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Formulation of Isomeric Reaction Types and Systematic Enumeration of Six-Electron Pericyclic Reactions

SHINSAKU FUJITA

Research Laboratories, Ashigara, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa, 250-01 Japan

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Reaction-center graphs (RCG), reaction graphs (RG), and basic reaction graphs (BRG), all of which are defined as substructures of imaginary transition structures (ITS), represent reaction types of various levels in ascending order of generality. The concept of isomeric RCGs is introduced for the systematic enumeration of the reaction types. The enumeration of six-electron pericyclic reactions is thereby translated into the counting of hexagonal and pentagonal RCGs. This issue is solved by regarding the hexagonal or pentagonal RCG as a derivative of a parent RG and by using Pólya's theorem generalized to be applicable to the cases in which the vertices are obliged to have different modes of substitution.

The systematic enumeration of reaction types is fundamentally important in providing organic chemistry with a logical format as well as in generating new possible reactions theoretically.[1] However, few approaches have succeeded, mainly because of three related factors. The first one is the absence of consistent definitions of reaction types.[2,3] The second factor is the deficiency of the strategy that realizes complete enumeration. The third factor is the lack of mathematical methods of verification.

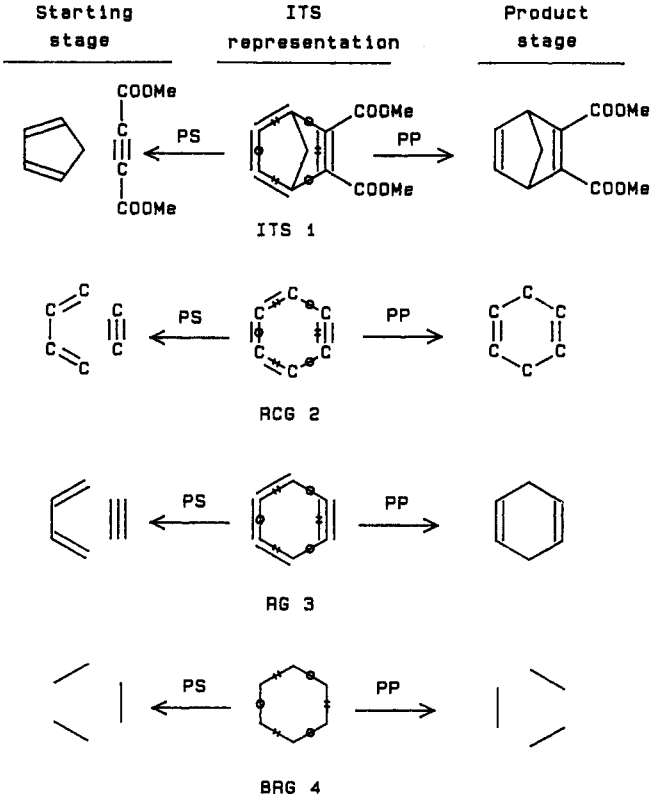
In previous papers,[4b,c] we have presented the concepts of *reaction graph* (RG) and *reaction-center graph* (RCG) with respect to the first factor. As for the second and third factors, we have already discussed the enumeration of the RGs. This enumeration, however, has considered only the modes of bond switching and not the variety of reacting atoms. The latter issue requires the enumeration of the RCGs, which will be discussed in the present paper.

FORMULATION OF REACTION TYPES

The unequivocal definitions of reaction types is necessary to the counting of them. Scheme I summarizes the representation, already introduced in the previous papers of this series,[5] based on the concept of *imaginary transition structure* (ITS). ITS **1** is obtained by superposing the left-hand side onto the right-hand side of the corresponding reaction diagram and by distinguishing the bonds into out- (-//-), in- (-⊖-), and par-bonds (—).

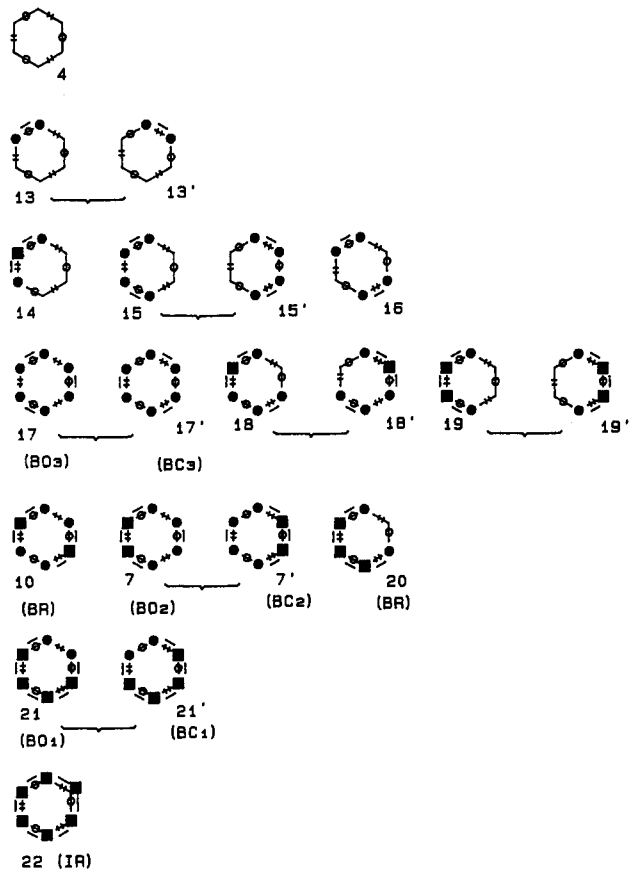
Each bond of a given ITS is called an *imaginary bond* (or an ITS bond) and consists of out-, in-, and/or par-bonds.[6] If we consider the imaginary bond as a figure, we can interpret the figure in various ways. In a chemical sense, the imaginary bond ⊖ represents an initial single bond that changes into a double bond. From another point of view (i.e., apart from a chemical meaning tentatively), we regard the imaginary bond also as a combination of a par-bond and an in-bond or as an in-bond modified by a single par-bond. Similarly, the imaginary bond ≡, which chemically indicates a triple bond converted into a double bond, is considered to be a combination of two par-bonds and one out-bond as well as an out-bond (-//-) modified by a double par-bond (=). These flexible modes of interpretation open the enumeration to a new treatment.

Scheme I



0095-2338/89/1629-0022$01.50/0

Table I. Parent Reaction Graphs of Hexagonal Class[a-c]



[a] The position marked ■ has a minimum valency of $v = 3$. The position marked ● has a minimum valency of $v = 2$. The unmarked position has a minimum valency of $v = 1$. [b] Each couple linked with a brace is a reaction pair (an RG pair). The isolated RG is a self-reaction pair. [c] BO_p is a bridge of ring opening of order p. BC_q is a bridge of ring closure of order q. BR is a bridge of rearrangement.

Table II. Cycle Indices Based on the Parent BRs of Hexagonal Class

RG[a]	symmetry	cycle index[b]	eq
4	D_3	G: $(1/6)(c_1^6 + 3c_2^3 + 2c_3^2)$	1
4s	D_6	P: $(1/12)(c_1^6 + 3c_1^2c_2^2 + 4c_2^3 + 2c_3^2 + 2c_6)$	2
13, 13′	C_2	G: $(1/2)(b_1^2c_1^4 + b_2c_2^2)$	3
14	C_1	G: $a_1b_1^2c_1^3$	4
14s	C_2	P: $(1/2)(a_1b_1^2c_1^3 + a_1b_2c_1c_2)$	5
15, 15′	C_2	G: $(1/2)(b_1^4c_1^2 + b_2^2c_2)$	6
16	C_2	G: $(1/2)(b_1^4c_1^2 + b_2^2c_2)$	7
16s	D_2	P: $(1/4)(b_1^4c_1^2 + b_2^2c_1^2 + 2b_2^2c_2)$	8
17, 17′	D_3	G: $(1/6)(b_1^6 + 3b_2^3 + 2b_3^2)$	9
18, 18′	C_1	G: $a_1b_1^4c_1$	10
19, 19′	C_2	G: $(1/2)(a_1^2b_1^2c_1^2 + a_2b_2c_2)$	11
10	C_2	G: $(1/2)(a_1^2b_1^4 + a_2b_2^2)$	12
10s	D_2	P: $(1/4)(a_1^2b_1^4 + a_1^2b_2^2 + 2a_2b_2^2)$	13
7, 7′	C_2	G: $(1/2)(a_1^2b_1^4 + a_2b_2^2)$	14
20	C_1	G: $a_1^3b_1^2c_1$	15
20s	C_2	P: $(1/2)(a_1^3b_1^2c_1 + a_1a_2b_2c_1)$	16
21, 21′	C_2	G: $(1/2)(a_1^4b_1^2 + a_2^2b_2)$	17
22	D_3	G: $(1/6)(a_1^6 + 3a_2^3 + 2a_3^2)$	18
22s	D_6	P: $(1/12)(a_1^6 + 3a_1^2a_2^2 + 4a_2^3 + 2a_3^2 + 2a_6)$	19

[a] The parent RGs are collected in Table I. [b] G: a cycle index for counting RCGs. P: a cycle index for counting RCG pairs.

