}$  so as to generate  $B_\theta$  non-equivalent stereoisomers. The numbers of non-equivalent stereoisomers  $B_\theta$  contained in equation (104) appear as the coefficients in a generating function represented as follows:

$$\sum_{[\theta]} B_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r} = \text{CI-CF}(\mathbf{G}, \mathcal{S}_d), \quad (116)$$

where the sphericity indices  $\mathcal{S}_d$  ( $a_d$ ,  $b_d$ , or  $c_d$ ) in the CI-CF are replaced by the ligand inventories shown in equations. (109), (110), or (111).  $\square$

For cases in which  $\mathbf{H}$  of the  $(\mathbf{H})\mathbf{G}$  moves on the subgroups of  $\mathbf{G}$  so as to construct two or more orbits, this theorem should be formulated generally on the basis of  $\sum_{\mathbf{H}}, (\mathbf{H})\mathbf{G}$ . This means that the components of the  $f_j$  should be expressed as  $f_j(i, i', \dots)$  ( $i = 1, 2, \dots, r (= |\mathbf{G}|/|\mathbf{H}|)$ ;  $i' = 1, 2, \dots, r' (= |\mathbf{G}|/|\mathbf{H}'|)$ ; as so on). Obviously, theorem 4 can be easily extended to satisfy such general cases.

**Example 15** [Achiral and chiral stereoisomers from a methane skeleton]. The products of cycles for the permutations of the right coset representation  $(\mathbf{C}_{3v})\mathbf{T}_d$  (figure 3) give the corresponding products of sphericity indices, as shown also in



figure 3. These are summed up in accord with equation (115) so as to give a CI-CF for this case:

$$\text{CI-CF}(\mathbf{T}_d, \mathbb{S}_d) = \frac{1}{24} \left( b_1^4 + 3b_2^2 + 8b_1b_3 + 6a_1^2c_2 + 6c_4 \right). \quad (117)$$

Let us consider the following set containing achiral and chiral ligands:

$$\mathbf{X} = \{\mathbf{A}, \mathbf{B}, \mathbf{X}, \mathbf{Y}; \mathbf{p}, \mathbf{q}, \mathbf{r}, \mathbf{s}; \bar{\mathbf{p}}, \bar{\mathbf{q}}, \bar{\mathbf{r}}, \bar{\mathbf{s}}\} \quad (118)$$

from which four ligands are selected as substituents, i.e.,  $\theta_{\mathbf{A}}$  of  $\mathbf{A}$ ,  $\theta_{\mathbf{B}}$  of  $\mathbf{B}$ ,  $\theta_{\mathbf{X}}$  of  $\mathbf{X}$ ,  $\theta_{\mathbf{Y}}$  of  $\mathbf{Y}$  (achiral ligands);  $\theta_{\mathbf{p}}$  of  $\mathbf{p}$ ,  $\theta_{\mathbf{q}}$  of  $\mathbf{q}$ ,  $\theta_{\mathbf{r}}$  of  $\mathbf{r}$ ,  $\theta_{\mathbf{s}}$  of  $\mathbf{s}$  (chiral ligands);  $\theta_{\bar{\mathbf{p}}}$  of  $\bar{\mathbf{p}}$ ,  $\theta_{\bar{\mathbf{q}}}$  of  $\bar{\mathbf{q}}$ ,  $\theta_{\bar{\mathbf{r}}}$  of  $\bar{\mathbf{r}}$ , and  $\theta_{\bar{\mathbf{s}}}$  of  $\bar{\mathbf{s}}$  (enantiomeric chiral ligands) so as to generate a stereoisomer having the following molecular formula:

$$M_f = \mathbf{A}^{\theta_{\mathbf{A}}} \mathbf{B}^{\theta_{\mathbf{B}}} \mathbf{X}^{\theta_{\mathbf{X}}} \mathbf{Y}^{\theta_{\mathbf{Y}}} \mathbf{p}^{\theta_{\mathbf{p}}} \mathbf{q}^{\theta_{\mathbf{q}}} \mathbf{r}^{\theta_{\mathbf{r}}} \mathbf{s}^{\theta_{\mathbf{s}}} \bar{\mathbf{p}}^{\theta_{\bar{\mathbf{p}}}} \bar{\mathbf{q}}^{\theta_{\bar{\mathbf{q}}}} \bar{\mathbf{r}}^{\theta_{\bar{\mathbf{r}}}} \bar{\mathbf{s}}^{\theta_{\bar{\mathbf{s}}}}. \quad (119)$$

The powers of the respective ligands contained in equation (119) satisfy the following partition:

$$[\theta] : \theta_{\mathbf{A}} + \theta_{\mathbf{B}} + \theta_{\mathbf{X}} + \theta_{\mathbf{Y}} + \theta_{\mathbf{p}} + \theta_{\mathbf{q}} + \theta_{\mathbf{r}} + \theta_{\mathbf{s}} + \theta_{\bar{\mathbf{p}}} + \theta_{\bar{\mathbf{q}}} + \theta_{\bar{\mathbf{r}}} + \theta_{\bar{\mathbf{s}}} = 4. \quad (120)$$

