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ORIGINAL PAPER

Stereoisograms of trigonal bipyramidal compounds: I. Chirality and *RS*-stereogenicity free from the conventional "chirality" and "stereogenicity"

Shinsaku Fujita

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Abstract The stereoisogram approach, which has originally been developed to rationalize organic stereochemistry (Fujita in J Org Chem 69:3158–3165, 2004; Fujita in Tetrahedron 62:691–705, 2006; 65:1581–1592, 2009), is extended and applied to inorganic stereochemistry by using trigonal bipyramidal compounds as examples. The point group $\mathbf{D}_{3h}$ of a trigonal bipyramidal skeleton is extended into the *RS*-stereoisomeric group of order 24, which is considered to control a stereoisogram of the trigonal bipyramidal skeleton. Stereoisograms of trigonal bipyramidal compounds derived from the skeleton correspond to subgroups of the *RS*-stereoisomeric group. Thereby, they are discussed in terms of attributive terms (chirality/achirality, *RS*-stereogenicity/*RS*-astereogenicity, and sclerality/asclerality) or equivalently in terms of relational terms (enantiomeric/self-enantiomeric, *RS*-diastereomeric/self-*RS*-diastereomeric, and holantimeric/self-holantimeric), where the stereoisograms are categorized into five types (Types I–V). Among them, stereoisograms of Types I, III, and V are shown to be capable of giving *C/A*-descriptors because of their *RS*-stereogenicity (or *RS*-diastereomeric relationships).

Keywords Trigonal bipyramidal compound · Stereoisogram · Inorganic stereochemistry · *RS*-diastereomeric · *C/A*-descriptor

1 Introduction

Although the terms "chirality" and "stereogenicity" are used widely in inorganic stereochemistry, the distinction between them has not been fully clarified, as found in

S. Fujita (✉)
Shonan Institute of Chemoinformatics and Mathematical Chemistry, Kaneko 479-7, Ooimachi, Ashigara-Kami-Gun, Kanagawa-Ken 258-0019, Japan
e-mail: shinsaku_fujita@nifty.com

the descriptions on *C/A*-descriptors in the IUPAC recommendations 2005 for inorganic chemistry [1] as well as in IUPAC Provisional Recommendations 2004 for organic chemistry [2]. As a typical example of such indistinct usage, we are able to point out the subsection title "IR-9.3.4 Describing absolute configuration—distinguishing between enantiomers" of [1] and the subsection title "P-92.1.9.4 Chirality" as well as the term "chirality symbol" for referring to *C/A*-descriptors. These descriptions claim that such *C/A*-descriptors are used to distinguish enantiomers or, in other words, to specify chirality. However, *C/A*-descriptors are also assigned to so-called pseudoasymmetric cases (cf. [3]), which are concerned with achiral compounds lacking enantiomeric relationships according even to the conventional terminology.

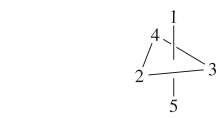
The description in the preceding paragraph means that *C/A*-descriptors specify both chiral and achiral cases, just as *R/S*-descriptors of the Cahn-Ingold-Prelog (CIP) system for organic stereochemistry specify both chiral and achiral cases [4,5]. To remedy this feature of *C/A*-descriptors, the term "stereogenicity" has been introduced as found in the title "Stereogenic Phosphorus" of a review on trigonal bipyramidal phosphorus compounds and so on [6]. According to the coinage of the term "stereogenicity" or "stereogenic center" (cf. [7, p. 58]), *C/A*-descriptors for achiral cases are ascribed to "stereogenicity", while *C/A*-descriptors for chiral cases are ascribed to "chirality", which is used as a subconcept of "stereogenicity". This is parallel to the revision of the CIP system for organic stereochemistry [5]. In spite of this revision, the rather incomplete distinction between "chirality" and "stereogenicity" has not provided us with fundamental solutions, so that such misuse as pointed out in the preceding paragraph is wide-spread even now and even in such rule books [1,2].

We have introduced the stereoisogram approach [8–10] to settle a similar kind of misleading situations that have been wide-spread in organic stereochemistry, where a newly-defined stereoisogram is proposed to define *chirality* (in a purely geometric meaning) and *RS-stereogenicity* as independent concepts. This independent feature exhibits sharp contrast to the conventional concepts "chirality" and "stereogenicity" which are dependent upon each other.

In the stereoisogram approach, such stereoisograms are classified into five types, where the existence of five types has been proven by considering *RS*-stereoisomeric groups [11], where stereoisograms of Type I, III, and V are characterized as being *RS*-stereogenic, so as to assure the assignment of *R/S*-descriptors. Then, the *R/S*-descriptors based on the *RS*-stereogenicity are linked to the chirality through chirality faithfulness [12].

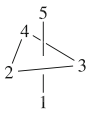
An advanced concept of *correlation diagrams of stereoisograms* has been later proposed to characterize cases having two or more *RS*-stereogenic centers, e.g., stereoisomers of cyclobutane derivatives [13] as well as binuclear and uninuclear promolecules [14,15]. Allene derivatives [16,17] and ethylene derivatives [18] have been discussed by more complicated treatments, where point groups, *RS*-stereoisomeric groups, stereoisomeric groups, and isoskeletal groups are introduced.

The present paper is devoted to show the versatility of the stereoisogram approach also in inorganic stereochemistry by using trigonal bipyramidal compounds as examples.



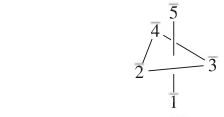
1

$\mathbf{D}_3$	
I	(1)(5)|(2)(3)(4)
C_3	(1)(5)|(2 3 4)
C_3^2	(1)(5)|(2 4 3)
$C_{2(1)}$	(1 5)|(2)(3 4)
$C_{2(2)}$	(1 5)|(2 4)(3)
$C_{2(3)}$	(1 5)|(2 3)(4)



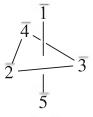
2

$\widetilde{\sigma}_h\mathbf{D}_3$	
$\widetilde{\sigma}_h$	(1 5)|(2)(3)(4)
$\widetilde{S}_3$	(1 5)|(2 3 4)
$\widetilde{S}_3^2$	(1 5)|(2 4 3)
$\widetilde{\sigma}_{v(1)}$	(1)(5)|(2)(3 4)
$\widetilde{\sigma}_{v(2)}$	(1)(5)|(2 4)(3)
$\widetilde{\sigma}_{v(3)}$	(1)(5)|(2 3)(4)



1

$\sigma_h\mathbf{D}_3$	
σ_h	(1 5)|(2)(3)(4)
S_3	(1 5)|(2 3 4)
S_3^2	(1 5)|(2 4 3)
$\sigma_{v(1)}$	(1)(5)|(2)(3 4)
$\sigma_{v(2)}$	(1)(5)|(2 4)(3)
$\sigma_{v(3)}$	(1)(5)|(2 3)(4)



2

$\widehat{I}\mathbf{D}_3$	
$\widehat{I}$	(1)(5)|(2)(3)(4)
$\widehat{C}_3$	(1)(5)|(2 3 4)
$\widehat{C}_3^2$	(1)(5)|(2 4 3)
$\widehat{C}_{2(1)}$	(1 5)|(2)(3 4)
$\widehat{C}_{2(2)}$	(1 5)|(2 4)(3)
$\widehat{C}_{2(3)}$	(1 5)|(2 3)(4)

Fig. 1 *RS*-Stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}(=\widetilde{\sigma}_h\mathbf{D}_{3h})$, which is derived from coset representations $\mathbf{D}_{3h}(/\mathbf{C}_{3v})$ (for vertices 1 and 5) and $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ (for vertices 2, 3, and 4)

2 Groups for characterizing trigonal bipyramidal compounds

2.1 Point groups for trigonal bipyramidal compounds

Let us first examine a trigonal bipyramidal skeleton **1** as *a reference skeleton*, in which the five substitution sites (vertices) are numbered from 1 to 5 as shown in Fig. 1. Although the skeleton **1** is depicted as a triangle with two vertical bonds, it is composed of a central atom, three bonds directing to the vertices of the triangle, and the two vertical bonds directing to the top and bottom vertices. The initial mode of numbering is selected arbitrarily from 5! (=120) modes of numbering, because the selection of any numbering does not lose generality.

The trigonal bipyramidal skeleton **1** belongs to a point group $\mathbf{D}_{3h}$ of order 12:

$$\begin{aligned}\mathbf{D}_{3h} = \{&I, C_3, C_3^2, C_{2(1)}, C_{2(1)}, C_{2(3)};\\ &\sigma_h, S_3, i, S_3^2, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}.\end{aligned} \tag{1}$$

Among the 12 elements, six proper rotations (chiral elements) construct the following subgroup $\mathbf{D}_3$:

$$\mathbf{D}_3 = \{I, C_3, C_3^2, C_{2(1)}, C_{2(1)}, C_{2(3)}\}, \tag{2}$$

which is the maximum chiral subgroup of $\mathbf{D}_{3h}$. By following Fujita's USCI (unit-subduced-cycle-index) approach [19], the two substitution sites numbered as 1 and 5 are determined to construct a two-membered orbit governed by a coset representation $\mathbf{D}_{3h}(/\mathbf{C}_{3v})$ of degree 2 ($= |\mathbf{D}_{3h}|/|\mathbf{C}_{3v}| = 12/6$), while the three substitution sites numbered as 2–4 are determined to construct a three-membered orbit governed by a coset representation $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ of degree 3 ($= |\mathbf{D}_{3h}|/|\mathbf{C}_{2v}| = 12/4$). The concrete forms of the coset representations are collected in the left part of Fig. 1 in the form of products of cycles, where the two coset representations at issue are separated with a vertical bar and where an overbar indicates the alternation of the configuration of each proligand. For a discussion on coset representations and a mark table of $\mathbf{D}_{3h}$, see Ref. [20,21].

