

The Sphericity Concept for an Orbit of Bonds. Formulation of Chirogenic Sites in a Homospheric Orbit and of Bond-Differentiating Chiral Reactions with Applications to C₆₀-Adducts

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After preparing the subduction table of I_h -group, buckminsterfullerene derivatives are combinatorially enumerated in an itemized manner concerning symmetries and molecular formulas. The symmetrical properties of the derivatives are discussed in terms of the sphericity concept. Bond-differentiating reactions are formulated in order to clarify possible routes to derivatives of several subsymmetries of I_h . Such bond-differentiating reactions are classified into four categories, *i.e.*, chemoselective achiral, chemoselective chiral, stereoselective chiral, and stereoselective achiral reactions. Chirogenic sites in a homospheric orbit are examined to show the possibility of direct chiral reactions. The terms *mesolocative*, *equilocative*, *diallocative*, and *semilocative* are proposed to characterize bond pairs in a homospheric orbit.

1. INTRODUCTION

The present paper aims at proposing a stereochemical concept *bond-differentiating chiral reactions* by using buckminsterfullerene as an example. Since buckminsterfullerene has 30 double bonds located between adjacent two six-membered rings, it provides a variety of possible cases in which the double bonds participate selectively in chiral reactions. As a result, a theoretical investigation on such possibilities inevitably requires combinatorial enumeration technique.

For the purpose of setting our problems appropriately, we should first mention the meaning of the present concept in the state of the art of stereochemistry. Asymmetric synthesis is one of the most active fields in organic chemistry, where various experimental results have been accumulated year after year.^{1–3} In order to communicate and discuss the results properly, several classification methods have been developed on the basis of empirical or theoretical criteria. Thus, in an earlier stage of the field, mechanisms on rather narrow ranges of reactions were successfully discussed in terms of empirical rules such as Prelog's rule⁴ and Cram's rule.⁵ For characterizing a wider range of asymmetric reactions, Mislow proposed the terms *enantiotopic* and *diastereotopic*, which entailed classification on the basis of pairwise relations.^{6,7} Hanson proposed the term *prochirality* and presented a practical nomenclature to specify stereochemical equivalency and nonequivalency.^{8,9} Although the term was widely accepted by organic chemists, some confusion emerged, since Hanson's prochirality involved two cases: a starting molecule may be achiral or chiral. In other words, Hanson's prochirality did not take the topicity terms into explicit consideration. Nakazaki pointed out that the two cases should be differentiated into enantio- and diastereoselective syntheses.^{10,11} Later, Mislow defined prochirality by starting from the local chirality of a site, where the terms *enantiotopic* and *diastereotopic* were rationally related to the term *prochirality*.¹² The term *stereogenic* proposed by McCasland¹³

was used to avoid confusion concerning Hanson's prochirality.^{12,14} Several reviews have appeared to discuss the terminology for specifying stereochemical processes.^{15,16}

We have recently presented a new definition of *prochirality* on the basis of the sphericity (chirality fittingness) of an orbit.^{17–19} Thus, the terms *enantiospheric*, *homospheric*, and *hemispheric* were proposed by examining a coset representation (CR) governing such an orbit so that the term prochirality was attributed to the enantiosphericity. In addition, the topicity terms were subsidiarily redefined from the sphericity concept, where the membership criterion was presented for determining such topicity.^{17,20} The sphericity concept was also applied to the redefinition of the stereogenicity.²⁰ We have later proposed the concepts *proligand* and *promolecule* to specify stereochemical properties of nonrigid molecules.^{21–23} For treating ligands as sites of chiral reactions, we have discussed *chirogenic sites* in an enantiospheric orbit.¹⁸

Although our previous consideration has shown fundamental aspects of stereochemical problems, more elaborate and important problems remain unsolved.

1. The previous consideration has been restricted within rather simple cases in which stereochemically nonequivalent atoms or the *re/si*-faces of a double bond are differentiated.²⁴ In order to pursue a universal theory of chiral synthesis, we should examine other possibilities in addition to such atom-differentiating and *re/si*-face-differentiating chiral reactions. Hence, one of the targets of the present paper is to formulate *bond-differentiating chiral reactions* as another possibility.

2. Although we have discussed *chirogenic sites*, we have dealt with a special case in which such chirogenic sites are placed in an enantiospheric orbit.¹⁸ Hence, such possibilities that chirogenic sites are placed in a homospheric orbit are open to further studies.

The formulation of bond-differentiating chiral reactions, on the other hand, aims at a contribution to fullerene chemistry, since the 30 double bonds of buckminsterfullerene (C₆₀) have recently attracted chemists' attention as interesting reaction sites.^{25–31} Although previous works have dealt with chemoselective reactions, the next step will be chiral

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Table 1. Subduction Table of I_h