Scheme II

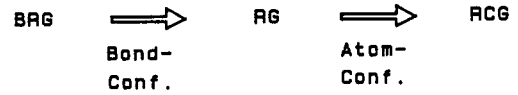
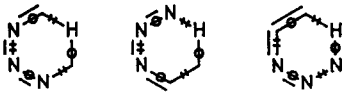
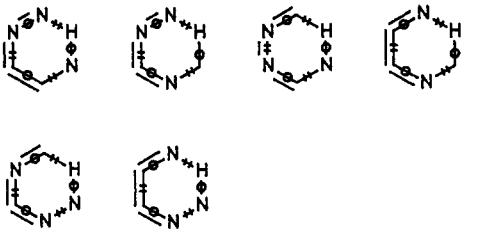
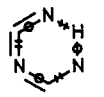


Table III. Isomeric RCGs with N_3H Based on the Parent RG **19**[a]

substitution mode[b]	RCG isomer (reaction type)
V	
L	
Δ	

[a] The number of isomeric RCGs is obtained as the coefficient of u^3w of eq 23. [b] The notation of a substitution mode is the same as described in the literature.[15]

The *reaction-center graph* (RCG) **2**[4b] is the subgraph of ITS **1** that contains all the reaction centers of **1** as well as the imaginary bonds between them. The *reaction graph* (RG) **3**, which has a more generic meaning, is created by neglecting the variation of atoms in RCG **2**. The *basic reaction graph* (BRG) **4** is a furthermore abstract subgraph, which arises from the deletion of the par-bonds modifying RG **3**.

In the ITS approach, *we regard these expressions* (**1**–**4**) *as* (*extended*) *structures or substructures that involve three kinds of bonds. We can thereby manipulate them as figures and then add their chemical meanings.*

In the light of the concept of reaction graphs and reaction-center graphs, we regard two reaction types as identical with one another if there exists an appropriate symmetry operation that can superpose the RCG (or RG) of the one reaction type onto the RCG (or RG) of the other.

METHODOLOGY OF ENUMERATION

Definition of Isomeric Reaction Types as Isomeric Reaction-Center Graphs (RCG Isomers). A reaction graph (RG) is a derivative of a basic reaction graph (BRG) with an appropriate bond configuration (Scheme II).[7] A reaction-center graph (RCG) is in turn regarded as a derivative of the RG with an appropriate atom configuration.[7] The latter step of Scheme II corresponds to the enumeration of RCGs presented in this paper.

Two different RCGs are defined as being *isomeric* (1) when they arise from a common parent RG and have the same set of atoms on their vertices or alternatively (2) when they come from a common parent BRG and have the same set of par-bonds on their edges as well as the same set of atoms on their vertices. Both of the definitions formulate the enumeration of more specific reaction types as the counting of RCGs. We adopt the former definition in the present paper. We will discuss the enumeration based on the latter definition elsewhere.

Scheme III illustrates the present methodology of enumeration. RCG **2** is a derivative of RG **3**, in which the vertices (nodes) are substituted by six carbon atoms. Since this case selects RG **3** as a parent, there are no other isomers than RCG **2**. In terms of the alternative definition that selects BRG **4**

Table IV. Enumeration of Reaction Types Based on Various Parent RGs[a]