According to equations (109)–(111), we obtain the following ligand inventories:

$$b_d = \mathbf{A}^d + \mathbf{B}^d + \mathbf{X}^d + \mathbf{Y}^d + \mathbf{p}^d + \mathbf{q}^d + \mathbf{r}^d + \mathbf{s}^d + \bar{\mathbf{p}}^d + \bar{\mathbf{q}}^d + \bar{\mathbf{r}}^d + \bar{\mathbf{s}}^d, \quad (121)$$

$$a_d = \mathbf{A}^d + \mathbf{B}^d + \mathbf{X}^d + \mathbf{Y}^d, \quad (122)$$

$$c_d = \mathbf{A}^d + \mathbf{B}^d + \mathbf{X}^d + \mathbf{Y}^d + 2\mathbf{p}^{d/2}\bar{\mathbf{p}}^{d/2} + 2\mathbf{q}^{d/2}\bar{\mathbf{q}}^{d/2} + 2\mathbf{r}^{d/2}\bar{\mathbf{r}}^{d/2} + 2\mathbf{s}^{d/2}\bar{\mathbf{s}}^{d/2}. \quad (123)$$

After these ligand inventories are introduced into the CI-CF (equation (117)), the resulting equation is expanded to give a generating function as follows:

$$\begin{aligned} F = & [\mathbf{ABXY}] + [\mathbf{p}\bar{\mathbf{p}}\bar{\mathbf{q}}\bar{\mathbf{q}} + \dots] + \left[ \frac{1}{2}(\mathbf{p}^4 + \bar{\mathbf{p}}^4) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{A}^3\mathbf{p} + \mathbf{A}^3\bar{\mathbf{p}}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}\mathbf{p}^3 + \mathbf{A}\bar{\mathbf{p}}^3) + \dots \right] + \left[ \frac{1}{2}(\mathbf{p}^3\mathbf{q} + \bar{\mathbf{p}}^3\bar{\mathbf{q}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{p}^3\bar{\mathbf{p}} + \bar{\mathbf{p}}^3\mathbf{p}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}^2\mathbf{p}^2 + \mathbf{A}^2\bar{\mathbf{p}}^2) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{p}^2\mathbf{q}^2 + \bar{\mathbf{p}}^2\bar{\mathbf{q}}^2) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}^2\mathbf{B}\mathbf{p} + \mathbf{A}^2\mathbf{B}\bar{\mathbf{p}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{A}^2\mathbf{p}\mathbf{q} + \mathbf{A}^2\bar{\mathbf{p}}\bar{\mathbf{q}}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}\mathbf{B}\mathbf{p}^2 + \mathbf{A}\mathbf{B}\bar{\mathbf{p}}^2) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{A}\mathbf{p}^2\bar{\mathbf{p}} + \mathbf{A}\bar{\mathbf{p}}^2\mathbf{p}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}\mathbf{p}^2\mathbf{q} + \mathbf{A}\bar{\mathbf{p}}^2\bar{\mathbf{q}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{p}^2\bar{\mathbf{p}}\mathbf{q} + \bar{\mathbf{p}}^2\mathbf{p}\bar{\mathbf{q}}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{p}^2\mathbf{q}\bar{\mathbf{q}} + \bar{\mathbf{p}}^2\bar{\mathbf{q}}\mathbf{q}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{p}^2\mathbf{q}\mathbf{r} + \bar{\mathbf{p}}^2\bar{\mathbf{q}}\bar{\mathbf{r}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\mathbf{A}\mathbf{B}\mathbf{X}\mathbf{p} + \mathbf{A}\mathbf{B}\mathbf{X}\bar{\mathbf{p}}) + \dots \right] + \left[ \frac{1}{2}(\mathbf{A}\mathbf{B}\mathbf{p}\mathbf{q} + \mathbf{A}\mathbf{B}\bar{\mathbf{p}}\bar{\mathbf{q}}) + \dots \right] \end{aligned}$$

$$\begin{aligned}
& +[\frac{2}{2}(A\overline{p}\overline{p}q + A\overline{p}p\overline{q}) + \dots] + [\frac{2}{2}(Apqr + A\overline{p}\overline{q}\overline{r}) + \dots] \\
& +[\frac{2}{2}(p\overline{p}qr + \overline{p}p\overline{q}\overline{r}) + \dots] + [\frac{2}{2}(pqrs + \overline{p}\overline{q}\overline{r}\overline{s}) + \dots] \\
& +[A^4 + \dots] + [A^3B + \dots] + [A^2B^2 + \dots] + [p^2\overline{p}^2 + \dots] \\
& +[A^2BX + \dots] + [A^2p\overline{p} + \dots] + [2ABp\overline{p} + \dots]. \tag{124}
\end{aligned}$$

The term in each pair of brackets in equation (124) is a representative for representing stereoisomers of the same kind of partitions. For example, the term  $\frac{1}{2}(p^4 + \overline{p}^4)$  in the third pair of brackets represents the terms,  $\frac{1}{2}(p^4 + \overline{p}^4)$ ,  $\frac{1}{2}(q^4 + \overline{q}^4)$ ,  $\frac{1}{2}(r^4 + \overline{r}^4)$ , and  $\frac{1}{2}(s^4 + \overline{s}^4)$ . The coefficient of each term (i.e., molecular formula) indicates the corresponding number of stereoisomers. For the numbers of chiral stereoisomers, a comment should be again added here. The term  $\frac{1}{2}(p^4 + \overline{p}^4)$  should be interpreted as designating  $1 \times \frac{1}{2}(p^4 + \overline{p}^4)$ , the coefficient 1 of which indicates the existence of one stereoisomer (one enantiomeric pair) having the molecular formula. On the other hand, the term  $\frac{2}{2}(ABXp + ABX\overline{p})$  should be interpreted as being  $2 \times \frac{1}{2}(ABXp + ABX\overline{p})$ , the coefficient 2 of which indicates the existence of two stereoisomers (two enantiomeric pairs) having the molecular formula. It should be noted that the terms  $ABXY$  and  $p\overline{p}q\overline{q}$  show special cases of chiral stereoisomers in which respective enantiomers have the same molecular formula. Hence, the terms should be interpreted as  $1 \times \frac{1}{2}(ABXY + \overline{ABXY})$  and  $1 \times \frac{1}{2}(p\overline{p}q\overline{q} + \overline{p}p\overline{q}q)$ .

