# Enantiomeric and diastereomeric relationships of ethylene derivatives. Restructuring stereochemistry by a group-theoretical and combinatorial approach

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To restructure stereochemistry into a systematic format, enantiomeric and diastereomeric relationships have been investigated by using ethylene derivatives as examples in the light of a new group-theoretical and combinatorial approach. On one hand, enantiomeric relationship for ethylene derivatives has been characterized by means of a point group of order 8 ($\mathbf{D}_{2h}$), where chirality fittingness based on the sphericity concept has been applied to the enumeration of stereoisomers. On the other hand, diastereomeric relationship for ethylene derivatives has been examined by a permutation group of order 8 ($\mathbf{S}_9^{[4]}$), which is a subgroup of the symmetric group of order 4 ($\mathbf{S}^{[4]}$) and isomorphic to a point group $\mathbf{D}_{2d}$. The subgroups of $\mathbf{S}_9^{[4]}$ have been classified into stereogenic and astereogenic ones. A stereogenic subgroup corresponds to a pair of diastereomers, while an astereogenic subgroup is assigned to a self-diastereomer. The relationship between diastereomers and constitutional isomers have been also discussed.

**KEY WORDS:** enantiomer, diastereomer, ethylene, stereochemistry

## 1.    Introduction

Enantiomeric relationship and diastereomeric one are essential items for stereochemistry, as described in textbooks of organic stereochemistry [1]. However, their total aspects have not been fully investigated. In particular, the term "diastereomeric" has been used pragmatically and experimentally so that it has attracted little attention of theoretical or mathematical basis. Moreover, because of the lack of mathematical tools, no comprehensive discussion for linking the two relationships has appeared during the history of stereochemistry.

Enantiomeric relationship is concerned with every pair of enantiomers that have opposite chiralities. It has been successfully discussed in the light of the sphericity concept and the USCI (unit-subduced-cycle-index) approach proposed by us [2], where point groups and coset representations have been applied to formulate such enantiomers.

On the other hand, diastereomeric relationship has not been so well defined from a group-theoretical point of view, since it has been indirectly defined as a stereoisomeric relationship except an enantiomeric one. Although it has been redefined by starting from the sphericity concept [3], diastereomeric relationship has merely described non-equivalence of molecules at issue, where the relevant equivalence has not been so well specified. As a result, no standard methodologies based on a sound mathematical foundation have not been reported to define diastereoisomerism. For example, *cis*- and *trans*-1,2-dichloroethylenes have been regarded as being diastereomeric, while they have not been diastereomeric to 1,1-dichloroethylene. This distinction has, of course, been based on the conventional scheme of organic stereochemistry, mathematical foundation has not been exploited to equalify *cis*- and *trans*-1,2-dichloroethylenes and to distinguish them from 1,1-dichloroethylene. Moreover, more complicated cases in which chiral ligands are taken into consideration have not been investigated because of the lack of mathematical foundation.

In this paper, we will first carry out combinatorial enumeration of ethylene derivatives with achiral and chiral ligands and shows the reason for the fact that diastereomeric relationship is not involved in this enumeration. Second, we will define a novel permutation group to characterize diastereomeric relationships between ethylene derivatives. Thereby, we will accomplish combinatorial enumeration under the permutation group. Further, we will discuss stereogenic and asterogenic subgroups in order to specify diastereoisomerism.

## 2. Results

### 2.1. Combinatorial enumeration of ethylene derivatives

#### 2.1.1. Desymmetrization and subduction of coset representations

An ethylene skeleton (**1**) belongs to a point group $\mathbf{D}_{2h}$, which involves eight symmetry operations as follows:

$$\mathbf{D}_{2h} = \{I, C_{2(1)}, C_{2(2)}, C_{2(3)}; \sigma_h, \sigma_{v(1)}, \sigma_{v(2)}, i\}, \tag{1}$$

where the symbol $I$ is an identity operation, $C_{2(1)}$ represents a rotation by 180° around the two-fold axis bisecting the C=C double bond, $C_{2(2)}$ represents a rotation by 180° around the two-fold axis through the C=C double bond, $C_{2(3)}$ represents a rotation by 180° around the two-fold axis perpendicular to the ethylene plane, $\sigma_h$ represents a reflection due to the reflection plane containing the ethylene molecule, $\sigma_{v(1)}$ is a reflection bisecting the C=C double bond, $\sigma_{v(2)}$ is a reflection due to the reflection plane containing the C=C double bond, and $i$ is an inversion with respect to the center of the C=C double bond (figure 1). When the four positions are numbered from 1 to 4, as shown figure 1, they construct an orbit (equivalence class) governed by a coset representation (CR) $\mathbf{D}_{2h}(/\mathbf{C}_s'')$ [2], where the local symmetry is determined to be $\mathbf{C}_s'' = \{I, \sigma_h\}$. The CR is represented as follows:
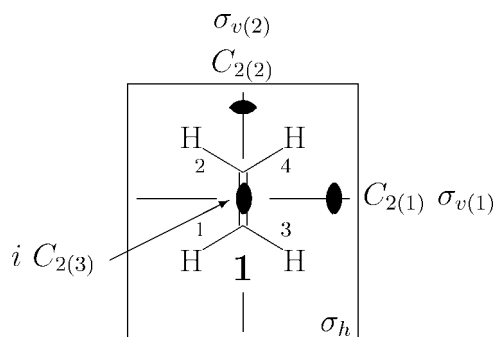
Figure 1. Numbering and symmetry operations for an ethylene skeleton. The frame represents the plane containing the atoms of the ethylene skeleton, where the reflection concerning the plane is denoted by the symbol $\sigma_h$. The symbol ● for $\mathbf{C}_{2(1)}$ or $\mathbf{C}_{2(2)}$ indicates that each straight line intersecting the symbol is a two-fold axis. The symbol ● for $\mathbf{C}_{2(3)}$ stands for the two-fold axis perpendicular to the ethylene plane.

$$\mathbf{D}_{2h}\left(/\mathbf{C}_s''\right) = \left\{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3);\right.$$
$$\left.\overline{(1)(2)(3)(4)}, \overline{(1\ 2)(3\ 4)}, \overline{(1\ 3)(2\ 4)}, \overline{(1\ 4)(2\ 3)}\right\}. \tag{2}$$

Note that the elements of equation (1) corresponds to the permutations of equation (2) in this order. Each permutation with an overline corresponds to an improper rotation of $\mathbf{D}_{2h}$, which produces a mirror image.

A derivative of ethylene is considered to be generated by putting a set of achiral ligands (A, B, C, or D) and chiral ones (p, q, r, or s; or $\overline{p}$, $\overline{q}$, $\overline{r}$, or $\overline{s}$) on the four positions of an ethylene skeleton (**1**)[1]. For example, ethylene itself is generated by putting four hydrogens on the four positions, as shown in figure 1. The derivation process is represented by a subduction of the CR $\mathbf{D}_{2h}(/\mathbf{C}_s'')$ into a subgroup $\mathbf{G}_i$ for the derivative and is denoted by $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{G}_i$ [2,5]. Such a subduction produces a sum of CRs for each subgroup, which can be precalculated algebraically by using mark tables and inverse mark tables for $\mathbf{D}_{2h}$ and the subgroup $\mathbf{G}_i$ [2]. The results are collected in table 1.

Each of the CRs corresponds to an orbit of ligands, which is characterized by its sphericity (enantiospheric, homospheric, and hemispheric) [2,5]. The sphericities are concisely represented by dummy variables, i.e., $a_d$ for an homospheric orbit, $b_d$ for an hemispheric orbit, and $c_d$ for an enantiospheric orbit, where the subscript $d$ represents the size of the orbit. Thereby, each of the results collected at the subduction column of table 1 is represented by a product of such dummy variables, which is called a unit subduced cycle index with chirality fittingness (USCI-CF) [2,5]. When such sphericity is ignored, a unit subduced cycle index (USCI) without chirality fittingness can be obtained, as listed also in table 1, where a dummy variable $s_d$ is substituted for $a_d$, $b_d$, and and $c_d$.