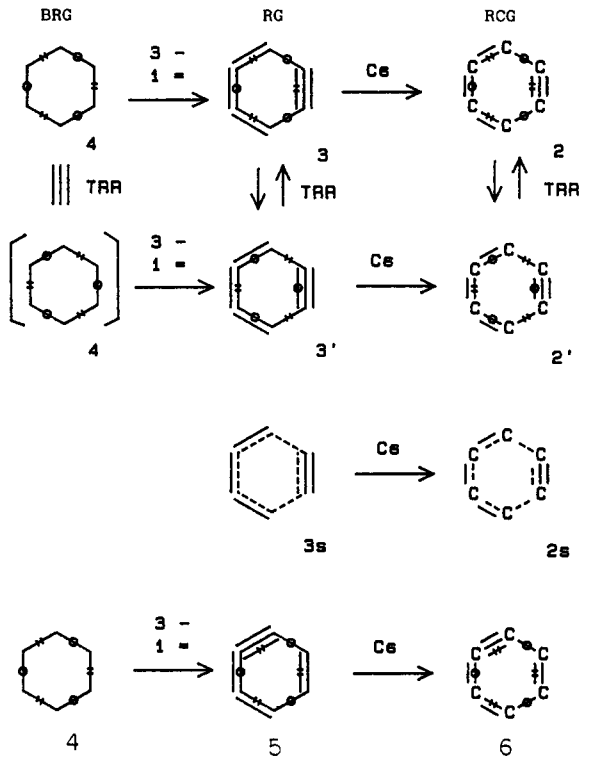
			no. of RCGs (RCG pairs)												
i	*j*	*k*	**4 (4s)**	**13, 13′**	**14 (14s)**	**15, 15′**	**16 (16s)**	**17, 17′**	**18, 18′**	**19, 19′**	**10 (10s)**	**7, 7′**	**20 (20s)**	**21, 21′**	**22 (22s)**
0	0	0	1 (1)	1	1 (1)	1	1 (1)	1	1	1	1 (1)	1	1 (1)	1	1 (1)
1	0	0	1 (1)	3	6 (4)	3	3 (2)	1	6	3	3 (2)	3	6 (4)	3	1 (1)
0	1	0	1 (1)	3	5 (3)	3	3 (2)	1	5	2	2 (1)	2	3 (2)	1	0 (0)
2	0	0	4 (3)	9	15 (9)	9	9 (6)	4	15	9	9 (6)	9	15 (9)	9	4 (3)
1	1	0	5 (3)	15	25 (13)	15	15 (8)	5	25	10	10 (5)	10	15 (8)	5	0 (0)
0	2	0	4 (3)	9	10 (6)	9	9 (6)	4	10	4	4 (3)	4	3 (2)	1	0 (0)
3	0	0	4 (3)	10	20 (12)	10	10 (6)	4	20	10	10 (6)	10	20 (12)	10	4 (3)
2	1	0	10 (6)	30	50 (26)	30	30 (16)	10	50	20	20 (10)	20	30 (16)	10	0 (0)
1	2	0	10 (6)	30	40 (22)	30	30 (16)	10	40	12	12 (7)	12	12 (7)	2	0 (0)
0	3	0	4 (3)	10	10 (6)	10	10 (6)	4	10	2	2 (1)	2	1 (1)	0	0 (0)
4	0	0	4 (3)	9	15 (9)	9	9 (6)	4	15	9	9 (6)	9	15 (9)	9	4 (3)
3	1	0	10 (6)	30	50 (26)	30	30 (16)	10	50	20	20 (10)	20	30 (16)	10	0 (0)
2	2	0	18 (11)	48	60 (32)	48	48 (27)	18	60	20	20 (12)	20	18 (10)	4	0 (0)
1	3	0	10 (6)	30	30 (16)	30	30 (16)	10	30	6	6 (3)	6	3 (2)	0	0 (0)
0	4	0	4 (3)	9	5 (3)	9	9 (6)	4	5	1	1 (1)	1	0 (0)	0	0 (0)
5	0	0	1 (1)	3	6 (4)	3	3 (2)	1	6	3	3 (2)	3	6 (4)	3	1 (1)
4	1	0	5 (3)	15	25 (13)	15	15 (8)	5	25	10	10 (5)	10	15 (8)	5	0 (0)
3	2	0	10 (6)	30	40 (22)	30	30 (16)	10	40	12	12 (7)	12	12 (7)	2	0 (0)
2	3	0	10 (6)	30	30 (16)	30	30 (16)	10	30	6	6 (3)	6	3 (2)	0	0 (0)
1	4	0	5 (3)	15	10 (6)	15	15 (8)	5	10	1	1 (1)	1	0 (0)	0	0 (0)
0	5	0	1 (1)	3	1 (1)	3	3 (2)	1	1	0	0 (0)	0	0 (0)	0	0 (0)
6	0	0	1 (1)	1	1 (1)	1	1 (1)	1	1	1	1 (1)	1	1 (1)	1	1 (1)
5	1	0	1 (1)	3	5 (3)	3	3 (2)	1	5	2	2 (1)	2	3 (2)	1	0 (0)
4	2	0	4 (3)	9	10 (6)	9	9 (6)	4	10	4	4 (3)	4	3 (2)	1	0 (0)
3	3	0	4 (3)	10	10 (6)	10	10 (6)	4	10	2	2 (1)	2	1 (1)	0	0 (0)
2	4	0	4 (3)	9	5 (3)	9	9 (6)	4	5	1	1 (1)	1	0 (0)	0	0 (0)
1	5	0	1 (1)	3	1 (1)	3	3 (2)	1	1	0	0 (0)	0	0 (0)	0	0 (0)
0	6	0	1 (1)	1	0 (0)	1	1 (1)	1	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	1	1 (1)	2	3 (2)	1	1 (1)	0	1	1	0 (0)	0	1 (1)	0	0 (0)
1	0	1	5 (3)	10	15 (8)	5	5 (3)	0	5	5	0 (0)	0	5 (3)	0	0 (0)
0	1	1	5 (3)	10	12 (6)	5	5 (3)	0	4	3	0 (0)	0	2 (1)	0	0 (0)
2	0	1	10 (6)	20	30 (16)	10	10 (6)	0	10	10	0 (0)	0	10 (6)	0	0 (0)
1	1	1	20 (10)	40	48 (24)	20	20 (10)	0	16	12	0 (0)	0	8 (4)	0	0 (0)
0	2	1	10 (6)	20	18 (10)	10	10 (6)	0	6	3	0 (0)	0	1 (1)	0	0 (0)
3	0	1	10 (6)	20	30 (16)	10	10 (6)	0	10	10	0 (0)	0	10 (6)	0	0 (0)
2	1	1	30 (16)	60	72 (36)	30	30 (16)	0	24	18	0 (0)	0	12 (6)	0	0 (0)
1	2	1	30 (16)	60	54 (28)	30	30 (16)	0	18	9	0 (0)	0	3 (2)	0	0 (0)
0	3	1	10 (6)	20	12 (6)	10	10 (6)	0	4	1	0 (0)	0	0 (0)	0	0 (0)
4	0	1	5 (3)	10	15 (8)	5	5 (3)	0	5	5	0 (0)	0	5 (3)	0	0 (0)
3	1	1	20 (10)	40	48 (24)	20	20 (10)	0	16	12	0 (0)	0	8 (4)	0	0 (0)
2	2	1	30 (16)	60	54 (28)	30	30 (16)	0	18	9	0 (0)	0	3 (2)	0	0 (0)
1	3	1	20 (10)	40	24 (12)	20	20 (10)	0	8	2	0 (0)	0	0 (0)	0	0 (0)
0	4	1	5 (3)	10	3 (2)	5	5 (3)	0	1	0	0 (0)	0	0 (0)	0	0 (0)
5	0	1	1 (1)	2	3 (2)	1	1 (1)	0	1	1	0 (0)	0	1 (1)	0	0 (0)
4	1	1	5 (3)	10	12 (6)	5	5 (3)	0	4	3	0 (0)	0	2 (1)	0	0 (0)
3	2	1	10 (6)	20	18 (10)	10	10 (6)	0	6	3	0 (0)	0	1 (1)	0	0 (0)
2	3	1	10 (6)	20	12 (6)	10	10 (6)	0	4	1	0 (0)	0	0 (0)	0	0 (0)
1	4	1	5 (3)	10	3 (2)	5	5 (3)	0	1	0	0 (0)	0	0 (0)	0	0 (0)
0	5	1	1 (1)	2	0 (0)	1	1 (1)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	2	4 (3)	4	3 (2)	1	1 (1)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
1	0	2	10 (6)	12	12 (7)	2	2 (1)	0	0	2	0 (0)	0	0 (0)	0	0 (0)
0	1	2	10 (6)	12	9 (5)	2	2 (1)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
2	0	2	18 (11)	20	18 (10)	4	4 (3)	0	0	4	0 (0)	0	0 (0)	0	0 (0)
1	1	2	30 (16)	36	27 (14)	6	6 (3)	0	0	3	0 (0)	0	0 (0)	0	0 (0)
0	2	2	18 (11)	20	9 (5)	4	4 (3)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
3	0	2	10 (6)	12	12 (7)	2	2 (1)	0	0	2	0 (0)	0	0 (0)	0	0 (0)
2	1	2	30 (16)	36	27 (14)	6	6 (3)	0	0	3	0 (0)	0	0 (0)	0	0 (0)
1	2	2	30 (16)	36	18 (10)	6	6 (3)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
0	3	2	10 (6)	12	3 (2)	2	2 (1)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
4	0	2	4 (3)	4	3 (2)	1	1 (1)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
3	1	2	10 (6)	12	9 (5)	2	2 (1)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
2	2	2	18 (11)	20	9 (5)	4	4 (3)	0	0	1	0 (0)	0	0 (0)	0	0 (0)
1	3	2	10 (6)	12	3 (2)	2	2 (1)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	4	2	4 (3)	4	0 (0)	1	1 (1)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	3	4 (3)	2	1 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
1	0	3	10 (6)	6	3 (2)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	1	3	10 (6)	6	2 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
2	0	3	10 (6)	6	3 (2)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
1	1	3	20 (10)	12	4 (2)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	2	3	10 (6)	6	1 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
3	0	3	4 (3)	2	1 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
2	1	3	10 (6)	6	2 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
1	2	3	10 (6)	6	1 (1)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	3	3	4 (3)	2	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	4	4 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)

Table IV (Continued)

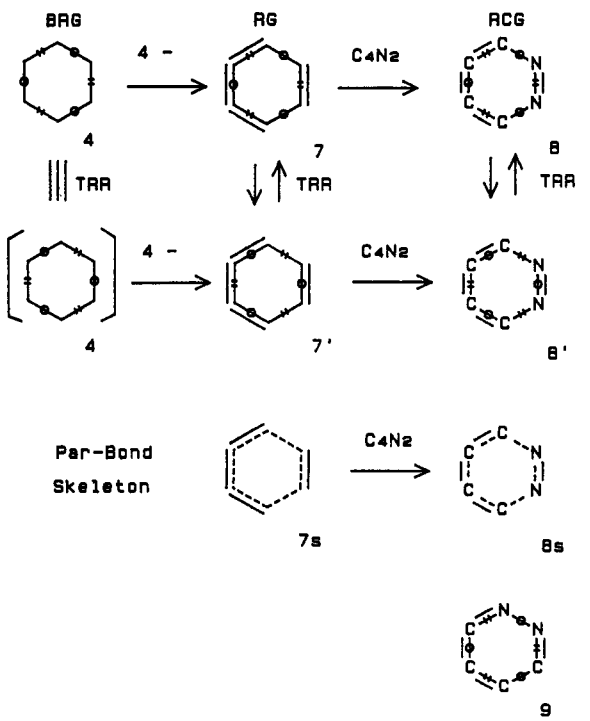
			no. of RCGs (RCG pairs)											
i	*j*	*k*	**4 (4s)**	**13, 13′**	**14 (14s)**	**15, 15′**	**16 (16s)**	**17, 17′**	**18, 18′**	**19, 19′**	**10 (10s)**	**7, 7′**	**20 (20s)**	**21, 21′**	**22 (22s)**
1	0	4	5 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	1	4	5 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
2	0	4	4 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
1	1	4	5 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	2	4	4 (3)	1	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	5	1 (1)	0	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
1	0	5	1 (1)	0	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	1	5	1 (1)	0	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)
0	0	6	1 (1)	0	0 (0)	0	0 (0)	0	0	0	0 (0)	0	0 (0)	0	0 (0)

[a] The coefficient of $u^i v^j w^k$ indicates the number of isomeric RCG with *i* nitrogens, *j* oxygens, and *k* hydrogens on each of parent RG.