Obviously, two diastereomers of  $ABp\overline{p}$  are correctly counted because the coefficient of the term is equal to 2. Thus, this result is in agreement with the stereochemical viewpoint (cf. figure 9). The existence of two enantiomeric pairs corresponding to such a term as  $\frac{2}{2}(pqrs + \overline{p}\overline{q}\overline{r}\overline{s})$  is also assured, as indicated by the coefficient 2 of the term  $2 \times \frac{1}{2}(pqrs + \overline{p}\overline{q}\overline{r}\overline{s})$ .

The results described here are in agreement with those described in [23, 24], which reported more detailed data itemized with subsymmetries.  $\square$

Theorem 4 has the same content as theorem 1 of Fujita's proligand method [9], which was proved otherwise without using the concept of double coset representations proposed in the present paper. Moreover, the discussions described for proving theorem 4 are expected to provide us with a common foundation for comprehending Fujita's USCI approach based on subduction of coset representations [11, 25], Fujita's characteristic-monomial (CM) method based on subduction of  $\mathbf{Q}$ -conjugacy representations [26, 27], and Fujita's enumeration method based on subduction of dominant representations [12, 13], where these result in the derivations of CI-CFs of the same kind as described in theorem 4. This point will be a further target to be pursued.

#### 4.3.2. Enumeration of achiral stereoisomers

In accord with the treatment described in [10], we consider the maximum chiral subgroup  $\mathbf{G}'$  of the group  $\mathbf{G}$ . Among the terms contained in equation

(115), the terms corresponding to the subgroup  $\mathbf{G}'$  are collected to give the following CI-CF:

$$\text{CI-CF}(\mathbf{G}', b_d) = \frac{1}{|\mathbf{G}'|} \sum_{g \in \mathbf{G}'} b_1^{v_1(p_g^{[R]})} b_2^{v_2(p_g^{[R]})} \dots b_d^{v_d(p_g^{[R]})} \dots b_r^{v_r(p_g^{[R]})}, \quad (125)$$

where only hemispheric indices remain and  $|\mathbf{G}'| = |\mathbf{G}|/2$ . Let us replace the CI-CF in equation (116) by the CI-CF in equation (125) so as to give the following equation:

$$\sum_{[\theta]} B'_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r} = \text{CI-CF}(\mathbf{G}', b_d), \quad (126)$$

where the sphericity indices  $b_d$  are replaced by the ligand inventories shown in equation (109). Then, we obtain a generating function for calculating the number of stereoisomers  $B'_\theta$ , where an achiral stereoisomer is counted once, while a chiral stereoisomer and its enantiomer are counted separately. Let the symbol  $\mathcal{A}$  represent a generating function for calculating achiral stereoisomers and the symbol  $\mathcal{C}$  represent a generating function for calculating enantiomeric pairs of chiral stereoisomers. Then, equation (126) means that

$$\text{CI-CF}(\mathbf{G}', b_d) = \mathcal{A} + 2\mathcal{C}, \quad (127)$$

while equation (116) means that

$$\text{CI-CF}(\mathbf{G}, \$_d) = \mathcal{A} + \mathcal{C}. \quad (128)$$

Hence  $\mathcal{A}$  and  $\mathcal{C}$  are calculated as follows:

$$\mathcal{A} = 2\text{CI-CF}(\mathbf{G}, \$_d) - \text{CI-CF}(\mathbf{G}', b_d), \quad (129)$$

$$\mathcal{C} = \text{CI-CF}(\mathbf{G}', b_d) - \text{CI-CF}(\mathbf{G}, \$_d). \quad (130)$$

The sphericity indices  $\$ _d$  (i.e.,  $a_d$ ,  $b_d$ , or  $c_d$ ) in the CI-CFs (equations (129) and (130)) are replaced by the ligand inventories shown in equations (109), (110), or (111). Obviously, the coefficient  $2B_\theta - B'_\theta$  ( $= A_\theta$ ) for achiral stereoisomers and the coefficient  $B'_\theta - B_\theta$  ( $= C_\theta$ ) for enantiomeric pairs of chiral stereoisomers appear in equations (129) and (130) after expansion.