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[1] Strictly speaking, the terms "proligand" and "promolecule" should be used in place of the term "ligand" and "molecule" [4].

Table 1
Subductions of $\mathbf{D}_{2h}(/\mathbf{C}_s'')$

| Subduction | USCI | USCI-CF | Sum |
|---|---|---|---|
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_1 = 4\mathbf{C}_1(/\mathbf{C}_1)$ | $s_1^4$ | $b_1^4$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_2 = 2\mathbf{C}_2(/\mathbf{C}_1)$ | $s_2^2$ | $b_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_2' = 2\mathbf{C}_2'(/\mathbf{C}_1)$ | $s_2^2$ | $b_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_2'' = 2\mathbf{C}_2''(/\mathbf{C}_1)$ | $s_2^2$ | $b_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_s = 2\mathbf{C}_s(/\mathbf{C}_1)$ | $s_2^2$ | $c_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_s' = 2\mathbf{C}_s'(/\mathbf{C}_1)$ | $s_2^2$ | $c_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_s'' = 4\mathbf{C}_s''(/\mathbf{C}_s'')$ | $s_1^4$ | $a_1^4$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_i = 2\mathbf{C}_i(/\mathbf{C}_1)$ | $s_2^2$ | $c_2^2$ | $\frac{1}{8}$ |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2v} = \mathbf{C}_{2v}(/\mathbf{C}_1)$ | $s_4$ | $c_4$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2v}' = 2\mathbf{C}_{2v}'(/\mathbf{C}_s')$ | $s_2^2$ | $a_2^2$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2v}'' = 2\mathbf{C}_{2v}''(/\mathbf{C}_s')$ | $s_2^2$ | $a_2^2$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2h} = 2\mathbf{C}_{2h}(/\mathbf{C}_s)$ | $s_2^2$ | $a_2^2$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2h}' = \mathbf{C}_{2h}'(/\mathbf{C}_1)$ | $s_4$ | $c_4$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{C}_{2h}'' = \mathbf{C}_{2h}''(/\mathbf{C}_1)$ | $s_4$ | $c_4$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{D}_2 = \mathbf{D}_2(/\mathbf{C}_1)$ | $s_4$ | $b_4$ | 0 |
| $\mathbf{D}_{2h}(/\mathbf{C}_s'') \downarrow \mathbf{D}_{2h} = \mathbf{D}_{2h}(/\mathbf{C}_s'')$ | $s_4$ | $a_4$ | 0 |

## 2.2. Enumeration of ethylene derivatives under point-group symmetry

Among the four methods of the USCI approach [6,7], we here use the PCI method [8] (the generating-function method based on partial cycle indices (PCIs)) after the extension taking account of chirality fittingness. By combining the data listed in table 1 and the inverse mark table for $\mathbf{D}_{2h}$ [9], the partial cycle indices with chirality fittingness (PCI-CFs) can be obtained as follows:

$$\text{PCI-CF}(\mathbf{C}_1, \$_d) = \frac{1}{8}b_1^4 - \frac{3}{8}b_2^2 - \frac{3}{8}c_2^2 - \frac{1}{8}a_1^4 + \frac{3}{4}c_4 + \frac{3}{4}a_2^2 + \frac{1}{4}b_4 - a_4, \qquad (3)$$

$$\text{PCI-CF}(\mathbf{C}_2, \$_d) = \frac{1}{4}b_2^2 - \frac{1}{4}c_4 - \frac{1}{4}a_2^2 - \frac{1}{4}b_4 + \frac{1}{2}a_4, \qquad (4)$$

$$\text{PCI-CF}(\mathbf{C}_2', \$_d) = \frac{1}{4}b_2^2 - \frac{1}{4}a_2^2 - \frac{1}{4}c_4 - \frac{1}{4}b_4 + \frac{1}{2}a_4, \qquad (5)$$

$$\text{PCI-CF}(\mathbf{C}_2'', \$_d) = \frac{1}{4}b_2^2 - \frac{1}{4}a_2^2 - \frac{1}{4}c_4 - \frac{1}{4}b_4 + \frac{1}{2}a_4, \qquad (6)$$

$$\text{PCI-CF}(\mathbf{C}_s, \$_d) = \frac{1}{4}c_2^2 - \frac{1}{2}c_4 - \frac{1}{4}a_2^2 + \frac{1}{2}a_4, \qquad (7)$$

$$\text{PCI-CF}(\mathbf{C}_s', \$_d) = \frac{1}{4}c_2^2 - \frac{1}{2}c_4 - \frac{1}{4}a_2^2 + \frac{1}{2}a_4, \qquad (8)$$

$$\text{PCI-CF}\big(\mathbf{C}_s'', \$_d\big) = \frac{1}{4}a_1^4 - \frac{3}{4}a_2^2 + \frac{1}{2}a_4, \tag{9}$$

$$\text{PCI-CF}(\mathbf{C}_i, \$_d) = \frac{1}{4}c_2^2 - \frac{1}{4}a_2^2 - \frac{1}{2}c_4 + \frac{1}{2}a_4, \tag{10}$$

$$\text{PCI-CF}(\mathbf{C}_{2v}, \$_d) = \frac{1}{2}c_4 - \frac{1}{2}a_4, \tag{11}$$

$$\text{PCI-CF}\big(\mathbf{C}_{2v}', \$_d\big) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4, \tag{12}$$

$$\text{PCI-CF}\big(\mathbf{C}_{2v}'', \$_d\big) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4, \tag{13}$$

$$\text{PCI-CF}(\mathbf{C}_{2h}, \$_d) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4, \tag{14}$$

$$\text{PCI-CF}\big(\mathbf{C}_{2h}', \$_d\big) = \frac{1}{2}c_4 - \frac{1}{2}a_4, \tag{15}$$

$$\text{PCI-CF}\big(\mathbf{C}_{2h}'', \$_d\big) = \frac{1}{2}c_4 - \frac{1}{2}a_4, \tag{16}$$

$$\text{PCI-CF}(\mathbf{D}_2, \$_d) = \frac{1}{2}b_4 - \frac{1}{2}a_4, \tag{17}$$

$$\text{PCI-CF}(\mathbf{D}_{2h}, \$_d) = a_4, \tag{18}$$

where the symbol $\$_d$ represents as set of $a_d$, $b_d$, or $c_d$, for the sake of simplicity. According to the three kinds of dummy variables, we use three kinds of ligand inventories as follows [2]:

$$a_d = A^d + B^d + C^d + D^d, \tag{19}$$

$$b_d = A^d + B^d + C^d + D^d + p^d + \overline{p}^d + q^d + \overline{q}^d + r^d + \overline{r}^d + s^d + \overline{s}^d, \tag{20}$$

$$c_d = A^d + B^d + C^d + D^d + 2p^{d/2}\overline{p}^{d/2} + 2q^{d/2}\overline{q}^{d/2} + 2r^{d/2}\overline{r}^{d/2} + 2s^{d/2}\overline{s}^{d/2}, \tag{21}$$

where the variables $A$ to $D$ correspond to achiral ligands A to D, while the lowercase letters such as $p$ and $\overline{p}$ represent a pair of enantiomeric ligands. They are introduced into the PCI-CFs (3)–(18) and the resulting equations are expanded to give generating functions for respective subgroups, e.g.,