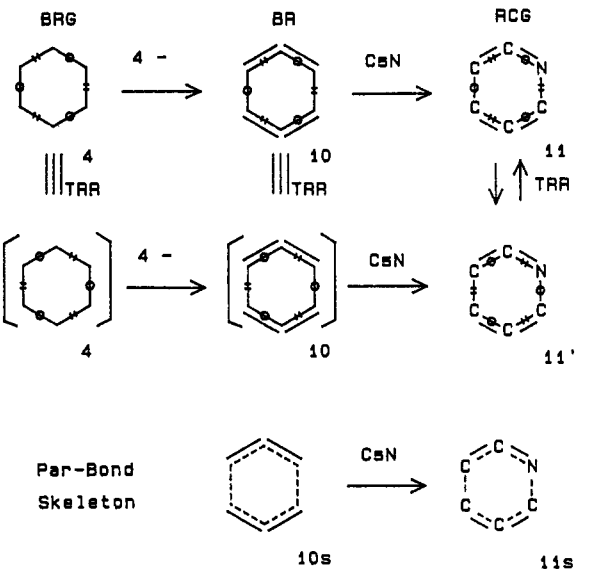
Scheme III



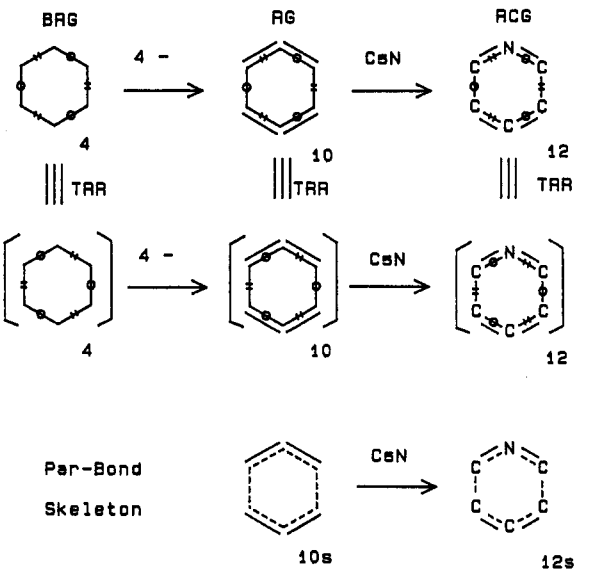
Scheme IV



Scheme V



Scheme VI

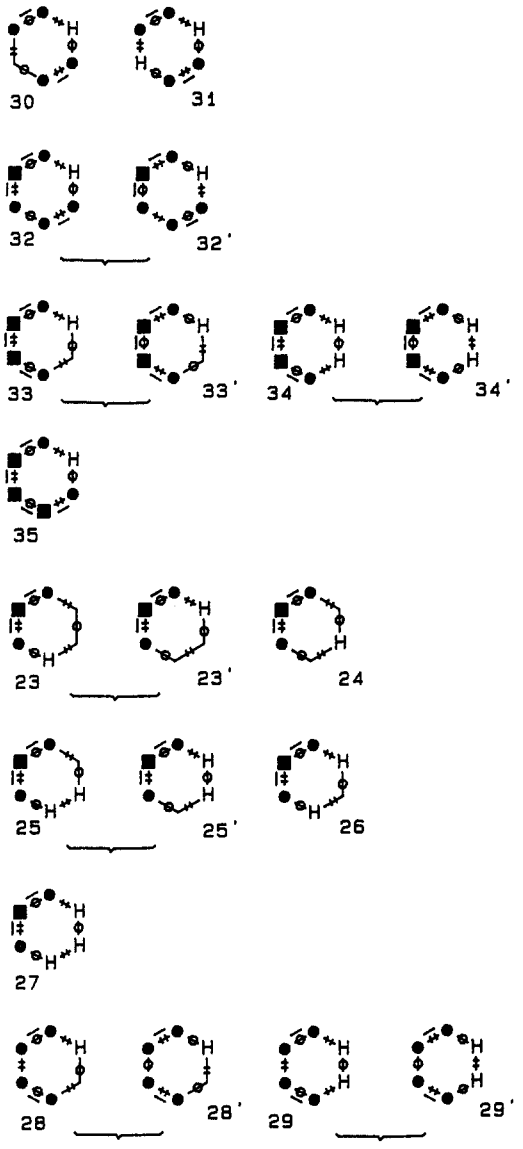


as a parent, there exist such isomers as RG **6**, since this isomer and RCG **2** are both generated by the addition of three single par-bonds and one double par-bond followed by the substitution of six carbon atoms.

Scheme IV depicts the other examples of the derivation of RCGs. RCG **8** is a derivative of RG **7** that has the specific mode of C_4N_2 substitutions (i.e., an atom configuration of C_4N_2). RCG **9** derived from RG **7** is isomeric to RCG **8**.

Definition of a Forward–Reverse Pair of Reaction Types as a Reaction Pair of Reaction-Center Graphs (an RCG Pair). Let us consider the operation that interchanges in-bonds and

Table V. Parent RGs of Hexagonal Class Preoccupied by Hydrogen Atoms[a,b]



[a] The position marked ■ has a minimum valency of $v = 3$. The position marked ● has a minimum valency of $v = 2$. The unmarked position has a minimum valency of $v = 1$. [b] Each couple linked with a brace is a reaction pair (an RG pair). The isolated RG is a self-reaction pair.

out-bonds with each other. We call this operation a *transformation to the reverse reaction* (TRR).[4b] The TRR operation on the reaction graph **3** gives RG **3'** that corresponds to the reverse reaction. Similarly, the TRR operation converts the reaction-center graph **2** into the reverse RCG **2'**. The pair of an RG and the reverse RG is defined as a reaction pair or, more specifically, as a *reaction pair of RG level* (RG pair). For example, the RGs **3** and **3'** construct an RG pair. The pair of RGs **7** and **7'** is another RG pair. A *reaction pair of RCG level* is defined similarly and abbreviated as an *RCG pair*. The pairs **2** and **2'** and **8** and **8'** illustrate the RCG pair.

There is a special case in which an RG is invariant on the TRR operation. We call this case a *self-reaction pair of RG level*, or a *self-RG pair* in an abbreviated fashion. The counterpart of RCG level is a *self-reaction pair of RCG level* (self-RCG pair). Scheme V shows an example that is a self-RG pair but not a self-RCG pair. Thus, RG **10** is converted into itself on the TRR operation. On the other hand, the TRR operation transforms RCG **11** into RCG **11'** of the reverse reaction.

Table VI. Cycle Indices of the Parent RGs Preoccupied with Hydrogen Atoms

RG[a]	symmetry	cycle index	eq
23, 23'	C_1	G: $a_1b_1^4$	27
24	C_1	G: $a_1b_1^4$	28
24s	C_2	P: $(1/2)(a_1b_1^4 + a_1b_2^2)$	29
25, 25'	C_1	G: $a_1b_1^3$	30
26	C_1	G: $a_1b_1^3$	31
26s	C_2	P: $(1/2)(a_1b_1^3 + a_1b_1b_2)$	32
27	C_1	G: $a_1b_1^2$	33
27s	C_2	P: $(1/2)(a_1b_1^2 + a_1b_2)$	34
28, 28'	C_1	G: b_1^5	35
29, 29'	C_2	G: $(1/2)(a_1^4 + b_2^2)$	36
30	C_1	G: b_1^5	37
30s	C_2	P: $(1/2)(b_4^5 + b_1b_2^2)$	38
31	C_2	G: $(1/2)(b_1^4 + b_2^2)$	39
31s	D_2	P: $(1/4)(b_1^4 + 3b_2^2)$	40
32, 32'	C_1	G: a_1b_4	41
33, 33'	C_1	G: $a_1^2b_1^3$	42
34, 34'	C_2	G: $(1/2)(a_1^2b_1^2 + a_2b_2)$	43
35	C_1	G: $a_1^3b_1^2$	44
35s	C_2	P: $(1/2)(a_1^3b_1^2 + a_1^2b_2)$	45

[a] The structures of RGs are collected in Table V.