Because of the relationship  $|\mathbf{G}'| = |\mathbf{G}|/2$ , the twice of the  $\text{CI-CF}(\mathbf{G}, \$ _d)$  (equation (115)) contains the  $\text{CI-CF}(\mathbf{G}', b_d)$  (equation (125)) once and only once, where the terms contained in the  $\text{CI-CF}(\mathbf{G}', b_d)$  are concerned with proper rotations. It follows that the remaining terms in the  $\mathcal{A}$  (equation (129)) is concerned with improper rotations only, i.e.,  $\bar{\mathbf{G}} = \mathbf{G} - \mathbf{G}'$ . Thereby, we can define the  $\text{CI-CF}_{\mathcal{A}}$  as follows:

$$\mathcal{A} = \text{CI-CF}_{\mathcal{A}}(\bar{\mathbf{G}}, \$ _d) = \frac{1}{|\bar{\mathbf{G}}|} \sum_{g \in \bar{\mathbf{G}}} \$ _1^{v_1(p_g^{[R]})} \$ _2^{v_2(p_g^{[R]})} \dots \$ _d^{v_d(p_g^{[R]})} \dots \$ _r^{v_r(p_g^{[R]})}, \quad (131)$$

where the sphericity indices  $\$d$  are  $a_d$  or  $c_d$  and no terms having  $b_d$  appear. It should be noted that the summation is concerned with improper rotations  $g \in \overline{\mathbf{G}}$  ( $= \mathbf{G} - \mathbf{G}'$ ) and the divisor is equal to  $|\overline{\mathbf{G}}| = |\mathbf{G}|/2$ . By using equation (131), the numbers of achiral stereoisomers  $A_\theta$  are calculated according to the following theorem:

**Theorem 5.** Suppose that the resulting set  $\mathbf{F}$  described in theorem 4 represents an achiral stereoisomer having a molecular formula of the partition  $[\theta]$  (equation (102)). The numbers of non-equivalent achiral stereoisomers  $A_\theta$  appear as the coefficients in a generating function represented as follows:

$$\sum_{[\theta]} A_\theta X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \bar{p}_1^{\theta''_1} \bar{p}_2^{\theta''_2} \dots \bar{p}_r^{\theta''_r} = \text{CI-CF}_{\mathcal{A}}(\overline{\mathbf{G}}, \$d), \quad (132)$$

where the sphericity indices  $\$d$  ( $a_d$  or  $c_d$ ) in the  $\text{CI-CF}_{\mathcal{A}}$  (equation (131)) are replaced by the ligand inventories shown in equations (110) or (111).  $\square$

**Example 16** [Achiral stereoisomers from a methane skeleton]. From the data collected in figure 3, the products of sphericity indices for the twelve improper rotations are summed up in accord with equation (131) so as to give a  $\text{CI-CF}_{\mathcal{A}}$  for this case:

$$\text{CI-CF}_{\mathcal{A}}(\overline{\mathbf{T}}_d, \$d) = \frac{1}{12} (6a_1^2 c_2 + 6c_4) = \frac{1}{2} (a_1^2 c_2 + c_4), \quad (133)$$

where we place  $\overline{\mathbf{T}}_d = \mathbf{T}_d - \mathbf{T}$ . From the set  $\mathbf{X}$  (equation (118)), four ligands are selected as substituents, i.e.,  $\theta_A$  of  $A$ ,  $\theta_B$  of  $B$ ,  $\theta_X$  of  $X$ ,  $\theta_Y$  of  $Y$  (achiral ligands);  $\theta_p$  of  $p$ ,  $\theta_q$  of  $q$ ,  $\theta_r$  of  $r$ ,  $\theta_s$  of  $s$  (chiral ligands);  $\theta_{\bar{p}}$  of  $\bar{p}$ ,  $\theta_{\bar{q}}$  of  $\bar{q}$ ,  $\theta_{\bar{r}}$  of  $\bar{r}$ , and  $\theta_{\bar{s}}$  of  $\bar{s}$  (enantiomeric chiral ligands) so as to generate a stereoisomer having the molecular formula  $M_f$  (equation (119)). The powers of the respective ligands contained in equation (119) satisfy the partition shown in equation (120). After the ligand inventories shown in equations (122) and (123) are introduced into the  $\text{CI-CF}_{\mathcal{A}}$  (equation (133)), the resulting equation is expanded to give a generating function as follows:

$$\begin{aligned} \overline{F} = & [A^4 + \dots] + [A^3 B + \dots] \\ & + [A^2 B^2 + \dots] + [p^2 \bar{p}^2 + \dots] + [A^2 B X + \dots] + [A^2 p \bar{p} + \dots] \\ & + [2ABp\bar{p} + \dots]. \end{aligned} \quad (134)$$

The term in each pair of brackets in equation (134) is a representative for representing achiral stereoisomers of the same kind of partitions.  $\square$

### 4.3.3. Enumeration of chiral stereoisomers

By combining equation (129) with equation (131), we obtain the following equation:

$$2\text{CI-CF}(\mathbf{G}, \$_d) = \text{CI-CF}(\mathbf{G}', b_d) + \text{CI-CF}_{\mathcal{A}}(\mathbf{G}', b_d). \quad (135)$$

This equation is introduced into equation (130) so as to generate the generating function  $\mathcal{C}$  for the numbers of chiral stereoisomers (enantiomeric pairs), i.e.,

$$\mathcal{C} = \frac{1}{2}\text{CI-CF}(\mathbf{G}', b_d) - \frac{1}{2}\text{CI-CF}_{\mathcal{A}}(\overline{\mathbf{G}}, \$_d). \quad (136)$$