Note that the subgroup $\mathbf{C}_{3v}$ represents the local symmetry of the vertex 1 (or 5), i.e.,

$$\mathbf{C}_{3v} = \{I, C_3, C_3^2, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}, \tag{3}$$

which generates a coset decomposition:

$$\mathbf{D}_{3h} = \mathbf{C}_{3v} + C_{2(1)}\mathbf{C}_{3v}. \tag{4}$$

The resulting set of cosets $\{\mathbf{C}_{3v}, C_{2(1)}\mathbf{C}_{3v}\}$ is concerned with the coset representation denoted by the symbol $\mathbf{D}_{3h}(/\mathbf{C}_{3v})$. In a similar way, the subgroup $\mathbf{C}_{2v}$ represents the local symmetry of the vertex 2 (or 3, or 4), i.e.,

$$\mathbf{C}_{2v} = \{I, C_{2(1)}, \sigma_h, \sigma_{v(1)}\} \tag{5}$$

(or its conjugate subgroups), which is concerned with the coset representation $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ through the corresponding coset decomposition, i.e.,

$$\mathbf{D}_{3h} = \mathbf{C}_{2v} + C_3\mathbf{C}_{2v} + C_3^2\mathbf{C}_{2v}. \tag{6}$$

2.2 *RS*-stereoisomeric group for a trigonal bipyramidal skeleton

The point group $\mathbf{D}_{3h}$ is composed of two cosets in terms of its subgroup $\mathbf{D}_3$:

$$\mathbf{D}_{3h} = \mathbf{D}_3 + \sigma_h\mathbf{D}_3, \tag{7}$$

where each element is equalized to the corresponding product of cycles derived from the coset representations $\mathbf{D}_{3h}(/\mathbf{C}_{3v})$ and $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$. Note that the product of cycles

for the coset $\sigma_h\mathbf{D}_3$ (i.e., reflections) has an overbar, which indicates the alternation of absolute configurations of ligands (reflection of ligand chirality).

Suppose that $\widetilde{\sigma}_h$ denotes the same permutation as σ_h but with no alternation of ligand configurations and that $\widehat{I}$ denotes the same permutation as I but with the alternation of ligand configurations. Thereby, there appear two additional groups derived from $\mathbf{D}_{3h}$ as follows:

$$\mathbf{D}_{3\widetilde{\sigma}} = \mathbf{D}_3 + \widetilde{\sigma}_h\mathbf{D}_3 \tag{8}$$

$$\mathbf{D}_{3\widehat{I}} = \mathbf{D}_3 + \widehat{I}\mathbf{D}_3, \tag{9}$$

where the group $\mathbf{D}_{3\widetilde{\sigma}}$ is called *an RS-permutation group* and the group $\mathbf{D}_{3\widehat{I}}$ is called *ligand-reflection group*. By following the formulation by Fujita [9,22,23], the resulting cosets, $\mathbf{D}_3$, $\sigma_h\mathbf{D}$, $\widetilde{\sigma}_h\mathbf{D}_3$, and $\widehat{I}\mathbf{D}_3$ are collected to give an *RS-stereoisomeric group*:

$$\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}} = \mathbf{D}_3 + \sigma_h\mathbf{D}_3 + \widetilde{\sigma}_h\mathbf{D}_3 + \widehat{I}\mathbf{D}_3, \tag{10}$$

whose concrete elements are shown in Fig. 1. This equation represents a coset decomposition of the resulting *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ by the subgroup $\mathbf{D}_3$, which contains rotations (proper rotations) only (Eq. 2).

2.3 Quadruplet of reference skeletons

The action of the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (order: $|\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}| = 24$) on the skeleton **1** (Fig. 1) generates 24 *RS*-stereoisomeric skeletons, which are divided into four parts in accord with the coset decomposition represented by Eq. 10. Because the subgroup $\mathbf{D}_3$ (order: $|\mathbf{D}_3| = 6$) is a normal subgroup of the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$, the coset decomposition represented by Eq. 10 provides the following factor group:

$$\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3 = \{\mathbf{D}_3, \sigma_h\mathbf{D}_3, \widetilde{\sigma}_h\mathbf{D}_3, \widehat{I}\mathbf{D}_3\}, \tag{11}$$

where the coset $\mathbf{D}_3$ plays as an identity element. The factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ is isomorphic to the Klein four-group. The transversal appearing in Eq. 11 constructs a group of order 4 as follows:

$$\mathrm{Tv}(\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3) = \{I, \sigma_h, \widetilde{\sigma}_h, \widehat{I}\}. \tag{12}$$

Once the mode of numbering is fixed for **1** (corresponding to the identity element $I = (1)(2)(3)(4)(5)$), the action of each element contained in the coset $I\mathbf{D}_3$ ($= \mathbf{D}_3$) produces a homomeric skeleton identical to the original skeleton **1**. This indicates that the skeleton **1** is a representative of the coset $I\mathbf{D}_3$ ($= \mathbf{D}_3$). In other words, the skeleton **1** is selected as a representative (a reference skeleton) from six skeletons (homomers) generated by the action of the six permutations of $\mathbf{D}_3$. Thus the reference skeleton **1** is regarded as corresponding to the the coset $I\mathbf{D}_3$ ($= \mathbf{D}_3$) of Eq. 11 and as corresponding to the element I of Eq. 12.

On the same line, each element of the transversal listed in the right-hand side of Eq. 11 (or Eq. 12) corresponds to a trigonal bipyramidal skeleton, **1**, $\overline{\mathbf{1}}$, **2**, or $\overline{\mathbf{2}}$, each of which is regarded as a representative of six reference skeletons contained in the corresponding coset, as collected in Fig. 1.

According to a general proof reported in [11], such a factor group as $\mathbf{D}_{3h\tilde{\sigma}\tilde{I}}/\mathbf{D}_3$ (Eq. 11) has only five subgroups, each of which corresponds to a subgroup of the *RS*-stereoisomeric group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}$ (Eq. 10). Note that the *RS*-stereoisomeric group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}$ (Eq. 10) is concerned with a reference skeleton (e.g., **1**). It follows that each trigonal bipyramidal derivative exhibits an appropriate subgroup of the *RS*-stereoisomeric group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}$ (Eq. 10). Discussions on the basis of factor groups are also effective even to the latter subgroup.

2.4 Three attributes and three relationships

According to the stereoisogram approach [8], the elements of the coset $\mathbf{D}_3$ (= $I\mathbf{D}_3$) in Fig. 1 are called *rotations*, the elements of the coset $\sigma_h\mathbf{D}_3$ are called *rotoreflections*, the elements of the coset $\tilde{\sigma}_h\mathbf{D}_3$ are called *RS-permutations*, and the elements of the coset $\hat{I}\mathbf{D}_3$ are called *ligand reflections*. When these four categories of elements are operated to trigonal bipyramidal derivatives, there appear three types of pairwise relationships, i.e.,

$$\text{rotoreflections } (\in \sigma_h\mathbf{D}_3): \quad \mathbf{1} \leftrightarrow \overline{\mathbf{1}} \text{ and } \mathbf{2} \leftrightarrow \overline{\mathbf{2}} \quad \Longrightarrow \text{enantiomeric} \tag{13}$$

$$RS\text{-permutations } (\in \tilde{\sigma}_h\mathbf{D}_3): \quad \mathbf{1} \leftrightarrow \mathbf{2} \text{ and } \overline{\mathbf{1}} \leftrightarrow \overline{\mathbf{2}} \quad \Longrightarrow RS\text{-diastereomeric} \tag{14}$$

$$\text{ligand reflections } (\in \hat{I}\mathbf{D}_3): \quad \mathbf{1} \leftrightarrow \overline{\mathbf{2}} \text{ and } \overline{\mathbf{1}} \leftrightarrow \mathbf{2} \quad \Longrightarrow \text{holantimeric}, \tag{15}$$

where the rotations ($\in \mathbf{D}_3$) convert **1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ into themselves so as to give homomeric relationships.

Keeping the three relationships in mind along with the homomeric relationships, we consider the point group $\mathbf{D}_{3h}$ (Eq. 1), the RS-permutation group $\mathbf{D}_{3\tilde{\sigma}}$ (Eq. 8), and the ligand-reflection group $\mathbf{D}_{3\hat{I}}$ (Eq. 9). Thereby, such relationships as described above are integrated to give *RS*-stereoisomeric relationships, which are related to attributive terms such as chirality and *RS*-stereogenicity, as summarized in Table 1. The symbols and notations used in Table 1 are in accord with Ref. [10].

2.5 Construction of stereoisograms

In order to exemplify procedures of constructing stereoisograms, we first show a procedure of constructing a stereoisogram of a trigonal bipyramidal complex [Ma_5], which exhibits Type IV character with a full symmetry, i.e., the *RS*-stereoisomeric group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}$ (Eq. 10). This procedure is based on the stereoisogram approach for organic stereochemistry [8–10], which is applied to the present case of a trigonal bipyramidal complex in inorganic stereochemistry.