Scheme VI demonstrates that both RG **10** and RCG **12** constitute respective self-reaction pairs. RCGs **11**, **11'**, and **12** are isomeric to each other, since they are derived by the C_5N substitution of the parent RG **10**. The two RCGs **11** and **11'** construct an RCG pair, whereas RCG **12** is a self-RCG pair. The pair **11** and **11'** is isomeric to the self-RCG pair **12**.

If a parent RG is not a self-reaction pair, there obviously emerge no RCG pairs based on the RG. Schemes III and IV are examples of this case. If a parent RG is a self-reaction pair, there exist one or more self-RCG pairs in the set of RCGs derived from the RG. Schemes V and VI are exmples of the latter case.

The two RGs of a reaction pair contain a common skeleton of par-bonds that is invariant on the TRR operation. We call the invariant a *par-bond skeleton*. The solid-line structure **3s** illustrates the par-bond skeleton that is common to RGs **3** and **3'**. It is noted that RG **3** and RG **3'** as well as the par-bond skeleton **3s** have the same symmetry. Schemes III and IV contain additional examples of this case.

Enumeration of Isomeric RCGs and Isomeric RCG Pairs. Suppose that a reaction graph (RG) is different from the reverse RG. Then the RG and the reverse RG along with the corresponding par-bond skeleton have the same symmetry. Hence we can obtain the same result in counting of RCG isomers (isomeric reaction-center graphs) if we start with either member of the RG pair as a parent. Furthermore, the resulting number of RCGs is equal to that of RCG pairs.

If an RG is a self-reaction pair, the par-bond skeleton generally has symmetry higher than the original RG. For example, the self-reaction pair **10** has C_2 symmetry, and the corresponding par-bond skeleton **10s** has D_2 symmetry. In this case, the number of RCG isomers is different from double the number of RCG pairs (cf. Schemes V and VI). Hence, both the enumerations of the RCGs and of the RCG pairs are necessary.

The definition discriminating between RCGs and RCG pairs affords a clear and fruitful basis to describe reaction types. The present procedure (Schemes II–VI) is also one of the methods that produces new possible reactions theoretically.

AUTHENTIC ENUMERATION OF HEXAGONAL REACTION-CENTER GRAPHS

Enumeration Starting from a Non-Self-RG Pair. As formulated in the last section, the enumeration of reaction types

Table VII. Enumeration of Hexagonal RCGs with Preoccupied Hydrogens[a]

		no. of RCGs (RCG pairs)			
i	j	**23, 23′**	**24 (24s)**	**25, 25′**	**26 (26s)**
0	0	1	1 (1)	1	1 (1)
1	0	5	5 (3)	4	4 (3)
0	1	4	4 (2)	3	3 (2)
2	0	10	10 (6)	6	6 (4)
1	1	16	16 (8)	9	9 (5)
0	2	6	6 (4)	3	3 (2)
3	0	10	10 (6)	4	4 (3)
2	1	24	24 (12)	9	9 (5)
1	2	18	18 (10)	6	6 (4)
0	3	4	4 (2)	1	1 (1)
4	0	5	5 (3)	1	1 (1)
3	1	16	16 (8)	3	3 (2)
2	2	18	18 (10)	3	3 (2)
1	3	8	8 (4)	1	1 (1)
0	4	1	1 (1)	0	0 (0)
5	0	1	1 (1)	0	0 (0)
4	1	4	4 (2)	0	0 (0)
3	2	6	6 (4)	0	0 (0)
2	3	4	4 (2)	0	0 (0)
1	4	1	1 (1)	0	0 (0)
0	5	0	0 (0)	0	0 (0)

[a] The coefficient of $u^i v^j$ indicates the number of isomeric RCGs with i nitrogens and j oxygens.

is accomplished by counting reaction-center graphs (RCGs) after the selection of an appropriate reaction graph (RG) as a parent graph. For enumerating six-electron pericyclic reactions, Table I collects the parent RGs that contain 0–6 single par-bonds. Each couple of RGs linked with a brace is an RG pair. Each of the isolated RGs without a brace is a self-RG pair. There emerge 20 RGs and 13 RG pairs, the numbers of which have been obtained by applying Pólya's theorem as reported in the previous paper.[4b,9]

To generate an RCG, we put an appropriate atom on each vertex of a parent RG. At this time, we must check their fitness, since the vertex has an obligatory minimum formal valency (v = 1–3). This is indicated by the number of out- plus par-bonds (or of in- plus par-bonds) incident to each vertex, because an equal number of in- and out- bonds are incident to each vertex. The vertices having minimum valency of v = 2 and 3 are indicated by different marks (i.e., ● and ■, respectively) in Table I. The unmarked positions have minimum valencies of v = 1. To simplify the following discussions, we choose carbon, nitrogen, oxygen, and hydrogen atoms as substituents. Obviously, each vertex of v = 1 can be substituted by C, N, O, or H. That of v = 2 (●) is capable of having C, N, or O but incapable of substitution of H. Each vertex of v = 3 (■) is able to have C or N as a substituent.

Table II summarizes the cycle indices for RGs collected in Table I. These equations are obtained by the application of Pólya's theorem. We introduce different variables, a_r, b_r, and c_r, in accord with the obligatory minimum formal valencies.

The variables of each equation of Table II are substituted by the atom-figure inventories

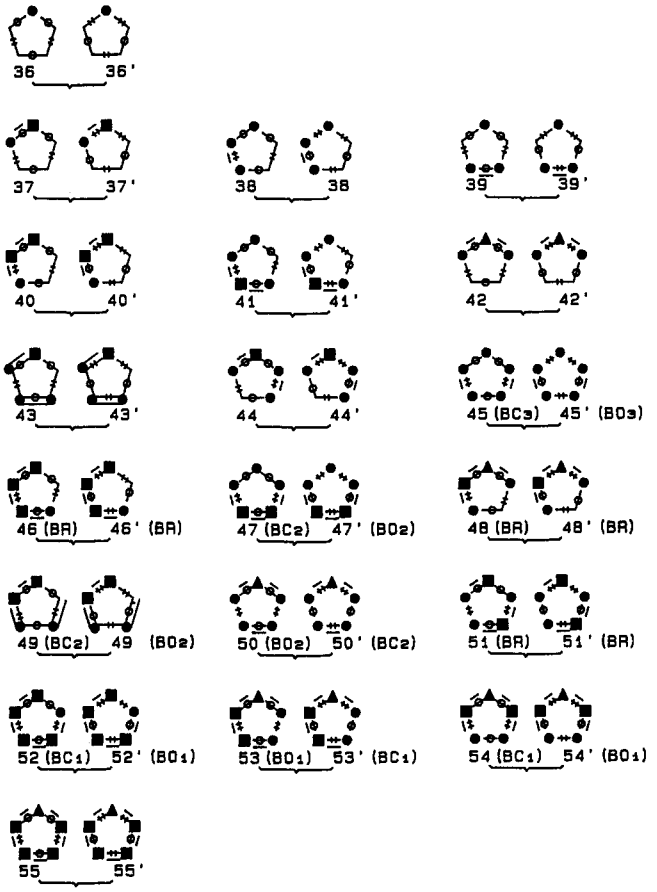
$$a_r = 1 + u^r \tag{20}$$

$$b_r = 1 + u^r + v^r \tag{21}$$

$$c_r = 1 + u^r + v^r + w^r \tag{22}$$

wherein the formal variables (u, v, and w) are introduced for counting nitrogens, oxygens, and hydrogens, respectively. The variable a_r is thereby an atom-figure inventory for N substitution, b_r for N, O substitution, and c_r for N, O, H substitution.[10] The use of the different inventories stems from the minimum formal valencies of the respective positions. For example, we obtain the following equation $G_{19}(u,v,w)$ as a generating function that counts RCGs on the basis of the parent RG **19**. Such equations are called *RCG-counting polynomial series*.