	Γ_{C_1}	Γ_{C_2}	Γ_{C_3}	Γ_{C_4}	Γ_{C_5}	Γ_{D_2}	$\Gamma_{C_{2\pi}}$	$\Gamma_{C_{2\theta}}$	Γ_{C_6}	Γ_{D_3}	$\Gamma_{C_{3\pi}}$	$\Gamma_{D_{2\theta}}$	Γ_{D_5}	$\Gamma_{C_{3\sigma}}$	$\Gamma_{C_{3\phi}}$	Γ_{D_7}	$\Gamma_{C_{3\tau}}$	Γ_{D_8}	$\Gamma_{C_{3\eta}}$	Γ_{D_9}	$\Gamma_{C_{3\zeta}}$	$\Gamma_{D_{10}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{11}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{12}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{13}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{14}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{15}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{16}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{17}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{18}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{19}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{20}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{21}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{22}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{23}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{24}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{25}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{26}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{27}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{28}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{29}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{30}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{31}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{32}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{33}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{34}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{35}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{36}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{37}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{38}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{39}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{40}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{41}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{42}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{43}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{44}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{45}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{46}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{47}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{48}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{49}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{50}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{51}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{52}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{53}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{54}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{55}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{56}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{57}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{58}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{59}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{60}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{61}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{62}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{63}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{64}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{65}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{66}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{67}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{68}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{69}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{70}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{71}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{72}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{73}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{74}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{75}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{76}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{77}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{78}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{79}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{80}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{81}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{82}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{83}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{84}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{85}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{86}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{87}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{88}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{89}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{90}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{91}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{92}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{93}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{94}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{95}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{96}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{97}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{98}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{99}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{100}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{101}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{102}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{103}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{104}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{105}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{106}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{107}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{108}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{109}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{110}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{111}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{112}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{113}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{114}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{115}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{116}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{117}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{118}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{119}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{120}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{121}}$	$\Gamma_{C_{3\lambda}}$	$\Gamma_{D_{122}}$	$\Gamma_{C_{3\mu}}$	$\Gamma_{D_{123}}$	$\Gamma_{C_{3\nu}}$	$\Gamma_{D_{124}}$	$\Gamma_{C_{3\xi}}$	$\Gamma_{D_{125}}$	$\Gamma_{C_{3\eta}}$	$\Gamma_{D_{126}}$	$\Gamma_{C_{3\theta}}$	$\Gamma_{D_{127}}$	$\Gamma_{C_{3\iota}}$	$\Gamma_{D_{128}}$	$\Gamma_{C_{3\kappa}}$	$\Gamma_{D_{129}}$	$\Gamma_{C_{3\$
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synthesis concerning derivatives of C_{60} .³² Since the I_h -symmetry of the C_{60} -skeleton is complex in nature, further studies will necessitate systematic consideration of the I_h -symmetry and its subsymmetries. Thus, equivalency or nonequivalency of bonds and atoms in such C_{60} -derivatives can only be comprehended by taking into consideration the subduction of coset representations (CRs) and the sphericity concept. In particular, the topicity terms should be reexamined in order to discuss pairwise relationships in fullerene derivatives.

The present paper deals with subduction of CRs for icosahedral (I_h) and tetrahedral symmetries (T_h), where necessary mark tables and their inverses are prepared. The subduction data are used in combinatorial enumeration of C_{60} -derivatives with given symmetries as well as in characterization of their symmetrical properties. Then, the concept of chirogenic sites is extended so as to characterize reaction sites in homospheric orbits. We also formulate bond-differentiating chiral reactions, where the sphericity concept is applied to an orbit containing equivalent edges (bonds). This formulation will be done by using the enumerated derivatives of C_{60} , where subduction tables for the groups (I_h and T_h) play an important role for discussing symmetrical relationships of the derivatives.

2. ENUMERATION OF FULLERENE ADDUCTS

2.1. Subduction of Coset Representations of Point Groups I_h and T_h . Subduction of coset representations (CRs) has originally been presented for combinatorial enumeration.³³ Later, the subduction has been applied to systematic classification of molecular symmetries³⁴ as well as to desymmetrization of achiral and chiral objects.^{17,19} Although subduction tables for several groups have been reported,¹⁹ we shall prepare here necessary tables for discussing I_h and related symmetries. Throughout the present paper, we use the symbols proposed in the previous paper:³³ *i.e.*, $G/(G_i)$ for designating a CR and $G/(G_i) \downarrow G_j$ for denoting a subduction, where G_i and G_j are subgroups of the group G .

The I_h skeleton of buckminsterfullerene (C_{60}) has 30 [6:6]-edges governed by coset representation (CR) $I_h/(C_{2v})$ and 60 [5:6]edges governed by CR $I_h/(C_s)$.^{35,36} Note that the notation [5:6] represents an edge between adjacent five- and six-membered rings, while [6:6] represents an edge between adjacent two six-membered rings. Suppose that 30 double bonds are placed on the [6:6]edges subject to the CR $I_h/(C_{2h})$ for simplicity of discussion, although thermal equilibration has been observed among several valence or positional isomers.³⁷ The enumeration of adducts and their symmetry characterization are conducted on the basis of the subduction of the CR $I_h/(C_{2v})$ and related tables derived from the subduction. For the purpose of the enumeration, tables such as a mark table, its inverse and a USCI (unit-subduced-cycle-index) table are necessary; they have previously been reported for the group I_h .³⁸ On the other hand, the symmetry characterization necessitates such raw subduction data as Table 1, which have not been reported for the group I_h .

For preparing the subduction table of I_h , the mark tables of all the subgroups of I_h are required.³³ For example, the subduction, $I_h/(C_{2v}) \downarrow T_h$, is calculated from the mark table (Table 2) or its inverse for the subgroup T_h (Table 3). These

Table 2. Mark Table of the T_h

	C_1	C_2	C_3	C_i	C_3	C_{2v}	C_{2h}	D_2	C_{3i}	D_{2h}	T	T_h
$T_h/(C_1)$	24	0	0	0	0	0	0	0	0	0	0	0
$T_h/(C_2)$	12	4	0	0	0	0	0	0	0	0	0	0
$T_h/(C_3)$	12	0	4	0	0	0	0	0	0	0	0	0
$T_h/(C_i)$	12	0	0	12	0	0	0	0	0	0	0	0
$T_h/(C_3)$	8	0	0	0	2	0	0	0	0	0	0	0
$T_h/(C_{2v})$	6	2	4	0	0	2	0	0	0	0	0	0
$T_h/(C_{2h})$	6	2	2	6	0	0	2	0	0	0	0	0
$T_h/(D_2)$	6	6	0	0	0	0	0	6	0	0	0	0
$T_h/(C_{3i})$	4	0	0	4	1	0	0	0	1	0	0	0
$T_h/(D_{2h})$	3	3	3	3	0	3	3	3	0	3	0	0
$T_h/(T)$	2	2	0	0	2	0	0	2	0	0	2	0
$T_h/(T_h)$	1	1	1	1	1	1	1	1	1	1	1	1

tables are in turn obtained from the multiplication table of T_h group and the mark tables of its subgroups.