$$
\begin{aligned}
f_{\mathbf{C}_1} = {} & \left[\frac{1}{2}\big(A^3 p + A^3\overline{p}\big) + \frac{1}{2}\big(A^3 q + A^3\overline{q}\big) + \cdots\right] \\
& + \left[\frac{3}{2}\big(A^2 Bp + A^2 B\overline{p}\big) + \frac{3}{2}\big(AB^2 p + AB^2\overline{p}\big) + \cdots\right] \\
& + \left[\frac{6}{2}(ABCp + ABC\overline{p}) + \frac{6}{2}(ABDp + ABD\overline{p}) + \cdots\right] + \cdots,
\end{aligned} \tag{22}
$$

$$
\begin{aligned}
f_{\mathbf{C}_2} = f_{\mathbf{C}_2'} = f_{\mathbf{C}_2''} = {} & \left[\frac{1}{2}\big(A^2 p^2 + A^2\overline{p}^2\big) + \frac{1}{2}\big(B^2 p^2 + B^2\overline{p}^2\big) + \cdots\right] \\
& + \left[\frac{1}{2}\big(p^2 q^2 + \overline{p}^2\overline{q}^2\big) + \frac{1}{2}\big(p^2 r^2 + \overline{p}^2\overline{r}^2\big) + \cdots\right],
\end{aligned} \tag{23}
$$

$$f_{\mathbf{C}_s} = f_{\mathbf{C}'_s} = f_{\mathbf{C}_i} = \left[A^2 p\overline{p} + B^2 p\overline{p} + \cdots\right] + [2p\overline{p}q\overline{q} + 2p\overline{p}r\overline{r} + \cdots]. \tag{24}$$

A pair of enantiomers is counted once as a coefficient of a combined term such as $(1/2)(A^3 p + A^3 \overline{p})$. On the same line, the term $(6/2)(ABCp + ABC\overline{p})$ is used in place of $3(ABCp + ABC\overline{p})$ to designate six pairs of enantiomers. A single term such as $A^2 p\overline{p}$ represents a so-called meso-compound. In equations (22), (23), terms in each pair of brackets represent derivatives of the same type.

The coefficients of equations (22), (23), and (24) are respectively collected in the $\mathbf{C}_1$-, $\mathbf{C}_2$- (also $\mathbf{C}'_2$- and $\mathbf{C}''_2$-column), and $\mathbf{C}_s$-column (also $\mathbf{C}'_s$- and $\mathbf{C}_i$-column) of tables 2 and 3, where an appropriate term is selected as a representative from each pair of brackets. Enumeration results for other subgroups are obtained similarly and collected also in the left parts of tables 2 and 3.

The data listed in tables 2 and 3 are illustrated in figures 2 and 3, where derivatives of the same type are depicted by an appropriate representative. As for a chiral derivative, an appropriate enantiomer is depicted as a representative. For the sake of simplicity, the $\mathbf{C}_1$ isomers with chiral ligands only are omitted in figure 3.

Table 2
Number of molecules derived from an ethylene skeleton (part I)

| Proligand partition | Number of molecules under point groups | | | | | | | | Number of molecules under permutation groups | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\mathbf{C}_1$ | $\mathbf{C}_2$ ($\mathbf{C}'_2$) ($\mathbf{C}''_2$) | $\mathbf{C}_s$ ($\mathbf{C}'_s$) ($\mathbf{C}_i$) | $\mathbf{C}''_s$ | $\mathbf{C}_{2v}$ ($\mathbf{C}'_{2h}$) ($\mathbf{C}''_{2h}$) | $\mathbf{C}'_{2v}$ ($\mathbf{C}''_{2v}$) ($\mathbf{C}_{2h}$) | $\mathbf{D}_2$ | $\mathbf{D}_{2h}$ | $\mathbf{S}_1^{[4]}$ | $\mathbf{S}_{2'}^{[4]}$ | $\mathbf{S}_3^{[4]}$ | $\mathbf{S}_7^{[4]}$ | $\mathbf{S}_9^{[4]}$ |
| $A^4$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 |
| $A^3B$ | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| $A^3p$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| $A^2B^2$ | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| $A^2BC$ | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $A^2Bp$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $A^2p^2$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| $A^2p\overline{p}$ | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $A^2pq$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $ABCD$ | 0 | 0 | 0 | 6 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $ABCp$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $ABp^2$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $ABp\overline{p}$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $ABpq$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $Ap^3$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| $Ap^2\overline{p}$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $Ap^2q$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $Ap\overline{p}q$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $Apqr$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |

Table 3
Number of molecules derived from an ethylene skeleton (part II)

| Proligand partition | Number of molecules under point groups | | | | | | | | Number of molecules under permutation groups | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\mathbf{C}_1$ | $\mathbf{C}_2$ $(\mathbf{C}_2')$ $(\mathbf{C}_2'')$ | $\mathbf{C}_s$ $(\mathbf{C}_s')$ $(\mathbf{C}_i)$ | $\mathbf{C}_s''$ | $\mathbf{C}_{2v}$ $(\mathbf{C}_{2h}')$ $(\mathbf{C}_{2h}'')$ | $\mathbf{C}_{2v}'$ $(\mathbf{C}_{2v}'')$ $(\mathbf{C}_{2h})$ | $\mathbf{D}_2$ | $\mathbf{D}_{2h}$ | $\mathbf{S}_1^{[4]}$ | $\mathbf{S}_{2'}^{[4]}$ | $\mathbf{S}_3^{[4]}$ | $\mathbf{S}_7^{[4]}$ | $\mathbf{S}_9^{[4]}$ |
| $p^4$ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 |
| $p^3\bar{p}$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| $p^3q$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| $p^2\bar{p}^2$ | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| $p^2\bar{p}q$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $p^2q^2$ | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| $p^2q\bar{q}$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $p^2qr$ | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 |
| $p\bar{p}q\bar{q}$ | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $p\bar{p}qr$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
| $pqrs$ | 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 |
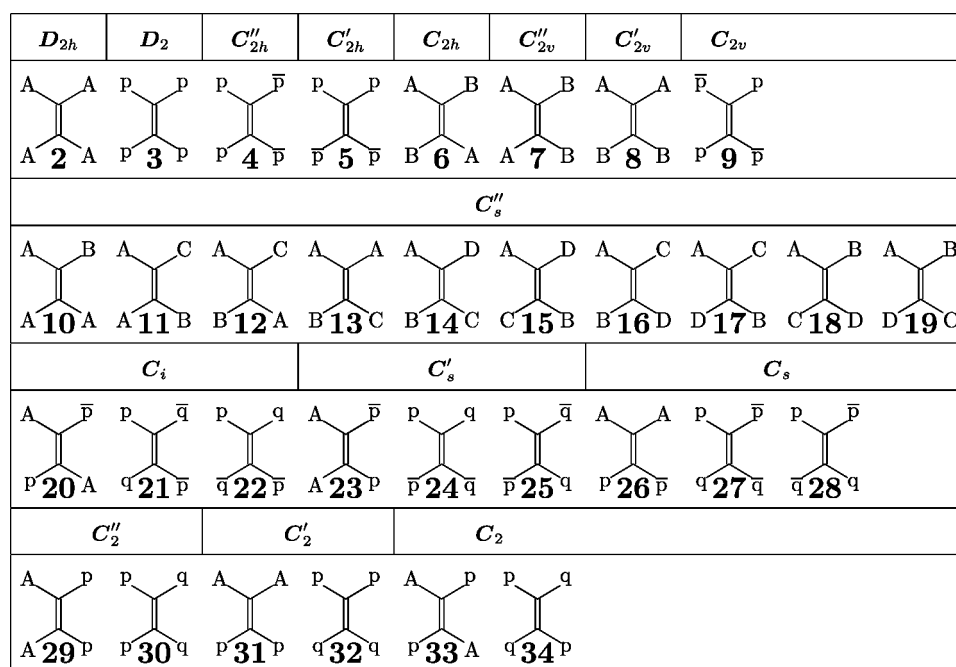


Figure 2. Derivatives of ethylene (part I).

