

Pseudo-Point Groups and Subsymmetry-Itemized Enumeration for Characterizing the Symmetries of 1,4-Dioxane and 1,4-Oxathiane Derivatives

Shinsaku Fujita

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606 Japan

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The pseudo-point group $\hat{\mathbf{D}}_{2h}$ is defined for characterizing the symmetries of 1,4-dioxane derivatives. The pseudo-point group $\hat{\mathbf{C}}'_{2v}$ is defined as a subgroup of $\hat{\mathbf{D}}_{2h}$ and is applied to the characterization of the symmetries of 1,4-oxathiane derivatives. The 1,4-dioxane derivatives with a given formula and a given symmetry are enumerated by the unit-subduced-cycle-index approach and compared with the 1,4-oxathiane derivatives. Each derivative enumerated belongs to a subsymmetry of $\hat{\mathbf{D}}_{2h}$ or $\hat{\mathbf{C}}'_{2v}$ so as to be classified into isoenergetic (type I, I', or II) or anisoenergetic (type III or IV). The orbits in the derivative are discussed by the sphericity and chonality terms.

1. INTRODUCTION

The *cis*–*trans* isomerism concerning six-membered saturated rings has been explained in most textbooks with a variety of expedient procedures based on simple polygon (planar) formulas and/or on chair-form formulas. For example, Fessenden–Fessenden's textbook¹ has described that *cis*-1,3-dimethylcyclohexane has an internal plane of symmetry (in the polygon formula or in its chair form) and is a *meso* form, while *cis*-1,2-dimethylcyclohexane is a *meso* form because of the presence of an internal plane of symmetry in the polygon formula (in spite of the absence of an internal plane of symmetry in its chair form). Hendrikson–Cram–Hammond's textbook² has given a complete analysis of substituted cyclohexanes, which is also based on the polygon (planar) formula. Pine's textbook³ has involved a discussion based on chair-form formulas, where *cis*-1,2-dimethylcyclohexane is concluded to be actually a *meso* form. Morrison–Boyd's textbook⁴ has depicted *cis*-1,2-dimethylcyclohexane as a chair-form formula and given its mirror conformation for comparison. Its conclusion is that the *cis*-1,2-dimethylcyclohexane is considered to be not literally a *meso* compound, but it is a nonresolvable racemic modification, which for most practical purposes amounts to the same thing. Solomon's textbook⁵ adopts a planar conformation based on a "time-average" of the various interconverting chair conformations. Mislow has proposed the term *stochastically achiral* to designate a system that contains a chiral molecule paired with its enantiomer and is strictly racemic even when the equilibrium is frozen.⁶ Eliel has proposed the term *residual isomers* for evaluating the number of isomers when conformational changes must be taken into consideration.⁷ Leonard *et al.*^{8,9} and Flurry^{10,11} have adopted related approaches in the enumeration of flexible cyclohexane isomers.

We have recently defined the pseudo-point group $\hat{\mathbf{D}}_{6h}$ for characterizing the stereochemistry of flexible cyclohexane isomers.^{12,13} Each isomer has been concluded to belong to a subgroup of $\hat{\mathbf{D}}_{6h}$. For example, the achirality of the *cis*-

1,2-dimethylcyclohexane is ascribed to the pseudo-point group $\hat{\mathbf{C}}_s$, which is categorized as an achiral and isoenergetic case (type I'). Thus, the terms based on the traditional stereochemistry have been replaced by the terms of the pseudo-point-group approach. More recently, we have reported an application of the pseudo-point-group approach to the symmetry characterization of tetrahydropyran and 1,3-dioxane derivatives, where we have dealt with the pseudo-point group $\hat{\mathbf{C}}'_{2v}$.¹⁴ However, the effectiveness of the pseudo-point-group approach has been examined only by using limited subjects. Conformational changes of 1,4-dioxane derivatives are suitable as further probes for testing the effectiveness, since 1,4-dioxane takes the chair-form conformation.¹⁵

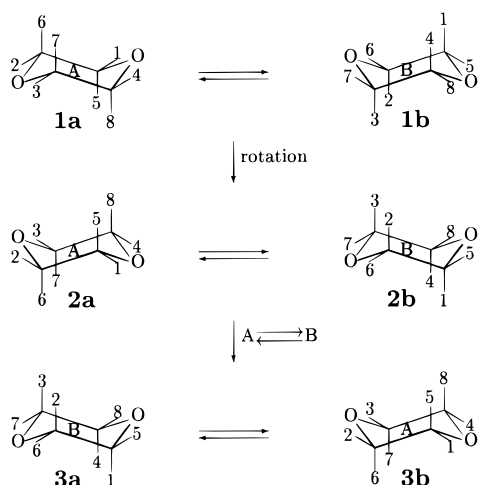
In the present paper, we define the pseudo-point group $\hat{\mathbf{D}}_{2h}$ for characterizing the symmetry of 1,4-dioxane. After 1,4-dioxane derivatives with a given formula and a given symmetry are combinatorially enumerated by the USCI (unit-subduced-cycle-index) approach,^{16,17} the symmetry of each derivative is discussed from the viewpoint of the pseudo-point-group approach. For comparison, we deal with 1,4-oxathiane of $\hat{\mathbf{C}}'_{2v}$ symmetry that can be derived by the desymmetrization of 1,4-dioxane. The present investigation of the pseudo-point group $\hat{\mathbf{C}}'_{2v}$ as a subgroup of the $\hat{\mathbf{D}}_{2h}$ will give a deeper prospect to the characterization of flexible molecules, since the $\hat{\mathbf{C}}'_{2v}$ -group is isomorphic to the $\hat{\mathbf{C}}_{2v}$ group reported previously to treat a global symmetry.¹⁴

2. THEORETICAL FOUNDATIONS AND RESULTS

A. Pseudorotations and Pseudo-Point Group $\hat{\mathbf{D}}_{2h}$. We take a pair of two chair conformers (**1a,b**) into consideration, since many conformational studies have indicated that the chair conformation is preferred for 1,4-dioxane.¹⁵ Although each conformer of 1,4-dioxane belongs to the point-group \mathbf{C}_{2h} ($=\{I, C_2, \sigma_h, i\}$) under fixed conditions, we do not examine the symmetry of each conformer itself. We instead focus our attention on the symmetry of the pair of the two conformers in order to treat the flipping of the 1,4-dioxane

Table 1. Subgroups of $\hat{\mathbf{D}}_{2h}$

subgroup	elements	chirality	energeticity	type	\mathbf{C}_{2h}	$\hat{\mathbf{D}}_2$	$\hat{\mathbf{C}}'_{2v}$
\mathbf{C}_1	{ I }	chiral	anisoenergetic	IV	*	*	*
\mathbf{C}_2	{ I, C_2 }	chiral	anisoenergetic	IV	*	*	
$\hat{\mathbf{C}}_2$	{ $I, \hat{C}_{2(1)}$ }	chiral	isoenergetic	II		*	*
$\hat{\mathbf{C}}_2$	{ $I, \hat{C}_{2(2)}$ }	chiral	isoenergetic	II		*	
\mathbf{C}_s	{ I, σ_h }	achiral	anisoenergetic	III	*		*
\mathbf{C}_s	{ $I, \hat{\sigma}_{v(1)}$ }	achiral	isoenergetic	I'			*
\mathbf{C}_s	{ $I, \hat{\sigma}_{v(2)}$ }	achiral	isoenergetic	I'			
\mathbf{C}_i	{ I, i }	achiral	anisoenergetic	III	*		
$\hat{\mathbf{C}}_{2v}$	{ $I, C_2, \hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)}$ }	achiral	isoenergetic	I'			
$\hat{\mathbf{C}}_{2v}'$	{ $I, \hat{C}_{2(1)}, \sigma_h, \hat{\sigma}_{v(1)}$ }	achiral	isoenergetic	I			*
$\hat{\mathbf{C}}_{2v}'$	{ $I, \hat{C}_{2(2)}, \sigma_h, \hat{\sigma}_{v(2)}$ }	achiral	isoenergetic	I			
\mathbf{C}_{2h}	{ I, C_2, σ_h, i }	achiral	anisoenergetic	III	*		
\mathbf{C}_{2h}	{ $I, \hat{C}_{2(1)}, i, \hat{\sigma}_{v(2)}$ }	achiral	isoenergetic	I			
\mathbf{C}_{2h}	{ $I, \hat{C}_{2(2)}, i, \hat{\sigma}_{v(1)}$ }	achiral	isoenergetic	I			
$\hat{\mathbf{D}}_2$	{ $I, C_2, \hat{C}_{2(1)}, i, \hat{C}_{2(2)}$ }	chiral	isoenergetic	II		*	
$\hat{\mathbf{D}}_{2h}$	{all operations}	achiral	isoenergetic	I			

**Figure 1.** Definition of the operation $\hat{C}_{2(1)}$ for 1,4-dioxane.

ring. It should be noted that, throughout the discussions of this paper, we regard a pair of two conformers as an isomer.