When we count fixed edges (double bonds) on all the symmetry operations of T_h , we obtain a fixed-point vector (FPV), (30,2,4,0,0,2,0,0,0,0,0,0), which can be also obtained by collecting the corresponding elements of the mark table of the I_h group. The FPV is multiplied by the inverse of the mark table (Table 3) which is regarded as a matrix (M^{-1}), *i.e.*

$$(30,2,4,0,0,2,0,0,0,0,0,0)M^{-1} = (1,0,0,0,0,1,0,0,0,0,0,0) \quad (1)$$

The resulting row vector indicates the appearance of CRs, $T_h/(C_1)$ and $T_h/(C_{2v})$, as shown in eq 2.

$$I_h/(C_{2v}) \downarrow T_h = T_h/(C_1) + T_h/(C_{2v}) \quad (2)$$

This procedure is repeated for every subgroup to prepare the subduction table shown in Table 1.

Since T_h -symmetrical hexakisadducts are representative products derived from C_{60} ,^{25,31} further desymmetrization provides potential routes to chiral compounds with interesting symmetries. For discussing such routes, we prepared Table 4 showing the subduction of the group T_h .

2.2. The Partial-Cycle-Index Method. The Pólya–Redfield theorem has been a standard tool for combinatorial enumeration.^{39–41} Although the theorem itself and its variation have been applied to enumeration of fullerenes,^{42,43} the enumeration results are itemized only with respect to molecular formulas, to chirality and achirality, or to irreducible representations. For the present purpose of discussing symmetry problems, more elaborate enumeration is desirable; that is to say, enumeration results should be itemized with respect to symmetries (point groups) as well as to molecular formulas. Several methods have later been reported for such elaborate enumeration: Hässelbarth's method based on mark tables,⁴⁴ Mead's method combining mark tables and double cosets,⁴⁵ Brocas' method combining double cosets and framework groups,⁴⁶ and Lloyd's mark version of the Readfield–Read superposition theorem.⁴⁷ As a more systematic approach to the elaborate enumeration, we have recently reported the USCI (unit-subduced-cycle-index) approach by starting from subduction of coset representations (CRs). The USCI approach involves four versatile methods: a generating-function method based on subduced cycle indices (method I),³³ a generating-function method based on partial cycle indices (method II),^{19,48} a method based on the elementary superposition theorem (method III),^{49,50} and a method based on the partial superposition theorem (method

Table 3. The Inverse Mark Table of T_h

	T_h (/C ₁)	T_h (/C ₂)	T_h (/C _s)	T_h (/C _i)	T_h (/C ₃)	T_h (/C _{2v})	T_h (/C _{2h})	T_h (/D ₂)	T_h (/C _{3i})	T_h (/D _{2h})	T_h (/T)	T_h (/T _h)	sum
C ₁	$\frac{1}{24}$	0	0	0	0	0	0	0	0	0	0	0	$\frac{1}{24}$
C ₂	$-\frac{1}{8}$	$\frac{1}{4}$	0	0	0	0	0	0	0	0	0	0	$\frac{1}{8}$
C _s	$-\frac{1}{8}$	0	$\frac{1}{4}$	0	0	0	0	0	0	0	0	0	$\frac{1}{8}$
C _i	$-\frac{1}{24}$	0	0	$\frac{1}{12}$	0	0	0	0	0	0	0	0	$\frac{1}{24}$
C ₃	$-\frac{1}{6}$	0	0	0	$\frac{1}{2}$	0	0	0	0	0	0	0	$\frac{1}{3}$
C _{2v}	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{2}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0	0
C _{2h}	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0
D ₂	$\frac{1}{12}$	$-\frac{1}{4}$	0	0	0	0	0	$\frac{1}{6}$	0	0	0	0	0
C _{3i}	$\frac{1}{6}$	0	0	$-\frac{1}{3}$	$-\frac{1}{2}$	0	0	0	1	0	0	0	$\frac{1}{3}$
D _{2h}	$-\frac{1}{3}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{6}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{6}$	0	$\frac{1}{3}$	0	0	0
T	$\frac{1}{6}$	0	0	0	$-\frac{1}{2}$	0	0	$-\frac{1}{6}$	0	0	$\frac{1}{2}$	0	0
T _h	$-\frac{1}{6}$	0	0	$\frac{1}{3}$	$\frac{1}{2}$	0	0	$\frac{1}{6}$	-1	$-\frac{1}{3}$	$-\frac{1}{2}$	1	0

