

Symmetry-itemized enumeration of *RS*-stereoisomers of allenes: II—the partial-cycle-index method of the USCI approach combined with the stereoisogram approach

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Abstract The partial-cycle-index (PCI) method of the unit-subduced-cycle-index approach (Fujita in *Symmetry and combinatorial enumeration of chemistry*. Springer, Berlin, 1991) is extended to meet the stereoisogram approach (Fujita in *J Org Chem* 69:3158–3165, 2004, *Tetrahedron* 60:11629–11638, 2004). Then, the PCI method is applied to the symmetry-itemized enumeration of quadruplets of stereoisograms, where an allene skeleton is considered to belong to the *RS*-stereoisomeric group $D_{2d\tilde{\sigma}\tilde{\tau}}$ derived from the point group D_{2d} . The resulting numbers of quadruplets are itemized in terms of subgroups of $D_{2d\tilde{\sigma}\tilde{\tau}}$, which are further categorized into five types (types I–V). The term ‘absolute configuration’, which has been correlated solely to chirality in the conventional stereochemistry, is extended to have three aspects (i.e., a chiral aspect, an *RS*-stereogenic aspect, and a scleral aspect) according to the three attributes of a stereoisogram (i.e., chirality, *RS*-stereogenicity, and sclerality). Thereby, the *RS*-stereodescriptors of the Cahn–Ingold–Prelog system are clarified to specify the *RS*-stereogenic aspect, not to specify the chiral aspect. They are assigned to a pair of *RS*-diastereomers contained in a type-I, type-III, or type-V stereoisogram, but not to a pair of enantiomers. To judge whether or not the *RS*-stereodescriptors (assigned originally on the basis of the *RS*-stereogenic aspect of an absolute configuration) are permitted to be applied to the chiral aspect, the concept of *chirality faithfulness* (Fujita in *J Comput Aided Chem* 10:16–29, 2009) is used after redefined by proposing *odd* and *even priority permutations*.

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1 Introduction

Although the Cahn-Ingold-Prelog (CIP) system [1] has been widely adopted in organic stereochemistry, its theoretical foundation still suffers from confusion between chirality and stereogenicity. For example, the revision of the CIP system [2] has adopted the term ‘stereogenic’ in the form of ‘chirality elements as stereogenic units of the CIP system’, where chirality is regarded as an aspect of stereogenicity. As a result, ‘stereogenic centers’ are categorized into ‘chirality centers’ (e.g., CABXY) and ‘pseudoasymmetric centers’ (e.g., CABp \bar{p}), as found in Table 1 of [3], where the symbols A, B, X, and Y denote achiral substituents, while a pair of p/ \bar{p} denotes an enantiomeric pair of chiral substituents. Even if we obey the conventional theoretical foundation of the CIP system [3], we are safe to say that ‘chirality centers’ refer to ‘chiral stereogenic centers’, while ‘pseudoasymmetric centers’ refer to ‘achiral stereogenic centers’. However, the distinction between chirality and stereogenicity has not well demonstrated in this statement.

In a parallel way, ‘stereogenic axes’ for characterizing allene skeletons are categorized into ‘chirality axes’ and ‘pseudoasymmetric axes’, as found also in Table 1 of [3]. In case of ‘axes’ along with ‘centers’, the distinction between chirality and stereogenicity has not well demonstrated.

Moreover, the CIP system is silent about non-stereogenic centers such as CXYp² and CXY \bar{p} ², even though each central carbon atom exhibits local chirality. There is no reliable rationalization in the principles of the CIP system why the chirality of CXYp² and CXY \bar{p} ² is not specified by the CIP system, even though chirality and stereogenicity are differentiated. This implies that *RS*-descriptors of the CIP system are not directly concerned with chirality, although the symmetry consistency of the CIP specification has been discussed in Section 1.1.5.3.4 of [3].

To avoid the confused situations described above, the author (Fujita) has proposed the concept of *stereoisograms* [4–6], where the conventional term ‘stereogenic’ is replaced by a more definite term *RS-stereogenic*. Such stereoisograms are characterized by applying *RS*-stereoisomeric groups, which are newly defined after the integration of the point-group theory and the permutation-group theory. After the *RS*-stereoisomeric groups are characterized by three attributes (i.e., chirality, *RS*-stereogenicity, and sclerality), they are categorized into five types (type I–V) [7]. Thereby, stereoisograms of type I (chiral, *RS*-stereogenic, and ascleral), III (chiral, *RS*-stereogenic, and scleral), and V (achiral, *RS*-stereogenic, and scleral) are differentiated by means of *RS*-descriptors, where the underlined *RS*-stereogenicity is found to be a common attribute but the chirality is not a common attribute [8]. This means that *RS*-descriptors of the CIP system are specified in terms of *RS*-stereogenicity (not chirality).

According to the stereoisogram approach, even non-stereogenic cases such as CXYp² and CXY \bar{p} ² can be characterized to be type II (chiral, *RS*-astereogenic, and

scleral), while such non-stereogenic cases as CA^2XY and $CA^2p\bar{p}$ can be characterized to be type IV (achiral, RS-astereogenic, and ascleral) at the same time. It follows that type-II and type-IV cases are concluded to be incapable of being specified by *RS*-descriptors because of their RS-astereogenic nature (not because of achiral nature). Note that the underlined *RS-astereogenicity* is found to be a common attribute but the achirality is not a common attribute [8].

On the other hand, the author (Fujita) has developed the unit-subduced-cycle-index (USCI) approach [9, 10] and the proligand method [11] in order to enumerating organic compounds as three-dimensional structures. These attempts are based on the point-group theory, where the numbers of pairs of enantiomers are calculated combinatorially. Now that point groups are extended to *RS*-stereoisomeric groups, we are able to enumerate chemical compounds under the action of *RS*-stereoisomeric groups in terms of the stereoisogram approach coupled with the USCI approach. This strategy has enabled us to enumerate quadruplets of *RS*-stereoisomers under the action of *RS*-stereoisomeric groups [12].

In Part I of the present series (the accompanying paper), the subgroups of the *RS*-stereoisomeric group for characterizing stereoisograms based on an allene skeleton have been discussed by considering the isomorphism between the *RS*-stereoisomeric group and the point group D_{4h} . Thereby, symmetry-itemized enumeration has been conducted under the action of *RS*-stereoisomeric groups, where the fixed-point matrix (FPM) method of the USCI approach has been adopted. For the purpose of demonstrating the usefulness of the strategy due to the combination of the USCI approach and the stereoisogram approach, the present article is devoted to the the partial-cycle-index (PCI) method of the USCI approach, which is adopted to enumerate quadruplets of *RS*-stereoisomers in a symmetry-itemized fashion under the action of the *RS*-stereoisomeric group on an allene skeleton.

2 Symmetry-itemized enumeration by the PCI method

2.1 Orbits and coset representations characterized by *RS*-stereoisomeric groups

The *RS*-stereoisomeric group for characterizing an allene skeleton is denoted by the symbol $D_{2d\tilde{\sigma}\hat{\Gamma}}$, which is constructed by starting from the point group D_{2d} [13, 14]. The *RS*-stereoisomeric group $D_{2d\tilde{\sigma}\hat{\Gamma}}$ is isomorphic to the the point group D_{4h} , so that it has 27 subgroups up to conjugacy to provide a non-redundant set of subgroups (SSG), as discussed in Part I of this series:

$$\text{SSG}_{D_{2d\tilde{\sigma}\hat{\Gamma}}} = \left\{ \begin{array}{l} 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 \\ C_1, C_2, C_2', C_{\tilde{\sigma}}, C_{\hat{\Gamma}}, C_s, C_{\hat{\Gamma}}, C_{\tilde{\sigma}}, S_4, S_4, C_{2\tilde{\sigma}}, C_{2v}, C_{2\hat{\Gamma}}, C_{s\tilde{\sigma}\hat{\Gamma}}, C_{2\hat{\Gamma}}', \\ C_{2\tilde{\sigma}}', C_{s\tilde{\sigma}\hat{\Gamma}}, D_2, C_{2\tilde{\sigma}}, S_{4\tilde{\sigma}}, S_{4\hat{\Gamma}}, D_{2d}, S_{4\tilde{\sigma}\hat{\Gamma}}, D_{2\hat{\Gamma}}, C_{2v\tilde{\sigma}\hat{\Gamma}}, D_{2\tilde{\sigma}}, D_{2d\tilde{\sigma}\hat{\Gamma}} \end{array} \right\}, \quad (1)$$

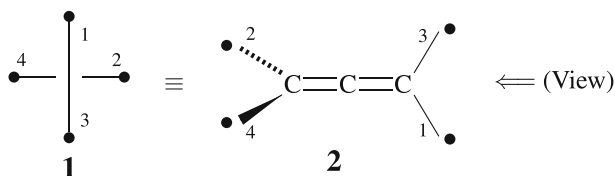


Fig. 1 Reference allene skeleton. The orbit of the four vertices corresponds to the coset representation $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}(/C_{s\tilde{\sigma}\hat{T}})$ under the *RS*-stereoisomeric group $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}$ and to the coset representation $\mathbf{D}_{2d}(/C_s)$ under the point group \mathbf{D}_{2d}

where the subgroups are aligned in the ascending order of their orders. For the convenience of cross reference, sequential numbers from 1 to 27 are attached to the respective subgroups.

The mark table of $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}$ as a 27×27 square matrix $M_{\mathbf{D}_{2d\tilde{\sigma}\hat{T}}}$ is identical with that of \mathbf{D}_{4h} (cf. Fig. 3 of [15]), because the $\text{SSG}_{\mathbf{D}_{2d\tilde{\sigma}\hat{T}}}$ is constructed in accordance with $\text{SSG}_{\mathbf{D}_{4h}}$. For practices of calculations, the corresponding inverse matrix $M_{\mathbf{D}_{2d\tilde{\sigma}\hat{T}}}^{-1}$ is also necessary, as reported in Eq. 110 of Part I of this series.

The coset representation $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}(/G_i)$ ($G_i \in \text{SSG}_{\mathbf{D}_{2d\tilde{\sigma}\hat{T}}}$) is calculated in a parallel way to the coset representation $\mathbf{D}_{4h}(/G_i)$ ($G_i \in \text{SSG}_{\mathbf{D}_{4h}}$), as shown in Part I of this series. For example, the coset representation $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}(/C_{s\tilde{\sigma}\hat{T}})$ is calculated to have an identical set of products of cycles with the coset representation $\mathbf{D}_{4h}(/C_{2v}''')$, as shown in Part I of this series.

The four positions of an allene skeleton **1** (or equivalently **2**) construct an orbit governed by the coset representation $\mathbf{D}_{d\tilde{\sigma}\hat{T}}(/C_{s\tilde{\sigma}\hat{T}})$, the degree of which is calculated to be $|\mathbf{D}_{2d\tilde{\sigma}\hat{T}}|/|C_{s\tilde{\sigma}\hat{T}}| (= 16/4 = 4)$. The *RS*-stereoisomeric group $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}$ exhibits the global symmetry of the allene skeleton **1**, while its subgroup $C_{s\tilde{\sigma}\hat{T}}$ exhibits the local symmetry of each of the four vertices (Fig. 1).

As reported in Eq. 47 of the Part I of this series, the group $C_{s\tilde{\sigma}\hat{T}}$ consists of the following set of operations:

$$C_{s\tilde{\sigma}\hat{T}}^{14} = \{I, \tilde{\sigma}_{d(1)}, \hat{T}, \sigma_{d(1)}\} \quad (\supset C_s) \quad (2)$$

The group $C_{s\tilde{\sigma}\hat{T}}$ as an *RS*-stereoisomeric group is constructed by extending the point group C_s :

$$C_s = \{I, \sigma_{d(1)}\} \quad (3)$$

according to a general procedure of constructing stereoisograms and *RS*-stereoisomeric groups [4,5].

It should be noted that the four positions of the allene skeleton **1** (or **2**) are alternatively regarded as being governed by the coset representation $\mathbf{D}_{2d}(/C_s)$, if the skeleton is considered to belong to the point group \mathbf{D}_{2d} . From this point of view, the point group \mathbf{D}_{2d} exhibits the global symmetry of the allene skeleton, while its subgroup C_s exhibits the local symmetry of each of the four vertices. Hence, it is one of the important targets of the present paper to compare between $\mathbf{D}_{2d\tilde{\sigma}\hat{T}}(/C_{s\tilde{\sigma}\hat{T}})$ and $\mathbf{D}_{2d}(/C_s)$, which are operated onto the same skeleton **1** (or **2**).

2.2 Partial cycle indices with chirality fittingness

According to the formulation of the USCI approach [9], the mark table $M_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}$ and its inverse $M_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}^{-1}$ are further used for subductions of coset representations, i.e., $\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\hat{G}_i) \downarrow \hat{G}_j$ (for $\hat{G}_i, \hat{G}_j \in \text{SSG}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}$). The results of such subductions are combined with the concept of sphericities to give unit subduced cycle indices with chirality fittingness (USCI-CFs), which are listed in a tabular form (the USCI-CF table). The USCI-CFs listed in the $\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})$ -row are shown as follows:

$$\begin{aligned} \text{USCI-CF}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})} &= \{b_1^4, b_2^2, b_2^2, b_1^2 b_2, c_2^2, a_1^2 c_2, a_1^4, c_2^2, b_4, c_4, \\ & c_4, a_2^2, a_2^2, a_1^2 a_2, a_2^2, c_4, a_2 c_2, b_4, b_2^2, a_4, \\ & a_4, a_4, c_4, a_4, a_2^2, b_4, a_4\} \end{aligned} \tag{4}$$

which has been listed in Table 3 of Part I of this series. The USCI-CFs listed in Eq. 4 are aligned in the order of $\text{SSG}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}$ (Eq. 1). Note that the symbols a_d, b_d, c_d denote sphericity indices, where a_d is assigned to a d -membered homospheric orbit of substitution positions, b_d is assigned to a d -membered hemispheric orbit, and c_d is assigned to a d -membered enantiospheric orbit.

Section 16.3 and Section 19.5 of [9] have discussed partial cycle indices without and with chirality fittingness (PCIs and PCI-CFs). According to Def. 19.6 of [9], PCI-CFs for enumerating RS -stereoisomers are calculated by using the $\text{USCI-CF}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})}$ (Eq. 4), which is multiplied by the inverse mark table of $\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}$ (Eq. 110 of Part I of this series):

$$\begin{aligned} \text{USCI-CF}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})} \times M_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}^{-1} &= (\text{PCI-CF}(\mathbf{C}_1), \dots, \\ \text{PCI-CF}(\hat{G}_i), \dots, \text{PCI-CF}(\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}})), \end{aligned} \tag{5}$$

where \hat{G}_i runs to cover the $\text{SSG}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}$ (Eq. 1). When the $\text{USCI-CF}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})}$ (Eq. 4) is regarded as a row vector of USCI-CFs, the result of Eq. 5 is also regarded as a row vector, in which each component (i.e., $\text{PCI-CF}(\hat{G}_i)$) as a polynomial of $a_d, b_d,$ and c_d corresponds to the PCI-CF of a subgroup at issue (\hat{G}_i). For example, the \mathbf{C}_1 -component of Eq. 5 (i.e., $\text{PCI-CF}(\mathbf{C}_1)$) is calculate as follows:

$$\begin{aligned} \text{PCI-CF}(\mathbf{C}_1) &= \text{USCI-CF}_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(\mathbf{C}_{s\bar{\sigma}\hat{\Gamma}})} \\ &\times {}^T \left(\frac{1}{16}, -\frac{1}{16}, -\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}, -\frac{1}{16}, -\frac{1}{16}, 0, 0, \right. \\ & \left. \frac{1}{8}, \frac{1}{8}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}, \frac{1}{4}, \frac{1}{4}, \frac{1}{8}, \frac{1}{8}, 0, 0, 0, 0, -\frac{1}{2}, -\frac{1}{2}, 0, 0 \right) \end{aligned} \tag{6}$$

where the symbol T of the last vector represents the transpose of the \mathbf{C}_1 -column of the inverse mark table $M_{\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}}^{-1}$.

The vector calculation of Eq. 6 gives Eq. 7. Similarly, PCI-CFs for every subgroups of $SSG_{D_{2d\bar{\sigma}\hat{\Gamma}}}$ (Eq. 1) are obtained as follows, where the sequential numbers are shown over the respective equality symbols for the convenience of cross reference.

$$\begin{aligned} \text{PCI-CF}(C_1) & \frac{1}{\text{III}} \frac{1}{16} b_1^4 - \frac{1}{16} a_1^4 - \frac{1}{8} b_1^2 b_2 + \frac{1}{4} a_1^2 a_2 - \frac{1}{8} a_1^2 c_2 - \frac{1}{16} b_2^2 \\ & + \frac{1}{4} a_2 c_2 - \frac{3}{16} c_2^2 + \frac{1}{8} b_4 + \frac{3}{8} c_4 - \frac{1}{2} a_4 \end{aligned} \quad (7)$$

$$\text{PCI-CF}(C_2) \stackrel{2}{=} 0 \quad (8)$$

$$\text{PCI-CF}(C'_2) \stackrel{3}{=} \frac{1}{\text{III}} \frac{1}{4} b_2^2 - \frac{1}{4} a_2^2 - \frac{1}{4} b_4 - \frac{1}{4} c_4 + \frac{1}{2} a_4 \quad (9)$$

$$\text{PCI-CF}(C_{\bar{\sigma}}) \stackrel{4}{=} \frac{1}{\text{II}} \frac{1}{4} b_1^2 b_2 - \frac{1}{4} a_1^2 a_2 - \frac{1}{4} b_2^2 + \frac{1}{2} a_2^2 - \frac{1}{4} a_2 c_2 \quad (10)$$

$$\text{PCI-CF}(C_{\hat{\sigma}}) \stackrel{5}{=} \frac{1}{\text{I}} \frac{1}{4} c_2^2 - \frac{1}{4} a_2^2 - \frac{1}{2} c_4 + \frac{1}{2} a_4 \quad (11)$$

$$\text{PCI-CF}(C_s) \stackrel{6}{=} \frac{1}{\text{V}} \frac{1}{4} a_1^2 c_2 - \frac{1}{4} a_1^2 a_2 + \frac{1}{4} a_2^2 - \frac{1}{4} a_2 c_2 \quad (12)$$

$$\text{PCI-CF}(C_{\hat{\Gamma}}) \stackrel{7}{=} \frac{1}{\text{I}} \frac{1}{8} a_1^4 - \frac{1}{4} a_1^2 a_2 - \frac{1}{8} a_2^2 + \frac{1}{4} a_4 \quad (13)$$

$$\text{PCI-CF}(C'_{\hat{\sigma}}) \stackrel{8}{=} \frac{1}{\text{I}} \frac{1}{8} a_2^2 - \frac{1}{4} a_2 c_2 + \frac{1}{8} c_2^2 - \frac{1}{4} c_4 + \frac{1}{4} a_4 \quad (14)$$

$$\text{PCI-CF}(S_4) \stackrel{9}{=} 0 \quad (15)$$

$$\text{PCI-CF}(S_4) \stackrel{10}{=} 0 \quad (16)$$

$$\text{PCI-CF}(C_{2\bar{\sigma}}) \stackrel{11}{=} 0 \quad (17)$$

$$\text{PCI-CF}(C_{2v}) \stackrel{12}{=} 0 \quad (18)$$

$$\text{PCI-CF}(C_{2\hat{\Gamma}}) \stackrel{13}{=} \frac{1}{\text{I}} \frac{1}{2} a_2^2 - \frac{1}{2} a_4 \quad (19)$$

$$\text{PCI-CF}(C_{s\bar{\sigma}\hat{\Gamma}}) \stackrel{14}{=} \frac{1}{\text{IV}} \frac{1}{2} a_1^2 a_2 - \frac{1}{2} a_2^2 \quad (20)$$

$$\text{PCI-CF}(C'_{2\hat{\Gamma}}) \stackrel{15}{=} 0 \quad (21)$$

$$\text{PCI-CF}(C'_{2\bar{\sigma}}) \stackrel{16}{=} \frac{1}{\text{I}} \frac{1}{2} c_4 - \frac{1}{2} a_4 \quad (22)$$

$$\text{PCI-CF}(C_{s\bar{\sigma}\hat{\sigma}}) \stackrel{17}{=} \frac{1}{\text{IV}} \frac{1}{2} a_2 c_2 - \frac{1}{2} a_2^2 \quad (23)$$

$$\text{PCI-CF}(D_2) \stackrel{18}{=} 0 \quad (24)$$

$$\text{PCI-CF}(C_{2\bar{\sigma}}) \stackrel{19}{=} \frac{1}{\text{II}} \frac{1}{4} b_2^2 - \frac{1}{4} a_2^2 - \frac{1}{4} b_4 - \frac{1}{4} c_4 + \frac{1}{2} a_4 \quad (25)$$

$$\text{PCI-CF}(\mathbf{S}_{4\tilde{\sigma}}) \stackrel{20}{\equiv} 0 \quad (26)$$

$$\text{PCI-CF}(\mathbf{S}_{4\tilde{\tau}}) \stackrel{21}{\equiv} 0 \quad (27)$$

$$\text{PCI-CF}(\mathbf{D}_{2d}) \stackrel{22}{\equiv} 0 \quad (28)$$

$$\text{PCI-CF}(\mathbf{S}_{4\tilde{\sigma}\tilde{\sigma}}) \stackrel{23}{\equiv} \frac{1}{2}c_4 - \frac{1}{2}a_4 \quad (29)$$

$$\text{PCI-CF}(\mathbf{D}_{2\tilde{\tau}}) \stackrel{24}{\equiv} 0 \quad (30)$$

$$\text{PCI-CF}(\mathbf{C}_{2v\tilde{\sigma}\tilde{\tau}}) \stackrel{25}{\equiv} \frac{1}{2}a_2^2 - \frac{1}{2}a_4 \quad (31)$$

$$\text{PCI-CF}(\mathbf{D}_{2\tilde{\sigma}}) \stackrel{26}{\equiv} \frac{1}{2}b_4 - \frac{1}{2}a_4 \quad (32)$$

$$\text{PCI-CF}(\mathbf{D}_{2d\tilde{\sigma}\tilde{\tau}}) \stackrel{27}{\equiv} a_4 \quad (33)$$

Note that a Roman numeral below each equality symbol represents the stereoisogram type at issue (types I–V) according to Fig. 4 (and Eqs. 27–53) of Part I of this series.