By introducing equations (125) and (131) into equation (136) (note that  $|\mathbf{G}'| = |\overline{\mathbf{G}}| = |\mathbf{G}|/2$ ), we can define the  $\text{CI-CF}_{\mathcal{C}}$  as follows:

$$\begin{aligned} \mathcal{C} &= \text{CI-CF}_{\mathcal{C}}(\mathbf{G}', \$_d) \\ &= \frac{1}{|\mathbf{G}|} \left\{ \sum_{g \in \mathbf{G}'} b_1^{v_1(p_g^{[R]})} b_2^{v_2(p_g^{[R]})} \dots b_d^{v_d(p_g^{[R]})} \dots b_r^{v_r(p_g^{[R]})} \right. \\ &\quad \left. - \sum_{g \in \overline{\mathbf{G}}} \$_1^{v_1(p_g^{[R]})} \$_2^{v_2(p_g^{[R]})} \dots \$_d^{v_d(p_g^{[R]})} \dots \$_r^{v_r(p_g^{[R]})} \right\}, \quad (137) \end{aligned}$$

where the sphericity indices  $\$_d$  in the latter summation are  $a_d$  or  $c_d$ . It should be noted that the first summation is concerned with proper rotations  $g \in \mathbf{G}'$ ; the second summation is concerned with improper rotations  $g \in \overline{\mathbf{G}}$  ( $= \mathbf{G} - \mathbf{G}'$ ); and the divisor is equal to  $|\mathbf{G}|$ . The comparison of the  $\text{CI-CF}_{\mathcal{C}}$  (equation (137)) with the  $\text{CI-CF}$  (equation (115)) reveals that the plus signs of the terms for the improper rotations appearing in the latter (equation (115)) are simply changed into minus signs so as to generate the former (equation (137)). By using equation (137), the numbers of achiral stereoisomers  $C_{\theta}$  are calculated according to the following theorem:

**Theorem 6.** Suppose that the resulting set  $\mathbf{F}$  described in theorem 4 represents a chiral stereoisomer having a molecular formula of the partition  $[\theta]$  (equation (102)). The numbers of chiral stereoisomers  $C_{\theta}$  appear as the coefficients in a generating function represented as follows:

$$\sum_{[\theta]} C_{\theta} X_1^{\theta_1} X_2^{\theta_2} \dots X_r^{\theta_r} p_1^{\theta'_1} p_2^{\theta'_2} \dots p_r^{\theta'_r} \overline{p}_1^{\theta''_1} \overline{p}_2^{\theta''_2} \dots \overline{p}_r^{\theta''_r} = \text{CI-CF}_{\mathcal{C}}(\mathbf{G}', \$_d), \quad (138)$$

where the sphericity indices  $\$_d$  ( $b_d$ ,  $a_d$ , or  $c_d$ ) in the  $\text{CI-CF}_{\mathcal{C}}$  (equation (137)) are replaced by the ligand inventories shown in equations (109), (110), or (111).  $\square$

**Example 17** [Chiral stereoisomers from a methane skeleton]. From the data collected in figure 3, the 24 products of sphericity indices are summed up or subtracted in accord with equation (137) so as to give a CI-CF<sub>C</sub> for this case:

$$\text{CI-CF}_C(\mathbf{T}, \mathcal{S}_d) = \frac{1}{24} (b_1^4 + 3b_2^2 + 8b_1b_3 - 6a_1^2c_2 - 6c_4). \quad (139)$$

From the set **X** (equation (118)), four ligands are selected as substituents, i.e.,  $\theta_A$  of **A**,  $\theta_B$  of **B**,  $\theta_X$  of **X**,  $\theta_Y$  of **Y** (achiral ligands);  $\theta_p$  of **p**,  $\theta_q$  of **q**,  $\theta_r$  of **r**,  $\theta_s$  of **s** (chiral ligands);  $\theta_{\bar{p}}$  of  $\bar{p}$ ,  $\theta_{\bar{q}}$  of  $\bar{q}$ ,  $\theta_{\bar{r}}$  of  $\bar{r}$ , and  $\theta_{\bar{s}}$  of  $\bar{s}$  (enantiomeric chiral ligands), so as to generate a chiral stereoisomer having the molecular formula  $M_f$  (equation (119)). The powers of the respective ligands contained in equation (119) satisfy the partition shown in equation (120). After the ligand inventories shown in equations (121)–(123) are introduced into the CI-CF<sub>C</sub> (equation (139)), the resulting equation is expanded to give a generating function as follows:

$$\begin{aligned} F' = & [\text{ABXY}] + [\text{p}\bar{p}\text{q}\bar{q} + \dots] + \left[ \frac{1}{2}(\text{p}^4 + \bar{\text{p}}^4) + \dots \right] + \left[ \frac{1}{2}(\text{A}^3\text{p} + \text{A}^3\bar{\text{p}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{A}\text{p}^3 + \text{A}\bar{\text{p}}^3) + \dots \right] + \left[ \frac{1}{2}(\text{p}^3\text{q} + \bar{\text{p}}^3\bar{\text{q}}) + \dots \right] + \left[ \frac{1}{2}(\text{p}^3\bar{\text{p}} + \bar{\text{p}}^3\text{p}) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{A}^2\text{p}^2 + \text{A}^2\bar{\text{p}}^2) + \dots \right] + \left[ \frac{1}{2}(\text{p}^2\text{q}^2 + \bar{\text{p}}^2\bar{\text{q}}^2) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{A}^2\text{Bp} + \text{A}^2\text{B}\bar{\text{p}}) + \dots \right] + \left[ \frac{1}{2}(\text{A}^2\text{pq} + \text{A}^2\bar{\text{p}}\bar{\text{q}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{ABp}^2 + \text{AB}\bar{\text{p}}^2) + \dots \right] + \left[ \frac{1}{2}(\text{Ap}^2\bar{\text{p}} + \text{A}\bar{\text{p}}^2\text{p}) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{Ap}^2\text{q} + \text{A}\bar{\text{p}}^2\bar{\text{q}}) + \dots \right] + \left[ \frac{1}{2}(\text{p}^2\bar{\text{p}}\text{q} + \bar{\text{p}}^2\text{p}\bar{\text{q}}) + \dots \right] \\ & + \left[ \frac{1}{2}(\text{p}^2\text{q}\bar{\text{q}} + \bar{\text{p}}^2\bar{\text{q}}\text{q}) + \dots \right] + \left[ \frac{1}{2}(\text{p}^2\text{qr} + \bar{\text{p}}^2\bar{\text{q}}\bar{\text{r}}) + \dots \right] \\ & + \left[ \frac{2}{2}(\text{ABXp} + \text{ABX}\bar{\text{p}}) + \dots \right] + \left[ \frac{2}{2}(\text{ABpq} + \text{AB}\bar{\text{p}}\bar{\text{q}}) + \dots \right] \\ & + \left[ \frac{2}{2}(\text{Ap}\bar{\text{p}}\text{q} + \text{A}\bar{\text{p}}\text{p}\bar{\text{q}}) + \dots \right] + \left[ \frac{2}{2}(\text{Apqr} + \text{A}\bar{\text{p}}\bar{\text{q}}\bar{\text{r}}) + \dots \right] \\ & + \left[ \frac{2}{2}(\text{p}\bar{\text{p}}\text{qr} + \bar{\text{p}}\text{p}\bar{\text{q}}\bar{\text{r}}) + \dots \right] + \left[ \frac{2}{2}(\text{pqrs} + \bar{\text{p}}\bar{\text{q}}\bar{\text{r}}\bar{\text{s}}) + \dots \right]. \quad (140) \end{aligned}$$

The term in each pair of brackets in equation (140) is a representative for representing chiral stereoisomers of the same kind of partitions.  $\square$

#### 4.4. Pólya's theorem as a special case

As found easily, Pólya's theorem is a special case of theorem 4, where the CI-CF (equation (115)) is reduced into the CI without CF (i.e., Pólya's CI). Thus, the sphericity indices,  $b_d$ ,  $a_d$ , and  $c_d$ , are replaced by a single dummy variable  $s_d$ . As a result, Pólya's theorem takes account of achiral ligands (or atoms) only as substituents although this fact had not been mentioned explicitly until Fujita's proligand method was proposed [9]. If chiral ligands are considered in an enumeration based on Pólya's Theorem, the result is inconsistent with stereochemistry, as shown in the following example:

**Example 18** [Stereoisomer enumeration without considering sphericities]. The sphericity indices ( $b_d$ ,  $a_d$ , and  $c_d$ ) appearing in equation (117) are replaced by a single dummy variable  $s_d$  so as to give the CI, which is equivalent to that derived by Pólya's theorem:

$$\text{CI}(\mathbf{T}_d, s_d) = \frac{1}{24} (s_1^4 + 3s_2^2 + 8s_1s_3 + 6s_1^2s_2 + 6s_4). \quad (141)$$

From the set  $\mathbf{X}$  (equation (118)), four ligands are selected as substituents, i.e.,  $\theta_A$  of A,  $\theta_B$  of B,  $\theta_X$  of X,  $\theta_Y$  of Y (achiral ligands);  $\theta_p$  of p,  $\theta_q$  of q,  $\theta_r$  of r,  $\theta_s$  of s (chiral ligands);  $\theta_{\bar{p}}$  of  $\bar{p}$ ,  $\theta_{\bar{q}}$  of  $\bar{q}$ ,  $\theta_{\bar{r}}$  of  $\bar{r}$ , and  $\theta_{\bar{s}}$  of  $\bar{s}$  (enantiomeric chiral ligands), so as to generate a stereoisomer having the molecular formula  $M_f$  (equation (119)). The powers of the respective ligands contained in equation (119) satisfy the partition shown in equation (120). In this case, we use a ligand inventory represented by the following equation:

$$s_d = \mathbf{A}^d + \mathbf{B}^d + \mathbf{X}^d + \mathbf{Y}^d + \mathbf{p}^d + \mathbf{q}^d + \mathbf{r}^d + \mathbf{s}^d + \bar{\mathbf{p}}^d + \bar{\mathbf{q}}^d + \bar{\mathbf{r}}^d + \bar{\mathbf{s}}^d. \quad (142)$$