We define a pseudorotation $\hat{C}_{2(1)}$ as a combination of the first rotation (a pair of **1a,b** into a pair of **2a,b**) and the subsequent exchange (**2a,b** into a pair of **3a,b**), as depicted in Figure 1. The $\hat{C}_{2(1)}$ operation corresponds to the permutation representation

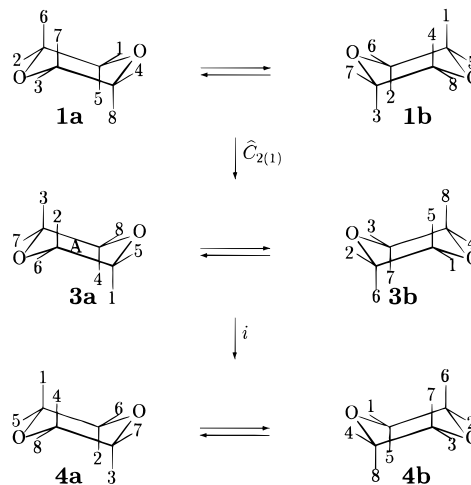
$$\hat{C}_{2(1)} \sim \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} = (1\ 8)(2\ 7)(3\ 6)(4\ 5) \quad (1)$$

by using the numbering shown in Figure 1. As shown by the direct comparison between the pair **1** and the pair **3**, the $\hat{C}_{2(1)}$ operation is presumed to be attributed to the hypothetical rotation axis (the pseudoaxis $\hat{C}_{2(1)}$) perpendicular to the original C_2 axis of the point group \mathbf{C}_{2h} .

By starting from \mathbf{C}_{2h} and the $\hat{C}_{2(1)}$ operation, we construct the set $\hat{\mathbf{D}}_{2h}$ by placing

$$\hat{\mathbf{D}}_{2h} = \mathbf{C}_{2h} + \mathbf{C}_{2h}\hat{C}_{2(1)} = \{I, C_2, \sigma_v, i; \hat{C}_{2(1)}, \hat{C}_{2(2)}, \hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)}\} \quad (2)$$

where the operations of the latter coset are defined by $\hat{C}_{2(1)}$, $I\hat{C}_{2(1)}$, $\hat{C}_{2(2)} = C_2\hat{C}_{2(1)}$, $\hat{\sigma}_{v(1)} = \sigma_v\hat{C}_{2(1)}$, and $\hat{\sigma}_{v(2)} = i\hat{C}_{2(1)}$. For example, Figure 2 indicates the definition of the operation $\hat{\sigma}_{v(2)}$, which is defined by the consecutive application of the $\hat{C}_{2(1)}$ operation and the usual inversion i . The total effect of

**Figure 2.** Definition of the operation $\hat{\sigma}_{v(1)}$ ($=i\hat{C}_{2(1)}$).

the $\hat{\sigma}_{v(2)}$ operation corresponds to the following permutation representation:

$$\hat{\sigma}_{v(2)} \sim \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ 6 & 5 & 8 & 7 & 2 & 1 & 4 & 3 \end{pmatrix} = (1\ 6)(2\ 5)(3\ 8)(4\ 7) \quad (3)$$

by using the numbering shown in Figure 2. The operations generated secondarily by eq 2 are called *pseudorotations*. For memorizing the pseudorotations, we can tentatively consider a planar 1,4-dioxane ring of the \mathbf{D}_{2h} symmetry. For example, the effect of the $\hat{\sigma}_{v(2)}$ operation can be memorized by relating it to the $\sigma_{v(2)}$ operation that stems from the mirror plain perpendicular to the planar 1,4-dioxane ring (\mathbf{D}_{2h}). This convention is allowable by the inspection of the permutation represented by eq 3.

The pseudorotations are classified into proper pseudorotations (e.g. $\hat{C}_{2(1)}$ and $\hat{C}_{2(2)}$) and improper pseudorotations (e.g. $\hat{\sigma}_{v(1)}$ and $\hat{\sigma}_{v(2)}$). Since the set appearing on the right side of eq 2 is closed with respect to their multiplication (consecutive application), the set $\hat{\mathbf{D}}_{2h}$ is concluded to be a group, which is isomorphic to the usual point group \mathbf{D}_{2h} .

B. Subductions of Coset Representations. In the previous paper, pseudopoint groups have been classified in terms of energeticity (isoenergetic and anisoenergetic).¹³ Thus, anisoenergetic groups contain only usual rotations (proper and improper), while isoenergetic groups are characterized by the presence of pseudorotations (proper and improper). The latter groups are denoted by a symbol with

Table 2. Subductions and USCIs for $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$

subduction	USCI
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_1 = 8\mathbf{C}_1/(\mathbf{C}_1)$	s_1^8
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_2 = 4\mathbf{C}_2/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_2 = 4\hat{\mathbf{C}}_2/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_2' = 4\hat{\mathbf{C}}_2'/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_s = 4\mathbf{C}_s/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_s = 4\hat{\mathbf{C}}_s/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_s' = 4\hat{\mathbf{C}}_s'/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_i = 4\mathbf{C}_i/(\mathbf{C}_1)$	s_2^4
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_{2v} = 2\mathbf{C}_{2v}/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_{2v}' = 2\hat{\mathbf{C}}_{2v}'/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_{2v}'' = 2\hat{\mathbf{C}}_{2v}''/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_{2h} = 2\mathbf{C}_{2h}/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_{2h} = 2\hat{\mathbf{C}}_{2h}/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_{2h}' = 2\hat{\mathbf{C}}_{2h}'/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{D}}_2 = 2\hat{\mathbf{D}}_2/(\mathbf{C}_1)$	s_4^2
$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{D}}_{2h} = \hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$	s_8

a hat (e.g., $\hat{\mathbf{D}}_{2h}$). Table 1 lists the subgroups of $\hat{\mathbf{D}}_{2h}$, which are classified into isoenergetic and anisoenergetic groups according to the procedure described in the previous paper.¹³ As a matter of course, the anisoenergetic groups concerning $\hat{\mathbf{D}}_{2h}$ are concluded to be the subgroup \mathbf{C}_{2h} and its subgroups, as shown in the \mathbf{C}_{2h} column of Table 1. On the other hand, pseudo-point groups are alternatively characterized in terms of chirality (chiral and achiral). The characterization due to the chirality is also shown in Table 1, where the subgroups of $\hat{\mathbf{D}}_2$ indicated in the $\hat{\mathbf{D}}_2$ column with an asterisk are concluded to be the sources of the chirality.