2.3 Generating functions for symmetry-itemized enumeration

Suppose that substituents for the four positions of **1** (or **2**) are selected from an inventory of proligands:

$$\mathbf{X} = \{A, B, X, Y; p, q, r, s; \bar{p}, \bar{q}, \bar{r}, \bar{s}\}, \quad (34)$$

where the letters A, B, X, and Y represent achiral proligands and the pairs of p/\bar{p} , q/\bar{q} , r/\bar{r} , and s/\bar{s} represent pairs of enantiomeric proligands in isolation. According to Theorem 19.6 (or Theorem 9.7) of [9], we use the following ligand-inventory functions:

$$a_d = A^d + B^d + X^d + Y^d \quad (35)$$

$$c_d = A^d + B^d + X^d + Y^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} + 2r^{d/2}\bar{r}^{d/2} + 2s^{d/2}\bar{s}^{d/2} \quad (36)$$

$$b_d = A^d + B^d + X^d + Y^d + p^d + q^d + r^d + s^d + \bar{p}^d + \bar{q}^d + \bar{r}^d + \bar{s}^d, \quad (37)$$

where the power $d/2$ appearing in Eq. 36 is an integer because the subscript d of c_d is always even in the light of the enantiosphericity of the corresponding orbit.

The ligand-inventory functions (Eqs. 35–37) are introduced into the PCI-CFs (Eqs. 7–33). Thereby we obtain the following generating functions:

$$f_{C_1} \stackrel{\text{III}}{\equiv} \left\{ \frac{1}{2}(A^2Bp + A^2B\bar{p}) + \dots \right\} + \left\{ \frac{1}{2}(A^2pq + A^2\bar{p}\bar{q}) + \dots \right\} \\ + \left\{ \frac{3}{2}(ABXp + ABX\bar{p}) + \dots \right\} + \left\{ \frac{1}{2}(ABp^2 + AB\bar{p}^2) + \dots \right\}$$

$$\begin{aligned}
& + \{ABp\bar{p} + \dots\} + \left\{ \frac{3}{2} (ABpq + AB\bar{p}\bar{q}) + \dots \right\} \\
& + \left\{ \frac{1}{2} (Ap^2\bar{p} + Ap\bar{p}^2) + \dots \right\} + \left\{ \frac{1}{2} (Ap^2q + A\bar{p}^2\bar{q}) + \dots \right\} \\
& + \left\{ \frac{3}{2} (Ap\bar{p}q + Ap\bar{p}\bar{q}) + \dots \right\} + \left\{ \frac{3}{2} (Apqr + A\bar{p}\bar{q}\bar{r}) + \dots \right\} \\
& + \left\{ \frac{1}{2} (p^2\bar{p}q + p\bar{p}^2\bar{q}) + \dots \right\} + \left\{ \frac{1}{2} (p^2q\bar{q} + \bar{p}^2q\bar{q}) + \dots \right\} \\
& + \left\{ \frac{1}{2} (p^2qr + \bar{p}^2\bar{q}\bar{r}) + \dots \right\} + \left\{ \frac{3}{2} (p\bar{p}qr + p\bar{p}\bar{q}\bar{r}) + \dots \right\} \\
& + \left\{ \frac{3}{2} (pqrs + \bar{p}\bar{q}\bar{r}\bar{s}) + \dots \right\} \tag{38}
\end{aligned}$$

$$f_{C'_2} \frac{3}{III} \left\{ \frac{1}{2} (A^2p^2 + A^2\bar{p}^2) + \dots \right\} + \left\{ \frac{1}{2} (p^2q^2 + \bar{p}^2\bar{q}^2) + \dots \right\} \tag{39}$$

$$\begin{aligned}
f_{C_{\bar{\sigma}}} \frac{4}{II} & \left\{ \frac{1}{2} (A^3p + A^3\bar{p}) + \dots \right\} + \left\{ \frac{1}{2} (A^2Bp + A^2B\bar{p}) + \dots \right\} \\
& + \left\{ \frac{1}{2} (A^2pq + A^2\bar{p}\bar{q}) + \dots \right\} + \left\{ \frac{1}{2} (ABp^2 + AB\bar{p}^2) + \dots \right\} \\
& + \left\{ \frac{1}{2} (Ap^3 + A\bar{p}^3) + \dots \right\} + \left\{ \frac{1}{2} (Ap^2\bar{p} + Ap\bar{p}^2) + \dots \right\} \\
& + \left\{ \frac{1}{2} (Ap^2q + A\bar{p}^2\bar{q}) + \dots \right\} + \left\{ \frac{1}{2} (p^3\bar{p} + p\bar{p}^3) + \dots \right\} \\
& + \left\{ \frac{1}{2} (p^3q + \bar{p}^3\bar{q}) + \dots \right\} + \left\{ \frac{1}{2} (p^2\bar{p}q + p\bar{p}^2\bar{q}) + \dots \right\} \\
& + \left\{ \frac{1}{2} (p^2q\bar{q} + \bar{p}^2q\bar{q}) + \dots \right\} + \left\{ \frac{1}{2} (p^2qr + \bar{p}^2\bar{q}\bar{r}) + \dots \right\} \tag{40}
\end{aligned}$$

$$f_{C_{\bar{\sigma}}} \frac{5}{I} \left\{ A^2p\bar{p} + A^2q\bar{q} + \dots \right\} + \{2p\bar{p}q\bar{q} + 2p\bar{p}\bar{r}\bar{r} + \dots\} \tag{41}$$

$$f_{C_s} \frac{6}{V} \{ABp\bar{p} + ABq\bar{q} + \dots\} \tag{42}$$

$$f_{C_{\bar{I}}} \frac{7}{I} \left\{ A^2BX + A^2BY \dots \right\} + \{3ABXY\} \tag{43}$$

$$f_{C'_{\bar{\sigma}}} \frac{8}{I} \{p\bar{p}q\bar{q} + \dots\} \tag{44}$$

$$f_{C_{2\bar{I}}} \frac{13}{I} \{A^2B^2 + \dots\} \tag{45}$$

$$f_{C_{s\bar{\sigma}\bar{I}}} \frac{14}{IV} \left\{ A^3B + \dots \right\} + \left\{ A^2BX + \dots \right\} \tag{46}$$

$$f_{C_{2\bar{\sigma}'}} \frac{16}{I} \left\{ p^2\bar{p}^2 + \dots \right\} \tag{47}$$

$$f_{C_{s\bar{\sigma}\bar{\sigma}}} \frac{17}{IV} \left\{ A^2p\bar{p} + \dots \right\} \tag{48}$$

$$f_{C_{2\bar{\sigma}}} \stackrel{19}{\equiv} \frac{1}{\Pi} \left\{ \frac{1}{2} (A^2 p^2 + A^2 \bar{p}^2) + \dots \right\} + \left\{ \frac{1}{2} (p^2 q^2 + \bar{p}^2 \bar{q}^2) + \dots \right\} \quad (49)$$

$$f_{S_{4\bar{\sigma}\hat{\sigma}}} \stackrel{23}{\equiv} \frac{1}{IV} \left\{ p^2 \bar{p}^2 + \dots \right\} \quad (50)$$

$$f_{C_{2v\bar{\sigma}\hat{\sigma}}} \stackrel{25}{\equiv} \frac{1}{IV} \left\{ A^2 B^2 + \dots \right\} \quad (51)$$

$$f_{D_{2\bar{\sigma}}} \stackrel{26}{\equiv} \frac{1}{\Pi} \left\{ \frac{1}{2} (p^4 + \bar{p}^4) + \dots \right\} \quad (52)$$

$$f_{D_{2d\bar{\sigma}\hat{\sigma}}} \stackrel{27}{\equiv} \frac{1}{IV} \left\{ A^4 + B^4 + X^4 + Y^4 \right\} \quad (53)$$

where generating functions of zero value are omitted (cf. the sequential numbers above the equality symbols). The coefficient of the term $A^a B^b X^x Y^y p^p \bar{p}^{\bar{p}} q^q \bar{q}^{\bar{q}} r^r \bar{r}^{\bar{r}} s^s \bar{s}^{\bar{s}}$ indicates the number of fixed promolecules (quadruplets) to be counted. Because A, B, etc. appear symmetrically, each pair of braces contains at least one representative of such symmetrically appearing terms, which can be represented by the following partition:

$$[\theta] = [a, b, x, y; p, \bar{p}, q, \bar{q}, r, \bar{r}, s, \bar{s}], \quad (54)$$

where we put $a \geq b \geq x \geq y, p \geq \bar{p}, q \geq \bar{q}, r \geq \bar{r}, s \geq \bar{s}$, and $p \geq q \geq r \geq s$ without losing generality.

The results collected in Eqs. 38–53 are consistent with those of Eqs. 112 and 114 reported in Part I of this series, where the 30 pairs of braces appearing in Eqs.38–53 corresponds to the partitions $[\theta]_1$ – $[\theta]_{30}$ discussed in Part I. As a result, Figs. 6–9 of Part I also illustrate the enumeration results collected in Eqs. 38–53.

3 Type-itemized enumeration by the PCI method

3.1 CI-CFs for characterizing five types of stereoisograms

The 27 subgroups of the *RS*-stereoisomeric group $D_{2d\bar{\sigma}\hat{\sigma}}$ are categorized into five types:

$$\text{Type I: SG}_{D_{2d\bar{\sigma}\hat{\sigma}}}^{[I]} = \{C_{\hat{\sigma}}, C_{\hat{\sigma}'}, C_{\bar{\sigma}}, C_{\bar{\sigma}'}, C_{2\hat{\sigma}}, C_{2\hat{\sigma}'}, C_{2\bar{\sigma}}, C_{2\bar{\sigma}'}, D_{2\hat{\sigma}}\} \quad (55)$$

$$\text{Type II: SG}_{D_{2d\bar{\sigma}\hat{\sigma}}}^{[II]} = \{C_{\bar{\sigma}}, S_{\bar{4}}, C_{2\bar{\sigma}}, D_{2\bar{\sigma}}\} \quad (56)$$

$$\text{Type III: SG}_{D_{2d\bar{\sigma}\hat{\sigma}}}^{[III]} = \{C_1, C_2, C'_2, D_2\} \quad (57)$$

$$\text{Type IV: SG}_{D_{2d\bar{\sigma}\hat{\sigma}}}^{[IV]} = \{C_{s\bar{\sigma}\hat{\sigma}}, C_{s\bar{\sigma}\bar{\sigma}}, S_{\bar{4}\hat{\sigma}}, S_{\bar{4}\bar{\sigma}}, S_{4\bar{\sigma}\hat{\sigma}}, S_{4\bar{\sigma}\bar{\sigma}}, C_{2v\bar{\sigma}\hat{\sigma}}, D_{2d\bar{\sigma}\hat{\sigma}}\} \quad (58)$$

$$\text{Type V: SG}_{D_{2d\bar{\sigma}\hat{\sigma}}}^{[V]} = \{C_s, S_4, C_{2v}, D_{2d}\} \quad (59)$$

These sets have been listed in Eqs. 115–119 of Part I of this series. These sets correspond to stereoisograms of type I–V, respectively.

According to Eqs. 55–59, cycle indices with chirality fittingness (CI-CFs) for characterizing five types are defined as follows:

$$\begin{aligned} \text{CI-CF}^{\text{[I]}} &= \text{PCI-CF}(\mathbf{C}_{\tilde{\sigma}}) + \text{PCI-CF}(\mathbf{C}_{\tilde{\tau}}) + \text{PCI-CF}(\mathbf{C}_{\tilde{\sigma}'}) + \text{PCI-CF}(\mathbf{C}_{2\tilde{\sigma}}) \\ &\quad + \text{PCI-CF}(\mathbf{C}_{2\tilde{\tau}}) + \text{PCI-CF}(\mathbf{C}'_{2\tilde{\tau}}) + \text{PCI-CF}(\mathbf{C}'_{2\tilde{\sigma}}) + \text{PCI-CF}(\mathbf{D}_{2\tilde{\tau}}) \end{aligned} \quad (60)$$

$$\text{PCI-CF}^{\text{[II]}} = \text{PCF-CF}(\mathbf{C}_{\tilde{\sigma}}) + \text{PCF-CF}(\mathbf{S}_{\tilde{4}}) + \text{PCF-CF}(\mathbf{C}_{2\tilde{\sigma}}) + \text{PCF-CF}(\mathbf{D}_{2\tilde{\sigma}}) \quad (61)$$

$$\text{PCI-CF}^{\text{[III]}} = \text{PCF-CF}(\mathbf{C}_1) + \text{PCF-CF}(\mathbf{C}_2) + \text{PCF-CF}(\mathbf{C}'_2) + \text{PCF-CF}(\mathbf{D}_2) \quad (62)$$

$$\begin{aligned} \text{PCI-CF}^{\text{[IV]}} &= \text{PCF-CF}(\mathbf{C}_{s\tilde{\sigma}\tilde{\tau}}) + \text{PCF-CF}(\mathbf{C}_{s\tilde{\sigma}\tilde{\sigma}}) + \text{PCF-CF}(\mathbf{S}_{\tilde{4}\tilde{\sigma}}) + \text{PCF-CF}(\mathbf{S}_{\tilde{4}\tilde{\tau}}) \\ &\quad + \text{PCF-CF}(\mathbf{S}_{\tilde{4}\tilde{\sigma}\tilde{\sigma}}) + \text{PCF-CF}(\mathbf{C}_{2v\tilde{\sigma}\tilde{\tau}}) + \text{PCF-CF}(\mathbf{D}_{2d\tilde{\sigma}\tilde{\tau}}) \end{aligned} \quad (63)$$

$$\text{PCI-CF}^{\text{[V]}} = \text{PCF-CF}(\mathbf{C}_s) + \text{PCF-CF}(\mathbf{S}_4) + \text{PCF-CF}(\mathbf{C}_{2v}) + \text{PCF-CF}(\mathbf{D}_{2d}), \quad (64)$$

where the PCI-CFs appearing in the right-hand sides are listed in Eqs. 7–33.

The PCI-CFs listed in Eqs. 7–33 are added according to the definitions shown by Eqs. 60–64. Note that the symbols I–V below the equality symbols in the PCI-CFs (Eqs. 7–33) represent the categories of the five types. Thereby, we obtain the following type-itemized CI-CFs:

$$\text{CI-CF}^{\text{[I]}} = \frac{1}{8}a_1^4 - \frac{1}{4}a_1^2a_2 + \frac{1}{4}a_2^2 - \frac{1}{4}a_2c_2 + \frac{3}{8}c_2^2 - \frac{1}{4}c_4 \quad (65)$$

$$\text{CI-CF}^{\text{[II]}} = \frac{1}{4}b_1^2b_2 - \frac{1}{4}a_1^2a_2 + \frac{1}{4}a_2^2 - \frac{1}{4}a_2c_2 + \frac{1}{4}b_4 - \frac{1}{4}c_4 \quad (66)$$

$$\begin{aligned} \text{CI-CF}^{\text{[III]}} &= \frac{1}{16}b_1^4 - \frac{1}{16}a_1^4 - \frac{1}{8}b_1^2b_2 + \frac{1}{4}a_1^2a_2 - \frac{1}{8}a_1^2c_2 \\ &\quad + \frac{3}{16}b_2^2 - \frac{1}{4}a_2^2 + \frac{1}{4}a_2c_2 - \frac{3}{16}c_2^2 - \frac{1}{8}b_4 + \frac{1}{8}c_4 \end{aligned} \quad (67)$$

$$\text{CI-CF}^{\text{[IV]}} = \frac{1}{2}a_1^2a_2 - \frac{1}{2}a_2^2 + \frac{1}{2}a_2c_2 + \frac{1}{2}c_4 \quad (68)$$

$$\text{CI-CF}^{\text{[V]}} = \frac{1}{4}a_1^2c_2 - \frac{1}{4}a_1^2a_2 + \frac{1}{4}a_2^2 - \frac{1}{4}a_2c_2 \quad (69)$$

These CI-CFs are verified by comparison with the data of the type-enumeration matrix (TEM), where $\text{USCI-CF}_{\mathbf{D}_{2d\tilde{\sigma}\tilde{\tau}}(\mathbf{C}_{s\tilde{\sigma}\tilde{\tau}})}$ (Eq. 4) regarded as a row vector is multiplied by the TEM shown in Table 3 of Part I of this series. It should be noted that the $\text{CI-CF}^{\text{[I]}}$ (Eq. 65) contains no sphericity index b_d in a similar way to the $\text{CI-CF}^{\text{[IV]}}$ (Eq. 68) or the $\text{CI-CF}^{\text{[V]}}$ (Eq. 69). This is in sharp contrast with the fact that quadruplets of type I are chiral from the viewpoint of the point-group theory, as discussed later.