Suppose that the five vertices of the skeleton **1** accommodate five achiral proligands of the same kind to produce a trigonal bipyramidal complex of the constitution [Ma_5] in accord with the function:

Table 1 Three relationships and the corresponding attributes appearing in stereoisograms [10]

symbol	relationship	attribute
(Concerned with reflections ◉)		
◉	enantiomeric	chiral
◉	(self-enantiomeric)	achiral
(Concerned with *RS*-permutations ○)		
○	*RS*-diastereomeric	*RS*-stereogenic
○	(self-*RS*-diastereomeric)	*RS*-astereogenic
(Concerned with ligand reflections ●)		
●	holantimeric	scleral
●	(self-holantimeric)	ascleral

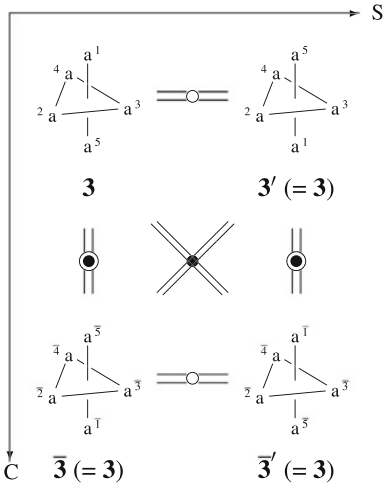


Fig. 2 Stereoisogram of Type IV for a trigonal bipyramidal complex with [Ma_5], which exhibits the full symmetry of $\mathbf{D}_{3h}$. The letter 'a' represents an achiral proligand and the central metal 'M' is omitted

$$f_1: \quad f_1(1) = f_1(2) = f_1(3) = f_1(4) = f_1(5) = \mathrm{a}. \tag{16}$$

Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates promolecules (named *RS*-stereoisomers) of the same kind (**3**, $\overline{\mathbf{3}}$, **3**′, and $\overline{\mathbf{3}}'$), which are aligned in a square planar fashion as depicted in Fig. 2. For the terms *proligands* and *promolecules*, see Refs. [19,24]. In most cases, they may be regarded as being equal to ligands and molecules, respectively. The three kinds of equality symbols with an open circle, a solid circle, and an encircled solid circle (Fig. 1) are added so as to construct a stereoisogram of Type IV. Thus, the resulting quadruplet of promolecules (**3**, $\overline{\mathbf{3}}$, **3**′, and $\overline{\mathbf{3}}'$) is degenerated into a single promolecule **3** in the stereoisogram of Type IV (Fig. 2), which belongs to the *RS*-stereoisomeric group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}$.

A stereoisogram (e.g., Fig. 2) characterizes a quadruplet of promolecules (named *RS*-stereoisomers). The terminology of the stereoisogram approach developed for organic stereochemistry [8–10] is applied to inorganic stereochemistry as follows:

1. The vertical axis (*C*-axis) of Fig. 2 is concerned with chirality (Table 1). A vertical equality symbol denotes a self-enantiomeric relationship so that the relevant

promolecules are degenerated to give an achiral promolecule. On the other hand, a vertical double-headed arrow denotes an enantiomeric relationship so that the relevant promolecules are chiral to give an enantiomeric pair. The term *enantiomers* is used to refer to the two promolecules of such an enantiomeric pair.

2. The horizontal axis (*S*-axis) of Fig. 2 is concerned with *RS*-stereogenicity (Table 1). A horizontal equality symbol denotes a self-*RS*-diastereomeric relationship so that the relevant promolecules are degenerated to give an *RS*-astereogenic promolecule. On the other hand, a horizontal double-headed arrow denotes an *RS*-diastereomeric relationship so that the relevant promolecules are *RS*-stereogenic to give an *RS*-diastereomeric pair. The term *RS-diastereomers* is used to refer to the two promolecules of such an *RS*-diastereomeric pair.
3. The diagonal axis of Fig. 2 is concerned with sclerality (Table 1). A diagonal equality symbol denotes a self-holantimeric relationship so that the relevant promolecules are degenerated to give an ascleral promolecule. On the other hand, a diagonal double-headed arrow denotes a holantimeric relationship so that the relevant promolecules are scleral to give a holantimeric pair. The term *holantimers* is used to refer to the two promolecules of such an holantimeric pair.

Each stereoisogram is characterized by a set of chiral/achiral, *RS*-stereogenic/*RS*-astereogenic, and scleral/ascleral attributes (Table 1), which is represented by a stereoisogram index, e.g., $[a, a, a]$ for such a Type IV stereoisogram as Fig. 2.

2.6 Five types of stereoisograms

As proven generally [11], a stereoisogram, which characterizes a quadruplet of promolecules (*RS*-stereoisomers), belongs to a factor group isomorphic to one of the five subgroups of the factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11). This subsection is devoted to discuss such stereoisograms of five types by taking trigonal bipyramidal compounds as examples. Thereby, the stereoisogram approach developed originally to comprehend organic stereochemistry [8–10] is shown to be equally effective to inorganic stereochemistry.

2.6.1 Stereoisograms of Type IV with a subsymmetry

Suppose that the five vertices of the skeleton **1** accommodate a set of five achiral proligands (2a, 2b, and c) in accord with the function:

$$f_2: \quad f_2(1) = f_2(5) = \mathrm{a}, \;\; f_2(2) = f_2(3) = \mathrm{b}, \;\; f_2(4) = \mathrm{c}, \tag{17}$$

which corresponds to the constitution $[\mathrm{Ma_2b_2c}]$. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates promolecules of the same kind, which construct a stereoisogram of Type IV depicted in Fig. 3. By following the stereoisogram approach [8], the resulting quadruplet of promolecules, i.e., **4**, $\overline{\mathbf{4}}$, $\mathbf{4}'$, and $\overline{\mathbf{4}}'$, is degenerated into a single promolecule **4**, which belongs to the point group $\mathbf{C}_{2v}$. The stereoisogram of Type IV (Fig. 3) is characterized by achiral, *RS*-astereogenic,

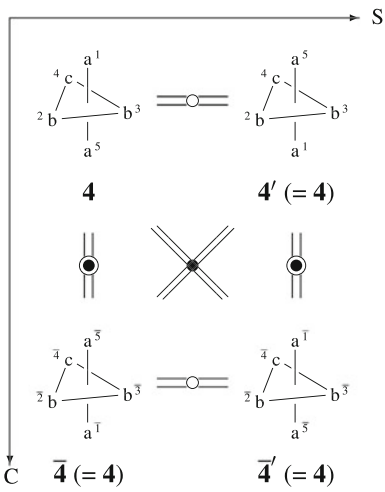


Fig. 3 Stereoisogram of Type IV for a trigonal bipyramidal complex with $[Ma_2b_2c]$, which exhibits the $\mathbf{C}_{2v}$-symmetry. The letters a, b, and c represent achiral proligands and the central metal 'M' is omitted

and ascleral attributes (stereoisogram index: $[a, a, a]$) according to the terminology summarized in Table 1.

Because the point group $\mathbf{D}_{3h}$ of **1** is subduced into its subgroup $\mathbf{C}_{2v}$ $(= \mathbf{C}_2 + \sigma_h \mathbf{C}_2)$, the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10) is subduced into its subgroup:

$$\mathbf{C}_{2v\widetilde{\sigma}\widehat{I}} = \mathbf{C}_2 + \sigma_h \mathbf{C}_2 + \widetilde{\sigma}_h \mathbf{C}_2 + \widehat{I}\mathbf{C}_2, \tag{18}$$

which indicates a group for characterizing the stereoisogram shown in Fig. 3. The group represented by Eq. 18 is also called *an RS-stereoisomeric group*, just as a subgroup (e.g., $\mathbf{C}_{2v}$) of a point group (e.g., $\mathbf{D}_{3h}$) is also called *a point group*. If necessary, the group represented by Eq. 18 is differentiated from the original *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10) by calling the original group *a maximum RS-stereoisomeric group*.

The corresponding factor group is obtained as follows:

$$\mathbf{C}_{2v\widetilde{\sigma}\widehat{I}}/\mathbf{C}_2 = \{\mathbf{C}_2, \sigma_h \mathbf{C}_2, \widetilde{\sigma}_h \mathbf{C}_2, \widehat{I}\mathbf{C}_2\}, \tag{19}$$

which is isomorphic to the factor group of Eq. 11. The factor group (Eq. 19) corresponding the following transversal:

$$\mathrm{Tv}(\mathbf{C}_{2v\widetilde{\sigma}\widehat{I}}/\mathbf{C}_2) = \{I, \sigma_h, \widetilde{\sigma}_h, \widehat{I}\}, \tag{20}$$

which is isomorphic to the transversal group of Eq. 12. It follows that the resulting quadruplet of promolecules ($\mathbf{4}$, $\overline{\mathbf{4}}$, $\mathbf{4}'$, and $\overline{\mathbf{4}}'$) is degenerated into a single promolecule **4**. The stereoisogram of Type IV (Fig. 3) belongs to the *RS*-stereoisomeric group $\mathbf{C}_{2v\widetilde{\sigma}\widehat{I}}$, which is a subgroup of $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$.