In the light of the pseudo-point-group approach, all of the eight atoms at the axial and equatorial positions of 1,4-dioxane are recognized to be equivalent. In other words, they construct one orbit governed by the coset representation $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$, the size of which is equal to $|\hat{\mathbf{D}}_{2h}|/|\mathbf{C}_1| = 8/1 = 8$. This recognition reflects the fact that the axial and equatorial positions are interchangeable under the unfixed condition. On the other hand, the fixed condition can be described by the subgroup \mathbf{C}_{2h} , which is the symmetry of each conformer (see eq 2) or the maximal anisoenergetic group of $\hat{\mathbf{D}}_{2h}$. Precisely speaking, the fixation of the conformation is assigned to the subduction of the coset representation:

$$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_{2h} = 2\mathbf{C}_{2h}/(\mathbf{C}_1) \quad (4)$$

This equation means that the original eight atoms are separated into two of four-membered sets, each of which is governed by the coset representation $\mathbf{C}_{2h}/(\mathbf{C}_1)$. In accord with the subduction, we define the unit subduced cycle index (USCI), s_d^2 , where the subscript represents the size of the orbit ($|\mathbf{C}_{2h}|/|\mathbf{C}_1| = 4/1 = 4$) and the power is the multiplicity of the orbit appearing in the right-hand side of eq 4. The subductions of the orbit $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$ into the respective subgroups of $\hat{\mathbf{D}}_{2h}$ as well as the corresponding USCIs can be obtained by similar procedures. The results are collected in Table 2. Note that the USCIs are mathematically equivalent to the data of Table 10 of ref 18, because $\hat{\mathbf{D}}_{2h}$ is isomorphic to \mathbf{D}_{2h} .

C. Enumeration of 1,4-Dioxane Derivatives. Let us consider the 8 positions of the 1,4-dioxane skeleton, which

Table 3. Numbers of 1,4-Dioxane Isomers

	\mathbf{C}_1	$\hat{\mathbf{C}}_2$, etc. ^a	$\hat{\mathbf{C}}_{2v}$, etc. ^b	$\hat{\mathbf{D}}_{2h}$	tot.
[8,0,0]	0	0	0	1	1
[7,1,0]	1	0	0	0	1
[6,2,0]	0	1	0	0	7
[6,1,1]	7	0	0	0	7
[5,3,0]	7	0	0	0	7
[5,2,1]	21	0	0	0	21
[4,4,0]	7	0	1	0	14
[4,3,1]	35	0	0	0	35
[4,2,2]	42	3	0	0	63
[3,3,2]	70	0	0	0	70

^a Represented for \mathbf{C}_2 , $\hat{\mathbf{C}}_2$, $\hat{\mathbf{C}}_2'$, \mathbf{C}_s , $\hat{\mathbf{C}}_s$, $\hat{\mathbf{C}}_s'$, and \mathbf{C}_i . ^b Represented for $\hat{\mathbf{C}}_{2v}$, $\hat{\mathbf{C}}_{2v}'$, $\hat{\mathbf{C}}_{2v}''$, \mathbf{C}_{2h} , $\hat{\mathbf{C}}_{2h}$, $\hat{\mathbf{C}}_{2h}'$, and $\hat{\mathbf{D}}_2$.

are numbered from 1 to 8 as shown in the pair of **1a** and **1b**. They are governed by $\hat{\mathbf{D}}_{2h}$ through a permutation representation \mathbf{P} , which is equal to $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$. Each element of the representation is a permutation of degree 8, as exemplified in eqs 1 and 3. Since there is one orbit to be considered, the USCIs are used as the subduced cycle indices (SCIs). Thereby, we obtain partial subduced indices (PCIs)^{19,20} of the respective subgroups as follows:

$$\text{PCI}(\mathbf{C}_1, s_d) = 1/8s_1^8 - 7/8s_2^4 + 7/4s_2^4 - s_8 \quad (5)$$

$$\text{PCI}(\mathbf{H}, s_d) = 1/4s_2^8 - 3/4s_2^4 + 1/2s_8 \text{ for } \mathbf{H} = \mathbf{C}_2, \hat{\mathbf{C}}_2, \hat{\mathbf{C}}_2', \mathbf{C}_s, \hat{\mathbf{C}}_s, \hat{\mathbf{C}}_s', \mathbf{C}_i \quad (6)$$

$$\text{PCI}(\mathbf{H}, s_d) = 1/2s_2^4 - 1/2s_8 \text{ for } \mathbf{H} = \hat{\mathbf{C}}_{2v}, \hat{\mathbf{C}}_{2v}', \hat{\mathbf{C}}_{2v}'', \mathbf{C}_{2h}, \hat{\mathbf{C}}_{2h}, \hat{\mathbf{C}}_{2h}', \hat{\mathbf{D}} \quad (7)$$

$$\text{PCI}(\hat{\mathbf{D}}_{2h}, s_d) = s_8 \quad (8)$$

Here each coefficient is adopted from Table 11 of ref 18, because $\hat{\mathbf{D}}_{2h}$ is isomorphic to \mathbf{D}_{2h} . Suppose that two kinds of substituents (X and Y) are substituted for the eight positions of the 1,4-dioxane skeleton. Then, we use the inventory represented by

$$s_d = 1 + x^d + y^d \quad (9)$$

After the inventory (eq 9) is introduced into eqs 5–8, the expansion of each equation produces the generating function for giving the numbers of isomers with a given subgroup. The coefficient of the term $1^k x^l y^m$ of each equation indicates the number of isomers with a given formula ($X^l Y^m$) and with a given symmetry (Table 3). Since the terms $1^k x^l y^m$, $1^l x^m y^k$, etc., have the same coefficient, the set of powers $[k, l, m]$ is used for representing them.

The CI for calculating the total number of isomers with each formula is obtained by summing up the SCIs (eqs 5–8):

$$\text{CI}(\mathbf{D}_{2h}, s_d) = 1/8s_1^8 + 7/8s_2^4 \quad (10)$$

The inventory (eq 9) is introduced into eq 10 to produce the generating function for giving the total numbers of isomers. They are collected in the rightmost column of Table 3. The values are equal to the sums for the respective rows of Table 3. Note that the $\hat{\mathbf{C}}_2$ column of Table 3 represents the seven subgroups of order 2 (\mathbf{C}_2 , $\hat{\mathbf{C}}_2$, $\hat{\mathbf{C}}_2'$, \mathbf{C}_s , $\hat{\mathbf{C}}_s$, $\hat{\mathbf{C}}_s'$, and \mathbf{C}_i) and

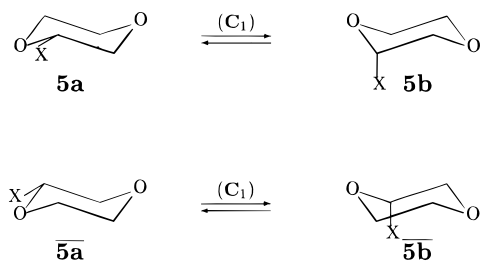


Figure 3. Monosubstituted 1,4-dioxane.