3.2 Generating functions for type-itemized enumeration

The ligand-inventory functions (Eqs. 35–37) are introduced into the CI-CFs (Eqs. 65–69) so as to give the following generating functions:

$$\begin{aligned}
 f^{[I]} = & \{A^2p\bar{p} + A^2q\bar{q} + \dots\} + \{3p\bar{p}q\bar{q} + 3p\bar{p}r\bar{r} + \dots\} \\
 & + \{A^2BX + A^2BY \dots\} + \{3ABXY\} \\
 & + \{A^2B^2 + \dots\} + \{p^2\bar{p}^2 + \dots\}
 \end{aligned} \tag{70}$$

$$\begin{aligned}
 f^{[II]} = & \left\{ \frac{1}{2}(A^3p + A^3\bar{p}) + \dots \right\} + \left\{ \frac{1}{2}(A^2Bp + A^2B\bar{p}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(A^2pq + A^2\bar{p}\bar{q}) + \dots \right\} + \left\{ \frac{1}{2}(ABp^2 + AB\bar{p}^2) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(Ap^3 + A\bar{p}^3) + \dots \right\} + \left\{ \frac{1}{2}(Ap^2\bar{p} + A\bar{p}p^2) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(Ap^2q + A\bar{p}^2\bar{q}) + \dots \right\} + \left\{ \frac{1}{2}(p^3\bar{p} + p\bar{p}^3) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(p^3q + p\bar{p}^3\bar{q}) + \dots \right\} + \left\{ \frac{1}{2}(p^2\bar{p}q + p\bar{p}^2\bar{q}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(p^2q\bar{q} + \bar{p}^2q\bar{q}) + \dots \right\} + \left\{ \frac{1}{2}(p^2qr + \bar{p}^2\bar{q}\bar{r}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(A^2p^2 + A^2\bar{p}^2) + \dots \right\} + \left\{ \frac{1}{2}(p^2q^2 + \bar{p}^2\bar{q}^2) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(p^4 + \bar{p}^4) + \dots \right\}
 \end{aligned} \tag{71}$$

$$\begin{aligned}
 f^{[III]} = & \left\{ \frac{1}{2}(A^2Bp + A^2B\bar{p}) + \dots \right\} + \left\{ \frac{1}{2}(A^2pq + A^2\bar{p}\bar{q}) + \dots \right\} \\
 & + \left\{ \frac{3}{2}(ABXp + ABX\bar{p}) + \dots \right\} + \left\{ \frac{1}{2}(ABp^2 + AB\bar{p}^2) + \dots \right\} \\
 & + \{ABp\bar{p} + \dots\} + \left\{ \frac{3}{2}(ABpq + AB\bar{p}\bar{q}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(Ap^2\bar{p} + A\bar{p}p^2) + \dots \right\} + \left\{ \frac{1}{2}(Ap^2q + A\bar{p}^2\bar{q}) + \dots \right\} \\
 & + \left\{ \frac{3}{2}(Ap\bar{p}q + A\bar{p}\bar{p}\bar{q}) + \dots \right\} + \left\{ \frac{3}{2}(Apqr + A\bar{p}\bar{q}\bar{r}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(p^2\bar{p}q + p\bar{p}^2\bar{q}) + \dots \right\} + \left\{ \frac{1}{2}(p^2q\bar{q} + \bar{p}^2q\bar{q}) + \dots \right\} \\
 & + \left\{ \frac{1}{2}(p^2qr + \bar{p}^2\bar{q}\bar{r}) + \dots \right\} + \left\{ \frac{3}{2}(p\bar{p}qr + p\bar{p}\bar{q}\bar{r}) + \dots \right\}
 \end{aligned}$$

$$\begin{aligned}
& + \left\{ \frac{3}{2} (pqrs + \bar{p}\bar{q}\bar{r}\bar{s}) + \dots \right\} + \left\{ \frac{1}{2} (A^2 p^2 + A^2 \bar{p}^2) + \dots \right\} \\
& + \left\{ \frac{1}{2} (p^2 q^2 + \bar{p}^2 \bar{q}^2) + \dots \right\} \quad (72)
\end{aligned}$$

$$\begin{aligned}
f^{[IV]} &= \{A^3 B + \dots\} + \{A^2 B X + \dots\} \\
&+ \{A^2 p \bar{p} + \dots\} + \{p^2 \bar{p}^2 + \dots\} + \{A^2 B^2 + \dots\} \\
&+ \{A^4 + B^4 + X^4 + Y^4\} \quad (73)
\end{aligned}$$

$$f^{[V]} = \{ABp\bar{p} + ABq\bar{q} + \dots\} \quad (74)$$

The generating functions (Eqs. 70–74) are also obtained by starting from the generating functions for the respective subgroups (Eq. 38–53), which are added according to the categories shown in Eqs. 60–64.

The constitution of each pair of parentheses appearing in Eqs. 70–74 corresponds to the representative of a stereoisogram. Examples of such representatives have been depicted in Figs. 6–9 of Part I of this series.

4 Examination of enumeration results

4.1 *RS*-stereoisomeric groups of Type I

Among the *RS*-stereoisomeric groups listed in Eq. 55 (Type I), there appear a quadruplet of $C_{\hat{T}}$ (Eq. 43) having $A^2 XY$ ($[\theta]_6$) and three quadruplets of $C_{\hat{T}}$ (Eq. 43) having $ABXY$ ($[\theta]_{10}$); a quadruplet of $C_{\hat{\sigma}}$ (Eq. 41) having $A^2 p\bar{p}$ ($[\theta]_8$) and two quadruplets of $C_{\hat{\sigma}}$ (Eq. 41) having $p\bar{p}q\bar{q}$ ($[\theta]_{28}$); a quadruplet of $C_{\hat{\sigma}'}$ (Eq. 44) having $p\bar{p}q\bar{q}$ ($[\theta]_{28}$); a quadruplet of $C_{2\hat{T}}$ (Eq. 45) having $A^2 B^2$ ($[\theta]_4$); as well as a quadruplet of $C_{2\hat{\sigma}'}$ (Eq. 47) having $p^2 \bar{p}^2$ ($[\theta]_{23}$). They are totally counted by Eq. 70.

4.1.1 Quadruplet of $C_{\hat{T}}$ with $A^2 XY$

The quadruplet of $C_{\hat{T}}$ having $A^2 XY$ ($[\theta]_6 = [2, 1, 1, 0; 0, 0, 0, 0, 0, 0, 0]$. cf. Eq. 73 of Part I) is counted once (Eq. 43) and characterized by the stereoisogram of type I, as shown in Fig. 2. The diagonal equality symbol shows the equivalence based on the following *RS*-stereoisomeric group (Eq. 40 of Part I):

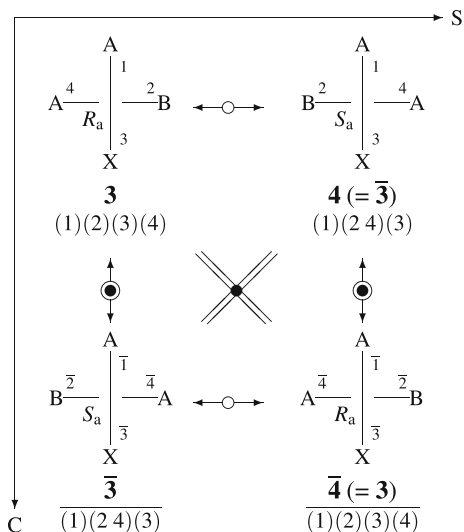
$$C_{\hat{T}} = \{I, \hat{T}\} \sim \{(1)(2)(3)(4), \overline{(1)(2)(3)(4)}\}, \quad (75)$$

which is a subgroup of the following *RS*-stereoisomeric group (Eq. 47 of Part I):

$$\begin{aligned}
C_{s\hat{\sigma}\hat{T}} &= \{I, \tilde{\sigma}_{d(1)}, \hat{T}, \sigma_{d(1)}\} \quad (76) \\
&\sim \{(1)(2)(3)(4), (1)(2\ 4)(3), \overline{(1)(2)(3)(4)}, \overline{(1)(2\ 4)(3)}\}. \quad (77)
\end{aligned}$$

Each of the four positions (1–4) of **3** constructs a one-membered $C_{\hat{T}}/(C_{\hat{T}})$ -orbit, which is fixed under the action of the *RS*-stereoisomeric group $C_{\hat{T}}$. In other words, the

Fig. 2 Stereoisogram of type I with the constitution A^2BX , where the reference promolecule **3** belongs to the RS -stereoisomeric group $C_{\hat{T}}$ and to the point group C_1 . The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $A(4) > B(2)$; $A(1) > X(3)$ (for **3** and **4**) and the priority sequence $A(\bar{4}) > B(\bar{2})$; $A(\bar{1}) > X(\bar{3})$ (for $\bar{\mathbf{3}}$ and $\bar{\mathbf{4}}$). This stereoisogram is chirality-faithful



stabilizer of each position is determined to be the local symmetry represented by $C_{\hat{T}}$. The global symmetry of **3** is determined to be $C_{\hat{T}}$, which is regarded as the stabilizer of **3** under the action of $D_{2d\hat{\sigma}\hat{T}}$. This behavior is consistent to the subduction:

$$D_{2d\hat{\sigma}\hat{T}} / (C_{s\hat{\sigma}\hat{T}}) \downarrow C_{\hat{T}} = 4C_{\hat{T}} / (C_{\hat{T}}), \tag{78}$$

which is shown in the 7th row of Table 3 of Part I. Note that the two A's are inequivalent under the action of the RS -stereoisomeric group $C_{s\hat{\sigma}\hat{T}}$ (Eq. 77), which is a subgroup of $D_{2d\hat{\sigma}\hat{T}}$.

It should be noted that the RS -stereoisomeric group $C_{s\hat{\sigma}\hat{T}}$ (Eq. 77) is isomorphic to the Klein four group, which is in turn isomorphic to the factor group $D_{2d\hat{\sigma}\hat{T}}/D_2$. Each promolecule of the quadruplet shown in Fig. 2 is transformed into its homomeric promolecule under the action of D_2 so that it is regarded as a representative of each coset appearing in the factor group $D_{2d\hat{\sigma}\hat{T}}/D_2$.

From the viewpoint of the point-group theory, the reference promolecule **3** belongs to the point group C_1 , so that a pair of $\mathbf{3}/\bar{\mathbf{3}}$ is counted once under the action of the point group D_{2d} [16]. From the viewpoint of the RS -stereoisomeric-group theory, on the other hand, the reference promolecule **3** belongs to the RS -stereoisomeric group $C_{\hat{T}}$, so that a quadruplet of $\mathbf{3}/\bar{\mathbf{3}}$ (doubly contained in the stereoisogram represented by Fig. 2) is counted once under the action of the RS -stereoisomeric group $D_{2d\hat{\sigma}\hat{T}}$.

The stereoisogram of type I (Fig. 2) indicates that **3** ($= \bar{\mathbf{4}}$) is enantiomeric (along the vertical C-axis) and RS -diastereomeric (along with the horizontal S-axis) to $\bar{\mathbf{3}}$ ($= \mathbf{4}$). The two relationships are superposed under the action of the RS -stereoisomeric group. This feature is diagrammatically demonstrated by the diagonal equality symbol. From an attributive viewpoint, each type-I stereoisogram is characterized by chirality (related to the enantiomeric relationship), RS -stereogenicity (related to the RS -diastereomeric relationship), and asclerality. The conventional methodology lays

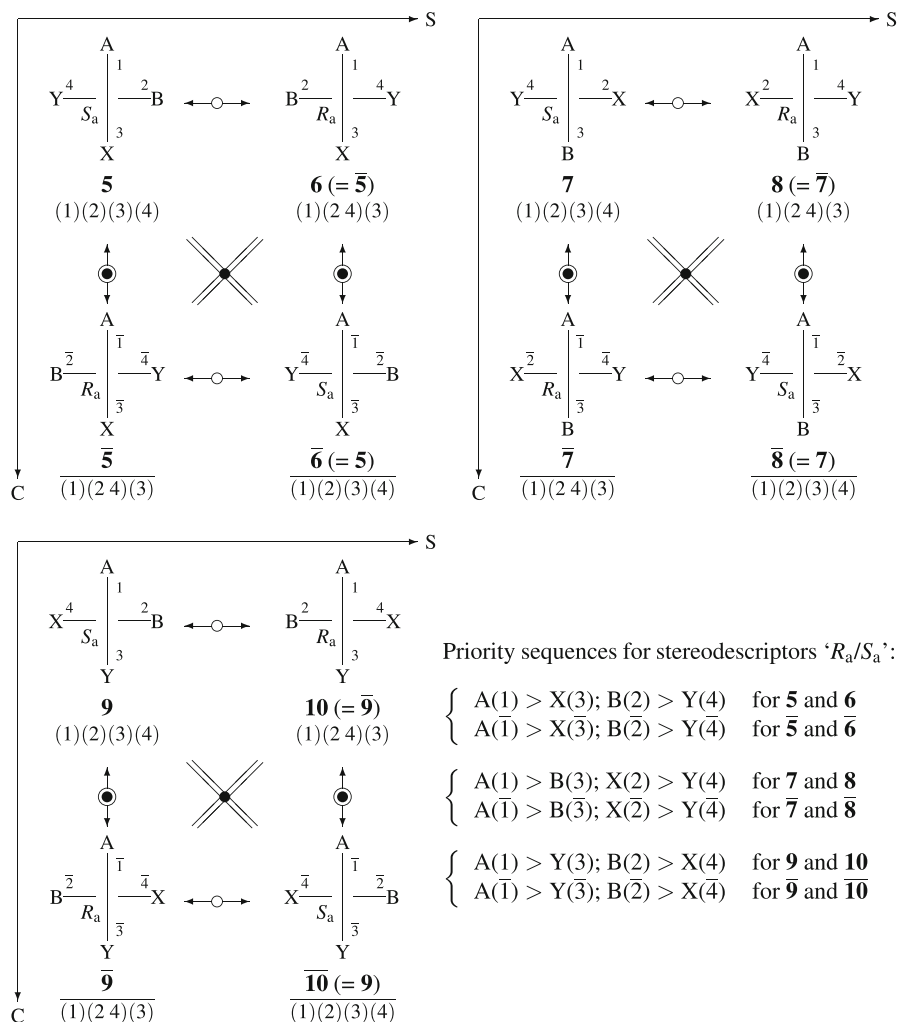


Fig. 3 Three stereoisograms of type I with the constitution ABXY. Each reference promolecule, **5**, **7**, or **9**, belongs to the *RS*-stereoisomeric group $C_{\hat{1}}$ and to the point group C_1 . The stereodescriptors 'R_a/S_a' are assigned by presuming the priority sequences listed in the lower-right part. These stereoisograms are chirality-faithful

stress on the enantiomeric relationship and erroneously ignore the *RS*-diastereomeric relationship, where the dichotomy between enantiomers and diastereomers has caused such unconscious confusion.

4.1.2 Quadruplets of $C_{\hat{1}}$ with ABXY

The coefficient 3 of the term 3ABXY in Eq. 43 indicates the presence of three quadruplets of $C_{\hat{1}}$ having a constitution ABXY ($[\theta]_{10} = [1, 1, 1, 1; 0, 0, 0, 0, 0, 0, 0]$, cf. Eq. 77 of Part I). They are shown in Fig. 3. The reference promolecule of each type-I stereoisogram (i.e., **5** of the upper-left stereoisogram, **7** of the upper-right stereoisogram,

gram, or **9** of the lower-left type-I stereoisogram) belongs to the *RS*-stereoisomeric group $C_{\hat{\tau}}$ shown in Eq. 75, which shows the equivalency due to the diagonal equality symbol.

Each of the four positions (1–4) of **5** (or **7**, or **9**) constructs a one-membered $C_{\hat{\tau}}(/C_{\hat{\tau}})$ -orbit, which is fixed by $C_{\hat{\tau}}$ under the action of the *RS*-stereoisomeric group $C_{s\hat{\sigma}\hat{\tau}}$ (Eq. 77) and more globally under the action of the *RS*-stereoisomeric group $D_{2d\hat{\sigma}\hat{\tau}}$. In other words, the stabilizer of **5** (or **7**, or **9**) is determined to be $C_{\hat{\tau}}$, and the stabilizer of each position is also determined to be $C_{\hat{\tau}}$. The four positions accommodate achiral substituents, A, B, X, and Y, which are different from one another. Note that the $C_{\hat{\tau}}(/C_{\hat{\tau}})$ -orbit is homospheric according to the extended concept of sphericities [17, 18]. This behavior is consistent to the subduction:

$$D_{2d\hat{\sigma}\hat{\tau}}(/C_{s\hat{\sigma}\hat{\tau}}) \downarrow C_{\hat{\tau}} = 4C_{\hat{\tau}}(/C_{\hat{\tau}}), \quad (79)$$

which is shown in the 7th row of Table 3 of Part I.

From the viewpoint of equivalence concerning quadruplets, the three quadruplets of Fig. 3 are inequivalent to one another under the *RS*-stereoisomeric group $D_{2d\hat{\sigma}\hat{\tau}}$, so that each of them is counted once during the enumeration under $D_{2d\hat{\sigma}\hat{\tau}}$, giving the term 3ABXY in Eq. 43.

Each quadruplet shown in Fig. 3 contains two pairs of enantiomers (e.g., $\overline{5/5}$ and $\overline{6/6}$), which coalesce to give a single pair of enantiomers (e.g., $\overline{5/5}$) because of a property of a type-I stereoisogram ($\mathbf{5} = \mathbf{6}$ and $\overline{\mathbf{5}} = \overline{\mathbf{6}}$). From an alternative point of view, each quadruplet shown in Fig. 3 contains two pairs of *RS*-diastereomers (e.g., $\mathbf{5/6}$ and $\overline{\mathbf{5/6}}$), which coalesce to give a single pair of *RS*-diastereomers (e.g., $\mathbf{5/6}$) because of the property of a type-I stereoisogram. Moreover, the single pair of enantiomers (e.g., $\overline{\mathbf{5/5}}$) coincides with the single pair of *RS*-diastereomers (e.g., $\mathbf{5/6}$) because of the property of a type-I stereoisogram.

Because the proligands A, B, X, and Y are achiral, each type-I quadruplet (e.g., $\mathbf{5}$, $\overline{\mathbf{5}}$, $\mathbf{6}$, and $\overline{\mathbf{6}}$) shown in Fig. 3 represents a set of *RS*-stereoisomers. The quadruplet degenerates into a single pair of enantiomers (e.g., $\overline{\mathbf{5/5}}$), which is alternatively regarded as a single pair of *RS*-diastereomers on the basis of the stereoisogram approach.

On the other hand, the pair $\overline{\mathbf{5/5}}$ (or $\overline{\mathbf{7/7}}$ or $\overline{\mathbf{9/9}}$) is selected as a set of stereoisomers from the viewpoint of the conventional stereochemistry, where the pair of enantiomers $\overline{\mathbf{5/5}}$ (or $\overline{\mathbf{7/7}}$ or $\overline{\mathbf{9/9}}$) is presumed as an entity to be recognized without considering a quadruplet of *RS*-stereoisomers. Thus, a pair of enantiomers such as $\overline{\mathbf{5/5}}$ represents a non-redundant set of stereoisomers, so that a pair of *RS*-diastereomers such as $\mathbf{5/6}$ ($= \overline{\mathbf{5/5}}$) is thoroughly ignored because of the conventional dichotomy between enantiomers and diastereomers.

The three quadruplets (concerning **5**, **7**, and **9**) shown in Fig. 3 are isomeric but not stereoisomeric, because they degenerate different graphs from each other. Note that the term ‘isomeric’ refers to equivalence as constitutions but inequivalence as graphs, and that the term ‘stereoisomeric’ refers to equivalence as graphs but inequivalence as configurations. From the viewpoint of the stereoisogram approach, they are not *RS*-stereoisomeric, although they are derived from the same allene skeleton **1** (or equivalently **2**). As a result, they are referred to as *being isoskeletal-isomeric* [19].