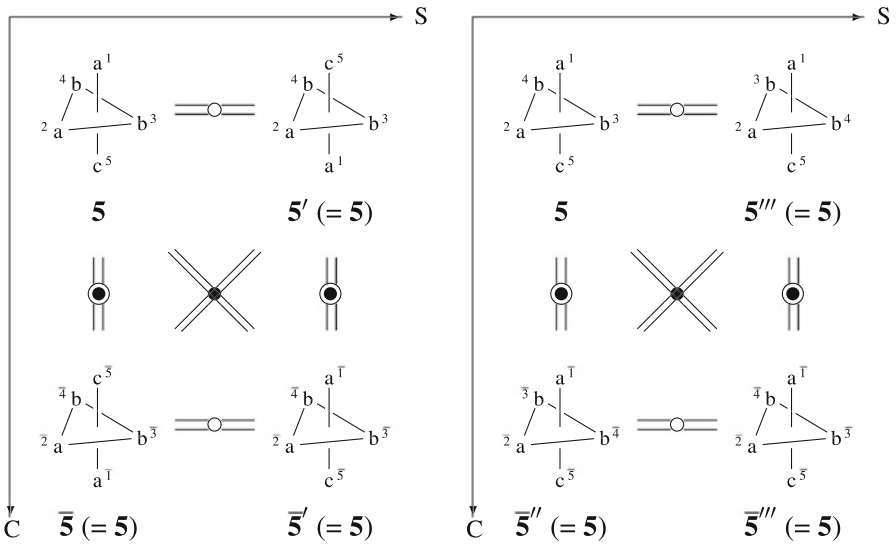


Fig. 4 Equivalent stereoisograms of Type IV for a trigonal bipyramidal complex with [Ma_2b_2c], which exhibits the $\mathbf{C}_s$-symmetry. The letters a, b, and c represent achiral proligands and the central metal 'M' is omitted. The *left* stereoisogram corresponds to the factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11), while the right stereoisogram corresponds to the factor group $\mathbf{C}_{s\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1$ (Eq. 25). Because of the isomorphism between these factor groups, the *left* and *right* stereoisograms are regarded as being equivalent under the *RS*-stereogenic group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$

As a next example, suppose that the five vertices of the skeleton **1** accommodate a set of five achiral proligands (2a, 2b, and c) in accord with the function:

$$f_3: \quad f_3(1) = f_3(2) = \mathrm{a}, \;\; f_3(3) = f_3(4) = \mathrm{b}, \;\; f_3(5) = \mathrm{c}, \tag{21}$$

which also corresponds to the constitution [Ma_2b_2c]. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates promolecules of the same kind, which construct a stereoisogram of Type IV depicted in Fig. 4 (left) by following the stereoisogram approach [8]. The resulting quadruplet of promolecules, i.e., **5**, $\overline{\mathbf{5}}$, **5**′, and $\overline{\mathbf{5}}'$, is degenerated into a single promolecule **5**, which belongs to the point group $\mathbf{C}_s$.

Strictly speaking, the equivalency of the four promolecules in Fig. 4 (left) is considered under the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10), if the numbering of vertices is taken into consideration. In other words, the promolecules **5**, $\overline{\mathbf{5}}$, **5**′, and $\overline{\mathbf{5}}'$ of the quadruplet are representatives of the four cosets of the factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11).

Another selection of reference skeletons provides us with an equivalent stereoisogram shown in Fig. 4 (right), which is more illustrative to show that the promolecule **5** belongs to the point group $\mathbf{C}_s$ ($= \{I, \sigma_{v(1)}\}$). Note that the element $C_{2(1)}$ ($\sim$ (1 5)(2)(3 4) $\in \mathbf{D}_3$) converts $\overline{\mathbf{5}}$ etc. (the left of Fig. 4) into $\overline{\mathbf{5}}''$ etc. (the right of Fig. 4). Thus, the two stereoisograms (the left and right of Fig. 4) are equivalent under the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10).

Because the point group $\mathbf{D}_{3h}$ of **1** is subduced into its subgroup $\mathbf{C}_s$:

$$\mathbf{C}_s = \mathbf{C}_1 + \sigma_{v(1)}\mathbf{C}_1, \tag{22}$$

the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10) is subduced into its subgroup:

$$\begin{aligned}\mathbf{C}_{s\widetilde{\sigma}\widehat{I}} &= \mathbf{C}_1 + \sigma_{v(1)}\mathbf{C}_1 + \widetilde{\sigma}_{v(1)}\mathbf{C}_1 + \widehat{I}\mathbf{C}_1 &(23)\\ &= \{I, \sigma_{v(1)}, \widetilde{\sigma}_{v(1)}, \widehat{I}\}, &(24)\end{aligned}$$

which indicates the *RS*-stereoisomeric group for the stereoisogram shown in Fig. 4. Although a derivation process is rather trivial, we obtain the following factor group:

$$\begin{aligned}\mathbf{C}_{s\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1 &= \{\mathbf{C}_1, \sigma_{v(1)}\mathbf{C}_1, \widetilde{\sigma}_{v(1)}\mathbf{C}_1, \widehat{I}\mathbf{C}_1\}\\ &= \{I, \sigma_{v(1)}, \widetilde{\sigma}_{v(1)}, \widehat{I}\}, &(25)\end{aligned}$$

which is identical with its transversal. The factor group represented by Eq. 25 is isomorphic to the factor group of Eq. 11 and to the transversal group of Eq. 12. It follows that the resulting quadruplet of promolecules (a quadruplet of **5**, $\overline{\mathbf{5}}$, **5**′, and $\overline{\mathbf{5}}'$; or a quadruplet of **5**, $\overline{\mathbf{5}}''$, **5**‴, and $\overline{\mathbf{5}}'''$) is degenerated into a single promolecule **5**. The stereoisogram of Type IV (Fig. 4, in particular, the right diagram) belongs to the *RS*-stereoisomeric group $\mathbf{C}_{s\widetilde{\sigma}\widehat{I}}$, which is a subgroup of $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$.

As exemplified by Figs. 2, 3, and 4, the stereoisograms of Type IV belong to the factor groups isomorphic to the Klein four-group, i.e., $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11) for Fig. 2, $\mathbf{C}_{2v\widetilde{\sigma}\widehat{I}}/\mathbf{C}_2$ (Eq. 19) for Fig. 3, and $\mathbf{C}_{s\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1$ (Eq. 25) for Fig. 4. Hence, the stereoisograms of Type IV are commonly discussed by using the maximum factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11) as a representative, as proven generally [11].

2.6.2 Stereoisograms of Type I with a subsymmetry

The five vertices of the skeleton **1** accommodate a set of five achiral proligands (2a, 2b, and c) in accord with the function:

$$f_4: \quad f_4(1) = f_4(2) = \mathrm{a},\ f_4(3) = f_4(5) = \mathrm{b},\ f_4(4) = \mathrm{c}, \tag{26}$$

which generates another example of a promolecule with the constitution $[\mathrm{Ma}_2\mathrm{b}_2\mathrm{c}]$. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates a quadruplet of promolecules (*RS*-stereoisomers), which construct a stereoisogram of Type I depicted in Fig. 5. The stereoisogram of Type I (Fig. 5) is characterized by chiral, *RS*-stereogenic, and ascleral attributes (stereoisogram index: $[-, -, a]$) according to the terminology summarized in Table 1.

By following the stereoisogram approach [8], the resulting quadruplet of promolecules, **6**, $\overline{\mathbf{6}}$, **7**, and $\overline{\mathbf{7}}$, can be regarded as being degenerated into an enantiomeric pair of promolecules **6**/$\overline{\mathbf{6}}$, which is equalized to another pair **7**/$\overline{\mathbf{7}}$ because of asclerality of the stereoisogram (i.e., **6** = $\overline{\mathbf{7}}$ and $\overline{\mathbf{6}}$ = **7**). Alternatively, the resulting quadruplet of promolecules can be regarded as being degenerated into an *RS*-diastereomeric pair

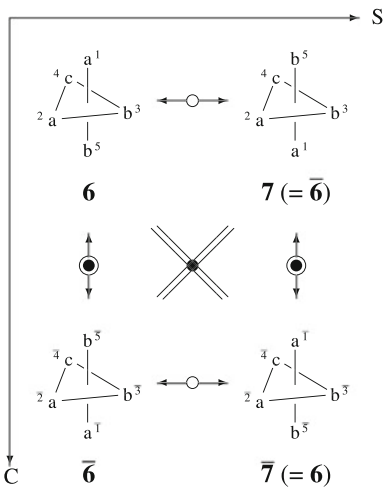


Fig. 5 Stereoisogram of Type I for a trigonal bipyramidal complex with $[Ma_2b_2c]$, which exhibits the $\mathbf{C}_1$-symmetry. The letters a, b, and c represent achiral proligands and the central metal 'M' is omitted

of promolecules **6**/**7**, which is equalized to another pair $\overline{\mathbf{6}}/\overline{\mathbf{7}}$. It should be noted that the conventional stereochemistry has adopted only the former standpoint, i.e., an enantiomeric pair of $\mathbf{6}/\overline{\mathbf{6}}$.

In the stereoisogram approach [8], two promolecules $\mathbf{6}/\overline{\mathbf{7}}$ (or $\mathbf{7}/\overline{\mathbf{6}}$) along a diagonal direction are identical to each other. Hence, **6** of the point group $\mathbf{C}_1$ is regarded as belonging to the following group:

$$\mathbf{C}_{1\widehat{I}} = \mathbf{C}_1 + \widehat{I}\mathbf{C}_1 = \{I, \widehat{I}\} \tag{27}$$

from the viewpoint of a stereoisogram of Type I. The identity pair $\mathbf{6}/\overline{\mathbf{7}}$ and the identity pair $\mathbf{7}/\overline{\mathbf{6}}$ are interchangeable in the stereoisogram shown by Fig. 5, which is characterized by the following group:

$$\mathbf{C}_{1\sigma\widetilde{\sigma}\widehat{I}} = \mathbf{C}_1 + \sigma_h\mathbf{C}_1 + \widetilde{\sigma}_h\mathbf{C}_1 + \widehat{I}\mathbf{C}_1. \tag{28}$$

Although a derivation process is rather trivial, we obtain the following factor group:

$$\begin{aligned}\mathbf{C}_{1\sigma\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1 &= \{\mathbf{C}_1, \sigma_h\mathbf{C}_1, \widetilde{\sigma}_h\mathbf{C}_1, \widehat{I}\mathbf{C}_1\} \\ &= \{I, \sigma_h, \widetilde{\sigma}_h, \widehat{I}\},\end{aligned} \tag{29}$$

which is identical with its transversal. The factor group represented by Eq. 29 is isomorphic to the factor group of Eq. 11 and to the transversal group of Eq. 12.