Table 4. Subduction Table of T_h

	↓ C ₁	↓ C ₂	↓ C _s	↓ C _i	↓ C ₃	↓ C _{2v}	↓ C _{2h}	↓ D ₂	↓ C _{3i}	↓ D _{2h}	↓ T	↓ T _h
T_h (/C ₁)	24C ₁ (/C ₁)	12C ₂ (/C ₁)	12C _s (/C ₁)	12C _i (/C ₁)	8C ₃ (/C ₁)	6C _{2v} (/C ₁)	6C _{2h} (/C ₁)	6D ₂ (/C ₁)	4C _{3i} (/C ₁)	3D _{2h} (/C ₁)	2T(/C ₁)	T_h (/C ₁)
T_h (/C ₂)	12C ₁ (/C ₁)	4C ₂ (/C ₁) +4C ₂ (/C ₂)	6C _s (/C ₁)	6C _i (/C ₁)	4C ₃ (/C ₁)	2C _{2v} (/C ₁) +2C _{2v} (/C ₂)	2C _{2h} (/C ₁) +2C _{2h} (/C ₂)	D ₂ (/C ₂) +D ₂ (/C ₂) +D ₂ (/C ₂)	2C _{3i} (/C ₁)	D _{2h} (/C ₂) +D _{2h} (/C ₂) +D _{2h} (/C ₂)	2T(/C ₂)	T_h (/C ₂)
T_h (/C _s)	12C ₁ (/C ₁)	6C ₂ (/C ₁)	4C _s (/C ₁) +4C _s (/C _s)	6C _i (/C ₁)	4C ₃ (/C ₁)	C _{2v} (/C ₁) +2C _{2v} (/C _s) +2C _{2v} (/C _s)	2C _{2h} (/C ₁) +2C _{2h} (/C _s)	3D ₂ (/C ₁)	2C _{3i} (/C ₁)	D _{2h} (/C _s) +D _{2h} (/C _s) +D _{2h} (/C _s)	T(/C ₁)	T_h (/C _s)
T_h (/C _i)	12C ₁ (/C ₁)	6C ₂ (/C ₁)	6C _s (/C ₁)	12C _i (/C _i)	4C ₃ (/C ₁)	3C _{2v} (/C ₁)	6C _{2h} (/C _i)	3D ₂ (/C ₁)	4C _{3i} (/C _i)	3D _{2h} (/C _i)	T(/C ₁)	T_h (/C _i)
T_h (/C ₃)	8C ₁ (/C ₁)	4C ₂ (/C ₁)	4C _s (/C ₁)	4C _i (/C ₁)	2C ₃ (/C ₁) +2C ₃ (/C ₃)	2C _{2v} (/C ₁)	2C _{2h} (/C ₁)	2D ₂ (/C ₁)	C _{3i} (/C ₁) +C _{3i} (/C ₃)	D _{2h} (/C ₁)	T(/C ₃)	T_h (/C ₃)
T_h (/C _{2v})	6C ₁ (/C ₁)	2C ₂ (/C ₁) +2C ₂ (/C ₂)	C _s (/C ₁) +4C _s (/C _s)	3C _i (/C ₁)	2C ₃ (/C ₁)	C _{2v} (/C _s) +2C _{2v} (/C _s) +2C _{2v} (/C _{2v})	C _{2h} (/C ₁) +2C _{2h} (/C _s)	D ₂ (/C ₂) +D ₂ (/C ₂) +D ₂ (/C ₂)	C _{3i} (/C ₁)	D _{2h} (/C _{2v}) +D _{2h} (/C _{2v}) +D _{2h} (/C _{2v})	T(/C ₂)	T_h (/C _{2v})
T_h (/C _{2h})	6C ₁ (/C ₁)	2C ₂ (/C ₁) +2C ₂ (/C ₂)	2C _s (/C ₁) +2C _s (/C _s)	6C _i (/C _i)	2C ₃ (/C ₁)	C _{2v} (/C ₂) +C _{2v} (/C _s) +C _{2v} (/C _s)	2C _{2h} (/C _i) +2C _{2h} (/C _{2h})	D ₂ (/C ₂) +D ₂ (/C ₂) +D ₂ (/C ₂)	2C _{3i} (/C _i)	D _{2h} (/C _{2h}) +D _{2h} (/C _{2h}) +D _{2h} (/C _{2h})	T(/C ₂)	T_h (/C _{2h})
T_h (/D ₂)	6C ₁ (/C ₁)	6C ₂ (/C ₂)	3C _s (/C ₁)	3C _i (/C ₁)	2C ₃ (/C ₁)	3C _{2v} (/C ₂)	3C _{2h} (/C ₂)	6D ₂ (/D ₂)	C _{3i} (/C ₁)	3D _{2h} (/D ₂)	2T(/D ₂)	T_h (/D ₂)
T_h (/C _{3i})	4C ₁ (/C ₁)	2C ₂ (/C ₁)	2C _s (/C ₁)	4C _i (/C _i)	C ₃ (/C ₁) +C ₃ (/C ₃)	2C _{2v} (/C ₁)	2C _{2h} (/C _i)	D ₂ (/C ₁)	C _{3i} (/C ₁) +C _{3i} (/C _{3i})	D _{2h} (/C _i)	T(/C ₃)	T_h (/C _{3i})
T_h (/D _{2h})	3C ₁ (/C ₁)	3C ₂ (/C ₂)	3C _s (/C _s)	3C _i (/C _i)	C ₃ (/C ₁)	3C _{2v} (/C _{2v})	3C _{2h} (/C _{2h})	3D ₂ (/D ₂)	C _{3i} (/C _i)	3D _{2h} (/D _{2h})	T(/D ₂)	T_h (/D _{2h})
T_h (/T)	2C ₁ (/C ₁)	2C ₂ (/C ₂)	C _s (/C ₁)	C _i (/C ₁)	2C ₃ (/C ₃)	C _{2v} (/C ₂)	C _{2h} (/C ₂)	2D ₂ (/D ₂)	C _{3i} (/C ₃)	D _{2h} (/D ₂)	2T(/T)	T_h (/T)
T_h (/T _h)	C ₁ (/C ₁)	C ₂ (/C ₂)	C _s (/C _s)	C _i (/C _i)	C ₃ (/C ₃)	C _{2v} (/C _{2v})	C _{2h} (/C _{2h})	D ₂ (/D ₂)	C _{3i} (/C _{3i})	D _{2h} (/D _{2h})	T(/T)	T_h (/T _h)

IV).⁵⁰ As compared by using digraphs as examples,⁵¹ the methods of the USCI approach are equally useful and can be applied to any combinatorial enumerations. We have already studied itemized enumeration of isomers derived from soccerane (C₆₀H₆₀) in which hydrogen atoms are replaced by other atoms.³⁵ In the present paper, we adopt method II for enumerating adducts derived by addition reactions to double bonds of buckminsterfullerene (C₆₀).