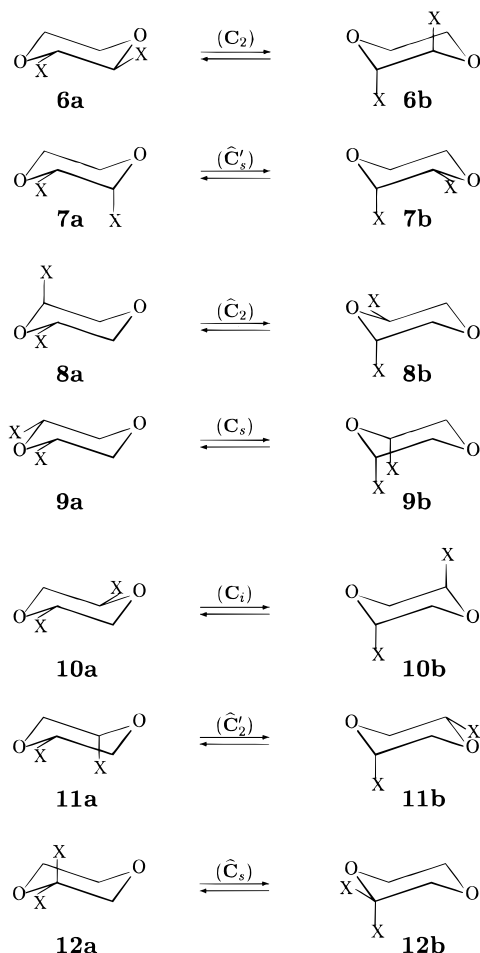
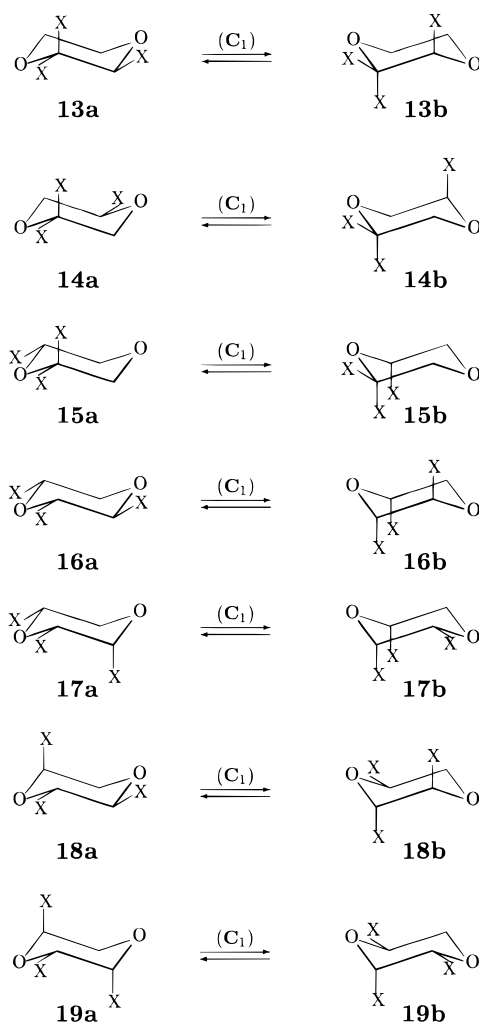


Figure 4. Disubstituted 1,4-dioxanes.

that the \hat{C}_{2v} column of Table 3 represents seven subgroups of order 4 (\hat{C}_{2v} , \hat{C}_{2v}' , \hat{C}_{2v}'' , C_{2h} , \hat{C}_{2h} , \hat{C}_{2h}' , and \hat{D}_2).

D. Symmetry Characterization of Enumerated 1,4-Dioxanes. The [7,1,0] row of Table 3 reveals that there is only one monosubstituted isomer, which belongs to C_1 . The C_1 [7,1,0] isomer (**5**) is illustrated in Figure 3. Since the C_1 [7,1,0] isomer is chiral, there exists the corresponding enantiomeric isomer $\bar{5}$. It should be noted that a pair of two conformers is regarded as an isomer in the present enumeration and that a set of enantiomeric pairs is counted once as an isomer if such a pair is chiral. For simplicity's sake, an arbitrary enantiomeric isomer (e.g. either one of **5** or $\bar{5}$) is depicted as a representative if chiral. The total number of disubstituted isomers is 7, as shown in the [6,2,0] row of Table 3. Each of these isomers belongs to every subsymmetry of order 2, as depicted in Figure 4. Although the *trans*-2,3- (**6**) and 2,6-isomers (**8**) are chiral, they are different in their energeticity. Thus, the former is anisoeenergetic (C_2) and the latter is isoenergetic (\hat{C}_2). This conclusion is easily

Figure 5. Trisubstituted 1,4-dioxanes with C_1 symmetry.

obtained by examining the presence or absence of a hat over the symmetry symbols. On the other hand, the corresponding *cis*-isomers **7** and **9** are achiral, where the former is isoenergetic (\hat{C}_s) and the latter is anisoeenergetic (C_s). The *trans*-2,5-isomer **10** is achiral and anisoeenergetic (C_i), while the *cis*-2,5-isomer **11** is chiral and isoenergetic (\hat{C}_2'). The 2,2-disubstituted isomer **12** is achiral and isoenergetic (\hat{C}_2).

The [5,3,0] row of Table 3 indicates that there exist seven trisubstituted isomers of C_1 symmetry and no isomers of other symmetries. They are depicted in Figure 5. The trisubstituted isomers **13**–**15** contain 2,2-geminal substitution. The remaining substitution of each isomer causes isoenergeticity so as to give an axial–equatorial change. The isomers **16**–**19** are 2,3,6-trisubstituted ones.

The [4,4,0] row of Table 3 indicates that there exists each one isomer belonging to every pseudo-point group of order 4. The corresponding seven isomers are depicted in Figure 6. The isomers **20**–**22**, which contain doubly geminal substitution, are all achiral and isoenergetic. The 2,3,5,6-tetrasubstituted isomers **23** and **25** are achiral and isoenergetic. The remaining 2,3,5,6-tetrasubstituted isomer **24** is achiral and anisoeenergetic, while the isomer **26** is chiral and isoenergetic.

E. Enumeration of 1,4-Oxathiane Derivatives. For characterizing the flipping of a 1,4-oxathiane ring, we define a pseudorotation \hat{C}_2 as depicted in Figure 7. Thereby, we

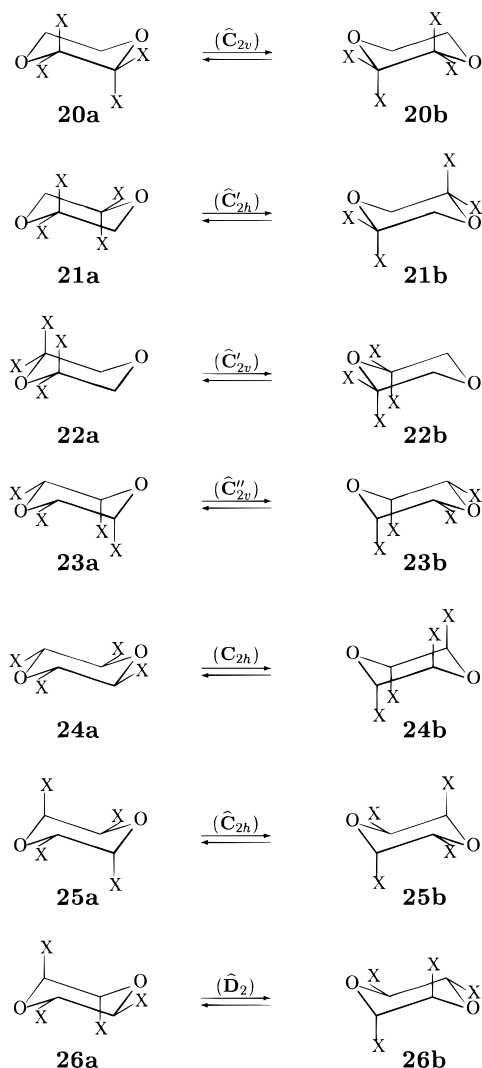


Figure 6. Tetrasubstituted 1,4-dioxanes belonging to the pseudo-point groups of order 4.

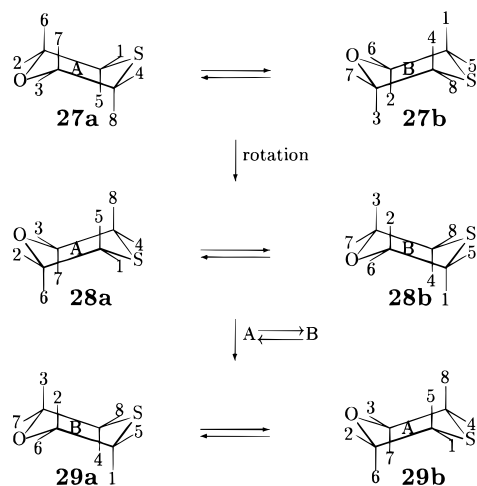


Figure 7. Definition of the operation \hat{C}_2 for 1,4-oxathiane.

are able to construct the pseudo-point group \hat{C}'_{2v} :

$$\hat{C}'_{2v} = C_s + C_s \hat{C}_2 = \{I, \sigma_v, \hat{C}_2, \hat{\sigma}_v\} \quad (11)$$

Since the pseudorotation \hat{C}_2 corresponds to $\hat{C}_{2(1)}$ defined in Figure 7, the group \hat{C}'_{2v} (eq 11) corresponds to the pseudo-point group \hat{C}'_{2v} whose subgroups are shown in the last