$C_1$

(Grid of ethylene derivative structures numbered 35–78)

35, 36, 37, 38, 39, 40, 41
42, 43, 44, 45, 46, 47, 48, 49, 50
51, 52, 53, 54, 55, 56, 57, 58, 59, 60
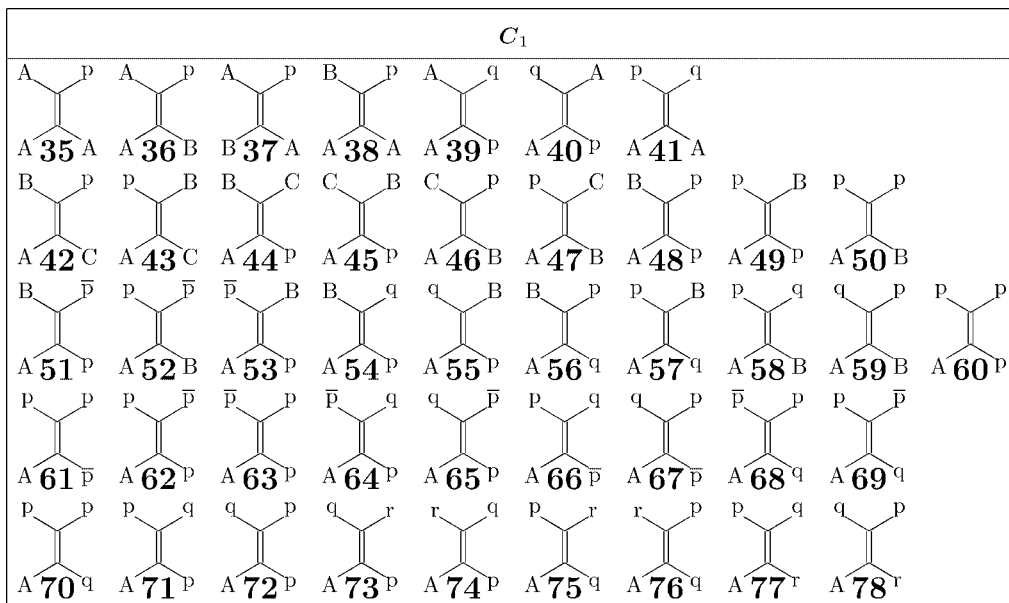61, 62, 63, 64, 65, 66, 67, 68, 69
70, 71, 72, 73, 74, 75, 76, 77, 78

Figure 3. Derivatives of ethylene (part II).

## 2.3. Enumeration of ethylene derivatives under permutation-group symmetry

The inspection of the permutations contained in equation (2) shows that the permutations corresponding to the proper rotations (i.e., $\mathbf{D}_2$) are the same as those for the improper rotations, if we ignore an overline on each permutation. In order to recognize distereoisomerism properly, we should add a permutation (1 3)(2)(4) to those of $\mathbf{D}_2$. Thereby, we can obtain the following permutation group $\mathbf{S}_9^{[4]}$:

$$\mathbf{S}_9^{[4]} = \big\{(1)(2)(3)(4),\, (1\,2)(3\,4),\, (1\,3)(2\,4),\, (1\,4)(2\,3);$$
$$(1\,3)(2)(4),\, (1\,2\,3\,4),\, (1)(3)(2\,4),\, (1\,4\,3\,2)\big\}. \tag{25}$$

The permutation representation $\mathbf{S}_9^{[4]}$ can be regarded as a permutation group that is isomorphic to that of $\mathbf{D}_{2d}$. The symbol $\mathbf{S}_9^{[4]}$ is used to indicate that the group generated from $\mathbf{D}_2$ and such a permutation as (1 3)(2)(4) is a subgroup of the symmetric group of degree 4 ($\mathbf{S}^{[4]}$).

According to the fact that $\mathbf{S}_9^{[4]}$ is isomorphic to the point group $\mathbf{D}_{2d}$, we obtain the corresponding PCIs for $\mathbf{S}_9^{[4]}$ by using the data of $\mathbf{D}_{2d}$ collected in our book [2]. Thus, we obtain the following PCIs:

$$\mathrm{PCI}\big(\mathbf{S}_1^{[4]}, s_d\big) = \frac{1}{8}s_1^4 - \frac{1}{8}s_2^2 - \frac{1}{4}s_1^2 s_2 + \frac{1}{4}s_4, \tag{26}$$

$$\mathrm{PCI}\big(\mathbf{S}_2^{[4]}, s_d\big) = 0, \tag{27}$$

$$\mathrm{PCI}\big(\mathbf{S}_{2'}^{[4]}, s_d\big) = \frac{1}{2}s_2^2 - \frac{1}{2}s_4, \tag{28}$$

$$\mathrm{PCI}\big(\mathbf{S}_3^{[4]}, s_d\big) = \frac{1}{2}s_1^2 s_2 - \frac{1}{2}s_2^2, \tag{29}$$

$$\mathrm{PCI}\big(\mathbf{S}_5^{[4]}, s_d\big) = 0, \tag{30}$$

$$\mathrm{PCI}\big(\mathbf{S}_7^{[4]}, s_d\big) = \frac{1}{2}s_2^2 - \frac{1}{2}s_4, \tag{31}$$

$$\mathrm{PCI}\big(\mathbf{S}_6^{[4]}, s_d\big) = 0, \tag{32}$$

$$\mathrm{PCI}\big(\mathbf{S}_9^{[4]}, s_d\big) = s_4. \tag{33}$$

As a result, we find several PCIs of zero value, i.e., PCI($\mathbf{S}_2^{[4]}$, $s_d$), PCI($\mathbf{S}_5^{[4]}$, $s_d$), and PCI($\mathbf{S}_6^{[4]}$, $s_d$). This means that there exist no molecules of these permutation symmetries. Since we now take no account of chirality fittingness, we use a single type of ligand inventory as follows:

$$s_d = A^d + B^d + C^d + D^d + p^d + \overline{p}^d + q^d + \overline{q}^d + r^d + \overline{r}^d + s^d + \overline{s}^d. \tag{34}$$

Note that the variable $s_d$ on the left-hand side and the $s^d$ on the right-hand side have different meanings. The inventory (equation (34)) is introduced into the PCI (equations (26)–(33)) and the resulting equations are expanded to give generating functions for respective subgroups. The coefficients of the generating functions are listed in the right parts of tables 2 and 3.

## 3.  Discussion

### 3.1.  Enantiomeric relationships

This section is devoted to a systematic recognition of enantiomeric relationship. Thereby, the relationship is found out to specify two objects (e.g., atoms) that belong to an equivalence class (orbit) under point-group symmetry.

#### 3.1.1. Derivatives with achiral ligands only

Achiral derivatives can be regarded as self-enantiomeric molecules, where each of them is identical with the corresponding enantiomer (mirror image). In this subsection, we first examine such extreme cases before we start manipulating pairs of enantiomers in general.

Equivalence under the point group $\mathbf{D}_{2h}$ is shown in figure 4 by using *cis*-1,2- (**79**), *trans*-1,2- (**80**), and 1,1-dichloroethylenes (**81**) as examples, where the positions 1 and 2 in each formula accommodate chlorine atoms, while the positions 3 and 4 take hydrogen atoms. As a result, each of them (**79**, **80**, or **81**) is converted into itself on the action of $\mathbf{D}_{2h}$. Note that a chlorine atom (or a hydrogen atom) is identical with its mirror image, because they are achiral in isolation.