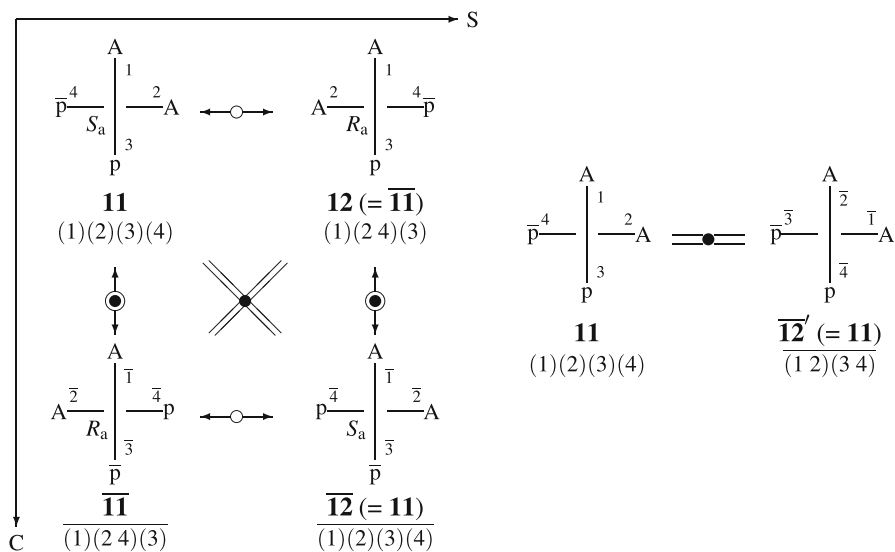


Fig. 4 Stereoisogram of type I with the constitution $A^2p\bar{p}$, where the reference promolecule **11** belongs to the RS -stereoisomeric group $C_{\hat{\sigma}}$ and to the point group C_1 . The holantimer $\bar{\mathbf{12}} (= \mathbf{11})$ is homomeric to $\bar{\mathbf{12}}' (= \mathbf{11})$, which is generated by the action of $\hat{C}_{2(1)}$ ($\sim (1\ 2)(3\ 4)$) operated on **11**, as shown in the right diagram. The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $A(1) > p(3)$; $A(2) > \bar{p}(4)$ (for **11** and **12**) and the priority sequence $A(\bar{1}) > p(\bar{4})$; $A(\bar{1}) > \bar{p}(\bar{3})$ (for $\bar{\mathbf{11}}$ and $\bar{\mathbf{12}}$). This stereoisogram is chirality-faithful

4.1.3 Quadruplet of $C_{\hat{\sigma}}$ with $A^2p\bar{p}$

The quadruplet of $C_{\hat{\sigma}}$ having $A^2p\bar{p}$ ($[\theta]_8 = [1, 1, 0, 0; 1, 1, 0, 0, 0, 0, 0, 0]$). cf. Eq. 75 of Part I) is counted once (Eq. 41) and characterized by a stereoisogram of type I, as shown in the left diagram of Fig. 4. The diagonal equality symbol shows the equivalence based on the following RS -stereoisomeric group (Eq. 39 of Part I):

$$C_{\hat{\sigma}} = \{I, \hat{C}_{2(1)}\} \sim \{(1)(2)(3)(4), \overline{(1\ 2)(3\ 4)}\}, \quad (80)$$

where the symbol $\hat{\sigma}$ in the subscript is used in place of $\hat{C}_{2(1)}$ for the sake of convenience. Note that the operation $\hat{C}_{2(1)}$ ($\sim (1\ 2)(3\ 4)$) is contained in the coset $\hat{I}\mathbf{D}_2$, the representative of which is selected to be the operation \hat{I} ($\sim (1)(2)(3)(4)$) in the drawing of the stereoisogram shown in Fig. 4. Thus, the promolecule $\bar{\mathbf{12}} (= \mathbf{11})$ in the stereoisogram is drawn by applying the operation \hat{I} ($\sim (1)(2)(3)(4)$), so that it is diagrammatically different from the reference promolecule **11**, strictly speaking. As shown in the right diagram of Fig. 4, the action of $\hat{C}_{2(1)}$ ($\sim (1\ 2)(3\ 4)$) on the reference promolecule **11** generates $\bar{\mathbf{12}}'$, which is the same as **11** diagrammatically without considering the mode of numbering (i.e., under the action of the RS -stereoisomeric group $\mathbf{D}_{2d\hat{\sigma}\hat{I}}$). Note that $\bar{\mathbf{12}} (= \mathbf{11})$ is homomeric to $\bar{\mathbf{12}}' (= \mathbf{11})$ under the action of \mathbf{D}_2 .

The 5th row of Table 3 in Part I of this series indicates that the four positions of the reference promolecule **11** is controlled by the following subduction:

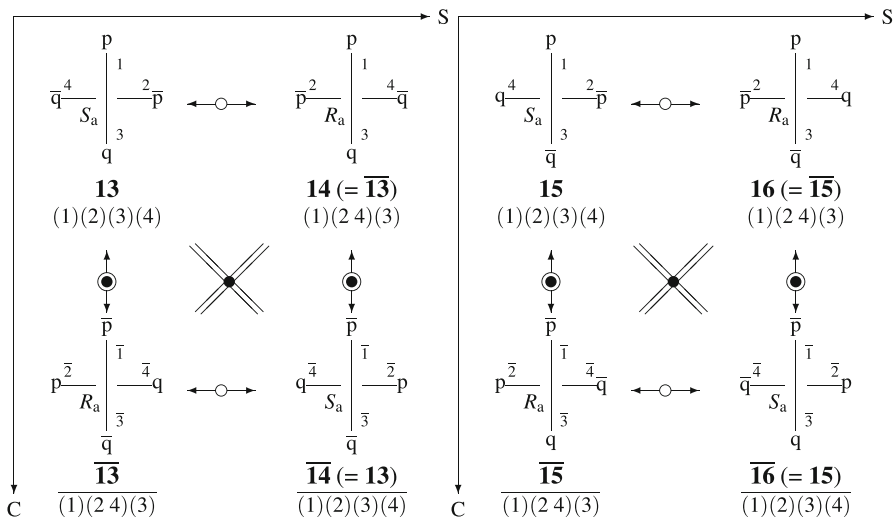


Fig. 5 Stereoisograms of type I with the constitution $p\bar{p}q\bar{q}$, where the reference promolecule **13** (or **15**) belongs to the RS -stereoisomeric group $C_{\hat{\sigma}}$ and to the point group C_1 . The stereodescriptors ‘ R_a/S_a ’ for the left stereoisogram are assigned by presuming the priority sequence $p(1) > q(3); \bar{p}(2) > \bar{q}(4)$ (for **13** and **14**) and the priority sequence $p(1) > q(\bar{3}); \bar{p}(1) > q(\bar{4})$ (for **13** and **14**). The stereodescriptors ‘ R_a/S_a ’ for the right stereoisogram are assigned by presuming the priority sequence $p(1) > \bar{q}(3); \bar{p}(2) > q(4)$ (for **15** and **16**) and the priority sequence $p(2) > \bar{q}(4); \bar{p}(1) > q(3)$ (for **15** and **16**). These stereoisograms are chirality-faithful

$$D_{2d\hat{\sigma}\hat{\tau}}/C_{s\hat{\sigma}\hat{\tau}} \downarrow C_{\hat{\sigma}} = 2C_{\hat{\sigma}}/C_1. \tag{81}$$

Thereby, two achiral proligands A’s occupy one two-membered enantiospheric $C_{\hat{\sigma}}/C_1$ -orbit (positions 1 and 2), while a pair of enantiomeric proligands p and \bar{p} in isolation occupy the other two-membered enantiospheric $C_{\hat{\sigma}}/C_1$ -orbit (positions 3 and 4). Totally, there appears the $C_{\hat{\sigma}}$ -promolecule **11**, which is the reference promolecule for generating the type-I stereoisogram shown in Fig. 4.

4.1.4 Quadruplets of $C_{\hat{\sigma}}$ and $C'_{\hat{\sigma}}$ Both with $p\bar{p}q\bar{q}$

The coefficient 3 of the term $3p\bar{p}q\bar{q}$ in Eq. 70 indicates the presence of three type-I quadruplets having $p\bar{p}q\bar{q}$ ($[\theta]_{28} = [0, 0, 0, 0; 1, 1, 1, 1, 0, 0, 0, 0]$. cf. Eq. 95 of Part I). Among them, two quadruplets belong to $C_{\hat{\sigma}}$ as found in Eq. 41, while the remaining one quadruplet belongs to $C'_{\hat{\sigma}}$ as found in Eq. 44.

The two quadruplets of $C_{\hat{\sigma}}$ having $p\bar{p}q\bar{q}$ are depicted in the form of stereoisograms of type I, as shown in Fig. 5. The diagonal equality symbol shows the equivalence based on the RS -stereoisomeric group (Eq. 80). Note that the corresponding holantimer $\bar{14}$ for the left stereoisogram (or $\bar{16}$ for the right stereoisogram) is homomeric to the reference promolecule **13** (or **15**) under the action of D_2 ($\subset D_{2d\hat{\sigma}\hat{\tau}}$). In other words, the reference promolecule **13** for the left stereoisogram (or **15** for the right stereoisogram) is fixed (stabilized) by $C_{\hat{\sigma}}$ (Eq. 80) under the action of the RS -stereoisomeric group $D_{2d\hat{\sigma}\hat{\tau}}$.

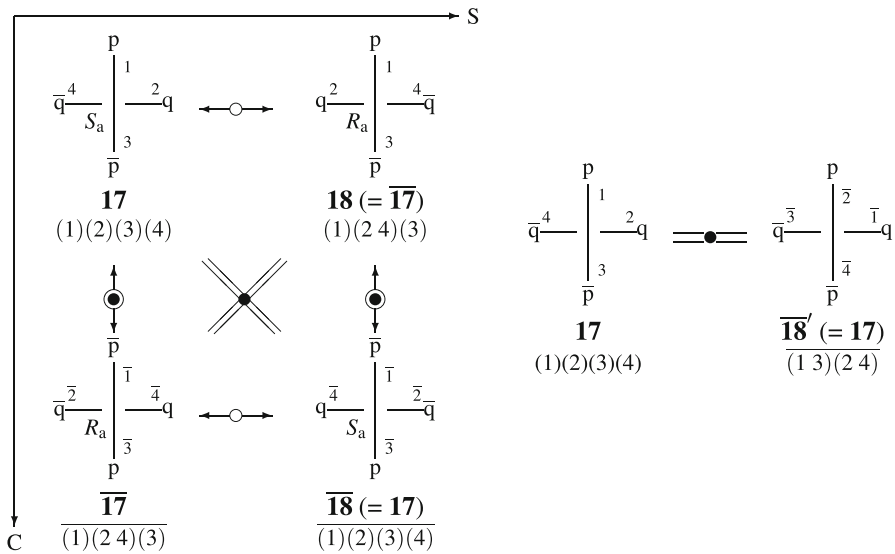


Fig. 6 Stereoisogram of type I with the constitution $\overline{p\bar{p}q\bar{q}}$, where the reference promolecule **17** belongs to the $R\bar{S}$ -stereoisomeric group C'_σ and to the point group C_1 . The holantimer **18** ($=\overline{\mathbf{17}}$) is homomeric to **18'** ($=\mathbf{17}$), which is generated by the action of $\widehat{C}_{2(3)}$ ($\sim (1\ 3)(2\ 4)$) operated on **17**, as shown in the *right diagram*. The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $p(1) > \bar{p}(3); q(2) > \bar{q}(4)$ (for **17** and **18**) and the priority sequence $p(3) > \bar{p}(1); q(4) > \bar{q}(2)$ (for **17** and **18**). This stereoisogram is chirality-faithful

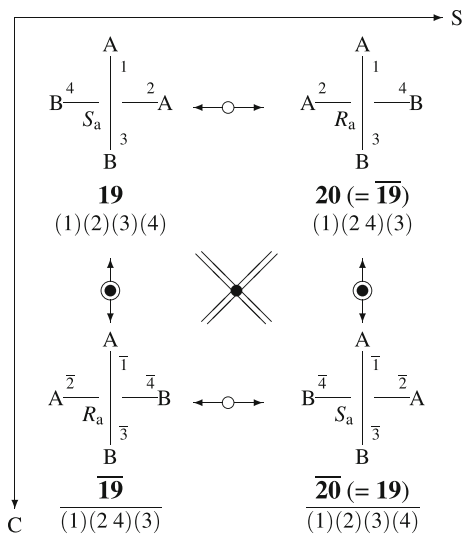
The four positions of the reference promolecule **13** (or **15**) are governed by the subduction represented by the right-hand side of Eq. 81. Thereby, a pair of enantiomeric proligands p and \bar{p} in isolation occupies one two-membered enantiospheric C'_σ ($/C_1$)-orbit (positions 1 and 2), while another pair of enantiomeric proligands q and \bar{q} in isolation occupies the other two-membered enantiospheric C'_σ ($/C_1$)-orbit (positions 3 and 4). Totally, there appears the C'_σ -promolecule **13** (or **15**), which is the reference promolecule for generating the type-I stereoisogram shown in the left (or right) diagram of Fig. 5.

The remaining one quadruplet having $\overline{p\bar{p}q\bar{q}}$ is depicted in Fig. 6, which shows a stereoisogram of type I. The reference promolecule **17** belongs to C'_σ represented as follows:

$$C'_\sigma = \{I, \widehat{C}_{2(3)}\} \sim \{(1)(2)(3)(4), \overline{(1\ 3)(2\ 4)}\}. \quad (82)$$

The corresponding holantimer **18** is generated by the action of $\widehat{I} (= \overline{(1)(2)(3)(4)})$, where **18** is homomeric to the reference promolecule **17**. The action of \widehat{I} is considered in place of the action of $\widehat{C}_{2(3)}$ to generate the holantimer (or its homomer), because these two ligand-reflections, $\widehat{C}_{2(3)}$ and \widehat{I} , are contained in the same coset, i.e., $\widehat{ID}_2 = \widehat{C}_{2(3)}D_2$. In fact, when the ligand-reflection $\widehat{C}_{2(3)}$ ($\sim (1\ 3)(2\ 4)$) is operated on **17**, there appears **18'**, which is identical with **17**, as shown in the right diagram of Fig. 6.

Fig. 7 Stereoisogram of type I with the constitution A^2B^2 , where the reference promolecule **19** belongs to the RS -stereoisomeric group $C_{2\hat{T}}$ and to the point group C'_2 . The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $A(1) > B(3)$; $A(2) > B(4)$ (for **19** and **20**) and the priority sequence $A(\bar{1}) > B(\bar{3})$; $A(\bar{2}) > B(\bar{4})$ (for **19** and **20**). This stereoisogram is chirality-faithful



The right diagram clearly shows that the reference promolecule **17** is fixed (stabilized) by C'_σ (Eq. 82) under the action of the RS -stereoisomeric group $D_{2d\sigma\hat{T}}$.

The four positions of **17** are governed by the subduction:

$$D_{2d\sigma\hat{T}}(/C_{s\sigma\hat{T}}) \downarrow C'_\sigma = 2C'_\sigma(/C_1), \tag{83}$$

which has been listed at the 8th row of Table 3 in Part I of this series. The resulting two-membered orbits governed by the coset representation $C'_\sigma(/C_1)$ are enantiospheric. Hence, one two-membered $C'_\sigma(/C_1)$ -orbit (positions 1 and 3) accommodates a pair of enantiomeric proligands (p and \bar{p}) in isolation, while the other two-membered $C'_\sigma(/C_1)$ -orbit (positions 2 and 4) accommodates another pair of enantiomeric proligands (q and \bar{q}) in isolation. Totally, there appears the reference promolecule **17**.

The two quadruplets listed in Fig. 5 are stereoisomeric, because they degenerate into a common graph. The relationship between the two quadruplets listed in Fig. 5 and the quadruplet shown in Fig. 6 is not stereoisomeric, but skeletal-isomeric.

4.1.5 Quadruplet of $C_{2\hat{T}}$ with A^2B^2

The coefficient 1 of the term A^2B^2 in Eq. 70 indicates the presence of one type-I quadruplet having A^2B^2 ($[\theta]_4 = [2, 2, 0, 0; 0, 0, 0, 0, 0, 0, 0, 0]$. cf. Eq. 71 of Part I). The reference promolecule **19** of this quadruplet belongs to $C_{2\hat{T}}$:

$$C_{2\hat{T}} = \{I, C_{2(1)}, \hat{C}_{2(1)}, \hat{T}\} \\ = \{(1)(2)(3)(4), (1\ 2)(3\ 4), \overline{(1\ 2)(3\ 4)}, \overline{(1)(2)(3)(4)}\}, \tag{84}$$

as found in Eq. 45. The corresponding stereoisogram is shown in Fig. 7.

The four positions of **19** are governed by the subduction:

$$\mathbf{D}_{2d\bar{\sigma}\hat{\Gamma}}(/C_{s\bar{\sigma}\hat{\Gamma}}) \downarrow C_{2\hat{\Gamma}} = 2C_{2\hat{\Gamma}}(/C_{\hat{\Gamma}}), \quad (85)$$

which has been listed at the 13th row of Table 3 in Part I of this series. Hence the four positions of **19** are divided into two orbits ($\{1, 2\}$ and $\{3, 4\}$), each of which is governed by the coset representation $C_{2\hat{\Gamma}}(/C_{\hat{\Gamma}})$. Because $C_{2\hat{\Gamma}}(/C_{\hat{\Gamma}})$ is homospheric, the orbit of positions $\{1, 2\}$ (or $\{3, 4\}$) accommodates two achiral proligands A's (or B's) so as to generate the reference promolecule **19**.

From the viewpoint of the point-group theory, the reference promolecule **19** belongs to the point group C'_2 . Each of the two orbits ($\{1, 2\}$ and $\{3, 4\}$) is governed by the coset representation $C'_2(/C_1)$, which is determined to be hemispheric if we obey the point-group theory. This means that A^2B^2 , A^2p^2 , p^2q^2 , etc. are permitted to occupy the hemispheric $C'_2(/C_1)$ -orbit [9, Fig. 21.5]. In contrast, the constitution A^2B^2 is differentiated from A^2p^2 , p^2q^2 , etc. from the *RS*-stereoisomeric-group-theoretical point of view, as described in the preceding paragraph.

4.1.6 Quadruplet of $C'_{2\bar{\sigma}}$ with $p^2\bar{p}^2$

The coefficient 1 of the term $p^2\bar{p}^2$ in Eq. 70 and in Eq. 47 indicates the presence of one type-I quadruplet having $p^2\bar{p}^2$ ($[\theta]_{23} = [0, 0, 0, 0; 2, 2, 0, 0, 0, 0, 0, 0]$. cf. Eq. 91 of Part I). The reference promolecule **21** of this quadruplet belongs to $C'_{2\bar{\sigma}}$:

$$\begin{aligned} C'_{2\bar{\sigma}} &= \{I, C_{2(1)}, \widehat{C}_{2(3)}, \widehat{C}_{2(2)}\} \\ &\sim \{(1)(2)(3)(4), (1\ 2)(3\ 4), \overline{(1\ 3)(2\ 4)}, \overline{(1\ 4)(2\ 3)}\}, \end{aligned} \quad (86)$$

which has been shown in Eq. 45 of Part I of this series.

The corresponding stereoisogram is shown in Fig. 8a, where the four representatives are generated by the operations of $C_{s\bar{\sigma}\hat{\Gamma}}$ (Eq. 77). The equality of each diagonal direction is assured under the action of \mathbf{D}_2 . Thus, the holantimer **22** is not diagrammatically identical with the reference promolecule **21**, although they are homomeric under \mathbf{D}_2 .