Table 4. Numbers of 1,4-Oxathiane Isomers

	C_1	\hat{C}_2	C_s	\hat{C}_s	\hat{C}'_{2v}	tot.
[8,0,0]	0	0	0	0	1	1
[7,1,0]	2	0	0	0	0	2
[6,2,0]	4	2	2	2	0	10
[6,1,1]	14	0	0	0	0	14
[5,3,0]	14	0	0	0	0	14
[5,2,1]	42	0	0	0	0	42
[4,4,0]	14	2	2	2	2	22
[4,3,1]	70	0	0	0	0	70
[4,2,2]	96	6	6	6	0	114
[3,3,2]	140	0	0	0	0	140
type	IV	II	III	I'	I	

column of Table 1. Let us consider the 8 positions of 1,4-oxathiane, which are numbered from 1 to 8 as shown in the pair of **27a,b** and governed by the pseudo-point group \hat{C}'_{2v} through a permutation representation P' . These positions are classified into two orbits in accord with

$$P' = 2\hat{C}'_{2v}/(C_1) \quad (12)$$

This equation indicates that the set of positions 1, 5, 4, and 8 (Figure 7) is governed by one $\hat{C}'_{2v}/(C_1)$, while the set of positions 2, 3, 6, and 7 is governed by the other $\hat{C}'_{2v}/(C_1)$. By starting from eq 12 and the USCI table for the usual point group C_{2v} ,¹⁷ we obtain a set of subduced cycle indices (SCIs), $(s_1^8, s_2^4, s_2^4, s_2^4, s_2^2)$. The set of SCIs is combined with the inverse mark table for the usual point group C_{2v} ¹⁷ to give a set of partial subduced indices (PCIs) for the enumeration of 1,4-oxathiane derivatives:

$$PCI(C_1, s_d) = 1/4 s_1^8 - 3/4 s_2^4 + 1/2 s_4^2 \quad (13)$$

$$PCI(\hat{C}_2, s_d) = 1/2 s_2^4 - 1/2 s_4^2 \quad (14)$$

$$PCI(C_s, s_d) = 1/2 s_2^4 - 1/2 s_4^2 \quad (15)$$

$$PCI(\hat{C}_s, s_d) = 1/2 s_2^4 - 1/2 s_4^2 \quad (16)$$

$$PCI(\hat{C}'_{2v}, s_d) = s_4^2 \quad (17)$$

The inventory (eq 9) is introduced into eqs 13–17, the expansion of which produces the generating functions for giving the numbers of isomers of the respective subgroups. The coefficient of the term $1^k x^l y^m$ of each equation indicates the number of isomers with $X^l Y^m$ and with a given symmetry. The results are listed in Table 4.

The total number of isomers with each formula can be obtained by using the CI that is in turn calculated by the SCIs.

$$CI(\hat{C}'_{2v}, s_d) = 1/4 s_1^8 + 3/4 s_2^4 \quad (18)$$

The introduction of the inventory (eq 9) into eq 18 and the expansion yield the generating function for giving the total numbers of isomers. The results are collected in the rightmost column of Table 4, the values of which are equal to the sums of the respective columns of Table 4.

It is worthwhile to mention the comparison between the present results with those reported for tetrahydropyran and 1,3-dioxane derivatives.¹⁴ The 10 positions of tetrahydropyran and the 8 positions of 1,3-dioxane have been reported

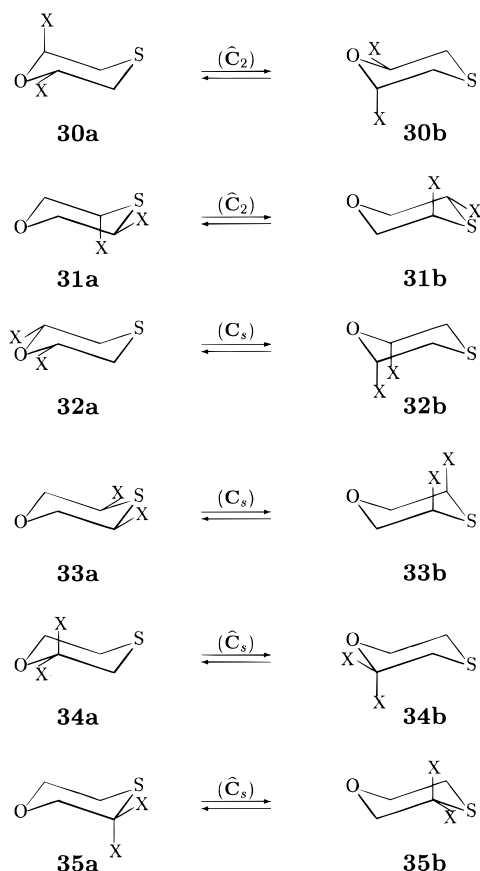


Figure 8. Disubstituted 1,4-oxathianes.

to be governed by respective coset representations according to the following equations:

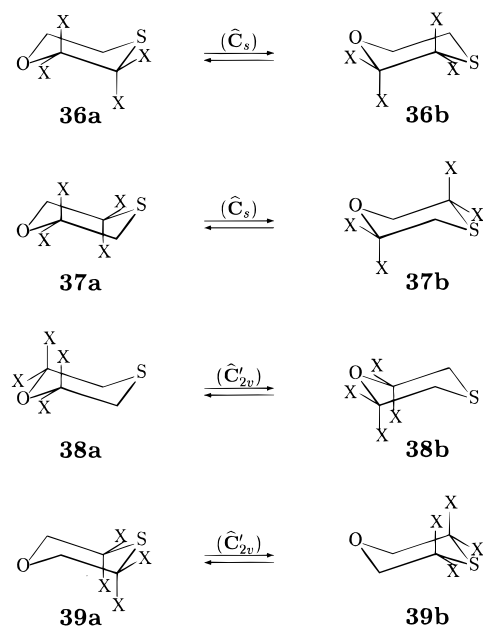
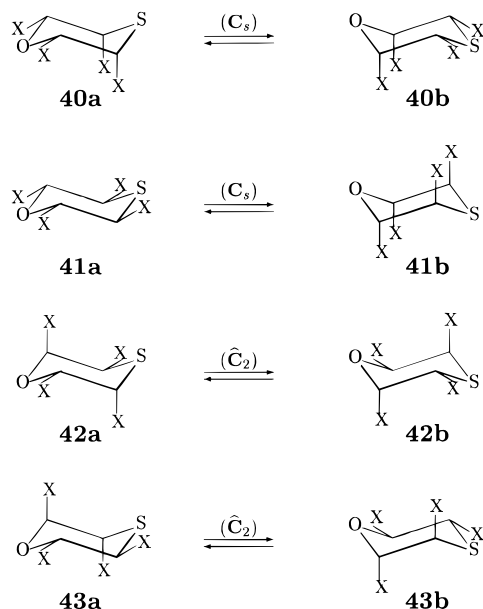
$$P_a = 2\hat{C}_{2v}/(C_1) + \hat{C}_{2v}/(C_s) \quad \text{for tetrahydropyran} \quad (19)$$

$$P_b = \hat{C}_{2v}/(C_1) + 2\hat{C}_{2v}/(C_s) \quad \text{for 1,3-dioxane} \quad (20)$$

Note that the prime symbol is omitted in these cases, since the \hat{C}_{2v} group has been used to represent a global symmetry in the previous paper. On the other hand, the 8 positions of 1,4-oxathiane are governed by coset representations according to eq 12. Hence, the numbers of isomers collected in Table 4 for 1,4-oxathiane derivatives are different from the results reported for tetrahydropyran and 1,3-dioxane derivatives.¹⁴

F. Symmetry Characterization of Enumerated 1,4-Oxathianes. The [6,2,0]-row of Table 4 indicates that there are two disubstituted pairs of \hat{C}_2 symmetry, two pairs of C_s symmetry, and two pairs of \hat{C}_s symmetry. They are depicted in Figure 8. The \hat{C}_{2v} [6,2,0] isomers (30 and 31) of 1,4-oxathiane are related to the \hat{C}_{2v} [6,2,0] isomer (8) of 1,4-dioxane. The desymmetrization of the 1,4-dioxanes into the 1,4-oxathianes (i.e. the replacement of either of the two oxygen atoms in 1,4-dioxane by a sulfur atom), however, maintains the \hat{C}_2 symmetry. The C_s [6,2,0] isomers (32 and 33) can be considered to be generated by the desymmetrization of the C_s [6,2,0] isomer (9) of 1,4-dioxane. The \hat{C}_s -[6,2,0] isomers (34 and 35) are related to the \hat{C}_s [6,2,0] isomer (12) of 1,4-dioxane.