By the inspection of the top row of figure 4, *cis*-1,2-dichloroethylene (**79**) is found to be converted into itself (**79**a, **79**b, $\overline{\textbf{79}}$a, and $\overline{\textbf{79}}$b) on the action of permutations, $\{(1)(2)(3)(4), (1\,2)(3\,4), \overline{(1)(2)(3)(4)}, \overline{(1\,2)(3\,4)}\}$. In other words, **79** is fixed during this action. Since these permutations correspond to the operations of $\mathbf{C}_{2v}''$, *cis*-1,2-dichloroethylene (**79**) is determined to belong to $\mathbf{C}_{2v}''$-symmetry. Thereby, the whole mode of conversions depicted in the top row of figure 4 is represented by a coset representation $\mathbf{D}_{2h}(/\mathbf{C}_{2v}'')$, where the local symmetry $\mathbf{C}_{2v}''$ corresponds to the symmetry of *cis*-1,2-dichloroethylene (**79**). The homosphericity of the $\mathbf{D}_{2h}(/\mathbf{C}_{2v}'')$-orbit indicates that *cis*-1,2-dichloroethylene (**79**) is achiral.

The $\mathbf{C}_{2v}''$-columns (the same as the $\mathbf{C}_{2v}'$-columns) in tables 2 and 3 show that derivatives of $\mathbf{C}_{2v}''$-symmetry should take a ligand partition $A^2B^2$. This is illustrated in figure 2 as the derivative **7**, which is a general case for the *cis*-1,2-dichloroethylene case.

The inspection of the middle row of figure 4 indicates that *trans*-1,2-dichloroethylene (**80**) belongs to $\mathbf{C}_{2h}$-symmetry, because the point group $\mathbf{C}_{2h}$ is assigned to the set of permutations $\{(1)(2)(3)(4), (1\,4)(2\,3), \overline{(1)(2)(3)(4)}, \overline{(1\,4)(2\,3)}\}$, which produces homomeric derivatives (**80**a, **80**b, $\overline{\textbf{80}}$a, and $\overline{\textbf{80}}$b). As a result, the whole mode of conversions depicted in the middle row of figure 4 is represented by a coset representation $\mathbf{D}_{2h}(/\mathbf{C}_{2h})$, where the local symmetry $\mathbf{C}_{2h}$ corresponds to the symmetry of *trans*-1,2-dichloroethylene (**79**).

The $\mathbf{C}_{2h}$-columns (the same as the $\mathbf{C}_{2v}'$-columns) in tables 2 and 3 show that derivatives of $\mathbf{C}_{2h}$-symmetry should take a ligand partition $A^2B^2$. The derivative **6** shown as an example in figure 2 is a general formula for the *trans*-1,2-dichloroethylene case.

The bottom row of figure 4 indicates that 1,1-dichloroethylene (**81**) belongs to $\mathbf{C}_{2v}'$, since the corresponding permutations $\{(1)(2)(3)(4), (1\,3)(2\,4), \overline{(1)(2)(3)(4)}, \overline{(1\,3)(2\,4)}\}$ fix **81** invariant. By considering $\mathbf{C}_{2v}'$ as a local symmetry, the whole mode is represented by a coset representation $\mathbf{D}_{2h}(/\mathbf{C}_{2v}')$.
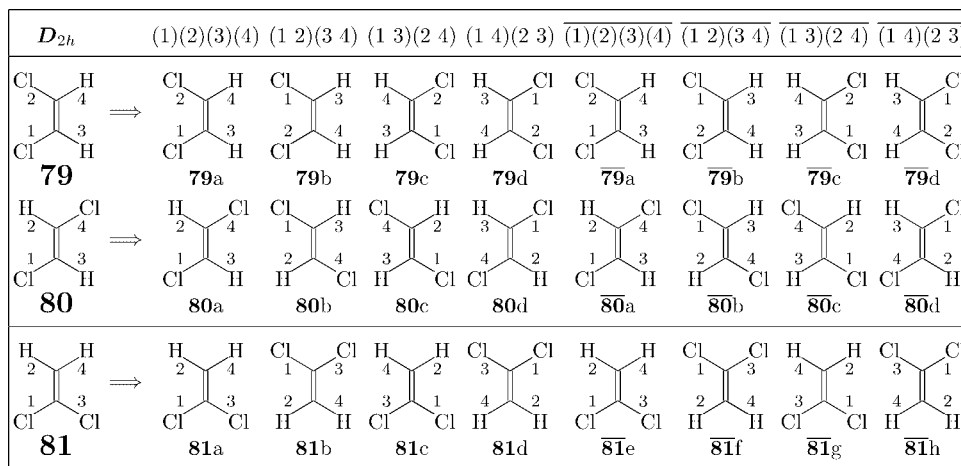


Figure 4. Dichloroethylenes under point-group symmetry.

The $\mathbf{C}'_{2v}$-columns in tables 2 and 3 indicate that derivatives of $\mathbf{C}'_{2v}$-symmetry should take a ligand partition $A^2B^2$. This is illustrated in figure 2 as a derivative **8**, which is a general case for the 1,1-dichloroethylene case.

### 3.1.2. Derivatives with chiral and achiral ligands

The systematic recognition of enantiomeric relationship is more clearly demonstrated by considering chiral ligands along with achiral ones (figure 5).

The top row of figure 5 depicts conversions for a *cis*-1,2-isomer with two chiral ligands p (**82**). The action of $\mathbf{D}_{2h}$ on **82** produces four homomers (**82**a–**82**d) and four enantiomers ($\overline{\textbf{82}}$a–$\overline{\textbf{82}}$d). Among them, **82**a and **82**b are identical with the original **82**, where this invariant processes are assigned to a set of permutations $\{(1)(2)(3)(4), (1\ 2)(3\ 4)\}$. This means that **82** belongs to $\mathbf{C}''_2$ that corresponds to the set of permutations.

The whole mode of conversions depicted in the top row of figure 5 is represented by a coset representation (CR) $\mathbf{D}_{2h}(/\mathbf{C}''_2)$, where the local symmetry $\mathbf{C}''_2$ corresponds to the symmetry of **82**. When the eight products (**82**a–**82**d and $\overline{\textbf{82}}$a–$\overline{\textbf{82}}$d) are considered to be governed by the CR $\mathbf{D}_{2h}(/\mathbf{C}''_2)$, they are divided into four sets of products, i.e., $\{\textbf{82}a, \textbf{82}b\}$, $\{\textbf{82}c, \textbf{82}d\}$, $\{\overline{\textbf{82}}a, \overline{\textbf{82}}b\}$, and $\{\overline{\textbf{82}}c, \overline{\textbf{82}}d\}$. These sets are recognized to construct a $\mathbf{D}_{2h}(/\mathbf{C}''_2)$-orbit of stereoisomerism, because the size of the orbit is calculated to be $|\mathbf{D}_{2h}|/|\mathbf{C}''_2| = 8/2 = 4$. Since the resulting $\mathbf{D}_{2h}(/\mathbf{C}''_2)$-orbit is enantiospheric, the orbit accommodates the four sets of products in a compensated chiral packing [2]. This packing corresponds to the enantiospheric relationship between **82** and its enantiomer.

The $\mathbf{C}''_2$-columns (the same as the $\mathbf{C}_2$-columns) in tables 2 and 3 show that derivatives of $\mathbf{C}''_2$-symmetry should have a ligand partition $A^2p^2$ or $p^2q^2$. These are illustrated in figure 2 as derivatives **29** and **30**, which are general cases for *cis*-1,2-disubstituted ethylenes.