The equality of each diagonal direction is more directly shown by selecting another set of representatives (Eq. 48 of Part I of this series):

$$\begin{aligned} C_{s\bar{\sigma}\hat{\sigma}} &= \{I, \tilde{\sigma}_{d(1)}, \widehat{C}_{2(3)}, \sigma_{d(2)}\} \\ &\sim \{(1)(2)(3)(4), (1)(2\ 4)(3), \overline{(1\ 3)(2)(4)}, \overline{(1\ 3)(2\ 4)}\}, \end{aligned} \quad (87)$$

which generates an alternative stereoisogram shown in Fig. 8b.

To show that the reference promolecule **21** is fixed by $C'_{\bar{\sigma}}$ under the action of $C_{s\bar{\sigma}\hat{\sigma}}$, the reference promolecule **21** is first shown to be fixed by the group $C'_2 (= \{I, C_{2(1)}\} \subset C'_{2\bar{\sigma}})$, which is a subgroup of \mathbf{D}_2 . Then, Eq. 86 provides the following factor group:

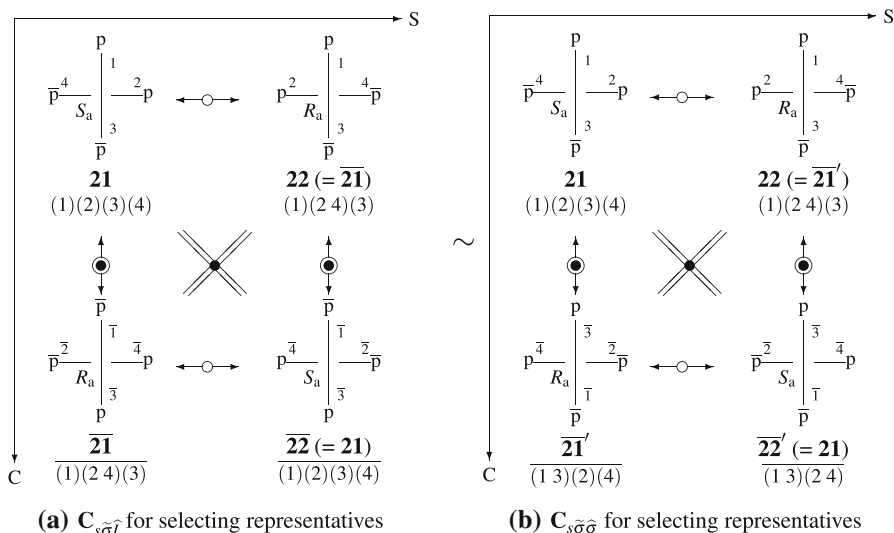


Fig. 8 Equivalent diagrams for a stereoisogram of type I with the constitution $p^2\bar{p}^2$, where the reference promolecule **21** belongs to the RS -stereoisomeric group $C'_{2\sigma}$ and to the point group C'_2 . **a** The quadruplet of promolecules is depicted by selecting $C_{S\sigma\bar{I}}$ as representatives. The stereodescriptors ‘ R_a/S_a ’ are assigned by presuming the priority sequence $p(1) > \bar{p}(3)$; $p(2) > \bar{p}(4)$ (for **21** and **22**) and the priority sequence $p(\bar{3}) > \bar{p}(\bar{1})$; $p(\bar{4}) > \bar{p}(\bar{2})$ (for **21** and **22**). This stereoisogram is chirality-faithful. **b** The quadruplet of promolecules is depicted by selecting $C_{S\sigma\sigma}$ as representatives. In a similar way to the left stereoisogram, the right stereoisogram is determined to be chirality-faithful

$$C'_{2\sigma}/C'_2 = \{C'_2, \widehat{C}_{2(3)}C'_2\} \cong \{I, \widehat{C}_{2(3)}\} = C'_\sigma, \tag{88}$$

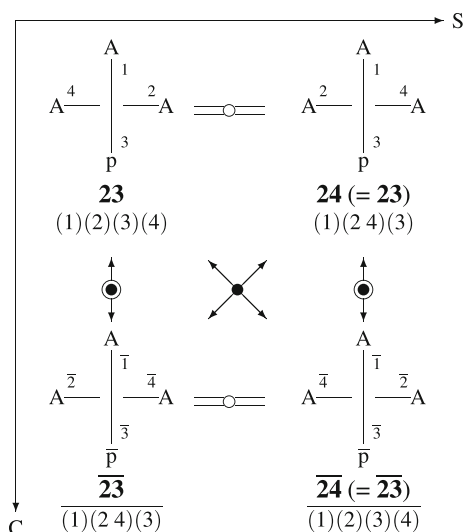
where the last side is identical with Eq. 82. The last side of Eq. 88 appears in the intersection between Eq. 86 and Eq. 87 as follows:

$$C'_{2\sigma} \cap C_{S\sigma\sigma} = C'_\sigma = \{I, \widehat{C}_{2(3)}\} \sim \{(1)(2)(3)(4), \overline{(1\ 3)(2\ 4)}\}. \tag{89}$$

The factor group $C'_{2\sigma}/C'_2$ (Eq. 88) is isomorphic to the factor group $D_{2\bar{I}}/D_2$, which is a subgroup of the factor group $D_{2d\sigma\bar{I}}/D_2$. As a result, Eq. 88 shows that the factor group $D_{2\bar{I}}/D_2 (\subset D_{2d\sigma\bar{I}}/D_2)$ can be correlated to $C'_\sigma (\subset C_{S\sigma\sigma})$. Note that the four elements of $C_{S\sigma\sigma}$ can be selected as the representatives of the four cosets appearing in the factor group $D_{2d\sigma\bar{I}}/D_2$. It follows that the reference promolecule **21** is found to be fixed by C'_σ under the action of $C_{S\sigma\sigma}$, just as **21** is fixed by $C'_{2\sigma}$ under the action of $D_{2d\sigma\bar{I}}$.

As found in the preceding paragraphs, the stereoisogram shown in Fig. 8a is equivalent with the stereoisogram shown in Fig. 8b under the action of $D_{2d\sigma\bar{I}}$. The holantimer $\bar{22}'$ is diagrammatically identical with the reference promolecule **21** in Fig. 8b, while the holantimer **22** is not diagrammatically identical with, but homomeric to the reference promolecule **21** in Fig. 8a. Note that $\bar{21}'$ is homomeric to $\bar{21}$, and that $\bar{22}' (= 21)$ is homomeric to **22**.

Fig. 9 Stereoisogram of type II with the constitution A^3p , where the reference promolecule **23** belongs to the RS -stereoisomeric group $C_{\bar{\sigma}}$ and to the point group C_1



4.2 RS -stereoisomeric groups of Type II

Among the RS -stereoisomeric groups listed in Eq. 56 (Type II), there appear quadruplets of $C_{\bar{\sigma}}$ (counted by Eq. 40), $C_{2\bar{\sigma}}$ (counted by Eq. 49), and $D_{2\bar{\sigma}}$ (counted by Eq. 52). They are totally counted by Eq. 71.

4.2.1 Quadruplet of $C_{\bar{\sigma}}$ with A^3p

The term $\frac{1}{2}(A^3p + A^3\bar{p})$ in Eq. 71 and in Eq. 40 indicates the presence of one type-II quadruplet having A^3p or $A^3\bar{p}$, which corresponds to the partition $[\theta]_3 = [3, 0, 0, 0; 1, 0, 0, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 70 of Part I). The reference promolecule **23** of this quadruplet belongs to $C_{\bar{\sigma}}$ (cf. Eq. 35 of Part I):

$$C_{\bar{\sigma}} = \{I, \bar{\sigma}_{d(1)}\} \\ \sim \{(1)(2)(3)(4), (1)(2\ 4)(3)\}. \quad (90)$$

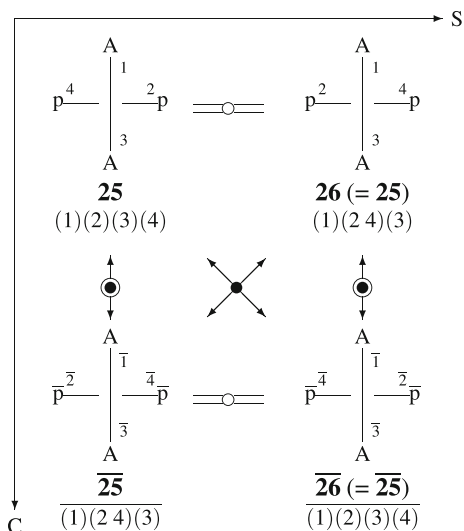
The corresponding stereoisogram is shown in Fig. 9.

The four positions of **23** are governed by the subduction:

$$D_{2d\bar{\sigma}}\bar{\Gamma}(/C_{s\bar{\sigma}}\bar{\Gamma}) \downarrow C_{\bar{\sigma}} = C_{\bar{\sigma}}(/C_1) + 2C_{\bar{\sigma}}(/C_{\bar{\sigma}}), \quad (91)$$

which has been listed at the 4th row of Table 3 in Part I of this series. Hence the four positions of **23** are divided into one two-membered hemispheric $C_{\bar{\sigma}}(/C_1)$ -orbit ($\{2, 4\}$) and two one-membered hemispheric $C_{\bar{\sigma}}(/C_{\bar{\sigma}})$ -orbits ($\{1\}$ and $\{3\}$). The $C_{\bar{\sigma}}(/C_1)$ -orbit accommodates two A's, while the $C_{\bar{\sigma}}(/C_{\bar{\sigma}})$ -orbits accommodate A and p separately. As a result, the reference promolecule **23** is generated so as to belong to the RS -stereoisomeric group $C_{\bar{\sigma}}$.

Fig. 10 Stereoisogram of type II with the constitution A^2p^2 , where the reference promolecule **25** belongs to the RS -stereoisomeric group $C_{2\bar{\sigma}}$ and to the point group C_2



From the point-group-theoretical point of view, the reference promolecule **23** belongs to the point group C_1 . The four positions are separated into four one-membered $C_1(/C_1)$ -orbits, so that three A's and p are inequivalent to one another. This means that the proligand A at position 2 is inequivalent to the proligand A at position 4 when considering the point group C_1 . Thereby, the two A's belonging to the $C_{\bar{\sigma}}(/C_1)$ -orbit are restricted to different chiral environments under the point group C_1 , so that they are chemically differentiated from each other.

The terms appearing in Eq. 40 correspond to respective reference promolecules of $C_{\bar{\sigma}}$, the stereoisograms of which can be drawn in a similar way to Fig. 9.

4.2.2 Quadruplet of $C_{2\bar{\sigma}}$ with A^2p^2

The term $\frac{1}{2}(A^2p^2 + A^2\bar{p}^2)$ in Eq. 71 indicates the presence of one type-II quadruplet having A^2p^2 or $A^2\bar{p}^2$, which corresponds to the partition $[\theta]_5 = [2, 0, 0, 0; 2, 0, 0, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 72 of Part I). As counted in Eq. 49, the reference promolecule **25** of this quadruplet belongs to $C_{2\bar{\sigma}}$ (cf. Eq. 37 of Part I):

$$C_{2\bar{\sigma}} = \{I, C_{2(3)}, \bar{\sigma}_{d(1)}, \bar{\sigma}_{d(2)}\} \sim \{(1)(2)(3)(4), (1\ 3)(2\ 4), (1)(2\ 4)(3), (1\ 3)(2)(4)\}. \quad (92)$$

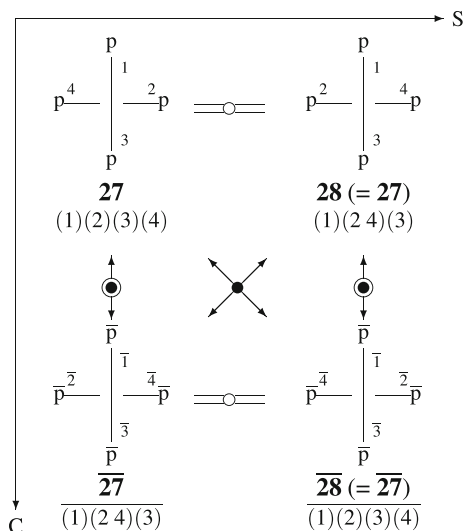
The corresponding stereoisogram is shown in Fig. 10.

The four positions of **25** are governed by the subduction:

$$D_{2d\bar{\sigma}\hat{I}}(/C_{s\bar{\sigma}\hat{I}}) \downarrow C_{2\bar{\sigma}} = C_{2\bar{\sigma}}(/C_{\bar{\sigma}}) + C_{2\bar{\sigma}}(/C'_{\bar{\sigma}}), \quad (93)$$

which has been listed at the 19th row of Table 3 in Part I of this series. Hence the four positions of **25** are divided into one two-membered hemispheric $C_{2\bar{\sigma}}(/C_{\bar{\sigma}})$ -

Fig. 11 Stereoisogram of type II with the constitution p^4 , where the reference promolecule **27** belongs to the RS -stereoisomeric group $D_{2\bar{\sigma}}$ and to the point group D_2



orbit $(\{1, 3\})$ and the other two-membered hemispheric $C_{2\bar{\sigma}}(/C'_{\bar{\sigma}})$ -orbit $(\{2, 4\})$. The $C_{2\bar{\sigma}}(/C_{\bar{\sigma}})$ -orbit accommodates two A 's, while the $C_{2\bar{\sigma}}(/C'_{\bar{\sigma}})$ -orbit accommodates two p 's. As a result, the reference promolecule **25** is generated so as to belong to the RS -stereoisomeric group $C_{2\bar{\sigma}}$.

From the point-group-theoretical point of view, the reference promolecule **25** belongs to the point group C_2 . The four positions are separated into two two-membered $C_2(/C_1)$ -orbits, which accommodate two A 's and two p 's separately.

The terms appearing in Eq. 49 correspond to respective reference promolecules of $C_{2\bar{\sigma}}$, the stereoisograms of which can be drawn in a similar way to Fig. 10.

4.2.3 Quadruplet of $D_{2\bar{\sigma}}$ with p^4

The term $\frac{1}{2}(p^4 + \bar{p}^4)$ in Eq. 71 indicates the presence of one type-II quadruplet having p^4 or \bar{p}^4 , which corresponds to the partition $[\theta]_{20} = [0, 0, 0, 0; 4, 0, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 87 of Part I). As counted in Eq. 52, the reference promolecule **25** of this quadruplet belongs to $D_{2\bar{\sigma}}$ (cf. Eq. 38 of Part I):

$$\begin{aligned} D_{2\bar{\sigma}} &= \{I, C_{2(1)}, C_{2(2)}, C_{2(3)}, \tilde{\sigma}_{d(1)}, \tilde{\sigma}_{d(2)}, \tilde{S}_{4(3)}, \tilde{S}_{4(3)}^3\} \\ &\sim \{(1)(2)(3)(4), (1\ 2)(3\ 4), (1\ 4)(2\ 3), (1\ 3)(2\ 4), \\ &\quad (1)(2\ 4)(3), (1\ 3)(2)(4), (1\ 2\ 3\ 4), (1\ 4\ 3\ 2)\}, \end{aligned} \quad (94)$$

which is a half subgroup of $D_{2d\bar{\sigma}\hat{I}}$. The corresponding stereoisogram is shown in Fig. 11.

The four positions of **27** are governed by the subduction:

$$D_{2d\bar{\sigma}\hat{I}}(/C_{s\bar{\sigma}\hat{I}}) \downarrow D_{2\bar{\sigma}} = D_{2\bar{\sigma}}(/C_{\bar{\sigma}}), \quad (95)$$

which has been listed at the 26th row of Table 3 in Part I of this series. Hence the four positions of **25** are not divided so as to give a four-membered hemispheric orbit governed by the coset representation $\mathbf{D}_{2\bar{\sigma}}(/C_{\bar{\sigma}})$. This orbit accommodates four p's to generate the reference promolecule **27**, which belongs to the *RS*-stereoisomeric group $\mathbf{D}_{2\bar{\sigma}}$.

From the point-group-theoretical point of view, the reference promolecule **27** belongs to the point group \mathbf{D}_2 . The four positions construct a four-membered $\mathbf{D}_2(/C_1)$ -orbit, which accommodate four p's because of the hemisphericity.

The terms appearing in Eq. 52 correspond to respective reference promolecules of $\mathbf{D}_{2\bar{\sigma}}$, the stereoisograms of which can be drawn in a similar way to Fig. 11.

4.3 *RS*-stereoisomeric groups of Type III

Among the *RS*-stereoisomeric groups listed in Eq. 57 (Type III), there appear quadruplets of \mathbf{C}_1 (counted by Eq. 38) and \mathbf{C}'_2 (counted by Eq. 39). They are totally counted by Eq. 72.

4.3.1 Quadruplet of \mathbf{C}_1 with ABXp

The coefficient $\frac{3}{2}(\text{ABXp} + \text{ABX}\bar{\text{p}})$ in Eq. 38 is interpreted to be $3 \times \frac{1}{2}(\text{ABXp} + \text{ABX}\bar{\text{p}})$, which indicates the presence of three quadruplets of \mathbf{C}_1 having a constitution ABXp or $\text{ABX}\bar{\text{p}}$ ($[\theta]_{11} = [1, 1, 1, 0; 1, 0, 0, 0, 0, 0, 0, 0]$. cf. Eq. 78 of Part I). They are shown in Fig. 12. The reference promolecule of each type-III stereoisogram (i.e., **29** of the upper-left stereoisogram, **31** of the upper-right stereoisogram, or **33** of the lower-left type-I stereoisogram) belongs to the *RS*-stereoisomeric group:

$$\mathbf{C}_1 = \{I\} \sim \{(1)(2)(3)(4)\}. \quad (96)$$

Each of the four positions (1–4) of **29** (or **31**, or **33**) constructs a one-membered $\mathbf{C}_1(/C_1)$ -orbit, where the stabilizer of each position is determined to be \mathbf{C}_1 . The four positions accommodate achiral substituents, A, B, and X as well as a chiral substituent p. This behavior is consistent to the subduction:

$$\mathbf{D}_{2d\bar{\sigma}\bar{\tau}}(/C_{s\bar{\sigma}\bar{\tau}}) \downarrow \mathbf{C}_1 = 4\mathbf{C}_1(/C_1), \quad (97)$$

which is shown in the first row of Table 3 of Part I.

Each quadruplet shown in Fig. 12 contains two pairs of enantiomers (e.g., **29/29** and **30/30**). The two pairs of enantiomers are diastereomeric (stereoisomeric) from the viewpoint of the conventional stereochemistry. In contrast, each quadruplet exhibits *RS*-stereoisomerism from the present viewpoint.

The three quadruplets shown in Fig. 12 are skeletal-isomeric to each other, not stereoisomeric.