Table VIII. Parent Reaction Graphs of Pentagonal Class[a-c]



[a] The positions marked ▲, ■, and ● have minimum valencies of v = 4, 3, and 2, respectively. Unmarked positions have valencies of v = 1. [b] Each couple linked with a brace is a reaction pair (an RG pair). The isolated RG is a self-reaction pair. [c] BO_p is a bridge of ring opening of order p. BC_q is a bridge of ring closure of order q. BR is a bridge of rearrangement.

Table IX. Cycle Indices Based on the Parent BRs of Pentagonal Class

RG	symmetry	cycle index	eq
36, 36′	C_2	G: $(1/2)(b_1c_1^4 + b_1c_2^2)$	31
37, 37′	C_1	G: $a_1b_1c_1^3$	32
38, 38′	C_1	G: $b_1^3c_1^2$	33
39, 39′	C_2	G: $(1/2)(b_1^3c_1^2 + b_1b_2c_2)$	34
40, 40′	C_1	G: $a_1^2b_1c_1^2$	35
41, 41′	C_1	G: $a_1b_1^3c_1$	36
42, 42′	C_2	G: $(1/2)(b_1^2c_1^2 + b_2c_2)$	37
43, 43′	C_1	G: $a_1b_1^3c_1$	38
44, 44′	C_1	G: $a_1b_1^3c_1$	39
45, 45′	C_2	G: $(1/2)(b_1^5 + b_1b_2^2)$	40
46, 46′	C_1	G: $a_1^3b_1c_1$	41
47, 47′	C_2	G: $(1/2)(a_1^2b_1^3 + a_2b_1b_2)$	42
48, 48′	C_1	G: $a_1b_1^2c_1$	43
49, 49′	C_1	G: $a_1^2b_1^3$	44
50, 50′	C_2	G: $(1/2)(b_4^4 + b_2^2)$	45
51, 51′	C_1	G: $a_1^2b_1^3$	46
52, 52′	C_1	G: $a_1^4b_1$	47
53, 53′	C_1	G: $a_1^2b_1^2$	48
54, 54′	C_2	G: $(1/2)(a_1^2b_1^2 + a_2b_2)$	49
55, 55′	C_2	G: $(1/2)(a_1^4 + a_2^2)$	50

Table X. Enumeration of Pentagonal RCGs[a]

			no. of RCGs																			
			36,	**37,**	**38,**	**39,**	**40,**	**41,**	**42,**	**43,**	**44,**	**45,**	**46,**	**47,**	**48,**	**49,**	**50,**	**51,**	**52,**	**53,**	**54,**	**55,**
i	*j*	*k*	**36′**	**37′**	**38′**	**39′**	**40′**	**41′**	**42′**	**43′**	**44′**	**45′**	**46′**	**47′**	**48′**	**49′**	**50′**	**51′**	**52′**	**53′**	**54′**	**55′**
0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	0	0	3	5	5	3	5	5	2	5	5	3	5	3	4	5	2	5	5	4	2	2
0	1	0	3	4	5	3	3	4	2	4	4	3	2	2	3	3	2	3	1	2	1	0
2	0	0	6	10	10	6	10	10	4	10	10	6	10	6	6	10	4	10	10	6	4	4
1	1	0	10	16	20	10	12	16	6	16	16	10	8	6	9	12	6	12	4	6	3	0
0	2	0	6	6	10	6	3	6	4	6	6	6	1	2	3	3	4	3	0	1	1	0
3	0	0	6	10	10	6	10	10	2	10	10	6	10	6	4	10	2	10	10	4	2	2
2	1	0	16	24	30	16	18	24	6	24	24	16	12	10	9	18	6	18	6	6	3	0
1	2	0	16	18	30	16	9	18	6	18	18	16	3	5	6	9	6	9	0	2	1	0
0	3	0	6	4	10	6	1	4	2	4	4	6	0	1	1	1	2	1	0	0	0	0
4	0	0	3	5	5	3	5	5	1	5	5	3	5	3	1	5	1	5	5	1	1	1
3	1	0	10	16	20	10	12	16	2	16	16	10	8	6	3	12	2	12	4	2	1	0
2	2	0	16	18	30	16	9	18	4	18	18	16	3	5	3	9	4	9	0	1	1	0
1	3	0	10	8	20	10	2	8	2	8	8	10	0	1	1	2	2	2	0	0	0	0
0	4	0	3	1	5	3	0	1	1	1	1	3	0	0	0	0	1	0	0	0	0	0
5	0	0	1	1	1	1	1	1	0	1	1	1	1	1	0	1	0	1	1	0	0	0
4	1	0	3	4	5	3	3	4	0	4	4	3	2	2	0	3	0	3	1	0	0	0
3	2	0	6	6	10	6	3	6	0	6	6	6	1	2	0	3	0	3	0	0	0	0
2	3	0	6	4	10	6	1	4	0	4	4	6	0	1	0	1	0	1	0	0	0	0
1	4	0	3	1	5	3	0	1	0	1	1	3	0	0	0	0	0	0	0	0	0	0
0	5	0	1	0	1	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
0	0	1	2	3	2	1	2	1	1	1	1	0	1	0	1	0	0	0	0	0	0	0
1	0	1	8	12	8	4	8	4	3	4	4	0	4	0	3	0	0	0	0	0	0	0
0	1	1	8	9	8	4	4	3	3	3	3	0	1	0	2	0	0	0	0	0	0	0
2	0	1	12	18	12	6	12	6	3	6	6	0	6	0	3	0	0	0	0	0	0	0
1	1	1	24	27	24	12	12	9	6	9	9	0	3	0	4	0	0	0	0	0	0	0
0	2	1	12	9	12	6	2	3	3	3	3	0	0	0	1	0	0	0	0	0	0	0
3	0	1	8	12	8	4	8	4	1	4	4	0	4	0	1	0	0	0	0	0	0	0
2	1	1	24	27	24	12	12	9	3	9	9	0	3	0	2	0	0	0	0	0	0	0
1	2	1	24	18	24	12	4	6	3	6	6	0	0	0	1	0	0	0	0	0	0	0
0	3	1	8	3	8	4	0	1	1	1	1	0	0	0	0	0	0	0	0	0	0	0
4	0	1	2	3	2	1	2	1	0	1	1	0	1	0	0	0	0	0	0	0	0	0
3	1	1	8	9	8	4	4	3	0	3	3	0	1	0	0	0	0	0	0	0	0	0
2	2	1	12	9	12	6	2	3	0	3	3	0	0	0	0	0	0	0	0	0	0	0
1	3	1	8	3	8	4	0	1	0	1	1	0	0	0	0	0	0	0	0	0	0	0
0	4	1	2	0	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	2	4	3	1	1	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	2	10	9	3	2	3	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
0	1	2	10	6	3	2	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	2	10	9	3	2	3	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	2	18	12	6	3	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
0	2	2	10	3	3	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	2	4	3	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	1	2	10	6	3	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	2	2	10	3	3	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	3	2	4	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	3	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	3	4	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	1	3	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	3	2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	3	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	2	3	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	0	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	1	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

[a] The coefficient of $u^i v^j w^k$ indicates the number of isomeric RCG with i nitrogens, j oxygens, and k hydrogens on each parent RG.

$$G_{19}(u,v,w) = Z(C_2; \mathbf{19}; 1+u^r, 1+u^r+v^r, 1+u^r+v^r+w^r) = (1/2)\{(1+u)^2(1+u+v)^2(1+u+v+w)^2 + (1+u^2)(1+u^2+v^2)(1+u^2+v^2+w^2)\} = (1 + 3u + 2v + 9u^2 + 10uv + 4v^2 + 10u^3 + 20u^2v + 12uv^2 + 2v^3 + \ldots) + w(1 + 5u + 3v + 10u^2 + 12uv + 3v^2 + 10u^3 + 18u^2v + 9uv^2 + v^3 + \ldots) + w^2(1 + 2u + v + 4u^2 + 3uv + v^2 + 2u^3 + 3u^2v + uv^2 + \ldots) \quad (23)$$

The expanded polynomial (eq 23) is a generating function in which the coefficient of $u^i v^j w^k$ indicates the number of isomers with i nitrogens, j oxygens, and k hydrogens (and, strictly speaking, $6-i-j-k$ implicit carbon atoms). Note the formal parallelism between $u^i v^j w^k$ and $N_i O_j H_k$. The full list of coefficients is shown in Table IV.