The [4,4,0] row of Table 4 indicates that there appear two isomers for every pseudo-point group of order 2 and of order 4. Figure 9 lists two \hat{C}_s [4,4,0] isomers and two \hat{C}'_{2v} [4,4,0]

Figure 9. Tetrasubstituted 1,4-oxathianes belonging to \hat{C}_s and \hat{C}'_{2v} .Figure 10. Tetrasubstituted 1,4-oxathianes belonging to C_s and \hat{C}_2 .

isomers. The \hat{C}_s [4,4,0] isomers (36) are generated by the desymmetrization of the \hat{C}_{2v} [6,2,0] isomer (20) of 1,4-dioxane. On the other hand, the other \hat{C}_s [4,4,0] isomers (37) are generated by the desymmetrization of the \hat{C}'_{2v} [6,2,0] isomer (21) of 1,4-dioxane. These desymmetrizations literally result in the reduction of the symmetries into their subsymmetries ($\hat{C}'_{2v} \rightarrow \hat{C}_s$, etc.). The \hat{C}'_{2v} [6,2,0] isomers (38 and 39) of 1,4-oxathiane are related to the \hat{C}'_{2v} [6,2,0] isomer (22) of 1,4-dioxane, where the change of heteroatoms provides no reduction of symmetry ($\hat{C}_{2v} \rightarrow \hat{C}'_{2v}$).

Figure 10 lists two C_s [4,4,0] isomers and two \hat{C}_2 [4,4,0] isomers. One of the C_s [4,4,0] isomers (40) is generated by the desymmetrization of the \hat{C}_{2v} [4,4,0] isomer (23) of 1,4-dioxane. The other isomer (41) comes from the desymmetrization of the C_{2h} [4,4,0] isomer (24) of 1,4-dioxane. The \hat{C}_s [4,4,0] isomer (42) is generated by the desymmetrization

Table 5. Types of Flexible Isomers

type	mode	subgroup of $\hat{\mathbf{D}}_{2h}$ (examples illustrated)
I	$A \rightleftharpoons A$	Isoenergetic $\hat{\mathbf{C}}'_{2v}$ (22 , 38 , 39) $\hat{\mathbf{C}}'_{2v}$ (23) $\hat{\mathbf{C}}_{2h}$ (25) $\hat{\mathbf{C}}'_{2h}$ (21) $\hat{\mathbf{D}}_{2h}$ (1)
I'	$Q \rightleftharpoons \bar{Q}$	$\hat{\mathbf{C}}_s$ (12 , 34 , 35 , 36 , 37) $\hat{\mathbf{C}}'_s$ (7) $\hat{\mathbf{C}}'_{2v}$ (20)
II	$Q \rightleftharpoons Q$ ($\bar{Q} \rightleftharpoons \bar{Q}$)	$\hat{\mathbf{C}}_2$ (8 , 30 , 31 , 42 , 43) $\hat{\mathbf{C}}'_2$ (11) $\hat{\mathbf{D}}_2$ (26)
III	$A \rightleftharpoons B$	Anisoenergetic \mathbf{C}_s (9 , 32 , 33 , 40 , 41) \mathbf{C}_i (10) \mathbf{C}_{2h} (24)
IV	$Q \rightleftharpoons R$ ($\bar{Q} \rightleftharpoons \bar{R}$)	\mathbf{C}_1 (5 , 13 , 14 , 15 , 16 , 17 , 18 , 19) \mathbf{C}_2 (6)

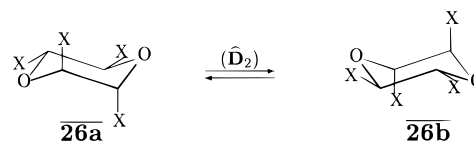
of the $\hat{\mathbf{C}}_{2h}$ [4,4,0] isomer (**25**) of 1,4-dioxane. The $\hat{\mathbf{C}}_2$ [4,4,0] isomer (**43**) of 1,4-oxathiane is related to the $\hat{\mathbf{C}}_{2h}$ [4,4,0] isomer (**25**) of 1,4-dioxane.

3. DISCUSSION

A. Iso- and Anisoenergetic Pairs. The subgroups of the pseudo-point group $\hat{\mathbf{D}}_{2h}$ are classified into two categories (isoenergetic and anisoenergetic) by the procedure described in the previous paper.¹² The categories for the respective subgroups are shown in the energeticity column of Table 1. Such isoenergetic groups are further classified into three types (type I, I', and II), while anisoenergetic ones are divided into two types (type III and IV).¹³ Table 5 lists the definition of types of flexible isomers, where the symbols A and B represent achiral conformers, Q and R represent chiral conformers, and \bar{Q} and \bar{R} represent the corresponding antipodal conformers.

Type I is assigned to a pseudo-point group that involves at least one improper pseudorotation as well as at least one improper (usual) rotation. Among the subgroups of $\hat{\mathbf{D}}_{2h}$, five pseudo-point groups, $\hat{\mathbf{C}}'_{2v}$, $\hat{\mathbf{C}}''_{2v}$, $\hat{\mathbf{C}}_{2h}$, $\hat{\mathbf{C}}'_{2h}$, and $\hat{\mathbf{D}}_{2h}$, are concluded to be type I. The presence of an improper pseudorotation and of an improper (usual) rotation indicates that the conformers of a pair of type I are homomeric and achiral in themselves, as denoted by the symbol A (Table 5). For example, the 2,2,6,6-tetrasubstituted 1,4-dioxane (**22**) belongs to $\hat{\mathbf{C}}'_{2v}$ symmetry and is classified into type I. Other examples are collected in Table 5.

Type I' comes from a pseudo-point group that involves at least one improper pseudorotation but no improper rotation. Each conformer (Q) of type I' is chiral because of the absence of improper rotation (Table 5). In agreement with the presence of at least one improper pseudorotation, the chiral conformer (Q) undergoes racemization to give its enantiomer (\bar{Q}). For example, the conformers **20a,b** are chiral and enantiomeric to each other. The resulting pair (**20**) belongs to $\hat{\mathbf{C}}_{2v}$ symmetry and is classified into type I'. Since any pairs of type I' are "stochastically achiral" in terms of Mislow's definition,⁶ the term "stochastically achiral" can be replaced by the more rigorous term type I' through pseudo-point groups such as $\hat{\mathbf{C}}_{2v}$.

**Figure 11.** Enantiomeric pair of **26** with $\hat{\mathbf{D}}_2$ symmetry.

Type II corresponds to a pseudo-point group that involves at least one proper pseudorotation but contains neither improper pseudorotation nor improper rotation. The two conformers (Qs) of a pair of type II are chiral and homomeric to each other. Hence, there exists the corresponding enantiomeric pair of \bar{Q} s (Table 5). For example, the pair **26** has the corresponding enantiomeric pair **26** shown in Figure 11.

Type III is ascribed to a pseudo-point group that involves at least one improper rotation but contains neither proper nor improper pseudorotations. As a result, the two conformers of a pair of type III are both achiral and different to each other. For example, the pair **24** belongs to the \mathbf{C}_{2h} symmetry and is classified into type III. It should be noted that the pseudo-point group of type III is a usual achiral point group, which also controls the respective conformers contained in the pair under fixed conditions.

Type IV is attributed to a pseudo-point group that involves at least one proper rotation but contains neither improper rotations nor any pseudorotations. In other words, the pseudo-point group of type IV is a usual chiral point group. As a result, the two conformers of a pair of type IV are both chiral and different from each other. Hence, there exists the corresponding antipode. This has been already illustrated in Figure 3.