Equation 27 generates the corresponding factor group:

$$\mathbf{C}_{1\widehat{I}}/\mathbf{C}_1 = \{\mathbf{C}_1, \widehat{I}\mathbf{C}_1\} = \{I, \widehat{I}\}, \tag{30}$$

which is isomorphic to the subgroup $\{\mathbf{D}_3, \widehat{I}\mathbf{D}_3\}$ of the factor group shown in Eq. 11. The factor group $\mathbf{C}_{1\widehat{I}}/\mathbf{C}_1$ (Eq. 30) is a subgroup of the factor group $\mathbf{C}_{1\sigma\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1$ (Eq. 29), just as the factor group $\mathbf{D}_{3\widehat{I}}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \widehat{I}\mathbf{D}_3\}$) is a subgroup of the maximum factor group

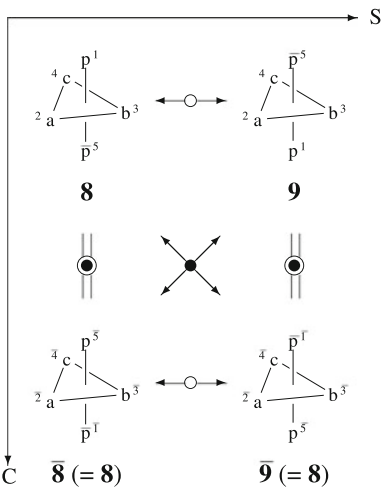


Fig. 6 Stereoisogram of Type V for a trigonal bipyramidal complex with [Mabcp$\bar{\text{p}}$], which exhibits the $\mathbf{C}'_s$-symmetry. The letters a, b, and c represent achiral proligands and a pair of p and $\bar{\text{p}}$ represents an enantiomeric pair of chiral proligands

$\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11). It follows that the factor group $\mathbf{C}_{1\widehat{I}}/\mathbf{C}_1$ (Eq. 30) is determined to be a subgroup of characterizing the stereoisogram type (Type I) of the stereoisogram shown in Fig. 5.

The discussions in the preceding paragraphs along with a general proof described in Ref. [11] show that the stereoisograms of Type I for trigonal bipyramidal compounds are commonly discussed by using the factor group $\mathbf{D}_{3\widehat{I}}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \widehat{I}\mathbf{D}_3\}$) as a representative, which is a subgroup of the maximum factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11).

2.6.3 Stereoisograms of Type V with a subsymmetry

Suppose that the five vertices of the skeleton **1** accommodate a set of five proligands (a, b, c, p and $\bar{\text{p}}$) in accord with the function:

$$f_5: \quad f_5(1) = \text{p},\ f_5(2) = \text{a},\ f_5(3) = \text{b},\ f_5(4) = \text{c},\ f_5(5) = \bar{\text{p}}, \tag{31}$$

where a, b, and c represent achiral proligands and a pair of p and $\bar{\text{p}}$ represents an enantiomeric pair of chiral proligands. Thereby, the quadruplet of skeletons (**1**, $\bar{\mathbf{1}}$, **2**, and $\bar{\mathbf{2}}$ shown in Fig. 1) generates two achiral promolecules, which construct a stereoisogram of Type V depicted in Fig. 6. The stereoisogram of Type V (Fig. 6) is characterized by achiral, *RS*-stereogenic, and scleral attributes (stereoisogram index: $[a, -, -]$) according to the terminology summarized in Table 1.

By following the stereoisogram approach [8], the resulting quadruplet of promolecules, **8**, $\bar{\mathbf{8}}$, **9**, and $\bar{\mathbf{9}}$, is degenerated into an *RS*-diastereomeric pair of achiral promolecules **8** and **9**, each of which belongs to the point group $\mathbf{C}'_s$.

Because the point group $\mathbf{D}_{3h}$ of **1** is subduced into its subgroup $\mathbf{C}'_s$, i.e.,

$$\mathbf{C}'_s = \mathbf{C}_1 + \sigma_h\mathbf{C}_1 = \{I, \sigma_h\}, \tag{32}$$

the *RS*-stereoisomeric group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}$ (Eq. 10) is subduced into its subgroup:

$$\mathbf{C}'_{s\widetilde{\sigma}\widehat{I}} = \mathbf{C}_1 + \sigma_h\mathbf{C}_1 + \widetilde{\sigma}_h\mathbf{C}_1 + \widehat{I}\mathbf{C}_1, \tag{33}$$

which indicates the *RS*-stereoisomeric group for characterizing the stereoisogram shown in Fig. 6. Although a derivation process is rather trivial, we obtain the following factor group:

$$\begin{aligned}\mathbf{C}'_{s\widetilde{\sigma}\widehat{I}}/\mathbf{C}_1 &= \{\mathbf{C}_1, \sigma_h\mathbf{C}_1, \widetilde{\sigma}_h\mathbf{C}_1, \widehat{I}\mathbf{C}_1\} \\ &= \{I, \sigma_h, \widetilde{\sigma}_h, \widehat{I}\},\end{aligned} \tag{34}$$

which is identical with its transversal. The factor group (Eq. 34) is isomorphic to the factor group represented by Eq. 11. The transversal group (Eq. 12) is also effective.

To treat the stereoisogram of Type V (Fig. 6) properly, the subgroup represented by Eq. 33 is further subduced into $\mathbf{C}'_s$ (Eq. 32), which indicates the *RS*-stereoisomeric group for the stereoisogram shown in Fig. 6. The corresponding factor group is obtained as follows:

$$\mathbf{C}'_s/\mathbf{C}_1 = \{\mathbf{C}_1, \sigma_h\mathbf{C}_1\} = \{I, \sigma_h\}. \tag{35}$$

The factor group $\mathbf{C}'_s/\mathbf{C}_1$ (Eq. 35) is isomorphic to $\mathbf{D}_{3h}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \sigma_h\mathbf{D}_3\}$), which is a subgroup of the factor group of Eq. 11. It follows that the stereoisograms of Type V for trigonal bipyramidal compounds can be discussed by using the factor group $\mathbf{D}_{3h}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \sigma_h\mathbf{D}_3\}$) as a representative, which is a subgroup of the maximum factor group $\mathbf{D}_{3h\widetilde{\sigma}\widehat{I}}/\mathbf{D}_3$ (Eq. 11).

2.6.4 Stereoisograms of Type II with a subsymmetry

Suppose that the five vertices of the skeleton **1** accommodate a set of five proligands (a, b, c, p and $\overline{\text{p}}$) in accord with the function:

$$f_6: \quad f_6(1) = f_6(5) = \text{p},\ \ f_6(2) = \text{a},\ \ f_6(3) = \text{b},\ \ f_6(4) = \text{c}, \tag{36}$$

where a, b, and c represent achiral proligands and a pair of p and $\overline{\text{p}}$ represents an enantiomeric pair of chiral proligands. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates an enantiomeric pair of chiral promolecules, which construct a stereoisogram of Type II depicted in Fig. 7. The stereoisogram of Type II (Fig. 7) is characterized by chiral, *RS*-astereogenic, and scleral attributes (stereoisogram index: $[-, a, -]$) according to the terminology summarized in Table 1.

By following the stereoisogram approach [8], the resulting quadruplet of promolecules, **10**, $\overline{\mathbf{10}}$, **10**′, and $\overline{\mathbf{10}}'$, is degenerated into an enantiomeric pair of chiral promolecules **10** and $\overline{\mathbf{10}}$, each of which belongs to the point group $\mathbf{C}_1$.

Two promolecules **10** and **10**′ (or $\overline{\mathbf{10}}$ and $\overline{\mathbf{10}}'$) are identical to each other on the action of an *RS*-permutation $\tilde{\sigma}_h$ ($\sim$ (1 5)(2)(4)(4) $\in \tilde{\sigma}_h\mathbf{D}_3$), so that the identity pair **10/10**′ (or $\overline{\mathbf{10}}/\overline{\mathbf{10}}'$) belongs to the following group:

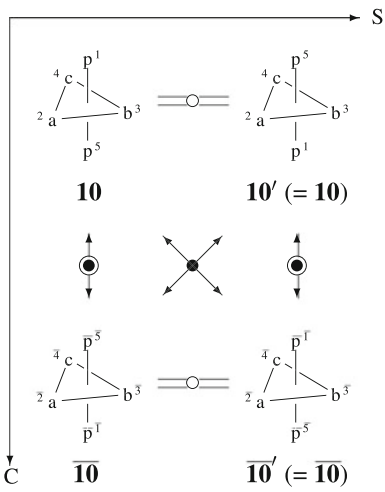


Fig. 7 Stereoisogram of Type II for a trigonal bipyramidal complex with [Mabcp^2] or [Mabcp̄^{2}], which exhibits the $\mathbf{C}_1$-symmetry. The letters a, b, and c represent achiral proligands and a pair of p and p̄ represents an enantiomeric pair of chiral proligands

$$\mathbf{C}_{1\tilde{\sigma}} = \mathbf{C}_1 + \tilde{\sigma}_h\mathbf{C}_1 = \{I, \tilde{\sigma}_h\}, \tag{37}$$

which indicates the *RS*-stereoisomeric group of the stereoisogram shown in Fig. 7. The group $\mathbf{C}_{1\tilde{\sigma}}$ (Eq. 37) is a subgroup of $\mathbf{C}'_{s\tilde{\sigma}\hat{I}}$ (Eq. 33).