It should be emphasized that the number of isomeric RCGs is obtained by mathematical treatment, and hence the present method affords a versatile probe to check the results of both a manual enumeration and a computational one. For example, the number of isomers with N_3H (strictly speaking, with C_2N_3H) is 10, which appears as the coefficient of the term u^3w ($=u^3v^0w^1$) of eq 23. Compare N_3H with u^3w. This number is equal to that of the manual enumeration collected in Table III.

Enumeration Starting from a Self-RG Pair. For the counting of the RCGs based upon RG **14**, we obtain the cycle index $Z(C_1, \mathbf{14})$ as found in Table II (eq 4). On substituting the variables of eq 4 by the atom-figure inventories (eq 20–22), we obtain an RCG-counting polynomial (eq 24) as a generating function.

$$G_{14}(u,v,w) = Z(C_1;\ \mathbf{14};\ 1+u^r,\ 1+u^r+v^r,\ 1+u^r+v^r+w^r) = (1+u)(1+u+v)^2(1+u+v+w)^3 \quad (24)$$

To calculate the number of *RG pairs*, we work out the corresponding par-bond skeleton (**14s**) as a parent graph. The graph (**14s**) that would be easily derived from RG **14** possesses C_2 symmetry. Hence we obtain $Z(C_2;\ \mathbf{14s})$ (eq 5) as a cycle index. When the atom-figure inventories (eq 20–22) are applied to the cycle index (eq 5), an RCG pair counting polynomial $P_{14}(u,v,w)$ is obtained as a generating function.

$$P_{14}(u,v,w) = Z(C_2;\ \mathbf{14s};\ 1+u^r,\ 1+u^r+v^r,\ 1+u^r+v^r+w^r) = (1/2)\{(1+u)(1+u+v)^2(1+u+v+w)^3 + (1+u)(1+u^2+v^2)(1+u+v+w)(1+u^2+v^2+w^2)\} \quad (25)$$

Table II contains also the cycle indices of the other parent RGs depicted in Table I. When the RG of Table I is a self-reaction pair, the corresponding par-bond skeleton and the cycle index are also listed in Table II. On substituting the variables of these cycle indices by the atom-figure inventories (e.g., eq 20–22), we obtain the RCG-counting polynomials for the respective parent RGs and also gain the RCG pair counting polynomials for the par-bond skeletons. The coefficients of these RCG or RCG pair counting polynomials are listed in Table IV.

Enumeration of RCGs Based on a Parent RG That Has Hydrogen Atoms Preoccupied. In this section, we discuss more detailed enumeration of isomeric RCGs, in which the sites of $v = 1$ are preoccupied by a given number of hydrogen atoms. To begin, we generate the parent RGs required for this treatment (Table V). There exist two cases in the derivation of the RGs of Table V from those of Table I.

The first case contains two or more isomeric RG pairs derived from one of the RGs of Table I.[12] For example, the RGs **23**, **23′**, and **24** are isomers (case 1), the number (i.e., 3) of which appears at **14**, $i = 0, j = 0$, and $k = 1$ in Table IV. The number of RG pairs is 2, which is the coefficient of the term **14s**, $i = 0, j = 0, k = 1$. A set of isomers, **25**, **25′**, and **26**, is another example of case 1.

The second case involves only one RG pair that is derived from one of the RGs of Table I.[13] RGs other than the above are examples of case 2. For instance, the pair of **28** and **28′** corresponds to the pair of **15** and **15′** ($i = 0, j = 0, k = 1$).[11]

Table VI collects the corresponding cycle indices for the RGs found in Table V. Their derivation can be accomplished similarly to that described in the last section. In this case, however, each unmarked vertex (Table V) is presumed to be capable of having an N or O substituent but unable to take a hydrogen atom, even if it is a position of $v = 1$.

The substitution of a_r and b_r contained in each cycle index (Table VI) by eq 20 and 21 affords the corresponding RCG or RCG pair counting polynomial series. Table VII collects only the cases that afford more detailed results than those of Table IV.[13] The other results have already appeared in Table IV. For example, Table IV contains the results for RG **28** at column **15** and lines of $k = 1$ as well as those from **29** at column **15** and lines of $k = 2$.[12]

AUTHENTIC ENUMERATION OF PENTAGONAL REACTION-CENTER GRAPHS

The procedures described above are applicable to any parent RGs with any modes of substitution. All we have to do are (1) find a permutation group of the parent RG, (2) consider an obligatory minimum formal valency of each position, (3) obtain the corresponding cycle index, and (4) substitute the variables of the cycle index by appropriate atom-figure inventories. In this section, we discuss the application of this method to enumerate pentagonal RCGs.

Table XI. Isomeric RCGs with N_2 Based on RGs **40–42**

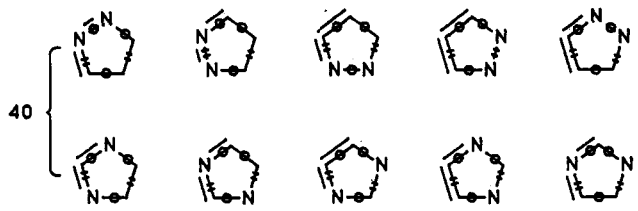
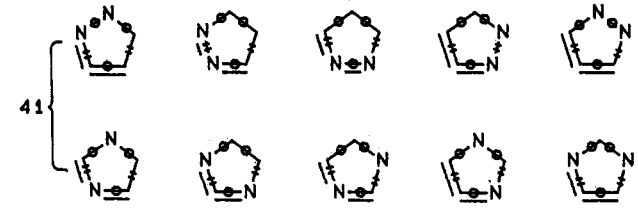
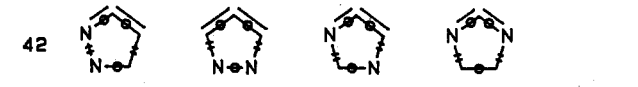
parent RG	RCG with N_2
40	
41	
42	

Table VIII lists parent RGs of pentagonal class.[4c] There are no self-reaction pairs in this series. Each of the RGs has one vertex to which two out-bonds (or two in-bonds) are incident. We call this a *valency-changed position* (*or vertex*) because of its chemical meaning. If it has no additional par-bonds, its obligatory minimum formal valency is $v = 2$ (marked by ●). When the valency-changed position has one additional incident par-bond, it has a minimum valency of $v = 3$ (marked by ■). Each vertex to which two par-bonds and two in-bonds (or two par-bonds and two out-bonds) are incident has an obligatory minimum formal valency of $v = 4$.[14] This is indicated by ▲ in Table VIII. The positions other than the valency-changed atom undergo ordinary interconversions. Their minimum valencies are the same as described in the previous sections.

Table IX summarizes cycle indices for the parent RGs of Table VIII. In Table IX, the variables a_r, b_r, and c_r are assigned to the vertices marked ■, ●, and none, respectively. The vertices ▲ have no variables assigned because of having only implicit carbons.

By substituting the variables of the cycle indices (Table IX) with the atom-figure inventories (eq 20–22), we obtain RCG-counting polynomials as generating functions. The coefficients of the RCG-counting polynomials are collected in Table X in which each column denotes a given parent RG, each line indicates the powers i, j, and k, and their intersection affords the coefficient of the term $u^i v^j w^k$. This value is the number of RCG isomers with i nitrogens, j oxygens, and k hydrogens.

Table XI presents a list of the RCGs derived from the parent RGs **40–42** by N_2 substitution. The numbers (10, 10, and 4) of the three cases are found at the intersections of the respective columns and the line $i = 2, j = 0$, and $k = 0$ in Table X. It should be noted that the valency-changed position of RG **42** has a valency of $v = 4$, and hence a nitrogen atom is incapable of occupying this position without the expansion of valency.