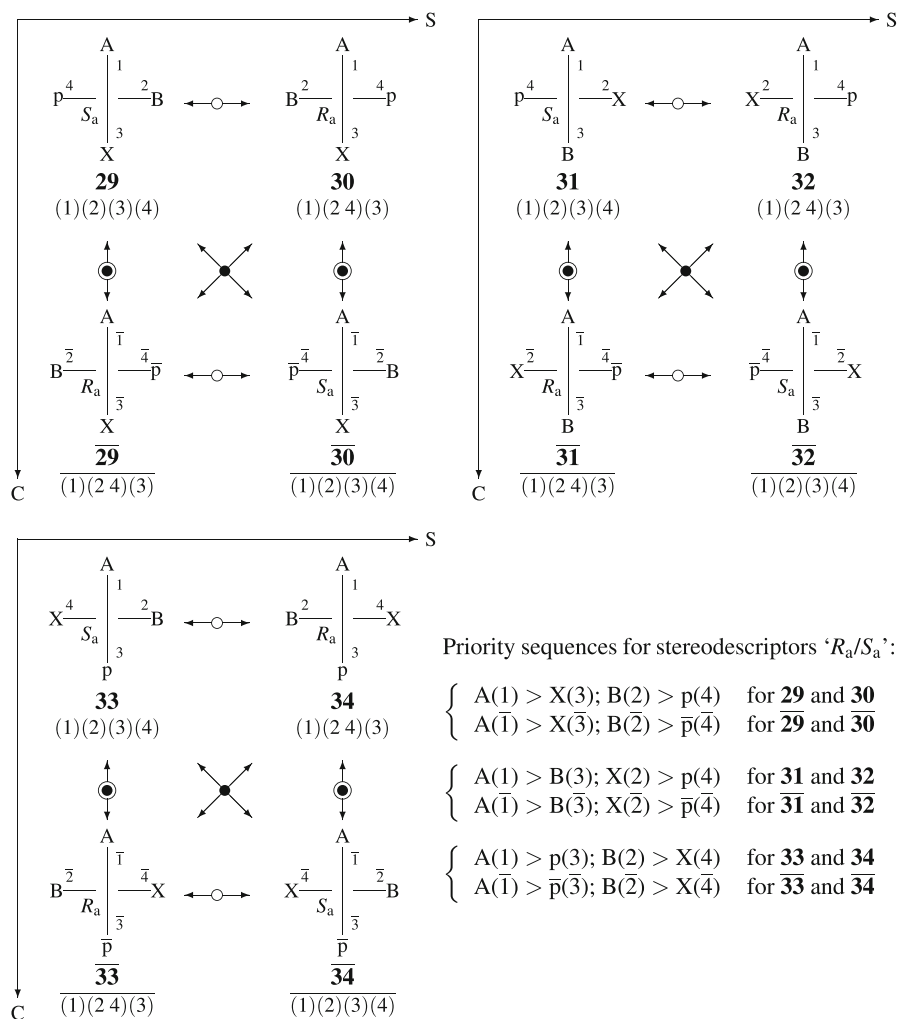
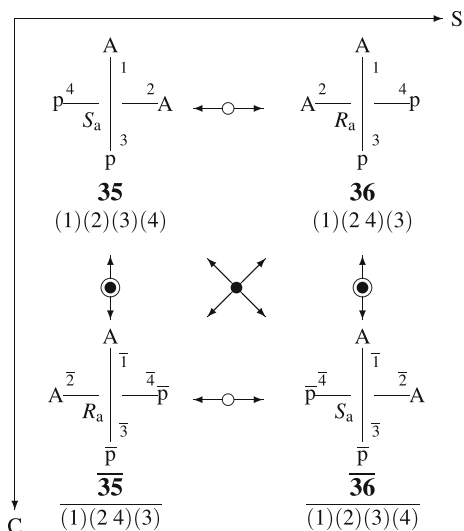


Fig. 12 Three stereoisograms of type III with the constitution ABXp. Each reference promolecule, **29**, **31**, or **33**, belongs to the RS -stereoisomeric group C_1 and to the point group C_1 . The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequences listed in the lower-right part. These stereoisograms are chirality-faithful

4.3.2 Quadruplet of C'_2 with A^2p^2

The term $\frac{1}{2}(A^2p^2 + A^2\bar{p}^2)$ in Eq. 39 indicates the presence of one quadruplet of C'_2 having a constitution A^2p^2 or $A^2\bar{p}^2$ ($[\theta]_5 = [2, 0, 0, 0; 2, 0, 0, 0, 0, 0, 0]$, cf. Eq. 72 of Part I). The corresponding type-III stereoisogram is depicted in Fig. 13. The reference promolecule **35** of the type-III stereoisogram belongs to the following RS -stereoisomeric group (cf. Eq. 29 of Part I):

Fig. 13 Stereoisogram of type III with the constitution A^2p^2 , where the reference promolecule **35** belongs to the RS -stereoisomeric group C'_2 , which is identical with the point group C'_2 . The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $A(1) > p(3)$; $A(2) > p(4)$ (for **35** and **36**) and the priority sequence $A(1) > \bar{p}(3)$; $A(\bar{2}) > \bar{p}(4)$ (for $\overline{\mathbf{35}}$ and $\overline{\mathbf{36}}$). This stereoisogram is chirality-faithful



$$C'_2 = \{I, C_{2(1)}\} \sim \{(1)(2)(3)(4), (1\ 2)(3\ 4)\}. \tag{98}$$

The four positions (1–4) of **35** are divided into two orbits according to the subduction (the third row of Table 3 of Part I):

$$D_{2d\tilde{\sigma}\hat{I}}(/C_{s\tilde{\sigma}\hat{I}}) \downarrow C'_2 = 2C'_2(/C_1). \tag{99}$$

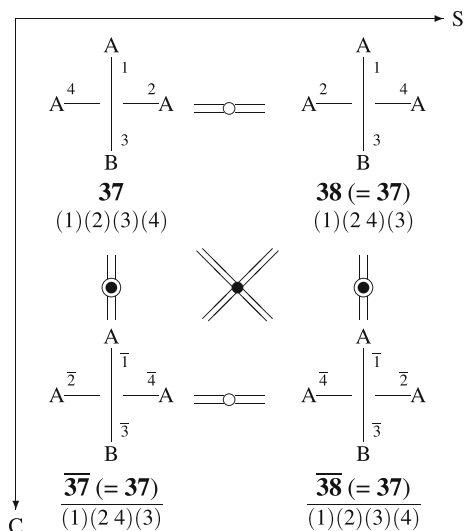
Each of the orbits ($\{1, 2\}$ and $\{3, 4\}$) is governed by the coset representation $C'_2(/C_1)$, which is determined to be hemispheric. Thereby, it accommodates two A 's (or two p 's) to generate the reference promolecule **35**.

The quadruplet shown in Fig. 13 contains two pairs of enantiomers ($\mathbf{35}/\overline{\mathbf{35}}$ and $\mathbf{36}/\overline{\mathbf{36}}$). The two pairs of enantiomers are diastereomeric (stereoisomeric) from the viewpoint of the conventional stereochemistry. In contrast, the quadruplet exhibits RS -stereoisomerism from the present viewpoint, where there appear three kind of pairwise relationships, i.e., enantiomeric (along the vertical directions), RS -diastereomeric (along the horizontal directions), and holantimeric relationships (along the diagonal directions).

As for the constitution A^2p^2 , there appear one type-II quadruplet of $C_{2\tilde{\sigma}}$ (Eq. 49) depicted in Fig. 10 and one type-III quadruplet of C'_2 (Eq. 39) depicted in Fig. 13. These two quadruplets are isoskeletal-isomeric to each other, but not stereoisomeric.

On the other hand, the type-I quadruplet of $C_{\tilde{\sigma}}$ depicted in Fig. 4 (the constitution $A^2p\bar{p}$) is stereoisomeric to the type-III quadruplet of C'_2 depicted in Fig. 13 (the constitution A^2p^2). Thus, stereoisomeric relationships are regarded as relationships between two (or more) quadruplets, where RS -stereoisomeric relationships (enantiomeric, RS -stereoisomeric, and holantimeric relationships) in each quadruplet are abstracted and differentiated from the stereoisomeric relationships. It should be noted that the conven-

Fig. 14 Stereoisogram of type IV with the constitution A^3B , where the reference promolecule **23** belongs to the RS -stereoisomeric group $C_{s\tilde{\sigma}\hat{I}}$ and to the point group C_s



tional stereochemistry overlooks RS -stereoisomeric relationships which are inherent in stereoisomeric relationships.

4.4 RS -stereoisomeric groups of Type IV

Among the RS -stereoisomeric groups listed in Eq. 58 (Type IV), there appear quadruplets of $C_{s\tilde{\sigma}\hat{I}}$ (counted by Eq. 46), $C_{s\tilde{\sigma}\hat{\sigma}}$ (counted by Eq. 48), $S_{4\tilde{\sigma}\hat{\sigma}}$ (counted by Eq. 50), $C_{2v\tilde{\sigma}\hat{I}}$ (counted by Eq. 51), and $D_{2d\tilde{\sigma}\hat{I}}$ (counted by Eq. 53). They are totally counted by Eq. 73.

4.4.1 Quadruplet of $C_{s\tilde{\sigma}\hat{I}}$ with A^3B

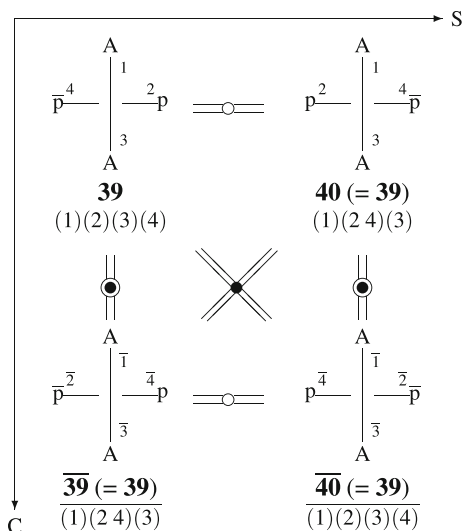
The term A^3B in Eq. 46 indicates the presence of one quadruplet of $C_{s\tilde{\sigma}\hat{I}}$ having a constitution A^3B ($[\theta]_2 = [3, 1, 0, 0; 0, 0, 0, 0, 0, 0, 0]$. cf. Eq. 69 of Part I). The corresponding type-IV stereoisogram is depicted in Fig. 14. The reference promolecule **37** of the type-IV stereoisogram belongs to the following RS -stereoisomeric group (cf. Eq. 47 of Part I):

$$\begin{aligned} C_{s\tilde{\sigma}\hat{I}} &= \{I, \tilde{\sigma}_{d(1)}, \hat{I}, \sigma_{d(1)}\} \\ &= \{(1)(2)(3)(4), (1)(2\ 4)(3), \overline{(1)(2)(3)(4)}, \overline{(1)(2\ 4)(3)}\}. \end{aligned} \quad (100)$$

The four positions (1–4) of **37** are divided into one two-membered orbit ($\{2, 4\}$) and two one-membered orbits ($\{1\}$ and $\{3\}$) according to the following subduction (the 14th row of Table 3 of Part I):

$$D_{2d\tilde{\sigma}\hat{I}}(/C_{s\tilde{\sigma}\hat{I}}) \downarrow C_{s\tilde{\sigma}\hat{I}} = C_{s\tilde{\sigma}\hat{I}}(/C_{\hat{I}}) + 2C_{s\tilde{\sigma}\hat{I}}(/C_{s\tilde{\sigma}\hat{I}}). \quad (101)$$

Fig. 15 Stereoisogram of type IV with the constitution $A^2p\bar{p}$, where the reference promolecule **39** belongs to the RS -stereoisomeric group $C_{s\tilde{\sigma}\hat{\Gamma}}$ and to the point group C_s



The two-membered $C_{s\tilde{\sigma}\hat{\Gamma}}(C_{\hat{\Gamma}})$ -orbit ($\{2, 4\}$) is homospheric so as to accommodate two achiral proligands A's in isolation. Each one-membered $C_{s\tilde{\sigma}\hat{\Gamma}}(C_{s\tilde{\sigma}\hat{\Gamma}})$ -orbit ($\{1\}$ and $\{3\}$) is homospheric so as to accommodate an achiral proligand A (or B) in isolation. Totally, there appears the reference promolecule **37**.

The subduction represented by Eq. 101 is more clearly demonstrated by the term A^2BX appearing in Eq. 46. The corresponding promolecule of $C_{s\tilde{\sigma}\hat{\Gamma}}$ having A^2BX can be generated through the replacement of the achiral proligand A at the position 1 of **37** by another achiral proligand X. The replacement causes no change of the RS -stereoisomeric group $C_{s\tilde{\sigma}\hat{\Gamma}}$, because the position 1 of **37** is governed by the one-membered homospheric orbit due to the coset representation $C_{s\tilde{\sigma}\hat{\Gamma}}(C_{s\tilde{\sigma}\hat{\Gamma}})$.

4.4.2 Quadruplet of $C_{s\tilde{\sigma}\hat{\Gamma}}$ with $A^2p\bar{p}$

The term $A^2p\bar{p}$ in Eq. 73 indicates the presence of one type-IV quadruplet having $A^2p\bar{p}$ which corresponds to the partition $[\theta]_8 = [2, 0, 0, 0; 1, 1, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 75 of Part I). As counted in Eq. 48, the reference promolecule **39** of this quadruplet belongs to $C_{s\tilde{\sigma}\hat{\Gamma}}$ (cf. Eq. 48 of Part I):

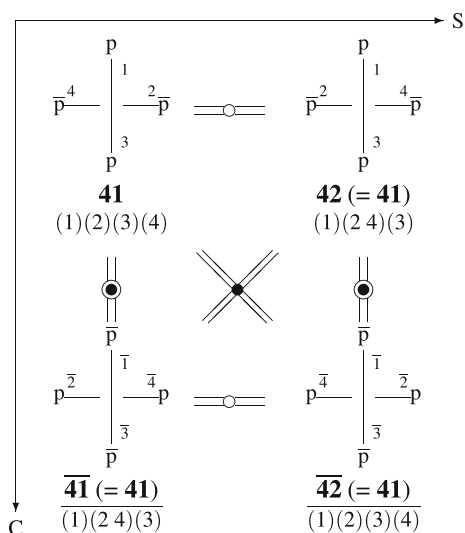
$$C_{s\tilde{\sigma}\hat{\Gamma}} = \{I, \tilde{\sigma}_{d(1)}, \hat{C}_{2(3)}, \sigma_{d(2)}\} \sim \{(1)(2)(3)(4), (1)(2\ 4)(3), \overline{(1\ 3)(2\ 4)}, \overline{(1\ 3)(2)(4)}\}. \quad (102)$$

The corresponding stereoisogram is shown in Fig. 15.

The four positions (1–4) of **39** are divided into two two-membered orbits ($\{1, 3\}$ and $\{2, 4\}$) according to the following subduction (the 17th row of Table 3 of Part I):

$$D_{2d\tilde{\sigma}\hat{\Gamma}}(C_{s\tilde{\sigma}\hat{\Gamma}}) \downarrow C_{s\tilde{\sigma}\hat{\Gamma}} = C_{s\tilde{\sigma}\hat{\Gamma}}(C_{\tilde{\sigma}}) + C_{s\tilde{\sigma}\hat{\Gamma}}(C_s). \quad (103)$$

Fig. 16 Stereoisogram of type IV with the constitution $p^2\bar{p}^2$, where the reference promolecule **41** belongs to the RS -stereoisomeric group $S_{4\tilde{\sigma}\hat{\sigma}}$ and to the point group S_4



The two-membered orbit ($\{2, 4\}$) governed by $C_{s\tilde{\sigma}\hat{\sigma}}(/C_{\tilde{\sigma}})$ is enantiospheric so as to accommodate a pair of p/\bar{p} , which is an enantiomeric pair in isolation. The two-membered orbit ($\{1, 3\}$) governed by $C_{s\tilde{\sigma}\hat{\sigma}}(/C_s)$ is homospheric so as to accommodate two A's, which are achiral in isolation. Totally, there appears the reference promolecule **39** of $C_{s\tilde{\sigma}\hat{\sigma}}$.

4.4.3 Quadruplet of $S_{4\tilde{\sigma}\hat{\sigma}}$ with $p^2\bar{p}^2$

The term $p^2\bar{p}^2$ in Eq. 73 indicates the presence of one type-IV quadruplet having $p^2\bar{p}^2$ which corresponds to the partition $[\theta]_{23} = [0, 0, 0, 0; 2, 2, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 90 of Part I). As counted in Eq. 50, the reference promolecule **41** of this quadruplet belongs to $S_{4\tilde{\sigma}\hat{\sigma}}$ (cf. Eq. 51 of Part I):

$$\begin{aligned}
 S_{4\tilde{\sigma}\hat{\sigma}} &= \{I, C_{2(3)}, \tilde{\sigma}_{d(1)}, \tilde{\sigma}_{d(2)}, \hat{C}_{2(1)}, \hat{C}_{2(2)}, S_{4(3)}, S_{4(3)}^3\} \\
 &\sim \{(1)(2)(3)(4), (1\ 3)(2\ 4), (1)(2\ 4)(3), (1\ 3)(2)(4), \\
 &\quad \overline{(1\ 2)(3\ 4)}, \overline{(1\ 4)(2\ 3)}, \overline{(1\ 2\ 3\ 4)}, \overline{(1\ 4\ 3\ 2)}\}. \quad (104)
 \end{aligned}$$

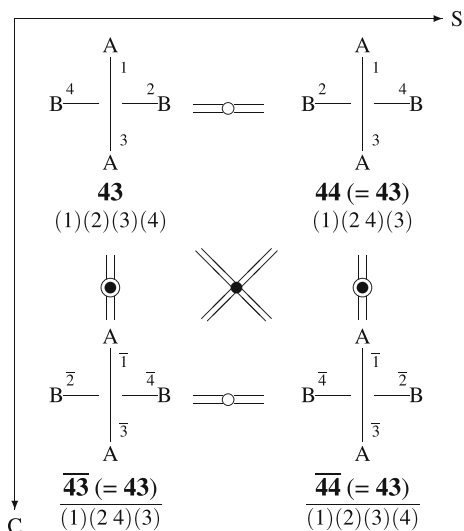
The corresponding stereoisogram is shown in Fig. 16.

The four positions (1–4) of **41** construct a single orbit according to the following subduction (the 23rd row of Table 3 of Part I):

$$\mathbf{D}_{2d\tilde{\sigma}\hat{\sigma}}(/C_{s\tilde{\sigma}\hat{\sigma}}) \downarrow S_{4\tilde{\sigma}\hat{\sigma}} = S_{4\tilde{\sigma}\hat{\sigma}}(/C_{\tilde{\sigma}}), \quad (105)$$

where no division of the four positions occurs. The four-membered orbit ($\{1, 2, 3, 4\}$) governed by $S_{4\tilde{\sigma}\hat{\sigma}}(/C_{\tilde{\sigma}})$ is enantiospheric so as to accommodate $p^2\bar{p}^2$, where a set of p^2 and a set of \bar{p}^2 are correlated by rotoreflection operations. Totally, there appears the reference promolecule **41** of $S_{4\tilde{\sigma}\hat{\sigma}}$.

Fig. 17 Stereoisogram of type IV with the constitution A^2B^2 , where the reference promolecule **43** belongs to the RS -stereoisomeric group $C_{2v}\tilde{\sigma}\hat{I}$ and to the point group C_{2v}



4.4.4 Quadruplet of $C_{2v}\tilde{\sigma}\hat{I}$ with A^2B^2

The term A^2B^2 in Eq. 73 indicates the presence of one type-IV quadruplet having A^2B^2 which corresponds to the partition $[\theta]_4 = [2, 2, 0, 0; 0, 0, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 71 of Part I). As counted in Eq. 51, the reference promolecule **43** of this quadruplet belongs to $C_{2v}\tilde{\sigma}\hat{I}$ (cf. Eq. 52 of Part I):

$$\begin{aligned}
 C_{2v}\tilde{\sigma}\hat{I} = \{ & I, C_{2(3)}, \tilde{\sigma}_{d(1)}, \tilde{\sigma}_{d(2)}, \hat{I}, \hat{C}_{2(3)}, \sigma_{d(1)}, \sigma_{d(2)} \} \\
 \sim \{ & (1)(2)(3)(4), (1\ 3)(2\ 4), (1)(2\ 4)(3), (1\ 3)(2)(4), \\
 & \overline{(1)(2)(3)(4)}, \overline{(1\ 3)(2\ 4)}, \overline{(1)(2\ 4)(3)}, \overline{(1\ 3)(2)(4)} \}. \quad (106)
 \end{aligned}$$

The corresponding stereoisogram is shown in Fig. 17.