A similar discussion on the middle row of figure 5 specifies the enantiomeric relationship between a *trans*-isomer **83** and its enantiomer. The isomers listed in the middle
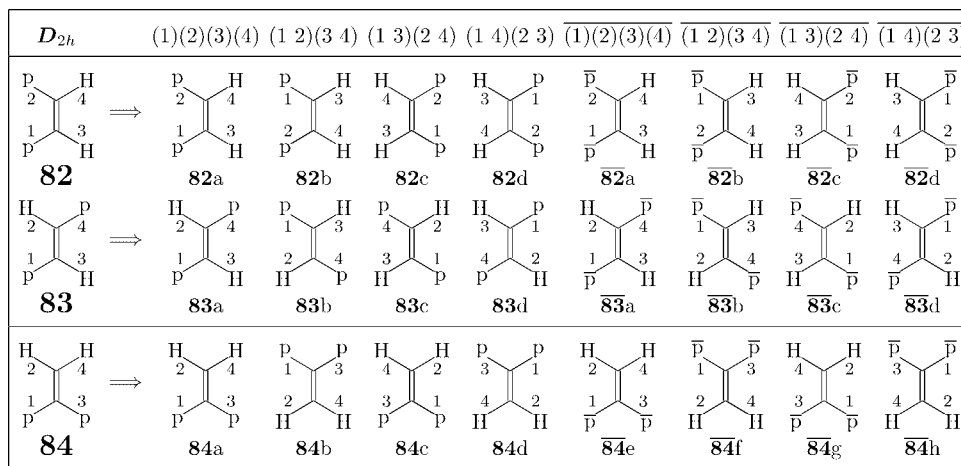


Figure 5. Ethylenes with two chiral ligands under point-group symmetry.

row are divided into four sets of isomers, i.e., {**83**a, **83**d}, {**83**b, **83**c}, {$\overline{\textbf{83}}$a, $\overline{\textbf{83}}$d}, and {$\overline{\textbf{83}}$b, $\overline{\textbf{83}}$c}. These four sets construct an orbit governed by a CR $\mathbf{D}_{2h}(/\mathbf{C}_2)$. where the local symmetry $\mathbf{C}_2$ corresponds to the symmetry of **83**. Note that $\mathbf{C}_2$ is assigned to a set of permutations {(1)(2)(3)(4), (1 4)(2 3)}, which keep **83** invariant, as shown in figure 5 (**83**a and **83**d). Since the resulting $\mathbf{D}_{2h}(/\mathbf{C}_2)$-orbit is enantiospheric, the orbit can accommodate the four sets of isomers in a compensated chiral packing [2]. This packing corresponds to the enantiomeric relationship between **83** and its enantiomer.

The $\mathbf{C}_2$-columns in tables 2 and 3 show that derivatives of $\mathbf{C}_2$-symmetry should take a ligand partition $A^2p^2$ or $p^2q^2$. These are illustrated in figure 2 as the derivatives **33** and **34**, which are general cases for *trans*-1,2-disubstituted ethylenes.

The bottom row of figure 5 specifies the enantiomeric relationship between a chiral 1,1-disubstituted ethylene **84** and its enantiomer, where the eight derivatives are divided into four sets of derivatives, i.e., {**84**a, **84**c}, {**84**b, **84**d}, {$\overline{\textbf{84}}$a, $\overline{\textbf{84}}$c}, and {$\overline{\textbf{84}}$b, $\overline{\textbf{84}}$d}. These sets construct an orbit governed by a CR $\mathbf{D}_{2h}(/\mathbf{C}'_2)$. The local symmetry $\mathbf{C}'_2$ is assigned to a set of permutations {(1)(2)(3)(4), (1 3)(2 4)} so that it corresponds to the symmetry of **83**. The $\mathbf{D}_{2h}(/\mathbf{C}'_2)$-orbit accommodates the four sets of derivatives in a compensated chiral packing according to its enantiosphericity [2]. This packing corresponds to the enantiomeric relationship between **84** and its enantiomer.

The $\mathbf{C}'_2$-columns (the same as the $\mathbf{C}_2$-columns) in tables 2 and 3 indicate that derivatives of $\mathbf{C}'_2$-symmetry should take a ligand partition $A^2p^2$ or $p^2q^2$. These are illustrated in figure 2 as the derivatives **31** and **32**, which are general cases for 1,1-disubstituted ethylenes.

## 3.2. Diastereomeric relationships

This section is devoted to a systematic recognition of diastereomeric relationship, which is determined to be a relationship between two objects (e.g., atoms) belonging to an equivalence class (orbit) under permutation-group symmetry.

### 3.2.1. Stereogenic and astereogenic groups

Each derivative listed in the right parts of tables 2 and 3 belongs to a subgroup of $\mathbf{S}_9^{[4]}$ equation (25). The elements of the subgroups are listed as follows:

$$\mathbf{S}_1^{[4]} = \big\{(1)(2)(3)(4)\big\}, \qquad\qquad\qquad\qquad\qquad\qquad\text{stereogenic,} \quad (35)$$

$$\mathbf{S}_2^{[4]} = \big\{(1)(2)(3)(4), (1\ 3)(2\ 4)\big\}, \qquad\qquad\qquad\qquad\text{stereogenic,} \quad (36)$$

$$\mathbf{S}_{2'}^{[4]} = \big\{(1)(2)(3)(4), (1\ 2)(3\ 4)\big\} \text{ or } \big\{(1)(2)(3)(4), (1\ 4)(2\ 3)\big\}, \quad\text{stereogenic,} \quad (37)$$

$$\mathbf{S}_3^{[4]} = \big\{(1)(2)(3)(4), (1\ 3)(2)(4)\big\}, \qquad\qquad\qquad\qquad\text{astereogenic,} \quad (38)$$

$$\mathbf{S}_4^{[4]} = \big\{(1)(2)(3)(4), (1\ 3)(2\ 4), (1\ 2\ 3\ 4), (1\ 4\ 3\ 2)\big\}, \qquad\text{astereogenic,} \quad (39)$$

$$\mathbf{S}_7^{[4]} = \big\{(1)(2)(3)(4), (1\ 3)(2)(4), (1)(3)(2\ 4)\big\}, \qquad\qquad\text{astereogenic,} \quad (40)$$

$$\mathbf{S}_6^{[4]} = \big\{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 3)(2\ 4), (1\ 4)(2\ 3)\big\}, \qquad\text{stereogenic,} \quad (41)$$

$$\mathbf{S}_9^{[4]} = \big\{(1)(2)(3)(4), \ldots; (1\ 3)(2)(4), \ldots\big\}, \qquad\qquad\qquad\text{astereogenic.} \quad (42)$$

The numbering of these subgroups (shown as the subscripts) is given according to the appearance order reported for the subgroups of the symmetric group of degree 4 (i.e., $\mathbf{S}^{[4]}$) [10]. Note that the conjugacy of the subgroup $\mathbf{S}_2^{[4]}$ in the $\mathbf{S}_{[4]}$ is broken during the restriction into the $\mathbf{S}_9^{[4]}$ of the present case so as to give $\mathbf{S}_2^{[4]}$ and $\mathbf{S}_{2'}^{[4]}$. The two sets given for $\mathbf{S}_{2'}^{[4]}$ (equation (37)) are conjugate to each other. The inverse order of $\mathbf{S}_7^{[4]}$ and $\mathbf{S}_6^{[4]}$ is in agreement with the order of the subgroups reported for $\mathbf{D}_{2d}$ [2].

The elements (permutations) of $\mathbf{S}_9^{[4]}$ (equation (25)) are classified into two categories. The elements of the one category are contained in $\mathbf{S}_6^{[4]}$ equation (41), which is isomorphic to $\mathbf{D}_2$ (the maximal chiral subgroup of $\mathbf{D}_{2d}$ and also that of $\mathbf{D}_{2h}$). These elements are here called *proper permutations*, which are related to proper rotations. The other category is the remaining part of $\mathbf{S}_9^{[4]}$ (i.e., $\mathbf{S}_9^{[4]} - \mathbf{S}_6^{[4]}$). The elements of this category are here called *improper permutations*, which are not always related to *improper rotations*.

The analogy between proper/improper permutations and proper/improper rotations indicates that we can obtain a new concept analogous to the concept chirality/achirality, since the latter is based on proper/improper rotations. Thus, if a subgroup of $\mathbf{S}_9^{[4]}$ contains proper permutations only, it is defined as a *stereogenic group*; and, if a subgroup contains at least one improper permutation, it is defined as an *astereogenic group*. Thereby, the subgroups of $\mathbf{S}_9^{[4]}$ are classified into stereogenic and astereogenic groups, as listed also in equations (35)–(42).