Hendrickson introduced a σ-shell as a novel concept for solving the enumeration problems.[15] The σ-shell is essentially equivalent to the present par-bond skeleton that has been defined in order to enumerate RCG pairs. In this sense, his method is limited only to the enumeration of RCG pairs,

although it has no definitions of an RCG pair or of a self-RCG pair.

CONCLUSION

A novel formulation of reaction types is described, based on the concept of imaginary transition structures (ITS). The reaction types are thus represented by basic reaction graphs (BRGs), reaction graphs (RGs), and reaction-center graphs (RCGs) in ascending order of specificity. The enumeration of reaction types is thereby transformed into the counting of the BRGs, the RGs, or the RCGs. The present paper deals with the enumeration of the RCGs.

The ITS method regards RCGs as derivatives of parent RGs in which the vertices are substituted by appropriate atoms. The concept of reaction pairs (RCG pairs) is also proposed.

For the purpose of the enumeration of six-electron pericyclic reactions, we discuss the counting of hexagonal and pentagonal RCGs substituted by C, H, N, and O. The enumeration problem is solved by applying Pólya's theorem, which is generalized to cover cases having two or more nonequivalent positions of substitution. The ITS approach gives a versatile probe to check the results of manual and computational enumeration, since the number of isomeric RCGs appears as the coefficient of a generating function called an RCG-counting polynomial series. Although the present paper deals only with limited examples, the method described is applicable generally to enumerate any reaction type.

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(5) The term "reaction-center graph" is used as an abbreviation of a reaction-center graph of level 1 described previously. A PS operation (projection to the starting stage) is the deletion of in-bonds. A PP operation (projection to the product stage), in turn, is the deletion of out-bonds. See ref 4b.

(6) The internal representation of an imaginary bond is a complex bond number (a,b), in which the integer a is the multiplicity of a starting stage and b is the difference between the multiplicity of the product stage and that of the starting stage. See ref 4a.

(7) A bond configuration is defined as a mode in which single or double par-bonds are attached to the edges of a parent BRG. An atom configuration is a mode in which appropriate atoms occupy the vertices of a parent RG.

(8) We use the term "derivative" here to indicate the one having extended meanings applicable to the ITS approach.

(9) For the enumeration of organic compounds, see: (a) Rouvray, D. H. *Chem. Soc. Rev.* **1974**, *3*, 355. (b) Balaban, A. T., Ed. *Chemical Applications of Graph Theory*; Academic Press: London, 1976. (c) Biggs, N. L.; Lloyd, E. K.; Wilson, R. J. *Graph Theory 1736–1936*; Clarendon Press: Oxford, U.K., 1976; Chapter 4. For Pólya's theorem, see: (d) Pólya, G. *Acta Math.* **1937**, *68*, 145. (e) Pólya, G.; Tarjan, R. E.; Woods, D. R. *Notes on Introductory Combinatorics*; Birkhaeuser: Boston, 1983; Chapter 6. (f) Liu, C. L. *Introduction to Combinatorial Mathematics*; McGraw-Hill: New York, 1969.

(10) The substitution of carbon atoms is presumed implicitly in all cases. If the presence of carbon atoms is necessary to be represented explicitly, the following atom-figure inventories should be used:

$$a_r = t^r + u^r \tag{20'}$$

$$b_r = t^r + u^r + v^r \tag{21'}$$

$$c_r = t^r + u^r + v^r + w^r \tag{22'}$$

The resulting RCG-counting polynomials have a coefficient of $t^h u^i v^j w^k$, which corresponds to the number of $C_hN_iO_jH_k$ isomers.

(11) The correspondence of the remaining RGs (case 1) is as follows: **29** and **29′** to **15** and **15′** ($i = 0, j = 0, k = 2$); **32** and **32′** to **18** and **18′** ($i = 0, j = 0, k = 1$); **33** and **33′** to **19** and **19′** ($i = 0, j = 0, k = 1$); **34** and **34′** to **19** and **19′** ($i = 0, j = 0, k = 2$); **27** to **14** ($i = 0, j = 0, k = 3$); **30** to **16** ($i = 0, j = 0, k = 1$); **31** to **16** ($i = 0, j = 0, k = 2$); **35** to **20** ($i = 0, j = 0, k = 1$).

(12) In case 1, all the terms of the generating function based upon one of the RGs in Table V have already emerged in the generating function derived from the corresponding RG of Table I. The following equations explain this situation:

$$G_{15}(u,v,w) = G_{15}{}^0(u,v) + wG_{28}(u,v) + w^2G_{29}(u,v)$$

$$G_{16}(u,v,w) = G_{16}{}^0(u,v) + wG_{30}(u,v) + w^2G_{31}(u,v)$$

$$G_{18}(u,v,w) = G_{18}{}^0(u,v) + wG_{32}(u,v)$$

$$G_{19}(u,v,w) = G_{19}{}^0(u,v) + wG_{33}(u,v) + w_2G_{34}(u,v)$$

$$G_{20}(u,v,w) = G_{20}{}^0(u,v) + wG_{35}(u,v)$$

$G_{xx}{}^0$ is a polynomial for counting RCGs with no hydrogen atoms (indicated by the superscript 0) and the subscript (xx) represents the parent RG. The example cited in the text is ascribed to $G_{15}(u,v,w)$.

(13) In case 2, the results collected in Table IV are subdivided into the ones of Table VII. These situations are explained by the equations

$$G_{14}(u,v,w) = G_{14}{}^0(u,v) + w[G_{23}(u,v) + G_{23'}(u,v) + G_{24}(u,v)] + w^2[G_{25}(u,v) + G_{25'}(u,v) + G_{26}(u,v)] + w^3G_{27}(u,v)$$

$$P_{14}(u,v,w) = P_{14}{}^0(u,v) + w[G_{23}(u,v) + P_{24}(u,v)] + w^2[G_{25}(u,v) + P_{26}(u,w)] + w^3P_{27}(u,v)$$

since $G_{23}(u,v)$ is equal to $G_{23'}(u,v)$ and $G_{25}(u,v)$ is equal to $G_{25'}(u,v)$.

(14) In this part of the section, we presume that only a carbon atom can occupy the vertex of $v = 4$.

(15) Hendrickson, J. B. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 47. This paper reported several values different from the present ones: (Table I) $B = 0$, N, $C_4Z_2(O)$; $B = 2(O)$, O, $C_3Z_3(O)$; $B = 2(P)$, N_2O, $C_3Z_3(V)$; $B = 2(P)$, NO_2, $C_3Z_3(V)$; $B = 3(/\Delta)$, N, $C_4Z_2(O)$; $B = 2(/\Delta)$, N, $C_3Z_3(L)$; $B = 2(/\Delta)$, O, $C_4Z_2(O)$; $B = 2(/\Delta)$, O, $C_3Z_3(L)$; $B = 2(/\Delta)$, NO, $C_4Z_2(M)$; (Table II) $B = 2(O)$, the first graph, N, $Z_2(M)$; $B = 2(O)$, the first graph, O, Z_2 (M); $B = 2(O)$, the first graph, O, $Z_3(L)$; $B = 2(O)$, the first graph, NO, $Z_2(M)$; $B = 2(O)$, the fourth graph, N, $Z_2(O)$; $B = 2(O)$, the fourth graph, $Z_2(O)$; $B = 2(M)$, the first graph, N, $Z_3(L)$; $B = 2(M)$, the first graph, O, $Z_3(L)$; $B = 2(M)$, the first graph, N_2O, $Z_3(V)$; $B = 2(M)$, the first graph, N_2O, $Z_3(L)$; $B = 2(M)$, the frist graph, NO_2, $Z_3(V)$; and $B = 2(M)$, the first graph, NO_2, $Z_3(L)$; (Table VI) $B = 4$, N_2O, $\alpha_3 = \beta_3$, $CQZ_3(V)$; $B = 4$, N_2O, $\alpha_3 = \beta_3$, $CQZ_3(S)$. The values for $B = 2(O)$ (the first graph) have been reported to be different from the ones for $B = 3(L)$ (Table II). Since the σ-shells of the two cases have the same symmetry, the results should be identical with one another.