Equation 37 generates the corresponding factor group:

$$\mathbf{C}_{1\tilde{\sigma}}/\mathbf{C}_1 = \{\mathbf{C}_1, \tilde{\sigma}_h\mathbf{C}_1\} = \{I, \tilde{\sigma}_h\}. \tag{38}$$

The factor group $\mathbf{C}_{1\tilde{\sigma}}/\mathbf{C}_1$ (Eq. 38) is isomorphic to the factor group $\mathbf{D}_{3\tilde{\sigma}}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \tilde{\sigma}_h\mathbf{D}_3\}$), which is a subgroup of the factor group shown in Eq. 11. Because the factor group $\mathbf{C}_{1\tilde{\sigma}}/\mathbf{C}_1$ (Eq. 38) is a subgroup of the factor group $\mathbf{C}'_{s\tilde{\sigma}\hat{I}}/\mathbf{C}_1$ (Eq. 34), the factor group (Eq. 38) characterizes the stereoisogram type (Type II) of the stereoisogram shown in Fig. 7. It follows that the stereoisograms of Type II for trigonal bipyramidal compounds can be discussed by using the factor group $\mathbf{D}_{3\tilde{\sigma}}/\mathbf{D}_3$ (= $\{\mathbf{D}_3, \tilde{\sigma}\mathbf{D}_3\}$) as a representative, which is a subgroup of the maximum factor group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}/\mathbf{D}_3$ (Eq. 11).

2.6.5 Stereoisograms of Type III with a subsymmetry

Suppose that the five vertices of the skeleton **1** accommodate a set of five proligands (a, b, c, d, p/p̄) in accord with the function:

$$f_7: \quad f_7(1) = \mathrm{a},\ f_7(2) = \mathrm{b},\ f_7(3) = \mathrm{c},\ f_7(4) = \mathrm{d},\ f_7(5) = \mathrm{p}, \tag{39}$$

where a, b, c, and d represent achiral proligands and a pair of p and p̄ represents an enantiomeric pair of chiral proligands. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates two enantiomeric pairs of chiral promolecules, which construct a stereoisogram of Type III depicted in Fig. 8. The stereoisogram of Type III

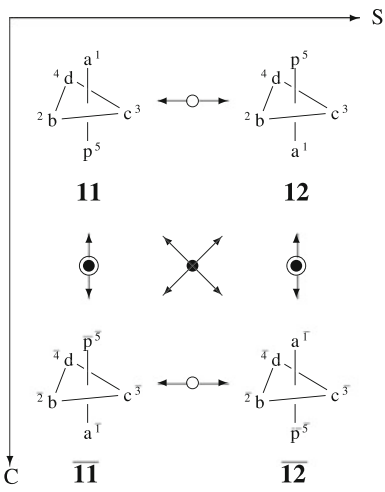


Fig. 8 Stereoisogram of Type III for a trigonal bipyramidal complex with [Mabcdp] or [Mabcdp̄], which exhibits the $\mathbf{C}_1$-symmetry

(Fig. 8) is characterized by chiral, *RS*-stereogenic, and scleral attributes (stereoisogram index: [−, −, −]) according to the terminology summarized in Table 1.

By following the stereoisogram approach [8], the resulting quadruplet of promolecules contains **11**, $\overline{\mathbf{11}}$, **12**, and $\overline{\mathbf{12}}$, each of which belongs to the point group $\mathbf{C}_1$.

Each of the promolecules (**11**, $\overline{\mathbf{11}}$, **12**, $\overline{\mathbf{12}}$) is inequivalent on the action of the *RS*-stereogenic group, i.e., $\mathbf{C}'_{s\tilde{\sigma}\hat{I}}$ (Eq. 33). Because of the point group $\mathbf{C}_1$ assigned to each promolecule, the factor group is trivial to be $\mathbf{C}_1/\mathbf{C}_1$, which is isomorphic to the factor group $\mathbf{D}_3/\mathbf{D}_3$ (= $\{\mathbf{D}_3\}$). The trivial factor group $\mathbf{C}_1/\mathbf{C}_1$ characterizes the stereoisogram type (Type III) of the stereoisogram shown in Fig. 8. Because the factor group $\mathbf{D}_3/\mathbf{D}_3$ (= $\{\mathbf{D}_3\}$) is a subgroup of the factor group shown in Eq. 11, stereoisograms of Type III can be discussed by using the factor group $\mathbf{D}_3/\mathbf{D}_3$ (= $\{\mathbf{D}_3\}$) as a representative, which is a subgroup of the maximum factor group $\mathbf{D}_{3h\tilde{\sigma}\hat{I}}/\mathbf{D}_3$ (Eq. 11).

2.6.6 Summary of five types by using simplified stereoisograms

As found in the preceding discussions, the factor group ($\mathbf{D}_{3h\tilde{I}}/\mathbf{D}_3$ of Eq. 11) and the factor groups for related Type I–V stereoisograms are isomorphic to the Klein four-group and its subgroups. Such isomorphism have been discussed generally by starting from appropriate point groups other than $\mathbf{D}_{3h}$ and the related subgroups [11]. As cited in Fig. 9, the above-mentioned results can be summarized by simplified stereoisograms reported in the general discussion [10].

Note that the term *ligand* is originally defined as "the atoms or groups joined to the central atom in an inorganic coordination entity" in inorganic terminology so as to be recommended to be replaced by "atom or group" in organic terminology (cf. P-91.1.1.1 (a) of IUPAC Provisional Recommendations 2004 [2]). In the stereoisogram approach, however, the term *ligand* and its abstract term *proligand* is also used to refer to atoms and groups which are regarded as substituents in organic chemistry. Because the stereoisogram approach aimed at integrating organic and inorganic

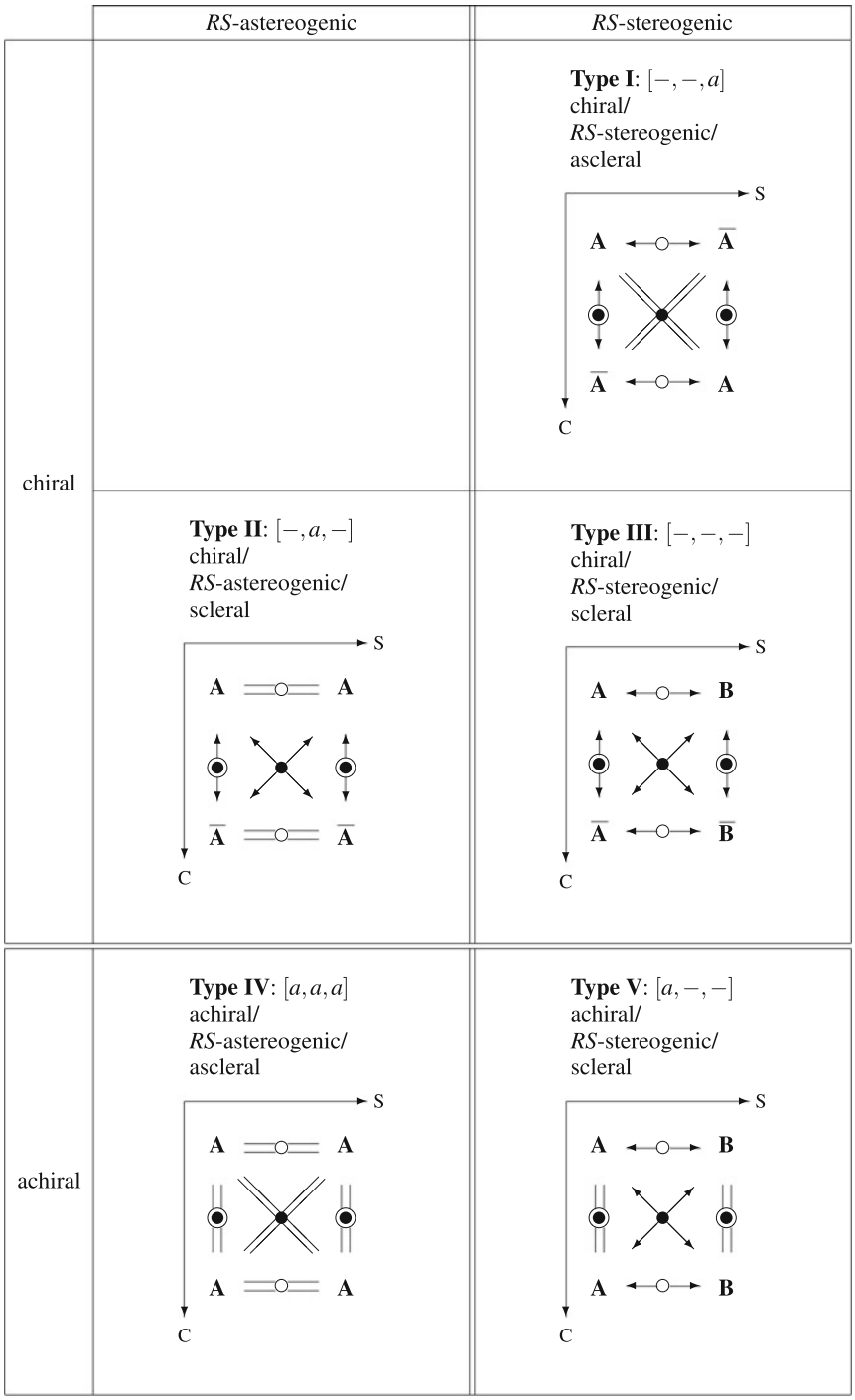


Fig. 9 Simplified stereoisograms of five types [10]. The symbols **A** and $\overline{\mathbf{A}}$ (or **B** and $\overline{\mathbf{B}}$) represent a pair of enantiomers

stereochemistry, such an extended usage provides us with a common theoretical basis to stereochemistry, both organic and inorganic.