After the ligand inventory is introduced into the CI (equation (141)), the resulting equation is expanded to give a generating function as follows:

$$\begin{aligned} F'' = & [\mathbf{ABXY}] + [\mathbf{p}\bar{\mathbf{p}}\mathbf{q}\bar{\mathbf{q}} + \dots] + [(\mathbf{p}^4 + \bar{\mathbf{p}}^4) + \dots] + [(\mathbf{A}^3\mathbf{p} + \mathbf{A}^3\bar{\mathbf{p}}) + \dots] \\ & + [(\mathbf{A}\mathbf{p}^3 + \mathbf{A}\bar{\mathbf{p}}^3) + \dots] + [(\mathbf{p}^3\mathbf{q} + \bar{\mathbf{p}}^3\bar{\mathbf{q}}) + \dots] + [(\mathbf{p}^3\bar{\mathbf{p}} + \bar{\mathbf{p}}^3\mathbf{p}) + \dots] \\ & + [(\mathbf{A}^2\mathbf{p}^2 + \mathbf{A}^2\bar{\mathbf{p}}^2) + \dots] + [(\mathbf{p}^2\mathbf{q}^2 + \bar{\mathbf{p}}^2\bar{\mathbf{q}}^2) + \dots] + [(\mathbf{A}^2\mathbf{B}\mathbf{p} + \mathbf{A}^2\mathbf{B}\bar{\mathbf{p}}) + \dots] \\ & + [(\mathbf{A}^2\mathbf{p}\mathbf{q} + \mathbf{A}^2\bar{\mathbf{p}}\bar{\mathbf{q}}) + \dots] + [(\mathbf{A}\mathbf{B}\mathbf{p}^2 + \mathbf{A}\mathbf{B}\bar{\mathbf{p}}^2) + \dots] \\ & + [(\mathbf{A}\mathbf{p}^2\bar{\mathbf{p}} + \mathbf{A}\bar{\mathbf{p}}^2\mathbf{p}) + \dots] + [(\mathbf{A}\mathbf{p}^2\mathbf{q} + \mathbf{A}\bar{\mathbf{p}}^2\bar{\mathbf{q}}) + \dots] \\ & + [(\mathbf{p}^2\bar{\mathbf{p}}\mathbf{q} + \bar{\mathbf{p}}^2\mathbf{p}\bar{\mathbf{q}}) + \dots] + [(\mathbf{p}^2\mathbf{q}\bar{\mathbf{q}} + \bar{\mathbf{p}}^2\bar{\mathbf{q}}\mathbf{q}) + \dots] + [(\mathbf{p}^2\mathbf{q}\mathbf{r} + \bar{\mathbf{p}}^2\bar{\mathbf{q}}\bar{\mathbf{r}}) + \dots] \\ & + [(\mathbf{A}\mathbf{B}\mathbf{X}\mathbf{p} + \mathbf{A}\mathbf{B}\mathbf{X}\bar{\mathbf{p}}) + \dots] + [(\mathbf{A}\mathbf{B}\mathbf{p}\mathbf{q} + \mathbf{A}\mathbf{B}\bar{\mathbf{p}}\bar{\mathbf{q}}) + \dots] \\ & + [(\mathbf{A}\mathbf{p}\bar{\mathbf{p}}\mathbf{q} + \mathbf{A}\bar{\mathbf{p}}\mathbf{p}\bar{\mathbf{q}}) + \dots] + [(\mathbf{A}\mathbf{p}\mathbf{q}\mathbf{r} + \mathbf{A}\bar{\mathbf{p}}\bar{\mathbf{q}}\bar{\mathbf{r}}) + \dots] \\ & + [(\mathbf{p}\bar{\mathbf{p}}\mathbf{q}\mathbf{r} + \bar{\mathbf{p}}\mathbf{p}\bar{\mathbf{q}}\bar{\mathbf{r}}) + \dots] + [(\mathbf{p}\mathbf{q}\mathbf{r}\mathbf{s} + \bar{\mathbf{p}}\bar{\mathbf{q}}\bar{\mathbf{r}}\bar{\mathbf{s}}) + \dots] + [\mathbf{A}^4 + \dots] + [\mathbf{A}^3\mathbf{B} + \dots] \\ & + [\mathbf{A}^2\mathbf{B}^2 + \dots] + [\mathbf{p}^2\bar{\mathbf{p}}^2 + \dots] + [\mathbf{A}^2\mathbf{B}\mathbf{X} + \dots] + [\mathbf{A}^2\mathbf{p}\bar{\mathbf{p}} + \dots] \\ & + [\mathbf{A}\mathbf{B}\mathbf{p}\bar{\mathbf{p}} + \dots]. \end{aligned} \quad (143)$$

The term in each pair of brackets in equation (143) is a representative for representing stereoisomers of the same kind of partitions.

Obviously, the two diastereomers of  $ABp\bar{p}$  are regarded as a single stereoisomer, which is in disagreement with the stereochemical viewpoint (cf. figure 9). The existence of two enantiomeric pairs corresponding to such a term as  $(ABXp + ABX\bar{p})$  cannot be clarified by equation (143), although the two enantiomeric pairs are so diastereomeric to be counted distinctly.

The result (equation (143)) contains another type of disagreement with the stereochemical viewpoint. Thus, the coefficient 1 of the term  $ABXY$  indicates that the two enantiomers of this molecular formula is counted once. On the other hand, such terms as appearing in  $(p^4 + \bar{p}^4)$  indicate that two enantiomers counted separately.  $\square$

In order to avoid the disagreement described in example 18, we should equalize chiral ligands (e.g.  $p$ ) and their enantiomeric ligands (e.g.,  $\bar{p}$ ). For this purpose, we should use the following ligand inventory:

$$s_d = A^d + B^d + X^d + Y^d + p^d + q^d + r^d + s^d \quad (144)$$

in place of equation (142). This means that ligands, even chiral, are regarded as graphs, not as three-dimensional objects within the scope of Pólya's theorem. In summary, Pólya's theorem is concluded to count graphs, not stereoisomers.