The suffixes of the USCI for each subduction (Table 1) are calculated from the orders of the corresponding group and subgroup. For example, the USCI for the subduction represented by eq 2 is calculated to be $\Phi_{T_h} = s_6s_{24}$, since we have $|T_h|/|C_1| = 24$ and $|T_h|/|C_{2v}| = 6$, where the orders of the respective subgroups are 24 for T_h , 1 for C_1 , and 4 for C_{2v} . This procedure is repeated for every subduction shown in Table 1, giving a complete USCI table of I_h group. For simplicity's sake, Table 5 indicates the USCIs concerning the CR I_h (/C_{2v}).

For the combinatorial enumeration of isomers with the subsymmetry \mathbf{G}_i (method II), partial cycle indices (PCIs)

have been defined by the following equation³⁵

$$\text{PCI}(\mathbf{G}_i; s_k) = \sum_{j=1}^s \bar{m}_{ji} \text{ZI}(\mathbf{G}_j; s_k) \quad (\text{for } i = 1, 2, \dots, s) \quad (3)$$

where the symbol \bar{m}_{ji} denotes each element of the inverse mark table and $\text{ZI}(\mathbf{G}_j; s_k)$ is a subduced cycle index (SCI).³³ The summation in eq 3 runs over a nonredundant set of subgroups, $\{\mathbf{G}_1, \mathbf{G}_2, \dots, \mathbf{G}_s\}$. Since only one orbit is taken into consideration, each SCI is equal to the corresponding USCI ($\Phi_{\mathbf{G}_j}$) in the present case. The dummy variable s_k in the right-hand side of eq 3 is replaced by the inventory

$$s_k = 1 + x^k \quad (4)$$

Then, the resulting equation for each subgroup \mathbf{G}_i ($i = 1, 2, \dots, s$) is expanded to produce a polynomial in which respective coefficients designate the numbers of derivatives.

Suppose that addition reactions occur at k of the 30 double bonds of buckminsterfullerene. Partial cycle indices (PCI)

for method II are calculated from USCIs collected in Table 5 and the elements appearing in the inverse matrix of the mark table for I_h .³⁸ The PCIs for all the subgroups are calculated as follows.

$$\text{PCI}_{T_h} = s_6 s_{24} - s_{30} = (1 + x^6)(1 + x^{24}) - (1 + x^{30}) = x^{24} + x^6 \quad (5)$$

$$\text{PCI}_{D_{5d}} = s_5^2 s_{10}^2 - s_{30} = (1 + x^5)^2 (1 + x^{10})^2 - (1 + x^{30}) = 3(x^{20} + x^{10}) \quad (6)$$

$$\begin{aligned} \text{PCI}_{D_{3d}} &= s_6^3 s_{12} - s_{30} = (1 + x^6)^3 (1 + x^{12}) - (1 + x^{30}) \\ &= 3(x^{24} + x^6) + 4(x^{18} + x^{12}) \end{aligned} \quad (7)$$

$$\begin{aligned} \text{PCI}_T &= \frac{1}{2}(x_6 s_{12}^2 - s_6 s_{24} - s_{30} + s_{30}) \\ &= \frac{1}{2}\{(1 + x^6)(1 + x^{12})^2 - (1 + x^6)(1 + x^{24})\} = x^{18} + x^{12} \end{aligned} \quad (8)$$

$$\text{PCI}_{C_{5i}} = \frac{1}{2}(s_{10}^3 - s_{10}^3) = 0 \quad (9)$$

$$\begin{aligned} \text{PCI}_{C_{5i}} &= \frac{1}{2}(s_5^4 s_{10} - s_{10}^3) = \frac{1}{2}\{(1 + x^5)^4 (1 + x^{10}) - (1 + x^{10})^3\} \\ &= 2(x^{25} + x^5) + 2(x^{20} + x^{10}) + 4x^{15} \end{aligned} \quad (10)$$

$$\text{PCI}_{D_5} = \frac{1}{2}s_5^2 s_{10}^2 - \frac{1}{2}s_{10}^3 = x^5 + 2x^{15} + \dots \quad (11)$$

$$\text{PCI}_{D_{2h}} = \frac{1}{3}s_2^3 s_8^3 - \frac{1}{3}s_6 s_{24} = x^8 + 3x^{10} + 3x^{12} + x^{14} + \dots \quad (12)$$

$$\text{PCI}_{C_{3i}} = \frac{1}{2}s_6^5 - \frac{1}{2}s_6^3 s_{12} - s_{30} + s_{30} = 3x^{12} + \dots \quad (13)$$

$$\begin{aligned} \text{PCI}_{C_{3v}} &= \frac{1}{2}s_3^4 s_6^3 - \frac{1}{2}s_6^3 s_{12} \\ &= 2x^3 + 3x^6 + 8x^9 + 9x^{12} + 12x^{15} + \dots \end{aligned} \quad (14)$$