The four positions (1–4) of **43** are divided into two two-membered orbits ($\{1, 3\}$ and $\{2, 4\}$) according to the following subduction (the 25th row of Table 3 of Part I):

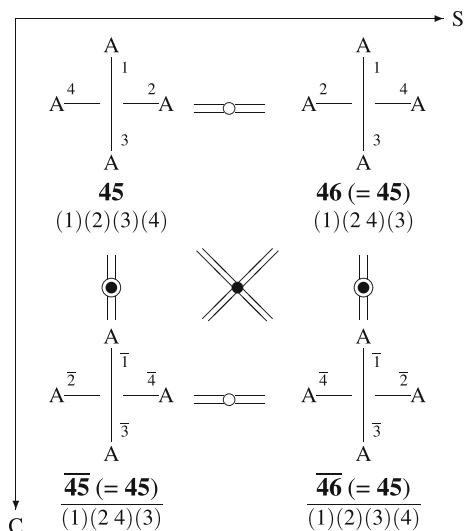
$$\mathbf{D}_{2d\tilde{\sigma}\hat{I}}(/C_{s\tilde{\sigma}\hat{I}}) \downarrow C_{2v}\tilde{\sigma}\hat{I} = C_{2v}\tilde{\sigma}\hat{I}(/C_{s\tilde{\sigma}\hat{I}}) + C_{2v}\tilde{\sigma}\hat{I}(/C'_{s\tilde{\sigma}\hat{I}}) \quad (107)$$

The two coset representations in the right-hand side of Eq. 107 are homospheric and permit identical modes of substitution, i.e., two A's for the two-membered orbit ($\{1, 3\}$) and two B's for the other two-membered orbit ($\{2, 4\}$). Totally, there appears the reference promolecule **43** of $C_{2v}\tilde{\sigma}\hat{I}$.

4.4.5 Quadruplet of $\mathbf{D}_{2d\tilde{\sigma}\hat{I}}$ with A^4

The term A^4 in Eq. 73 indicates the presence of one type-IV quadruplet having A^4 which corresponds to the partition $[\theta]_1 = [4, 0, 0, 0; 0, 0, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 68 of

Fig. 18 Stereoisogram of type IV with the constitution A^4 , where the reference promolecule **45** belongs to the RS -stereoisomeric group $D_{2d}\bar{\sigma}\hat{\tau}$ and to the point group D_{2d}



Part I). As counted in Eq. 53, the reference promolecule **45** exhibits the full symmetry of the allene skeleton (cf. Eq. 53 of Part I). The corresponding stereoisogram is shown in Fig. 18.

4.5 RS -stereoisomeric groups of Type V

Among the RS -stereoisomeric groups listed in Eq. 59 (Type V), there appear quadruplets of C_s (counted by Eq. 47). There are no other quadruplets of type V, as counted by Eq. 74.

4.5.1 Quadruplet of C_s with $ABp\bar{p}$

The term $A^2p\bar{p}$ in Eq. 74 indicates the presence of one type-V quadruplet having $ABp\bar{p}$ which corresponds to the partition $[\theta]_{13} = [1, 1, 0, 0; 1, 1, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 80 of Part I). As counted in Eq. 42, the reference promolecule **47** of this quadruplet belongs to C_s (cf. Eq. 31 of Part I):

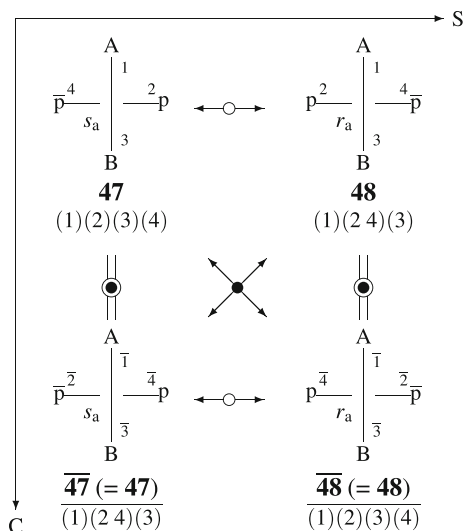
$$\begin{aligned} C_s &= \{I, \sigma_{d(1)}\} \\ &\sim \{(1)(2)(3)(4), \overline{(1)(2 4)(3)}\}. \end{aligned} \quad (108)$$

The corresponding stereoisogram is shown in Fig. 19.

The 6th row of Table 3 in Part I of this series indicates that the four positions of the reference promolecule **47** is controlled by the following subduction:

$$D_{2d}\bar{\sigma}\hat{\tau}/C_{s\bar{\sigma}\hat{\tau}} \downarrow C_s = C_s(/C_1) + 2C_s(/C_s). \quad (109)$$

Fig. 19 Stereoisogram of type V with the constitution $A^2p\bar{p}$, where the reference promolecule **47** belongs to the RS -stereoisomeric group C_s , which is identical with the point group C_s . The stereodescriptors ‘ R_a/S_a ’ are assigned by presuming the priority sequence $A(1) > B(3)$; $p(2) > \bar{p}(4)$ (for **47** and **48**). Although these promolecules are achiral, the hypothetical self-enantiomers are treated by using the priority sequence $A(\bar{1}) > B(\bar{3})$; $p(\bar{4}) > \bar{p}(\bar{2})$ (for **47** and **48**). This stereoisogram is chirality-unfaithful



Thereby, one two-membered enantiospheric C_s ($/C_1$)-orbit ($\{2, 4\}$) accommodates a pair of enantiomeric proligands p/\bar{p} , while the two one-membered homospheric C_s ($/C_s$)-orbits ($\{1\}$ and $\{3\}$) accommodate achiral proligands A and B separately. Totally, there appears the C_s -promolecule **47**, which is the reference promolecule for generating the type-V stereoisogram shown in Fig. 19.

5 Configurational notations for allene derivatives

5.1 Three-aspects of absolute configurations

In the glossary of the IUPAC Recommendations 1996 [20], the term *absolute configuration* is defined as “The spatial arrangement of the atoms of a chiral molecular entity (or group) and its stereochemical description, e.g., *R* or *S*.” It follows that the term ‘absolute configuration’ is directly combined with the ‘*R/S*’-stereodescriptor and with the term ‘chirality’ in the conventional stereochemistry. This is because the chirality/achirality is postulated to be a sole pairwise attribute for specifying ‘absolute configuration’ in the conventional stereochemistry.

The postulate described in the preceding paragraph causes a serious confusion that ‘absolute configuration’ is correlated solely to ‘chirality’ so that the stereodescriptors ‘*R*’ and ‘*S*’ are erroneously recognized to specify chirality. For example, Rule P-93.1.2 of Provisional Recommendations 2004 [21] for allenes states “... Chirality is thus described by the stereodescriptors ‘ R_a ’ and ‘ S_a ’ or ‘ M ’ and ‘ P ’ ...”. Strictly speaking, however, both chirality and achirality are described by the stereodescriptors of the Cahn-Ingold-Prelog (CIP) system. Note that achirality is sometimes described by the stereodescriptors of the CIP system (e.g., for a ‘pseudoasymmetric’ center or axis), although the lowercase letters ‘*r*’ and ‘*s*’ are used for the purpose for demonstrating their exceptional features [2, 3]. In other words, the ‘absolute configuration’ described by the stereodescriptors of the Cahn-Ingold-Prelog (CIP) system are correlated to

chirality and (sometimes) to achirality, where no reliable rationalization has been provided in the conventional stereochemistry.

On the other hand, the stereoisogram approach takes account of three types of pairwise attributes, i.e., chirality/achirality (along the vertical direction of a stereoisogram), *RS*-stereogenicity/*RS*-astereogenicity (along the horizontal direction of a stereoisogram), and sclerality/asclerality (along the diagonal direction of a stereoisogram), as depicted above [4–6]. Thereby, there appear three types of pairwise relationships, i.e., enantiomeric relationships, *RS*-diastereomeric relationships, and holantimeric relationships, for the purpose of discussing the term *absolute configuration*. This is in sharp contrast with the conventional stereochemistry which postulates enantiomeric relationships (between two entities of a pair) and diastereomeric relationships (between two or more entities).

On the basis of the stereoisogram approach, the term *absolute configuration* is extended to have three aspects:

1. Chiral aspect: The chiral aspect of the term *absolute configuration* is generated by reflection operations and corresponds to enantiomeric relationships, each of which is concerned with the appearance of a pair of enantiomers.
2. *RS*-Stereogenic aspect: The *RS*-stereogenic aspect of the term *absolute configuration* is generated by *RS*-permutation operations and corresponds to *RS*-diastereomeric relationships, each of which is concerned with the appearance of a pair of *RS*-diastereomers. The *RS*-diastereomers of each pair are differentiated by the *RS*-stereodescriptors due to the CIP system.
3. Scleral aspect: The scleral aspect of the term *absolute configuration* is generated by ligand-reflection operations and corresponds to holantimeric relationships, each of which is concerned with the appearance of a pair of holantimers. The scleral aspect is important to discuss *chirality faithfulness*, which harmonizes the *RS*-stereogenic aspect with the chiral aspect during notation processes giving *RS*-stereodescriptors [8].

By means of the formulation of stereoisograms, the *RS*-stereodescriptors due to the CIP system is concluded to be concerned with the *RS*-stereogenic aspect, not with the chiral aspect. In other words, the stereodescriptors '*R/S*' are assigned to a pair of *RS*-diastereomers, not to a pair of enantiomers. Hence, a quadruplet of type I, III, or V is characterized by *RS*-stereodescriptors because of its *RS*-stereogenicity (note that types I and III are chiral while type V is achiral); on the other hand, a quadruplet of type II or IV is not characterized by *RS*-stereodescriptors because of its *RS*-astereogenicity (note that type II is chiral while type IV is achiral).

The features of stereoisograms of type II should be added to demonstrate chiral but *RS*-astereogenic cases, in which enantiomers of each pair are not differentiated by the stereodescriptors '*R/S*' for the allene axes at issue. For example, the stereodescriptors '*R/S*' are not assigned to the enantiomeric pair of **23/23** (Fig. 9), **25/25** (Fig. 10), and **27/27** (Fig. 11), although the allene axes exhibit chiral properties. These type-II cases are properly formulated to be one of the five types (types I–V) by the stereoisogram approach. Note that the original principles of the CIP system [2] eliminate these enantiomeric pairs of type-II stereoisograms before starting procedure of assigning *RS*-stereodescriptors.

5.2 The stereodescriptors ' R_a/S_a ' for allene derivatives

Rule P-92.1.5.3 of Provisional Recommendations 2004 [21] defines the stereodescriptors ' R_a/S_a ' to specify the arrangement of substituents (atoms or groups) in the elongated tetrahedral system such as an allene skeleton. The stereodescriptors ' R_a/S_a ' are preferred to the stereodescriptors ' M/P ', as described in Rules P-92.1.5.4 (for the elongated tetrahedral system) and P-93.1.2 (for the allene skeleton).

The stereoisogram approach reveals that the stereodescriptors ' R_a/S_a ' are assigned to a pair of *RS*-diastereomers, not to a pair of enantiomers. In other words, the stereodescriptors ' R_a/S_a ' are correlated to the *RS*-stereogenic aspect of absolute configuration. It follows that a quadruplet of type I, III, or V is characterized by the stereodescriptors R_a/S_a , because it is determined to be *RS*-stereogenic, as illustrated by horizontal double-headed arrows with an open circle.

5.2.1 Stereodescriptors for Type-V stereoisograms

In order to demonstrate that the stereodescriptors ' R_a/S_a ' are assigned to a pair of *RS*-diastereomers, not to a pair of enantiomers, let us examine the stereoisogram of type V shown in Fig. 19. Because the priority sequence is determined to be $A(1) > B(3); p(2) > \bar{p}(4)$, the stereodescriptor ' s_a ' is assigned to the reference promolecule **47**. The lowercase letter ' s_a ' is used in place of the uppercase letter ' S_a ' to clarify the achirality of **47**. The same priority sequence is applied to the *RS*-diastereomer **48**, which is characterized by the stereodescriptor ' r_a '. Obviously, the pair of *RS*-diastereomers **47/48** is characterized by the pair of stereodescriptors ' s_a/r_a ' according to the stereoisogram approach.

Because both **47** and **48** are achiral, the pair of stereodescriptors s_a/r_a does not concern with a pair of enantiomers. Hence, the CIP system treated this case as an exceptional one in terms of 'pseudoasymmetric axis'.

5.2.2 Stereodescriptors for Type-I stereoisograms

Let us next examine the type-I stereoisogram shown in Fig. 2. Because the priority sequence is determined to be $A(4) > B(2); A(1) > X(3)$, the stereodescriptor ' R_a ' is assigned to the reference promolecule **3**. The same priority sequence is applied to the *RS*-diastereomer **4**, which is characterized by the stereodescriptor ' S_a '.

As for the enantiomer **3** of the reference promolecule, the priority sequence is determined to be $A(4) > B(2); A(\bar{1}) > X(3)$, which is identical with $A(4) > B(2); A(1) > X(3)$. Hence, the stereodescriptor ' S_a ' is assigned to the enantiomer **3**. Because the *RS*-diastereomer **4** is identical with the enantiomer **3** in this case, the pair of stereodescriptors ' R_a/S_a ' may be considered to be assigned to the pair of *RS*-diastereomers or the pair of enantiomers. However, the pair of stereodescriptors ' R_a/S_a ' should be considered to be assigned to the pair of *RS*-diastereomers in order to harmonize this case with the type-V case described above.

5.2.3 Stereodescriptors for Type-III stereoisograms

Let us now examine the type-III stereoisograms shown in Fig. 12 in order to demonstrate the three aspects of absolute configuration.

Because the priority sequence is determined to be $A(1) > X(3); B(2) > p(4)$, the stereodescriptor ' S_a ' is assigned to the reference promolecule **29**. The same priority sequence is applied to the *RS*-diastereomer **30**, which is characterized by the stereodescriptor ' R_a '. The pair of stereodescriptors ' R_a/S_a ' is assigned to the pair of *RS*-diastereomers **30/29**, where the common priority sequence $A(1) > X(3); B(2) > p(4)$ is used.

As for the enantiomer $\overline{\mathbf{29}}$ of the reference promolecule, another priority sequence $A(\overline{1}) > X(\overline{3}); B(\overline{2}) > \overline{p}(\overline{4})$ should be applied. Thereby, the stereodescriptor ' R_a ' is assigned to $\overline{\mathbf{29}}$. The same priority sequence is applied to $\overline{\mathbf{30}}$, which is the *RS*-diastereomer of $\overline{\mathbf{29}}$. Hence, $\overline{\mathbf{30}}$ is characterized by the stereodescriptor ' S_a '. The pair of stereodescriptors ' R_a/S_a ' is assigned to the pair of *RS*-diastereomers $\overline{\mathbf{29}}/\overline{\mathbf{30}}$, where the common priority sequence $A(\overline{1}) > X(\overline{3}); B(\overline{2}) > \overline{p}(\overline{4})$ is used.

Similar assignments can be conducted to the other stereoisograms of Fig. 12. The pair of stereodescriptors ' R_a/S_a ' is assigned to the pair of *RS*-diastereomers **32/31** (or **31/32**) in the second stereoisogram of Fig. 12. The pair of stereodescriptors ' R_a/S_a ' is assigned to the pair of *RS*-diastereomers **34/33** (or **33/34**) in the third stereoisogram of Fig. 12.

Strictly speaking, the pairing of the descriptor ' S_a ' of **29** (or **31** or **33**) with the descriptor ' R_a ' of **29** (or **31** or **33**) would be permitted only if the priority sequence such as $A(1) > X(3); B(2) > p(4)$ is presumed to be equalized to the other priority sequence such as $A(\overline{1}) > X(\overline{3}); B(\overline{2}) > \overline{p}(\overline{4})$. This presumption is implicit in the conventional stereochemistry so that the stereodescriptors '*R/S*' for describing 'absolute configuration' are directly combined with the term 'chirality' without considering the three aspects of absolute configuration.

5.3 Chirality faithfulness

5.3.1 Chirality faithful stereodescriptors for Type-I stereoisograms

The priority sequence $A(4) > B(2); A(1) > X(3)$, which is applied to the type-I stereoisogram shown in Fig. 2 (cf. Sect. 5.2.2), indicates that the stereodescriptor ' R_a ' is assigned to the reference promolecule **3**. The ligand reflection operated to the priority sequence produces another priority sequence $A(\overline{4}) > B(\overline{2}); A(\overline{1}) > X(\overline{3})$, which indicates that the stereodescriptor ' R_a ' is assigned to the holantimeric promolecule $\overline{\mathbf{4}}$. This conversion can be expressed by the following permutation called a *priority permutation*:

$$\left(\begin{array}{ccc} 4 & 2 & 1 \\ \overline{4} & \overline{2} & \overline{1} \end{array} \begin{array}{c} 3 \\ 3 \\ 3 \end{array} \right) = \overline{(1)(2)(3)(4)}, \quad (110)$$

which is determined to an even permutation (a zero swap). The even priority permutation assigns the same stereodescriptor ' R_a ' to the reference promolecule **3** and

its holantimer $\bar{4}$. As a result of a type-I stereoisogram, the pair of stereodescriptors ' R_a/S_a ' assigned to the pair of *RS*-diastereomers can be regarded as being assigned to the pair of enantiomers. It follows that this case referred to as a chirality-faithful case.

Let us examine the type-I stereoisograms shown in Fig. 3. By applying the priority sequence $A(1) > X(3); B(2) > Y(4)$, the stereodescriptor ' S_a ' is assigned to the reference promolecule **5**, while the stereodescriptor ' R_a ' is assigned to its *RS*-diastereomeric promolecule **6**. The ligand reflection operated to the priority sequence produces another priority sequence $A(\bar{1}) > X(\bar{3}); B(\bar{2}) > Y(\bar{4})$, which indicates that the stereodescriptor ' S_a ' is assigned to its holantimer $\bar{6}$. This conversion can be expressed by the following priority permutation:

$$\left(\begin{array}{cccc} 1 & 3 & 2 & 4 \\ \bar{1} & \bar{3} & \bar{2} & \bar{4} \end{array} \right) = \overline{(1)(2)(3)(4)}, \quad (111)$$

which is determined to be an even permutation (zero swap). Thus, the first stereoisogram for **5** etc. is concluded to be chirality-faithful. Hence, the pair of stereodescriptors ' R_a/S_a ' assigned to the pair of *RS*-diastereomers (**5/6**) can be regarded as being assigned to the pair of enantiomers (**5/5**).

Similar discussions are applicable to the second and third stereoisograms of type I shown in Fig. 3. Thereby they are concluded to be chirality-faithful. Thus, the pair of stereodescriptors ' R_a/S_a ' assigned to the pair of *RS*-diastereomers (**7/8** or **9/10**) can be regarded as being assigned to the pair of enantiomers (**7/8** or **9/9**).

The type-I stereoisogram shown in Fig. 4 exhibits another mode of a priority permutation. By applying the priority sequence $A(1) > p(3); A(2) > \bar{p}(4)$, the stereodescriptor ' S_a ' is assigned to the reference promolecule **11**, while the stereodescriptor ' R_a ' is assigned to its *RS*-diastereomeric promolecule **12**. The ligand reflection operated to the priority sequence produces another priority sequence $A(\bar{2}) > p(\bar{4}); A(\bar{1}) > \bar{p}(\bar{3})$, which indicates that the stereodescriptor ' S_a ' is assigned to its holantimer $\bar{12}$. This conversion can be expressed by the following priority permutation:

$$\left(\begin{array}{cccc} 1 & 3 & 2 & 4 \\ \bar{2} & \bar{4} & \bar{1} & \bar{3} \end{array} \right) = \overline{(1\ 2)(3\ 4)}, \quad (112)$$

which is determined to be an even permutation (two swaps). Hence, the stereoisogram shown in Fig. 4 is concluded to be chirality-faithful because of the even priority permutation. As a result, the pair of stereodescriptors ' R_a/S_a ' assigned to the pair of *RS*-diastereomers (**11/12**) can be regarded as being assigned to the pair of enantiomers (**11/11**).