3 Chirality and *RS*-stereogenicity

This section is devoted to demonstrate that the conventional methodology has mixed up *RS*-diastereomeric relationships (or *RS*-stereogenicity) with enantiomeric relationships (or chirality).

3.1 Independence between chirality and *RS*-stereogenicity

One of the merits of introducing stereoisograms (and *RS*-stereoisomers) is a definite demonstration that chirality (along its *C*-axis) and *RS*-stereogenicity (along its *S*-axis) are independent concepts. Or equivalently, we can say that enantiomeric relationships (along its *C*-axis) are independent to *RS*-diastereomeric relationships (along its *S*-axis). The independence between these concepts is clearly demonstrated by differentiating between rotoreflections ($\in \sigma_h \mathbf{D}_3$, Eq. 13) and *RS*-permutations ($\in \widetilde{\sigma}_h \mathbf{D}_3$, Eq. 14), or equivalently between the point group $\mathbf{D}_{3h}$ (Eq. 1) and the *RS*-permutation group $\mathbf{D}_{3\widetilde{\sigma}}$ (Eq. 8).

It should be emphasized that an *RS*-diastereomeric relationship is a pairwise relationship, just as an enantiomeric relationship is a pairwise relationship, as shown in Table 1. This means that *RS*-stereogenicity for characterizing permutational properties can be discussed in parallel ways to chirality for characterizing mirror-image properties. Although they are independent, chirality and *RS*-stereogenicity (or enantiomeric and *RS*-diastereomeric relationships) interact, as formulated by the presence of five types of stereoisograms, as shown in Fig. 9. For concrete examples, see Fig. 3 for Type IV, Fig. 5 for Type I, Fig. 6 for Type V, Fig. 7 for Type II, and Fig. 8 for Type III.

In contrast, the conventional stereochemistry has nullified the interaction between permutational properties and mirror-image properties by preferring enantiomeric relationships rather than "diastereomeric" relationships. In other words, the conventional stereochemistry has lacked the formulation of Type I stereoisograms, so that *RS*-diastereomeric relationships of the stereoisogram approach are misleadingly equalized to enantiomeric relationships.

The case of Type V (Fig. 6) provides us with another example which shows the independence between enantiomeric relationships and *RS*-diastereomeric ones. As clearly shown by the stereoisogram of Type V (Fig. 6), an achiral promolecule **8** (= $\overline{\mathbf{8}}$) is *RS*-diastereomeric to another achiral promolecule **9** (= $\overline{\mathbf{9}}$). The respective enantiomeric relationships are degenerated into achiral promolecules, **8** and **9**.

3.2 Problematic situations in the conventional terminology

In the conventional stereochemistry, such Type V cases as formulated by the stereoisogram approach are exceptionally treated as pseudoasymmetric cases [3], where, for example, a "diastereomeric" relationship between **8** and **9** is presumed as a result of

the conventional dichotomy between enantiomeric relationships and "diastereomeric" relationships. It should be noted that the relationship (a) between **6** (= $\overline{\mathbf{7}}$) and **7** (= $\overline{\mathbf{6}}$) (cf. Fig. 5) has the same feature as the relationship (b) between **8** and **9** (cf. Fig. 6), if we focus our attention on *RS*-permutations along the *S*-axes of Figs. 5 and 6. On the basis of the conventional terminology, however, the relationship (a) is called an "enantiomeric" relationship (i.e., the nullification of *RS*-permutations, with considering the reflection of ligand chirality), while the relationship (b) is called a "diastereomeric" relationship (i.e. the adoption of *RS*-permutations, without considering the reflection of ligand chirality). In other words, the conventional stereochemistry has a preference for "enantiomeric" relationships (along the *C*-axes) in Type I cases, while it has a preference for "diastereomeric" relationships (along the *S*-axes) in Type V cases. The two modes of decision are obviously inconsistent.

To do well with the relationship (a) called an "enantiomeric" relationship and the relationship (b) called a "diastereomeric" relationship, the dichotomy "diastereomers are stereoisomers other than enantiomers" has been adopted in the conventional stereochemistry (cf. [25, p. 1196] and [7, p. 237]). Although the dichotomy is apparently simple in practices of testing "enantiomers" and "diastereomers", its conceptual basis is not so simple. Note that the "enantiomeric" relationship is accompanied by the reflection of ligand chirality while the "diastereomeric" relationship does not refer to whether it is accompanied by the reflection of ligand chirality or not. Moreover, the "diastereomeric" relationship for **8** and **9** lacks enantiomeric relationships to be compared, because these "diastereomers" are both achiral.

The conventional methodology described in the preceding paragraph is based on a concealed prerequisite (a two-step procedure) that the first test for stereoisomeric relationships is applied to two compounds whether they generate an identical graph, and then the second test for enantiomeric relationships is applied to the two stereoisomers in order to detect a pair of enantiomers or an achiral compound. Thereby, the two-step procedure has been done because of the above-mentioned dichotomy, so that no detection of a pair of enantiomers or of an achiral compound is interpreted as being "diastereomeric".

Obviously, the two-step procedure only tests stereoisomeric relationships and enantiomeric relationships, so that a test for "diastereomeric" relationships is not directly conducted. It follows that "diastereomeric" relationships are subsidiary so as to specify relationships between pairs of enantiomers and/or achiral compounds, which are detected by the second test. Although such "diastereomeric" relationships obtained implicitly are otherwise linked to permutations as found in the formulation of the Cahn-Ingold-Prelog (CIP) system [26, p. 32], a theoretical basis for the linkage has not been fully demonstrated in the conventional stereochemistry.

3.3 *C/A*-descriptors for trigonal bipyramidal compounds

3.3.1 C/A-descriptors based on RS-diastereomeric relationships

According to Section IR-9.3.4.5 of the IUPAC recommendations 2005 [1], *C/A*-descriptors for describing absolute configurations are assigned to trigonal bipyramidal

centers, where *C* (clockwise) or *A* (anticlockwise) is specified as an *RS*-stereogenicity symbol (a revision of an original "chirality symbol") after each ligand is assigned a priority number based on the rules developed by Cahn, Ingold, and Prelog (the CIP rules) [4,5].

When the CIP priority is presumed to be a > b > c, the trigonal bipyramidal compounds with [Ma_2b_2c] (Type I, Fig. 5) are differentiated by *C/A*-descriptors as follows,

$$\left.\begin{array}{l} \mathbf{6}(=\overline{\mathbf{7}}):\ \textit{TBPY-5-12-A} \\ \mathbf{7}(=\overline{\mathbf{6}}):\ \textit{TBPY-5-12-C} \end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair,} \tag{40}$$

According to the stereoisogram approach, the *C/A*-descriptors are regarded as being pairwise assigned to the pair of *RS*-diastereomers **6** and **7**. Because the pair of *RS*-diastereomers coincides with the pair of enantiomers **6** and $\overline{\mathbf{6}}$, the *C/A*-descriptors are interpreted to be reassigned to the latter pair of enantiomers **6** and $\overline{\mathbf{6}}$ in terms of *chirality faithfulness* [12]. The above Type I case is chirality-faithful because the CIP priority a > b > c remains unchanged on the action of reflections.

When the CIP priority is presumed to be a > b > c > p > $\overline{\text{p}}$, the trigonal bipyramidal compounds with [Mabcp$\overline{\text{p}}$] (Type V, Fig. 6) are differentiated by the following *C/A*-descriptors:

$$\left.\begin{array}{l} \mathbf{8}(=\overline{\mathbf{8}}):\ \textit{TBPY-5-45-a} \\ \mathbf{9}(=\overline{\mathbf{9}}):\ \textit{TBPY-5-45-c} \end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair} \tag{41}$$

Because **8** and **9** are achiral, they are not chirality-faithful [12]. Hence, the uppercase letters *C* and *A* are changed into lowercase letters *c* and *a*. According to the stereoisogram approach, the *C/A*-descriptors are regarded as being pairwise assigned to the pair of *RS*-diastereomers **8** and **9**, which are not enantiomeric obviously. Hence, the original name "chirality symbol" [1] is inadequate so as to be renamed into a more appropriate term *RS-stereogenicity symbol*.

It should be added that the conventional name "chirality symbol" [1] has been based on a transmuted term "chirality", as found in the subsection title "IR-9.3.4 Describing absolute configuration—distinguishing between enantiomers", which appears in the so-called Red Book for inorganic chemistry [1]. This subsection title means that "describing absolute configuration" (by *C/A*-descriptors) is directly linked to "chirality" (i.e., "distinguishing between enantiomers"), so that the term "chirality" has been transmuted to "describe absolute configuration" apart from the original connotation of a purely geometric meaning. The subsection title "P-92.1.9.4 Chirality" and the term "chirality symbol" used in IUPAC Provisional Recommendations 2004 for organic chemistry [2] indicate the direct linkage between "chirality" and *C/A*-descriptors, so that the term "chirality" is found to suffer from such transmutation. The term "chirality center" referred to as the classical example of a stereogenic unit in P-91.1.1.1 (a) of IUPAC Provisional Recommendations 2004 [2] also shows the transmutation of "chirality" in the formulation of *R/S*-descriptors, which are the organic counterpart of *C/A*-descriptors. Thus the transmutation of the term "chirality" is widely spread in organic stereochemistry as well as in inorganic stereochemistry.

It should emphasized that chirality (in a purely geometric meaning) distinguishes between enantiomers, while *C/A*-descriptors and *R/S*-descriptors for describing absolute configuration are not based on chirality (in a purely geometric meaning), nor on the conventional "stereogenicity", but stem from *RS*-stereogenicity of the stereoisogram approach.