$$\begin{aligned} \text{PCI}_{D_3} &= \frac{1}{2}s_3^2 s_6^4 - \frac{1}{2}s_6^3 s_{12} - \frac{1}{2}s_{30} + \frac{1}{2}s_{30} \\ &= x^3 + x^6 + 4x^9 + 3x^{12} + 6x^{15} + \dots \end{aligned} \quad (15)$$

$$\begin{aligned} \text{PCI}_{C_5} &= \frac{1}{4}s_5^6 - \frac{1}{4}s_5^2 s_{10}^2 - \frac{1}{4}s_5^4 s_{10} - \frac{1}{4}s_{10}^3 + \frac{1}{2}s_{10}^3 \\ &= 2x^{10} + 2x^{15} + \dots \end{aligned} \quad (16)$$

$$\text{PCI}_{C_{2h}} = \frac{1}{2}s_2^3 s_4^6 - \frac{1}{2}s_2^3 s_8^3 - s_6^3 s_{12} - s_{10}^3 + 2s_{30}$$

$$= 3x^4 + 6x^6 + 15x^8 + 18x^{10} + 24x^{12} + 36x^{14} + \dots \quad (17)$$

$$\begin{aligned} \text{PCI}_{C_{2v}} &= \frac{1}{2}s_1^2 s_2^2 s_4^6 - \frac{1}{2}s_2^3 s_8^3 \\ &= x + 2x^3 + 3x^4 + 7x^5 + 9x^6 + 12x^7 + 15x^8 + 21x^9 + \\ &\quad 21x^{10} + 30x^{11} + 28x^{12} + 35x^{13} + 36x^{14} + \\ &\quad 40x^{15} + \dots \end{aligned} \quad (18)$$

$$\begin{aligned} \text{PCI}_{D_2} &= \frac{1}{6}s_2^3 s_4^6 - \frac{1}{6}s_2^3 s_8^3 - \frac{1}{6}s_6^2 s_{12} + \frac{1}{6}s_6^2 s_{24} \\ &= x^4 + 3x^6 + 5x^8 + 7x^{10} + 9x^{12} + 12x^{14} + \dots \end{aligned} \quad (19)$$

$$\begin{aligned} \text{PCI}_{C_3} &= \frac{1}{4}s_3^{10} - \frac{1}{4}s_3^2 s_6^4 - \frac{1}{4}s_3^4 s_6^3 - \frac{1}{4}s_6^5 - \frac{1}{2}s_6^2 s_{12}^2 + \\ &\quad \frac{1}{2}s_6^3 s_{12} + \frac{1}{2}s_6^2 s_{24} + \frac{1}{2}s_{30} - \frac{1}{2}s_{30} \\ &= x^3 + 8x^6 + 24x^9 + 43x^{12} + 54x^{15} + \dots \end{aligned} \quad (20)$$

$$\begin{aligned} \text{PCI}_{C_i} &= \frac{1}{60}s_2^{15} - \frac{1}{4}s_2^3 s_4^6 - \frac{1}{6}s_6^5 + \frac{1}{6}s_2^3 s_8^3 - \frac{1}{10}s_{10}^3 + \\ &\quad \frac{1}{2}s_6^3 s_{12} + \frac{1}{3}s_6^2 s_{24} - s_{30} \\ &= 4x^6 + 15x^8 + 40x^{10} + 69x^{12} + 89x^{14} + \dots \end{aligned} \quad (21)$$

$$\begin{aligned} \text{PCI}_{C_s} &= \frac{1}{4}s_1^4 s_2^{13} - \frac{1}{2}s_1^2 s_2^2 s_4^6 - \frac{1}{4}s_2^3 s_4^6 - \frac{1}{2}s_3^4 s_6^3 + \frac{1}{2}s_2^3 s_8^3 - \\ &\quad \frac{1}{2}s_5^4 s_{10} + \frac{1}{2}s_6^3 s_{12} + \frac{1}{2}s_{10}^3 \\ &= 4x^2 + 10x^3 + 34x^4 + 82x^5 + 175x^6 + 352x^7 + \\ &\quad 604x^8 + 972x^9 + 1430x^{10} + 1972x^{11} + 2485x^{12} + \\ &\quad 2968x^{13} + 3270x^{14} + 3376x^{15} + \dots \end{aligned} \quad (22)$$

$$\begin{aligned} \text{PCI}_{C_2} &= \frac{1}{4}s_1^2 s_2^{14} - \frac{1}{4}s_2^3 s_4^6 - \frac{1}{4}s_1^2 s_2^2 s_4^6 - \frac{1}{4}s_2^3 s_4^6 - \frac{1}{2}s_3^2 s_6^4 + \\ &\quad \frac{1}{2}s_2^3 s_8^3 - \frac{1}{2}s_5^2 s_{10}^2 + \frac{1}{2}s_6^3 s_{12} + \frac{1}{2}s_{10}^3 + s_{30} - s_{30} \\ &= 3x^2 + 5x^3 + 21x^4 + 41x^5 + 99x^6 + 176x^7 + \\ &\quad 318x^8 + 486x^9 + 717x^{10} + 986x^{11} + 1204x^{12} + \\ &\quad 1484x^{13} + 1554x^{14} + 1688x^{15} + \dots \end{aligned} \quad (23)$$