Because the reference promolecule (e.g., **3** for Fig. 2) is identical (or homomeric) to its holantimer (e.g., $\bar{4}$), the above discussions are seemingly artificial and complicated in the case of type-I stereoisograms. However, such a common mathematical framework is necessary to explain all of the type-I, III, and V stereoisograms.

5.3.2 Chirality unfaithful stereodescriptors for Type-V stereoisograms

The priority sequence $A(1) > B(3); p(2) > \bar{p}(4)$ has been applied to the reference promolecule **47** of the type-V stereoisogram shown in Fig. 19 (cf. Sect. 5.2.1). The ligand reflection operated to the priority sequence produces another priority sequence $A(\bar{1}) > B(\bar{3}); p(\bar{4}) > \bar{p}(\bar{2})$, so that the following priority permutation is obtained:

$$\left(\begin{array}{cccc} 1 & 3 & 2 & 4 \\ \bar{1} & \bar{3} & \bar{4} & \bar{2} \end{array} \right) = \overline{(1)(24)(3)}, \quad (113)$$

which is determined to be an odd permutation (one swap). Hence, the stereoisogram shown in Fig. 19 is concluded to be chirality-unfaithful because of the odd priority permutation. The stereodescriptor 's_a' is assigned to the reference promolecule **47**, which is achiral. The stereodescriptor 'r_a' is assigned to the reference promolecule **48**, which is also achiral. The pair of stereodescriptors s_a/r_a assigned to the pair of *RS*-diastereomers (**47/48**), which has no counterpart pair of enantiomers. The chirality-unfaithful feature results in the fact that the pair of stereodescriptors s_a/r_a is assigned to the pair of holantimers (the reference promolecule **47** and its holantimer $\overline{\mathbf{48}}$ (= **48**)). Note that the pair of *RS*-diastereomers (e.g., **47/48**) generally coincides with the pair of holantimers (e.g., **47/48**) in the case of a type-V stereoisogram.

5.3.3 Chirality-faithful and -unfaithful stereodescriptors for Type-III stereoisograms

Type-III stereoisograms may be chirality-faithful or chirality-unfaithful. They are determined by examining priority permutations. If chirality-faithful, the pair of stereodescriptors 'R_a/S_a' assigned originally to the pair of *RS*-diastereomers is permitted to be applied to the pair of enantiomers. If chirality-unfaithful, in contrast, the pair of stereodescriptors 'R_a/S_a' assigned originally to the pair of *RS*-diastereomers cannot be applied to the pair of enantiomers. To differentiate these two cases, the pair for a chirality-unfaithful case is designated by the lowercase letters 'r_a/s_a'.

Chirality-Faithful Stereodescriptors for Type-III Stereoisograms. Let us now reexamine the stereoisograms of type III described in Sect. 5.2.3 from the viewpoint of chirality faithfulness.

The priority sequence $A(1) > X(3); B(2) > p(4)$ for **29** (cf. the first stereoisogram of Fig. 12) is converted into another priority sequence $A(\bar{1}) > X(\bar{3}); B(\bar{2}) > \bar{p}(\bar{4})$ under a reflection operation. Thereby, the following priority permutation is obtained:

$$\left(\begin{array}{cccc} 1 & 3 & 2 & 4 \\ \bar{1} & \bar{3} & \bar{2} & \bar{4} \end{array} \right) = \overline{(1)(2)(3)(4)}, \quad (114)$$

which is determined to be an even permutation (zero swap). Hence, the first stereoisogram of Fig. 12 is concluded to be chirality-faithful because of the even priority permutation. On the basis of the stereoisogram approach, the pair of stereodescriptors

' R_a/S_a ' is assigned to the pair of *RS*-diastereomers **30/29**. Because the stereoisogram at issue is chirality-faithful, the pair of stereodescriptors ' R_a/S_a ' is permitted to be applied to the pair of enantiomers $\overline{29/29}$. Strictly speaking, however, the priority sequence $A(1) > X(3); B(2) > p(4)$ applied to **29** is different from the priority sequence $A(\overline{1}) > X(\overline{3}); B(\overline{2}) > \overline{p}(\overline{4})$ applied to $\overline{29}$.

In similar ways, the priority sequence $A(1) > B(3); X(2) > p(4)$ for **31** (cf. the second stereoisogram of Fig. 12) and the priority sequence $A(1) > p(3); B(2) > X(4)$ for **33** (cf. the third stereoisogram of Fig. 12) give even priority permutations, so that the stereoisograms at issue are concluded to be chirality-faithful. Hence, the pair of stereodescriptors ' R_a/S_a ' assigned originally to the pair of *RS*-diastereomers is permitted to be applied to the pair of enantiomers.

The priority sequence $A(1) > p(3); A(2) > p(4)$ is applied to the type-III stereoisogram shown in Fig. 13. Thereby, the stereodescriptor ' S_a ' is assigned to the reference promolecule **35**. By applying the same priority sequence to its *RS*-diastereomer **36**, this is characterized by the stereodescriptor ' R_a '. Hence, the pair of stereodescriptors ' S_a/R_a ' is assigned to the pair of *RS*-diastereomers **35/36**. On the other hand, a reflection operated to the above priority sequence produces another priority sequence $A(\overline{1}) > \overline{p}(\overline{3}); A(\overline{2}) > \overline{p}(\overline{4})$. Thereby, the stereodescriptor ' R_a ' is assigned to the promolecule $\overline{35}$, while the stereodescriptor ' S_a ' is assigned to the promolecule **36**. Hence, the pair of stereodescriptors ' R_a/S_a ' is assigned to the pair of *RS*-diastereomers $\overline{35/36}$.

The two priority sequences described above give the following priority permutation:

$$\begin{pmatrix} 1 & 3 & 2 & 4 \\ \overline{1} & \overline{3} & \overline{2} & \overline{4} \end{pmatrix} = \overline{(1)(2)(3)(4)}, \quad (115)$$

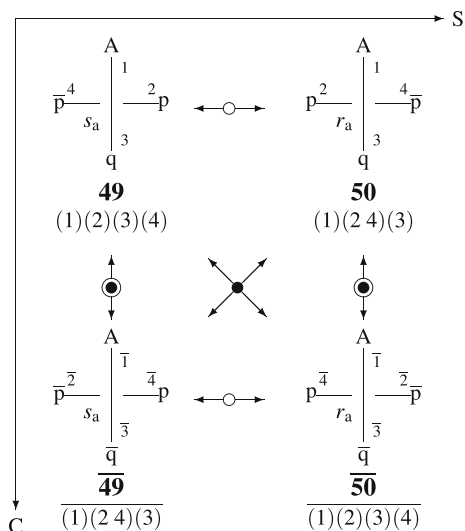
which is determined to be an even permutation (zero swap). Hence, the type-III stereoisogram shown in Fig. 13 is concluded to be chirality-faithful. It follows that the pair of stereodescriptors ' S_a/R_a ' assigned originally to the pair of *RS*-diastereomers (**35/36**) can be regarded as being assigned to the pair of enantiomers (**35/35**), where the difference in the priority sequences ($A(1) > p(3); A(2) > p(4)$ vs. $A(\overline{1}) > \overline{p}(\overline{3}); A(\overline{2}) > \overline{p}(\overline{4})$) is neglected.

In the above process of rationalization, the reference promolecule **35** and its holantimer $\overline{36}$ are characterized by the same stereodescriptor ' S_a ' because of the chirality-faithful property of the stereoisogram at issue. This fact reveals the concealed meaning of the neglect of the difference in the priority sequences ($A(1) > p(3); A(2) > p(4)$ vs. $A(\overline{1}) > \overline{p}(\overline{3}); A(\overline{2}) > \overline{p}(\overline{4})$).

Chirality-Unfaithful Stereodescriptors for Type-III Stereoisograms. The term $\frac{3}{2}$ ($A\overline{p}\overline{p}q + A\overline{p}q$) in Eq. 72 indicates the presence of three type-III quadruplets having $A\overline{p}\overline{p}q$ which corresponds to the partition $[\theta]_{18} = [1, 0, 0, 0; 1, 1, 1, 0, 0, 0, 0, 0]$ (cf. Eq. 85 of Part I). The reference promolecules belong to the *RS*-stereoisomeric group C_1 , as counted in Eq. 38.

To illustrate a chirality-unfaithful case, a stereoisogram with **49** as a reference promolecule is shown in Fig. 20. The four positions of **49** are inequivalent under $D_{2d\overline{\sigma}\widehat{I}}$, because they are divided into four one-membered orbits according to Eq. 97.

Fig. 20 Stereoisogram of type III with the constitution $A\bar{p}\bar{q}$, where the reference promolecule **49** belongs to the RS -stereoisomeric group C_1 and to the point group C_1 . The stereodescriptors ' R_a/S_a ' are assigned by presuming the priority sequence $A(1) > q(3)$; $p(2) > \bar{p}(4)$ (for **49** and **50**) and the priority sequence $A(\bar{1}) > \bar{q}(\bar{3})$; $\bar{p}(\bar{4}) > \bar{p}(\bar{2})$ (for **49** and **50**). This stereoisogram is chirality-unfaithful



The priority sequence $A(1) > q(3)$; $p(2) > \bar{p}(4)$ is applied to the reference promolecule **49** (Fig. 20), so that the stereodescriptor ' s_a ' is assigned to **49**, while the stereodescriptor ' r_a ' is assigned to **50**. Thus, the pair of stereodescriptors ' s_a/r_a ' is assigned to the pair of RS -diastereomers **49/50**, where the lowercase letters are used for emphasizing the chirality-unfaithful nature described below. On the other hand, the priority sequence $A(\bar{1}) > \bar{q}(\bar{3})$; $\bar{p}(\bar{4}) > \bar{p}(\bar{2})$ is applied to the pair of RS -diastereomers **49/50**, which are characterized by the pair of stereodescriptors ' s_a/r_a '.

As a result, the same stereodescriptor ' s_a ' is assigned to the pair of enantiomers **49/49**; and the same stereodescriptor ' r_a ' is assigned to the pair of enantiomers **50/50**. Hence, the pair of stereodescriptors ' r_a/s_a ' assigned originally to the pair of RS -diastereomers is not permitted to be applied to the pair of enantiomers.

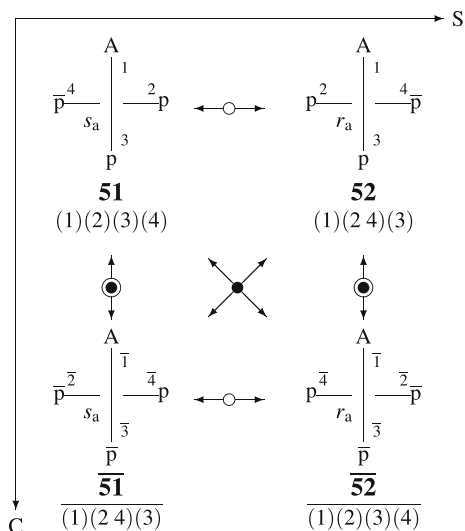
The nature of the stereoisogram shown in Fig. 20 is rationalized in terms of chirality unfaithfulness. The conversion of the priority sequence $A(1) > q(3)$; $p(2) > \bar{p}(4)$ into another sequence $A(\bar{1}) > \bar{q}(\bar{3})$; $\bar{p}(\bar{4}) > \bar{p}(\bar{2})$ by the action of reflection is represented by the following priority permutation:

$$\begin{pmatrix} 1 & 3 & 2 & 4 \\ \bar{1} & \bar{3} & \bar{4} & \bar{2} \end{pmatrix} = \overline{(1)(2\ 4)(3)}, \quad (116)$$

which is determined to be an odd permutation (one swap). Hence, the type-III stereoisogram shown in Fig. 20 is concluded to be chirality-unfaithful, where the reference promolecule **49** and its holantimer **50** are characterized by opposite stereodescriptors. The lowercase letters ' s_a/r_a ' are used to emphasize chirality unfaithfulness.

The term $\frac{1}{2}(Ap^2\bar{p} + Ap\bar{p}^2)$ in Eq. 72 indicates the presence of one type-III quadruplets having $Ap^2\bar{p}$ which corresponds to the partition $[\theta]_{16} = [1, 0, 0, 0; 2, 1, 0, 0, 0, 0, 0, 0]$ (cf. Eq. 83 of Part I). The reference promolecule **51** shown in Fig. 21 belongs to

Fig. 21 Stereoisogram of type III with the constitution $Ap^2\bar{p}$, where the reference promolecule **51** belongs to the RS -stereoisomeric group C_1 , which is identical with the point group C_1 . The stereodescriptors ‘ R_a/S_a ’ are assigned by presuming the priority sequence $A(1) > p(3); p(2) > \bar{p}(4)$ (for **51** and **52**) and the priority sequence $A(\bar{1}) > \bar{p}(\bar{3}); p(\bar{4}) > \bar{p}(\bar{2})$ (for **51** and **52**). This stereoisogram is chirality-unfaithful



the RS -stereoisomeric group C_1 , as counted in Eq. 38. The four positions of **51** are inequivalent under $D_{2d\bar{\sigma}\bar{\tau}}$, because they are divided into four one-membered orbits according to Eq. 97.

The priority sequence $A(1) > p(3); p(2) > \bar{p}(4)$ is converted into another sequence $A(\bar{1}) > \bar{p}(\bar{3}); p(\bar{4}) > \bar{p}(\bar{2})$ under reflection, so that the corresponding priority permutation is identical with Eq. 116. Hence, the type-III stereoisogram shown in Fig. 21 is concluded to be chirality-unfaithful. It follows that the pair of stereodescriptors ‘ s_a/r_a ’ assigned originally to the pair of RS -diastereomers **51/52** is not permitted to be applied to the pair of enantiomers **51/51**.

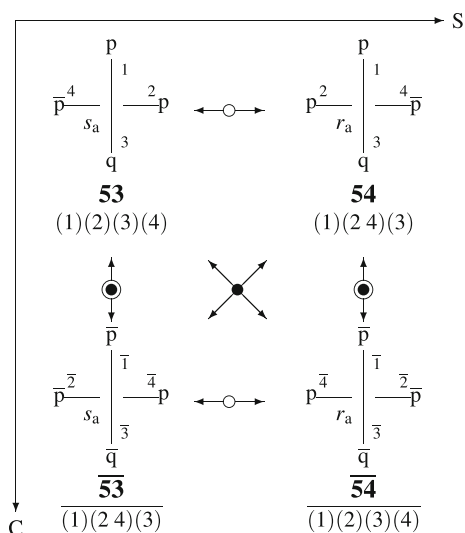
The term $\frac{1}{2}(p^2\bar{p}q + p\bar{p}^2\bar{q})$ in Eq. 72 indicates the presence of one type-III quadruplets having $p^2\bar{p}q$ which corresponds to the partition $[\theta]_{24} = [0, 0, 0, 0; 2, 1, 1, 0, 0, 0, 0, 0]$ (cf. Eq. 91 of Part I). The reference promolecule **53** shown in Fig. 22 belongs to the RS -stereoisomeric group C_1 , as counted in Eq. 38. The four positions of **53** are inequivalent under $D_{2d\bar{\sigma}\bar{\tau}}$, because they are divided into four one-membered orbits according to Eq. 97.

The priority sequence $p(2) > \bar{p}(4); p(1) > q(3)$ is converted into another sequence $p(\bar{4}) > \bar{p}(\bar{2}); \bar{p}(\bar{1}) > \bar{q}(\bar{3})$ under reflection, so that the corresponding priority permutation is calculated as follows:

$$\left(\begin{array}{cccc} 2 & 4 & 1 & 3 \\ \bar{4} & \bar{2} & \bar{1} & \bar{3} \end{array} \right) = \overline{(1)(2\ 4)(3)}, \quad (117)$$

which is determined to be an odd permutation (one swap). Hence, the type-III stereoisogram shown in Fig. 22 is concluded to be chirality-unfaithful. It follows that the pair of stereodescriptors ‘ s_a/r_a ’ assigned originally to the pair of RS -diastereomers **53/54** is not permitted to be applied to the pair of enantiomers **53/53**.

Fig. 22 Stereoisogram of type III with the constitution $p^2\bar{p}q$, where the reference promolecule **53** belongs to the *RS*-stereoisomeric group C_1 , which is identical with the point group C_1 . The stereodescriptors ‘ R_a/S_a ’ are assigned by presuming the priority sequence $p(2) > \bar{p}(4)$; $p(1) > q(3)$ (for **53** and **54**) and the priority sequence $p(4) > \bar{p}(2)$; $\bar{p}(1) > \bar{q}(3)$ (for **53** and **54**). This stereoisogram is chirality-unfaithful



5.3.4 Chirality-unfaithful stereodescriptors versus reflection-invariant stereodescriptors

The CIP system adopts the term ‘reflection-invariant (stereo)descriptors’ [3, p. 31] without considering the concept of stereoisograms. By obeying the discussions on the CIP system [3, p. 31], the promolecule **51** (‘ s_a ’) is compared with its enantiomer $\overline{\mathbf{51}}$ (‘ s_a ’), where the stereodescriptor ‘ s_a ’ is referred to as a ‘reflection-invariant descriptor’. This means that the term ‘reflection-invariant descriptor’ is unaware of *RS*-diastereomeric relationships which should be considered as the subjects of stereodescriptors. In other words, the discussions on the CIP system [3, p. 31] overlook the fact that the pair of stereodescriptors ‘ s_a/r_a ’ should be assigned to the pair of *RS*-diastereomers **51/52**, not to the pair of enantiomers **51/51**. Note that *RS*-diastereomers or *RS*-diastereomeric relationships stem from the concept of *RS*-stereogenicity, which is a definite restriction of stereogenicity for the purpose of constructing a stereoisogram.

By obeying the stereoisogram approach, on the other hand, the pair of stereodescriptors ‘ s_a/r_a ’ is first assigned to the pair of *RS*-diastereomers **51/52** (or $\overline{\mathbf{51/52}}$), and then the chirality (un)faithfulness is considered to determine whether or not the assignment is applicable to the pair of enantiomers **51/51**. It should be emphasized that the chirality (un)faithfulness is systematically determined by using a priority permutation.

6 Conclusion

The partial-cycle-index (PCI) method of the USCI approach [9] is extended to accomplish the symmetry-itemized enumeration of quadruplets of stereoisograms, where an allene skeleton is considered to belong to the *RS*-stereoisomeric group $D_{2d\bar{\sigma}\bar{\tau}}$. The resulting numbers of quadruplets are itemized in terms of subgroups of $D_{2d\bar{\sigma}\bar{\tau}}$, which

are further categorized into five types (types I–V). Three aspects of absolute configurations, i.e., a chiral aspect, an *RS*-stereogenic aspect, and a scleral aspect, are formulated by applying the stereoisogram approach to the allene skeleton. The *RS*-stereodescriptors of the Cahn-Ingold-Prelog (CIP) system are clarified to specify the *RS*-stereogenic aspect, not to specify the chiral aspect, where they are assigned to a pair of *RS*-diastereomers contained in a type-I, type-III, or type-V stereoisogram, but not to a pair of enantiomers. To apply the *RS*-stereodescriptors to the chiral aspect of an absolute configuration, the concept of *chirality faithfulness* is redefined by proposing *odd* and *even priority permutations*.

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