## 5. Conclusions

The concept of *double coset representations* is proposed to characterize stereoisomerism. Thus, when a skeleton belongs to a point group  $\mathbf{G}$ , its substitution positions are governed by right coset representations  $(\mathbf{H})\backslash\mathbf{G}$ , where the  $\mathbf{H}$  is a subgroup of  $\mathbf{G}$ . Then, a set of homomeric stereoisomers of  $\mathbf{K}$ -symmetry is governed by a double coset representation  $(\mathbf{H})\backslash\mathbf{G}/(\mathbf{K})$ , which is based on double cosets  $\mathbf{H}g\mathbf{K}$  ( $g \in \mathbf{G}$ ). This is generalized to describe sets of homomeric stereoisomers, which are governed by double coset representations  $(\mathbf{H})\backslash\mathbf{G}/(g_j\mathbf{K}g_j^{-1})$  based on double cosets  $\mathbf{H}g(g_j\mathbf{K}g_j^{-1})$ , where the operations  $g_j$  ( $j = 1, 2, \dots, s (= |\mathbf{G}|/|\mathbf{K}|)$ ) are representatives of a left coset decomposition of  $\mathbf{G}$  by  $\mathbf{K}$  and  $g_1 = I$ . In order to treat chiral ligands as well as achiral ligands, the concept of *sphericities of double cosets* is proposed so that double cosets are classified into *homospheric* double cosets, *enantiospheric* double cosets, or *hemispheric* double cosets. The sphericities of double cosets determine modes of substitutions (i.e., chirality fittingness), where homospheric double cosets permit achiral ligands only; enantiospheric double cosets permit achiral ligands or enantiomeric pairs; and hemispheric double cosets permit achiral and chiral ligands. These results hold true when  $\mathbf{H}$  and  $\mathbf{K}$  run over the subgroups of  $\mathbf{G}$ .



In order to apply the sphericities of double cosets to combinatorial enumeration of stereoisomers, they are linked to the sphericities of cycles which are ascribed to the right coset representation  $(\mathbf{H} \setminus) \mathbf{G}$ . The resulting products of sphericity indices are used to construct a CI-CFs, which is proved to be identical with the CI-CF introduced in Fujita's proligand method [9].

## References

- [1] G. Pólya, *Acta Math.* 68 (1937) 145–254.
- [2] G. Pólya and R.C. Read, *Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds* (Springer-Verlag, New York, 1987).
- [3] F. Harary and E. M. Palmer, *Graphical Enumeration* (Academic Press, New York, 1973).
- [4] A.T. Balaban (ed), *Chemical Applications of Graph Theory* (Academic Press, London, 1976).
- [5] G. Pólya, R.E. Tarjan and D.R. Woods, *Notes on Introductory Combinatorics* (Birkhäuser, Boston, 1983).
- [6] K. Balasubramanian, *Chem. Rev.* 85 (1985) 599–618.
- [7] E.K. Lloyd, in: *Studies in Physical and Theoretical Chemistry. Graph Theory and Topology in Chemistry*, vol. 51 eds. R.B. King and D.H. Rouvray, (Elsevier, Amsterdam, 1987), pp. 537–543.
- [8] A.T. Balaban, in: *Chemical Group Theory. Introduction and Fundamentals*, eds. D. Bonchev and D.H. Rouvray (Gordon & Breach, Switzerland, 1994) pp. 159–208.
- [9] S. Fujita, *Theor. Chem. Acc.* 113 (2005) 73–79.
- [10] S. Fujita, *Theor. Chem. Acc.* 113 (2005) 80–86.
- [11] S. Fujita, *Symmetry and Combinatorial Enumeration in Chemistry* (Springer-Verlag, Berlin-Heidelberg, 1991).
- [12] S. Fujita, *Theor. Chem. Acta.* 91 (1995) 291–314.
- [13] S. Fujita, *Theor. Chem. Acta.* 91 (1995) 315–332.
- [14] S. Fujita, *Bull. Chem. Soc. Jpn.* 71 (1998) 1587–1596.
- [15] S. Fujita, *Bull. Chem. Soc. Jpn.* 72 (1999) 2409–2416.
- [16] E. Ruch and D.J. Klein, *Theor. Chim. Acta.* 63 (1983) 447–472.
- [17] J. Brocas, *J. Amer. Chem. Soc.* 108 (1986) 1135–1145.
- [18] W. Hässelbarth, *Theor. Chim. Acta.* 67 (1985) 427–437.
- [19] C.A. Mead, *J. Amer. Chem. Soc.* 109 (1987) 2130–2137.
- [20] E. Ruch, W. Hässelbarth and B. Richter, *Theor. Chim. Acta.* 19 (1970) 288–300.
- [21] S. Fujita, *J. Graph Theor.* 18 (1994) 349–371.
- [22] S. Fujita, *J. Chem. Educ.* 63 (1986) 744–746.
- [23] S. Fujita, *Chem. Rec.* 2 (2002) 164–176.
- [24] S. Fujita, *J. Math. Chem.* 35 (2004) 261–283.
- [25] S. Fujita, *Bull. Chem. Soc. Jpn.* 63 (1990) 203–215.
- [26] S. Fujita, *Theor. Chem. Acc.* 99 (1998) 224–230.
- [27] S. Fujita, *J. Chem. Inf. Comput. Sci.* 40 (2000) 1101–1112.