$$\begin{aligned} \text{PCI}_{C_1} &= \frac{1}{120}s_1^{30} - \frac{1}{8}s_1^2 s_2^{14} - \frac{1}{8}s_1^4 s_2^{13} - \frac{1}{120}s_2^{15} - \frac{1}{12}s_3^{10} + \\ &\quad \frac{1}{12}s_3^2 s_4^6 + \frac{1}{4}s_1^2 s_2^2 s_4^6 + \frac{1}{4}s_2^3 s_4^6 - \frac{1}{20}s_5^6 + \frac{1}{4}s_3^2 s_6^4 + \frac{1}{4}s_3^4 s_6^3 + \\ &\quad \frac{1}{12}s_6^5 - \frac{1}{3}s_2^3 s_8^3 + \frac{1}{4}s_5^2 s_{10}^2 + \frac{1}{4}s_5^4 s_{10} + \frac{1}{20}s_{10}^3 + \frac{1}{6}s_6^2 s_{12}^2 - \\ &\quad \frac{1}{2}s_6^3 s_{12} - \frac{1}{2}s_{10}^3 - \frac{1}{6}s_6^2 s_{24} - \frac{1}{2}s_{30} + \frac{1}{2}s_{30} \\ &= 25x^3 + 199x^4 + 1124x^5 + 4801x^6 + 16698x^7 + \\ &\quad 48297x^8 + 118482x^9 + 249269x^{10} + 453741x^{11} + \\ &\quad 718865x^{12} + 995764x^{13} + 1209378x^{14} + \\ &\quad 1290082x^{15} + \dots \end{aligned} \quad (24)$$

The coefficient of each term x^k in the expanded equations (eqs 5–24) indicates the number of derivatives with the

Table 5. Subductions and USCIs of the $I_h(C_{2v})$ Orbit

subgroup (G_j)	subduction $I_h(C_{2v}) \downarrow G_j$	USCI (=SCI=ZI($G_j; s_k$))	sum $\sum_{i=1}^s \bar{m}_{ji}$
C_1	$30C_1/(C_1)$	$\Phi_{C_1} = s_1^{30}$	1/120
C_2	$14C_2/(C_1) + 2C_2/(C_2)$	$\Phi_{C_2} = s_1^2 s_2^{14}$	1/8
C_s	$13C_s/(C_1) + 4C_s/(C_s)$	$\Phi_{C_s} = s_1^4 s_2^{13}$	1/8
C_i	$15C_i/(C_1)$	$\Phi_{C_i} = s_2^{15}$	1/120
C_3	$10C_3/(C_1)$	$\Phi_{C_3} = s_3^{10}$	1/6
D_2	$6D_2/(C_1) + D_2/(C_2) + D_2/(C'_2) + D_2/(C''_2)$	$\Phi_{D_2} = s_2^3 s_4^6$	0
C_{2v}	$6C_{2v}/(C_1) + C_{2v}/(C_s) + C_{2v}/(C'_s) + 2C_{2v}/(C_{2v})$	$\Phi_{C_{2v}} = s_1^2 s_2^2 s_4^6$	0
C_{2h}	$6C_{2h}/(C_1) + C_{2h}/(C_2) + 2C_{2h}/(C'_s)$	$\Phi_{C_{2h}} = s_2^3 s_4^6$	0
C_5	$6C_5/(C_1)$	$\Phi_{C_5} = s_5^6$	1/5
D_3	$4D_3/(C_1) + 2D_3/(C_2)$	$\Phi_{D_3} = s_3^2 s_6^4$	0
C_{3v}	$3C_{3v}/(C_1) + 4C_{3v}/(C_s)$	$\Phi_{C_{3v}} = s_3^4 s_6^3$	0
C_{3i}	$5C_{3i}/(C_1)$	$\Phi_{C_{3i}} = s_6^5$	1/6
D_{2h}	$3D_{2h}/(C_1) + D_{2h}/(C_{2v}) + D_{2h}/(C'_{2v}) + D_{2h}/(C''_{2v})$	$\Phi_{D_{2h}} = s_2^3 s_8^3$	0
D_5	$2D_5/(C_1) + 2D_5/(C_2)$	$\Phi_{D_5} = s_5^2 s_{10}^2$	0
C_{5v}	$C_{5v}/(C_1) + 4C_{5v}/(C_s)$	$\Phi_{C_{5v}} = s_5^4 s_{10}$	0
C_{5i}	$3C_{5i}/(C_1)$	$\Phi_{C_{5i}} = s_{20}^3$	1/5
T	$2T/(C_1) + T/(C_2)$	$\Phi_T = s_6^2 s_{12}$	0
D_{3d}	$D_{3d}/(C_1) + D_{3d}/(C_2) + 2D_{3d}/(C_s)$	$\Phi_{D_{3d}} = s_6^3 s_{12}$	0
D_{5d}	$D_{5d}/(C_2) + 2D_{5d}/(C_s)$	$\Phi_{D_{5d}} = s_{10}^3$	0
T_h	$T_h/(C_1) + T_h/(C_{2v})$	$\Phi_{T_h} = s_6^5 s_{24}$	0
I	$I/(C_2)$	$\Phi_I = s_{30}$	0
I_h	$I_h/(C_{2v})$	$\Phi_{I_h} = s_{30}$	0

corresponding symmetry in which k of the double bonds are attacked. Obviously, the coefficient of x^k is the same as that of x^{30-k} for the present enumeration. The present results obtained by means of method II (eqs 5–24) are mathematically equivalent to the previous result that has been reported for the enumeration of dodecahedrane derivatives by using method I.³⁸ Note that the bonds (edges) of dodecahedrane construct an orbit governed by the same CR $I_h(C_{2v})$ as the present case. The comparison of the two enumerations exemplifies the relationship between the methods of the USCI approach and indicates the equal usefulness of them.