3.3.2 Chirality faithfulness of C/A-descriptors

When the CIP priority is presumed to be a (1) > b (2) > c (3) > d (4) > p (5) > $\overline{\text{p}}$ (6), the trigonal bipyramidal compounds with [Mabcdp] or [Mabcd$\overline{\text{p}}$] (Fig. 8) are differentiated by the following *C/A*-descriptors:

$$\left.\begin{array}{ll} \mathbf{11}: & \textit{TBPY-5-15-A} \\ \mathbf{12}: & \textit{TBPY-5-15-C} \end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair} \tag{42}$$

$$\left.\begin{array}{ll} \overline{\mathbf{11}}: & \textit{TBPY-5-16-C} \\ \overline{\mathbf{12}}: & \textit{TBPY-5-16-A} \end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair.} \tag{43}$$

According to the stereoisogram approach, the *C/A*-descriptors are pairwise assigned to each pair of *RS*-diastereomers as linked with a brace. Note that the configuration index *TBPY-5-15* for **11** (or *TBPY-5-16* for $\overline{\mathbf{11}}$) is identical with that for **12** (or that for $\overline{\mathbf{12}}$).

If we obey the conventional methodology, we are forced to consider pairs of enantiomers in place of the above-mentioned pairs of *RS*-diastereomers, so that the following pairs of *C/A*-descriptors are presumed:

$$\left.\begin{array}{ll} \mathbf{11}: & \textit{TBPY-5-15-A} \\ \overline{\mathbf{11}}: & \textit{TBPY-5-16-C} \end{array}\right\} \text{an enantiomeric pair} \tag{44}$$

$$\left.\begin{array}{ll} \mathbf{12}: & \textit{TBPY-5-15-C} \\ \overline{\mathbf{12}}: & \textit{TBPY-5-16-A} \end{array}\right\} \text{an enantiomeric pair.} \tag{45}$$

Although the pairing of *A* and *C* is satisfied in each pair (i.e., chirality-faithful [12]), the configuration index for one of the pair is different from the other of the pair, i.e., *TBPY-5-15* vs. *TBPY-5-16*. If we strictly take account of chirality faithfulness [12], we should tentatively change the configuration index *TBPY-5-16* into *TBPY-5-15* for $\overline{\mathbf{11}}$ and $\overline{\mathbf{12}}$, where the CIP priority a > b > c > d > $\overline{\text{p}}$ (5) is tentatively adopted in place of the CIP priority a > b > c > d > p (5) > $\overline{\text{p}}$ (6).

As an example of a chirality-unfaithful case, suppose that the five vertices of the skeleton **1** accommodate a set of five achiral proligands (a, b, p, $\overline{\text{p}}$, q/$\overline{\text{q}}$) in accord with the function:

$$f_8: \quad f_8(1) = \text{a},\ f_8(2) = \text{b},\ f_8(3) = \text{p},\ f_8(4) = \overline{\text{p}},\ f_8(5) = \text{q}, \tag{46}$$

where a and b represent achiral proligands as well as a pair of p and $\overline{\text{p}}$ or a pair of q and $\overline{\text{q}}$ represents an enantiomeric pair of chiral proligands. Thereby, the quadruplet of skeletons (**1**, $\overline{\mathbf{1}}$, **2**, and $\overline{\mathbf{2}}$ shown in Fig. 1) generates two enantiomeric pairs of chiral

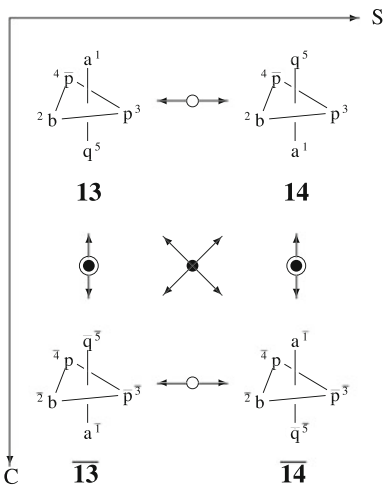


Fig. 10 Stereoisogram of Type III for a trigonal bipyramidal complex with [Mabp$\overline{\text{p}}$q] or [Mabp$\overline{\text{p}}\overline{\text{q}}$], which exhibits the $\mathbf{C}_1$-symmetry

promolecules, which construct a stereoisogram of Type III depicted in Fig. 10. By following the stereoisogram approach [8], the resulting quadruplet consists of promolecules, **13**, $\overline{\mathbf{13}}$, **14**, and $\overline{\mathbf{14}}$, each of which belongs to the point group $\mathbf{C}_1$.

When the CIP priority is presumed to be a (1) > b (2) > p (3) > $\overline{\text{p}}$(4) > q (5) > $\overline{\text{q}}$ (6), the trigonal bipyramidal compounds with [Mabp$\overline{\text{p}}$q] or [Mabp$\overline{\text{p}}\overline{\text{q}}$] (Fig. 10) are differentiated by the following *C/A*-descriptors:

$$\left.\begin{array}{l}\mathbf{13}: \textit{TBPY-5-15-a}\\ \mathbf{14}: \textit{TBPY-5-15-c}\end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair} \tag{47}$$

$$\left.\begin{array}{l}\overline{\mathbf{13}}: \textit{TBPY-5-16-a}\\ \overline{\mathbf{14}}: \textit{TBPY-5-16-c}\end{array}\right\} \text{an } \textit{RS}\text{-diastereomeric pair.} \tag{48}$$

According to the stereoisogram approach, the *C/A*-descriptors are pairwise assigned to each pair of *RS*-diastereomers as linked with a brace. Note again that the configuration index *TBPY-5-15* for **13** (or *TBPY-5-16* for $\overline{\mathbf{13}}$) is identical with that for **14** (or that for $\overline{\mathbf{14}}$).

If we obey the conventional methodology, we are force to consider pairs of enantiomers in place of the above-mentioned pairs of *RS*-diastereomers. This convention provides us with an inconsistent result that the pairing of *A* and *C* is not satisfied in each pair (i.e., chirality-unfaithful [12]). Hence, the lowercase letters *c* and *a* are used in place of the uppercase letters *C* and *A*. Moreover, the configuration indices are different, i.e., *TBPY-5-15* vs. *TBPY-5-16*. If we strictly take account of chirality faithfulness [12], we should change the configuration indices *TBPY-5-16* for $\overline{\mathbf{13}}$ ($\overline{\mathbf{14}}$) into *TBPY-5-15*, where the CIP priority a > b > p > $\overline{\text{p}}$ > $\overline{\text{q}}$ (5) is adopted in place of the CIP priority a > b > p > $\overline{\text{p}}$ > q (5) > $\overline{\text{q}}$ (6). However, the feature of being chirality-unfaithful remains unchanged.

Table 2 Single criterion for giving *C/A*-descriptors in the stereoisogram approach

	chirality	*RS*-stereogenicity
Type I	enantiomeric	*RS*-diastereomeric
Type III	enantiomeric	*RS*-diastereomeric
Type V	self-enantiomeric	*RS*-diastereomeric

(chirality-faithfulness)

3.3.3 Single criterion in the stereoisogram approach

As summarized in Table 1, chirality/achirality and *RS*-stereogenicity/*RS*-astereogenicity are independent concepts. The discussions on Type I (Fig. 5), III (Figs. 8 and 10), and V (Fig. 6) have revealed that *C/A*-descriptors are assigned to *RS*-diastereomeric relationships along the *S*-axes of stereoisograms of Type I, III, and V, The capability of naming *C/A*-descriptors is summarized as a single criterion shown in Table 2. This criterion for giving *C/A*-descriptors in inorganic chemistry is consistent with the single criterion for giving *RS*-descriptors in organic chemistry (cf. Table 10.2 of [27]).

Such *C/A*-descriptors as assigned originally by *RS*-diastereomeric relationships (due to *RS*-stereogenicity) should be subsequently reinterpreted in terms of chirality faithfulness in order to specify enantiomeric relationships (due to chirality). This type of reinterpretation in inorganic stereochemistry is parallel to the chirality faithfulness proposed for assigning *RS*-descriptors in organic stereochemistry [12].

On the other hand, the conventional inorganic stereochemistry has adopted an entangled criterion in which *C/A*-descriptors are based on "enantiomeric" relationships (or chirality) for Type I cases, on "diastereomeric" relationships (or "stereogenicity") for Type V cases, and on both "enantiomeric" and "diastereomeric" relationships for Type III cases. This entangled criterion has succeeded to the terminology of organic stereochemistry, in which *RS*-descriptors of the CIP system suffer from confusion due to the misleading differentiation between the terms "enantiomeric" and "diastereomeric".

4 Conclusion

The point group $\mathbf{D}_{3h}$ is extended into the *RS*-stereoisomeric group in order to characterize a trigonal bipyramidal skeleton. Respective trigonal bipyramidal compounds are considered to be controlled by subgroups of the *RS*-stereoisomeric group, which are linked with stereoisograms as diagrammatic devices. Such stereoisograms as assigned to trigonal bipyramidal compounds are discussed in terms of attributive terms (chirality/achirality, *RS*-stereogenicity/*RS*-astereogenicity, and sclerality/asclerality) or equivalently in terms of relational terms (enantiomeric/self-enantiomeric, *RS*-diastereomeric/self-*RS*-diastereomeric, and holantimeric/self-holantimeric). After they are categorized into five types, stereoisograms of Types I, III, and V are shown to be capable of giving *C/A*-descriptors because of their *RS*-stereogenicity (or *RS*-diastereomeric relationships). Thereby, the stereoisogram approach, which has originally been developed to rationalize organic stereochemistry [8,28,29], is clarified to be effective to inorganic stereochemistry.

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