### 3.2.2. Derivatives with achiral ligands only

Equivalence under a permutation group $\mathbf{S}_9^{[4]}$ is shown in figure 6 by using dichloroethylenes as examples. Under the action of $\mathbf{S}_9^{[4]}$, *cis*-1,2-dichloroethylene (**79**) is converted into *cis*-1,2-dichloroethylene (**80**a)–(**80**d) as well as into *trans*-1,2-dichloroethylene (**79**a)–(**79**d), while *trans*-1,2-dichloroethylene (**80**) is converted into *trans*-1,2-dichloroethylene (**80**e)–(**80**h) as well as into *cis*-1,2-dichloroethylene (**79**e)–(**79**h). The *cis*- and *trans*-isomers, which are regarded as being diastereomeric in conventional stereochemistry, are equivalent under the permutation group $\mathbf{S}_9^{[4]}$. They are determined to belong to $\mathbf{S}_{2'}^{[4]}$-symmetry (equation (37)), which is isomorphic to $\mathbf{C}_2'$. Note that they are non-equivalent under $\mathbf{D}_2$ and $\mathbf{D}_{2h}$ (i.e., under point-group symmetry). As a result, the diastereomeric relationship between *cis*- and *trans*-1,2-dichloroethylene is assigned to the stereogenic group $\mathbf{S}_{2'}^{[4]}$. In other words, such a stereogenic group is capable of predicting the presence of diastereomers.

The whole mode of conversions shown in the top row of figure 6 is represented by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$, which governs four sets ($|\mathbf{S}_9^{[4]}|/|\mathbf{S}_{2'}^{[4]}|$) of isomers, i.e., {**79**a, **79**b}, {**79**c, **79**d}, {**80**a, **80**b}, and {**80**a, **80**b}. The packing of the $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$-orbit with the four sets of isomers is a compensated packing of two *cis*-isomer sets ({**79**a, **79**b} and {**79**c, **79**d}) and two *trans*-isomer sets ({**80**a, **80**b} and {**80**a, **80**b}), which is mathematically analogous to a compensated chiral packing of an enantiospheric orbit. The whole mode of conversions shown in the middle row of figure 6 is also represented by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$ and can be characterized in the same way. Since $\mathbf{S}_9^{[4]}$ is astereogenic and $\mathbf{S}_{2'}^{[4]}$ is stereogenic,
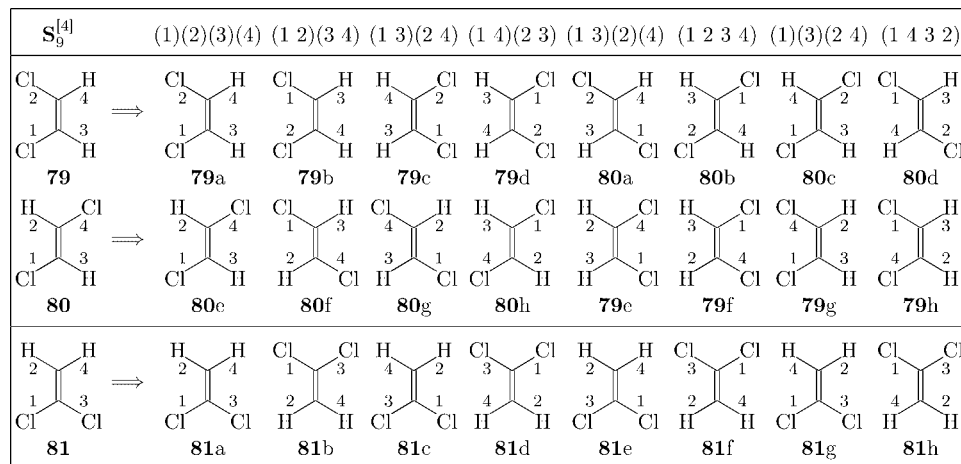
Figure 6. Dichloroethylenes under permutation-group symmetry.

the CR $S_9^{[4]}(/S_{2'}^{[4]})$ for the whole mode of conversions shown in the top or middle row of figure 6 is characterized by the combination "asterogenic/stereogenic", which is akin to the combination "achiral/chiral" for defining enantiosphericity. Thereby, the same sort of discussion explains the diastereoisomerism. It follows that *diastereomers are contained in an orbit characterized by such a combination as "asterogenic/stereogenic"*.

The intersection between the $S_{2'}^{[4]}$-column and the $A^2B^2$-row in table 2 predicts that one derivative exists if diastereomers are regarded as being equivalent and counted once. This case corresponds to the diastereomeric pair of *cis-* and *trans-*1,2-dichloroethylene, which are equalified under the permutation group $S_9^{[4]}$ as discussed in the preceding paragraph.

On the other hand, 1,1-dichloroethylene (**81**) is converted into itself (**81**a and **81**c; and **81**e and **81**g), as shown in the bottom row of figure 6. It is called a *self-diastereomric* isomer. This isomer is determined to belong to $S_7^{[4]}$-symmetry (equation (40)), which is asterogenic and isomorphic to $C_{2v}$. As a result, the self-diastereomeric nature of 1,1-dichloroethylene is assigned to the asterogenic group $S_7^{[4]}$. In other words, such an asterogenic group is capable of predicting the absence of diastereomers.

The whole mode of conversions shown in the bottom row of figure 6 is represented by a CR $S_9^{[4]}(/S_7^{[4]})$. Since both $S_9^{[4]}$ and $S_7^{[4]}$ is asterogenic, the CR is characterized by the combination "asterogenic/asterogenic", which is akin to the combination "achiral/achiral" for defining homosphericity.

The intersection between the $S_7^{[4]}$-column and the $A^2B^2$-row in table 2 predicts that one derivative, which is identical with its diastereomer, is available. This case corresponds to the self-diastereomeric case of 1,1-dichloroethylene.

### 3.2.3. Derivatives with chiral and achiral ligands

The systematic recognition of diastereomeric relationship is illustrated in figure 7 by considering chiral ligands along with achiral ones.
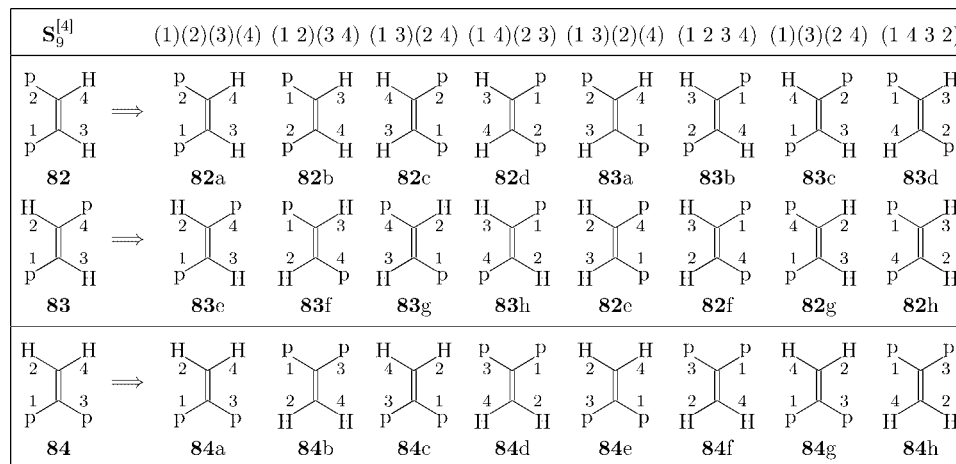
Figure 7. Ethylenes with two chiral ligands under permutation-group symmetry.