B. Cis–Trans Isomerism. In this section, we discuss the cis–trans isomerism of 1,4-dioxane and 1,4-oxathiane rings from the viewpoint of flexible-isomer types (I, I', II, III, IV).

We first discuss the *cis*-2,3-disubstituted 1,4-dioxane (**7**), since this is in the same situation as *cis*-1,2-dimethylcyclohexane described in the Introduction. The isomer **7** belongs to $\hat{\mathbf{C}}'_s$, which is classified into type I' (Table 5). Obviously, one conformer **7a** is enantiomeric to the other conformer **7b** in accord with the general mode ($Q \rightleftharpoons \bar{Q}$). The essential aspect derived from the present approach is the introduction of a hypothetical symmetry element, $\hat{\sigma}_{v(2)}$ (Table 1 and Figure 2), which is formulated as an improper pseudorotation. Thereby, the conventions adopted in various textbooks (see Introduction) can be replaced by the present terminology.

The next object is the *cis*-2,6-disubstituted 1,4-dioxane (**9**), which is in the same situation as *cis*-1,3-dimethylcyclohexane. The isomer **9** belongs to \mathbf{C}_s , which is classified into type III (Table 5). Note that the reflection σ_h contained in \mathbf{C}_s is a usual symmetry operation. As a result of the anisoenergetic character of type III, one conformer **9a** is different (diastereomeric) from the other conformer **9b**, which agrees with the general mode ($A \rightleftharpoons B$). The *cis*-2,6- (**32**) and the *cis*-3,5-disubstituted 1,4-oxathianes (**33**) behave in the same manner, since they belong to \mathbf{C}_s that is classified into type III (Table 5).

Geminal disubstituted 1,4-dioxanes (**12**) and 1,4-oxathianes (**34** and **35**) belong to $\hat{\mathbf{C}}_s$ (type I'), while 1,1-disubstituted cyclohexanes belong to $\hat{\mathbf{C}}'_{2v}$ (type I). The behavior of the former set of heterocycles stems from the desymmetrization

Table 6. Sphericities and Chronalities for $\hat{\mathbf{D}}_{2h}$ and $\hat{\mathbf{C}}'_{2v}$

group	orbit	size	sphericity	chronality
$\hat{\mathbf{D}}_{2h}$	$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$	$ \hat{\mathbf{D}}_{2h}/\mathbf{C}_1 = 8/1 = 8$	enantiospheric	enantiochronal
	$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_2)$	$ \hat{\mathbf{D}}_{2h}/\mathbf{C}_2 = 8/2 = 4$	enantiospheric	enantiochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}_2)$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}_2 = 8/2 = 4$	enantiospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}'_2)$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}'_2 = 8/2 = 4$	enantiospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_s)$	$ \hat{\mathbf{D}}_{2h}/\mathbf{C}_s = 8/2 = 4$	homospheric	enantiochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}_s)$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}_s = 8/2 = 4$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}'_s)$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}'_s = 8/2 = 4$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_i)$	$ \hat{\mathbf{D}}_{2h}/\mathbf{C}_i = 8/2 = 4$	homospheric	enantiochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}_{2v})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}_{2v} = 8/2 = 4$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}'_{2v})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}'_{2v} = 8/2 = 4$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}''_{2v})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}''_{2v} = 8/2 = 4$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_{2h})$	$ \hat{\mathbf{D}}_{2h}/\mathbf{C}_{2h} = 8/2 = 4$	homospheric	enantiochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}_{2h})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}_{2h} = 8/4 = 2$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{C}}'_{2h})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{C}}'_{2h} = 8/4 = 2$	homospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{D}}_2)$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{D}}_2 = 8/4 = 2$	enantiospheric	homochronal
	$\hat{\mathbf{D}}_{2h}/(\hat{\mathbf{D}}_{2h})$	$ \hat{\mathbf{D}}_{2h}/\hat{\mathbf{D}}_{2h} = 8/8 = 1$	homospheric	homochronal
$\hat{\mathbf{C}}'_{2v}$	$\hat{\mathbf{C}}'_{2v}/(\mathbf{C}_1)$	$ \hat{\mathbf{C}}'_{2v}/\mathbf{C}_1 = 4/1 = 4$	enantiospheric	enantiochronal
	$\hat{\mathbf{C}}'_{2v}/(\hat{\mathbf{C}}_2)$	$ \hat{\mathbf{C}}'_{2v}/\hat{\mathbf{C}}_2 = 4/2 = 2$	enantiospheric	homochronal
	$\hat{\mathbf{C}}'_{2v}/(\mathbf{C}_s)$	$ \hat{\mathbf{C}}'_{2v}/\mathbf{C}_s = 4/2 = 2$	homospheric	enantiochronal
	$\hat{\mathbf{C}}'_{2v}/(\hat{\mathbf{C}}_s)$	$ \hat{\mathbf{C}}'_{2v}/\hat{\mathbf{C}}_s = 4/2 = 2$	homospheric	homochronal
	$\hat{\mathbf{C}}'_{2v}/(\hat{\mathbf{C}}'_{2v})$	$ \hat{\mathbf{C}}'_{2v}/\hat{\mathbf{C}}'_{2v} = 4/4 = 1$	homospheric	homochronal

due to heteroatoms or, in other words, from the absence of the usual improper rotation σ_h .

C. Sphericity and Chronality. The sphericity terms (enantiospheric, homospheric, and hemispheric) have been proposed for characterizing the symmetries of rigid molecules²¹ and for describing flexible cyclohexanes.¹³ In addition, the chronality terms (enantiochronal, homochronal, and hemichronal) have been proposed by characterizing the flipping processes of flexible compounds.¹³ Table 6 lists the sphericities and chronalities of the coset representations to be considered for the pseudo-point groups $\hat{\mathbf{D}}_{2h}$ and $\hat{\mathbf{C}}'_{2v}$.

The orbit of the eight positions in 1,4-dioxane is enantiospheric (Table 6), since it is governed by the coset representation $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$. This means that the orbit can be separated into two halves in a chiral environment. Suppose that 1,4-dioxane (**1**) is placed under an appropriate chiral condition (e.g. in the presence of a chiral reagent). Then, the eight atoms (for the numbering, see Figure 1) are divided in accord with the subduction into $\hat{\mathbf{D}}_2$, since $\hat{\mathbf{D}}_2$ is the maximal chiral subgroup of $\hat{\mathbf{D}}_{2h}$. Table 2 gives

$$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{D}}_2 = 2\hat{\mathbf{D}}_2/(\mathbf{C}_1) \quad (21)$$

This result corresponds to the separation represented schematically as follows:

$$\underbrace{\{1, 2, 3, 4, 5, 6, 7, 8\}}_{\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)} \xrightarrow{\downarrow \hat{\mathbf{D}}_2} \underbrace{\{1, 2, 7, 8\}}_{\hat{\mathbf{D}}_2/(\mathbf{C}_1)} + \underbrace{\{3, 4, 5, 6\}}_{\hat{\mathbf{D}}_2/(\mathbf{C}_1)} \quad (22)$$

Hence, one half $\{1, 2, 7, 8\}$ governed by $\hat{\mathbf{D}}_2/(\mathbf{C}_1)$ is unequivalent to the other half $\{3, 4, 5, 6\}$ governed by $\hat{\mathbf{D}}_2/(\mathbf{C}_1)$ under the chiral conditions. It should be noted the 1,4-dioxane ring is *not* fixed in the present situation. Thus, each of the halves, $\{1, 2, 7, 8\}$ or $\{3, 4, 5, 6\}$, is an equivalence class (orbit) of the $\hat{\mathbf{D}}_2$ group so as to contain equatorial and axial atoms.

The desymmetrization process due to eq 21 (or eq 22) can be visualized by producing derivatives. For example, each atom of the set $\{3, 4, 5, 6\}$ is replaced by the atom X to give the pair **26** of the $\hat{\mathbf{D}}_2$ symmetry. On the other hand,

the replacement at the set $\{1, 2, 7, 8\}$ produces the enantiomeric pair **26** shown in Figure 11.

The same $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$ orbit of the eight positions in 1,4-dioxane is alternatively recognized as being enantiochronal (Table 6). This means that the orbit can be separated into two halves under a fixed condition (e.g. at a low temperature). As a result, the eight atoms are divided in accord with the subduction into \mathbf{C}_{2h} (eq 4), since \mathbf{C}_{2h} is the maximal anisoenergetic subgroup of $\hat{\mathbf{D}}_{2h}$. It follows that the separation is represented schematically as follows:

$$\underbrace{\{1, 2, 3, 4, 5, 6, 7, 8\}}_{\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)} \xrightarrow{\downarrow \mathbf{C}_{2h}} \underbrace{\{1, 2, 3, 4\}}_{\mathbf{C}_{2h}/(\mathbf{C}_1)} + \underbrace{\{5, 6, 7, 8\}}_{\mathbf{C}_{2h}/(\mathbf{C}_1)} \quad (23)$$

Hence, one half $\{1, 2, 3, 4\}$ governed by $\mathbf{C}_{2h}/(\mathbf{C}_1)$ corresponds to the equatorial positions of the conformer **1a** (or to the axial positions of the conformer **1b**), while the other half $\{5, 6, 7, 8\}$ governed by $\mathbf{C}_{2h}/(\mathbf{C}_1)$ corresponds to the axial positions of the conformer **1a** (or to the equatorial positions of the conformer **1b**). Hence, the eight hydrogen atoms of 1,4-dioxane show an average signal under unfixed condition, while they are capable of showing two signals of equal intensity under fixed condition.

It should be emphasized that the mode of separation due to eq 22 is different from that due to eq 23 in agreement with the different external effects. To take account of the cooperation of the chiral effect and the fixing one, we consider the intersection of $\hat{\mathbf{D}}_2$ and \mathbf{C}_{2h} :

$$\hat{\mathbf{D}}_2 \cap \mathbf{C}_{2h} = \mathbf{C}_2 \quad (24)$$

Then, the subduction of the $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$ orbit into \mathbf{C}_2 is represented by

$$\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_2 = 4\mathbf{C}_2/(\mathbf{C}_1) \quad (25)$$

as shown in Table 2. In accord with this subduction, the $\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)$ orbit is divided into four orbits governed by $\mathbf{C}_2/(\mathbf{C}_1)$:

$$\underbrace{\{1, 2, 3, 4, 5, 6, 7, 8\}}_{\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1)} \xrightarrow{\downarrow \mathbf{C}_2} \underbrace{\{1, 2\}}_{\mathbf{C}_2/(\mathbf{C}_1)} + \underbrace{\{3, 4\}}_{\mathbf{C}_2/(\mathbf{C}_1)} + \underbrace{\{5, 6\}}_{\mathbf{C}_2/(\mathbf{C}_1)} + \underbrace{\{7, 8\}}_{\mathbf{C}_2/(\mathbf{C}_1)} \quad (26)$$

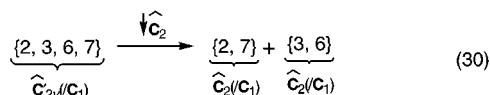
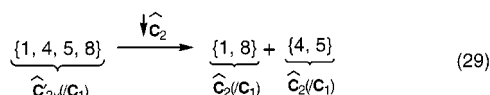
The right-hand side of eq 26 indicates the mode of separation under a chiral and fixed condition. Obviously, the desymmetrization represented by $\hat{\mathbf{D}}_{2h} \rightarrow \hat{\mathbf{D}}_2 \rightarrow \mathbf{C}_2$ gives an effect equivalent to the one resulting from the desymmetrization of $\hat{\mathbf{D}}_{2h} \rightarrow \mathbf{C}_{2h} \rightarrow \mathbf{C}_2$:

$$(\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \hat{\mathbf{D}}_2) \downarrow \mathbf{C}_2 = (\hat{\mathbf{D}}_{2h}/(\mathbf{C}_1) \downarrow \mathbf{C}_{2h}) \downarrow \mathbf{C}_2 \quad (27)$$

The eight positions in 1,4-oxathiane are divided into two $\hat{\mathbf{C}}'_{2v}/(\mathbf{C}_1)$ orbits (i.e. $\{1, 4, 5, 8\}$ and $\{2, 3, 6, 7\}$ in the pair **27**) in accord with eq 12. Since each of these orbits is enantiospheric, it is further divided into two halves under a chiral condition. This division is controlled by the subduction

$$\hat{\mathbf{C}}'_{2v}/(\mathbf{C}_1) \downarrow \hat{\mathbf{C}}_2 = 2\hat{\mathbf{C}}_2/(\mathbf{C}_1) \quad (28)$$

since the maximal chiral group of \hat{C}_{2v}' is \hat{C}_2 . This result corresponds to the separation represented schematically as follows:

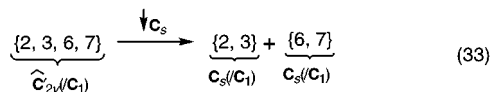
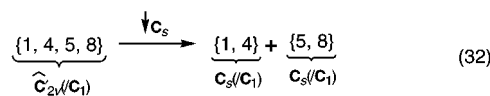


The right-hand sides of eqs 29 and 30 indicate the modes of separation under a chiral (and unfixed) condition. Each mode is related to the derivation of **30** (or **31**) by the replacement of {3, 6} (or {4, 5}) by Xs.

From the viewpoint of chronality, each of these $\hat{C}_{2v}'(\hat{C}_1)$ orbits is enantiochronal. Hence, it is further divided to give another set of two halves under a fixed condition. Since the maximal anisoenergetic group of \hat{C}_{2v}' is C_s , the division is controlled by the subduction

$$\hat{C}_{2v}'(\hat{C}_1) \downarrow C_s = 2C_s(\hat{C}_1) \quad (31)$$

Hence, the division is schematically represented as follows:



The right-hand sides of eqs 32 and 33 indicate the modes of separation under a fixed condition. This separation is related to the derivation of **32** (or **33**) by the replacement of {2,3} (or {1,4}) by Xs.

The behaviors of homospheric orbits and of homochronal orbits are exemplified also by the flipping of 1,4-dioxane. The four carbon atoms of 1,4-dioxane construct an orbit governed by $\hat{D}_{2h}(\hat{C}_s)$. As shown in Table 6, this orbit is homospheric and homochronal. The $\hat{D}_{2h}(\hat{C}_s)$ orbit is subduced into \hat{D}_2 and into C_{2h} to give the following results:

$$\hat{D}_{2h}(\hat{C}_s) \downarrow \hat{D}_2 = \hat{D}_2(\hat{C}_1) \quad (34)$$

$$\hat{D}_{2h}(\hat{C}_s) \downarrow C_{2h} = C_{2h}(\hat{C}_1) \quad (35)$$

The homosphericity of the $\hat{D}_{2h}(\hat{C}_s)$ orbit is characterized by eq 34. Hence, no division of the orbit occurs under a chiral condition. On the other hand, eq 35 indicates the behavior of the homochronal $\hat{D}_{2h}(\hat{C}_s)$ orbit. Thus, the four carbons of 1,4-dioxane are equivalent to each other under fixed conditions.

The pair **24** has an orbit of four Xs (or another orbit of the remaining hydrogens), which shows the hemichronality due to $C_{2h}(\hat{C}_1)$. When we substitute a fluorine atom for each X, these four fluorine atoms are predicted to show an

average signal under unfixed condition, while they are capable of showing two signals of unequal intensities under fixed condition.

4. CONCLUSION

The pseudo-point-group approach is effective to characterize the symmetries of 1,4-dioxanes and 1,4-oxathianes. After the combinatorial enumeration of their derivatives, the symmetries of the resulting derivatives are discussed in terms of chirality and energeticity. The symmetries of orbits (equivalence classes) are successfully discussed by means of the sphericity terms and the chronality terms.

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