The top row of figure 7 is explained by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$. This is analogous to the top row of figure 6, where the replacement of achiral ligands by chiral ones brings out no effect to the conversion modes of this case. Thus, two *cis*-isomer sets ({**82**a, **82**b} and {**82**c, **82**d}) and two *trans*-isomer sets ({**83**a, **83**d} and {**83**b, **83**c}) are governed by the CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$. The permutation group $\mathbf{S}_9^{[4]}$ does not contain reflection operations, there appear no isomers with $\overline{\mathrm{p}}$. The middle row of figure 7 is explained similarly by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$. The stereogenicity of the group $\mathbf{S}_{2'}^{[4]}$ predicts the presence of diastereomers.

The above discussion is reinforced by the data at the intersection between the $\mathbf{S}_{2'}^{[4]}$-column and the $A^2p^2$-row in table 2, which predicts that one derivative exists if diastereomers are regarded as being equivalent and counted once. This case corresponds to the diastereomeric pair of *cis*- and *trans*-1,2-disubstituted ethylenes, which are equalified under the permutation group $\mathbf{S}_9^{[4]}$.

The bottom row of figure 7 is explained by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_7^{[4]})$, which is analogous to the one for the bottom row of figure 6. The replacement of achiral ligands by chiral ones brings out no effect to the conversion modes of this case. The asterogenicity of the group $\mathbf{S}_7^{[4]}$ predicts the absence of diastereomers (i.e., the presence of a self-diastereomer).

The intersection between the $\mathbf{S}_7^{[4]}$-column and the $A^2p^2$-row in table 2 shows that one derivative, which is identical with its diastereomer, is available. This case corresponds to the self-diastereomeric case of 1,1-disubstituted ethylene.

### 3.2.4. Diastereomers and constitutional isomers

Each ethylene derivative that belongs to a stereogenic group $\mathbf{S}_i^{[4]}$ ($i = 1, 2, 2', 6$) has its diastereomer(s). It is regarded as a member of an orbit governed by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_i^{[4]})$, where the local symmetry $\mathbf{S}_i^{[4]}$ corresponds to the permutation symmetry of the derivative. On the other hand, each ethylene derivative that belongs to an astere-

ogenic group $\mathbf{S}_i^{[4]}$ ($i = 3, 4, 7, 9$) has no diastereomers. It is regarded as a member of an orbit governed by a CR $\mathbf{S}_9^{[4]}(/\mathbf{S}_i^{[4]})$.

Two ethylene derivatives belonging to distinct orbits are considered to be constitutional isomers. For example, a diastereomeric pair of *cis-* and *trans-*1,2-disubstituted ethylenes is regarded as being constitutionally isomeric to a 1,1-disubstituted ethylene, since they belong to distinct orbits (i.e., $\mathbf{S}_9^{[4]}(/\mathbf{S}_{2'}^{[4]})$ and $\mathbf{S}_9^{[4]}(/\mathbf{S}_7^{[4]})$).

Diastereomers and constitutional isomers for ethylene derivatives with ABCD should be mentioned to obtain a deeper insight into the relationship between them. As found in the ABCD-row of table 2, there are six isomers of $\mathbf{C}_s''$-symmetry under point-group symmetry, whereas there are three isomers of $\mathbf{S}_7^{[1]}$-symmetry under permutation-group symmetry. Since $\mathbf{S}_7^{[1]}$ is stereogenic, the data at the ABCD-row of table 2 predict three pairs of diastereomers. They are depicted in figure 2, i.e., **14** and **15**; **16** and **17**; and **18** and **19**. The relationship between any two of these pairs is determined to be constitutionally isomeric.

### 3.3. Other types of enumeration

The importance of the selection of groups should be emphasized in treating stereochemical phenomena. The enumeration under point groups takes account of chirality fittingness in order to count stereoisomers with chiral and achiral ligands. If we disregard such chirality fittingness (violation of chirality fittingness), we can use PCIs without chirality fittingess. These PCIs are obtained by placing $s_d = a_d = b_d = c_d$ in the PCI-CFs (equations (3)–(18)) as follows:

$$\text{PCI}(\mathbf{C}_1, s_d) = 0, \tag{43}$$

$$\text{PCI}(\mathbf{C}_2, s_d) = \text{PCI}(\mathbf{C}_2', s_d) = \text{PCI}(\mathbf{C}_2'', s_d) = 0, \tag{44}$$

$$\text{PCI}(\mathbf{C}_s, s_d) = \text{PCI}(\mathbf{C}_s', s_d) = \text{PCI}(\mathbf{C}_i, s_d) = \text{PCI}(\mathbf{C}_{2v}, s_d) = 0, \tag{45}$$

$$\text{PCI}(\mathbf{C}_s'', s_d) = \frac{1}{4}s_1^4 - \frac{3}{4}s_2^2 + \frac{1}{2}s_4, \tag{46}$$

$$\text{PCI}(\mathbf{C}_{2v}', s_d) = \text{PCI}(\mathbf{C}_{2v}'', s_d) = \text{PCI}(\mathbf{C}_{2h}, s_d) = \frac{1}{2}s_2^2 - \frac{1}{2}s_4, \tag{47}$$

$$\text{PCI}(\mathbf{C}_{2h}', s_d) = \text{PCI}(\mathbf{C}_{2h}'', s_d) = \text{PCI}(\mathbf{D}_2, s_d) = 0, \tag{48}$$

$$\text{PCI}(\mathbf{D}_{2h}, s_d) = s_4. \tag{49}$$

Note that the symbols for point groups are tentatively used to represent isomorphic permutation groups. To do this type of enumeration, we introduce the ligand inventory described in equation (34). This type of enumeration, however, does not produce useful results, since these are essentially identical with the PCI-CF enumeration with achiral ligands only. Compare equations (46), (47), and (49) with the corresponding PCI-CFs (equation (9) etc.; equation (13) etc.; and equation (18) etc.) that contain terms of $a_d$ only. As a result, the above results of the term A$^3$B correspond to those of such terms as A$^3$p and p$^3$q in this enumeration; the term A$^2$BC corresponds to terms such as A$^2$Bp and A$^2$pq; and the term ABCD corresponds to the terms such as ABCp and ABpq.

If we use the symmetric group of degree 4 ($\mathbf{S}^{[4]}$) in the counting of ethylene derivatives, we obtain indisciminative results only. For example, *cis*-1,2-, *trans*-1,2-, and 1,1-disubstituted ethylenes are regarded as being equivalent in this enumeration. To recognize distereoisomerism properly, *cis*-1,2- and *trans*-1,2-disubstituted ethylenes (diastereoisomers) should be discriminated from a 1,2-disubstituted ethylene (constitutional isomers). This task can be accomplished by the use of $\mathbf{S}_9^{[4]}$ in place of $\mathbf{S}^{[4]}$.

## 4.   Conclusion

To characterize the stereoisomerism of ethylene derivatives, two types of groups have been considered to act on an ethylene skeleton. One is a point group of order 8 ($\mathbf{D}_{2h}$) to characterize enantiomeric relationship, where chirality fittingness based on the sphericity concept have been used in the enumeration of stereoisomers. The other is a permutation group of order 8 ($\mathbf{S}_9^{[4]}$), which is a subgroup of the symmetric group of degree 4 ($\mathbf{S}^{[4]}$) and isomorphic to a point group $\mathbf{D}_{2d}$. This group has been used to enumerate stereoisomers under $\mathbf{S}_9^{[4]}$ and to characterize diastereomeric relationship. The subgroups of $\mathbf{S}_9^{[4]}$ are classified into stereogenic and astereogenic ones. A stereogenic subgroup corresponds to a pair of diastereomers, while an astereogenic subgroup is assigned to a self-diastereomer. Thereby, diastereomers such as *cis*- and *trans*-1,2-disubstituted ethylenes are related to each other as belonging to the same orbit of stereoisomerism.

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