Total numbers without consideration of subsymmetries are calculated by summing up all of the PCIs shown in eq 3. Since the terms other than those of cyclic groups vanish during the summation, we obtain a definition of a cycle index (CI).⁵²

$$CI = \sum_{i=1}^s PCI(G_i; s_k) \quad (25)$$

$$= \sum_{j=1}^s \left(\sum_{i=1}^s \bar{m}_{ji} \right) ZI(G_j; s_k) \quad (\text{for } i = 1, 2, \dots, s) \quad (26)$$

The sum $\sum_{i=1}^s \bar{m}_{ji}$ in eq 26 is calculated by summing up the elements appearing in each row of the inverse of a mark table, as shown in the rightmost column of Table 5 for the group I_h . By introducing the inventory (eq 4) into the CI of the present case (derived from eq 26), we have the following generating function

$$CI = \frac{1}{120} s_1^{30} + \frac{1}{8} s_1^2 s_2^{14} + \frac{1}{8} s_1^4 s_2^{13} + \frac{1}{120} s_2^{15} + \frac{1}{6} s_3^{10} + \frac{1}{5} s_5^6 + \frac{1}{6} s_6^5 + \frac{1}{5} s_{10}^3$$

$$= 1 + x + 8x^2 + 46x^3 + 262x^4 + 1257x^5 + 5113x^6 + 17238x^7 + 49270x^8 + 119997x^9 + 251512x^{10} + 456729x^{11} + 722750x^{12} + 1000251x^{13} + 1214376x^{14} + 1295266x^{15} + \dots \quad (27)$$

To illustrate the results, Figure 1 shows one x^6 -derivative with T_h symmetry (**1**), one x^{12} -derivative with T symmetry (**2**), and three x^{10} -derivatives with D_{5d} symmetry (**3** to **5**), where boldfaced edges indicate double bonds attacked, while unreacted double bonds on [6:6]edges are not designated. The point group of each adduct remains unchanged if we exchange attacked double bonds with unattacked ones. Note that the original double bonds are placed on the 30 [6:6]-edges of C_{60} . Hence, there exist complementary series of derivatives: one $[x^{24}, T_h]$ -derivative, one $[x^{18}, T]$ -derivative, and three $[x^{20}, D_{5d}]$ -derivatives. For simplicity of illustration, we show either one from such a complementary pair. In the present enumeration, each pair of antipodes is counted once; hence an arbitrary antipode of the T -derivative (**2**) is shown in Figure 1. Figure 2 illustrates three x^6 -derivatives (**6**–**8**) and four x^{12} -derivatives (**9**–**12**), both having D_{3d} symmetry.

3. SYMMETRICAL PROPERTIES OF BUCKMINSTERFULLERENE ADDUCTS

3.1. Locativity for Specifying Bond Pairs. We use Greek letters to designate pairwise relationships between a given standard bond and another [6:6]bond in a bond pair of C_{60} . As shown in Figure 3, a top horizontal [6:6]bond (at the north pole) is selected as a standard bond, and each representative of a set of equivalent positions is denoted by

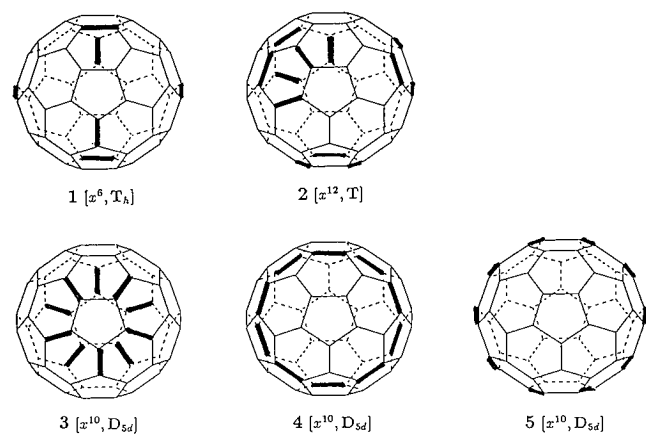


Figure 1. Derivatives with the symmetries T_h , T , and D_{5d} .

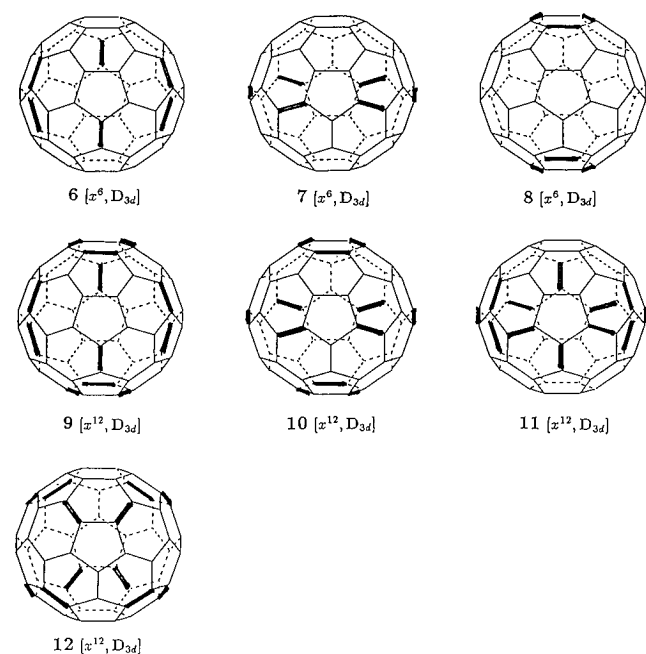


Figure 2. Derivatives with the symmetry D_{3d} .

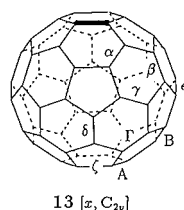


Figure 3. Positional relationships between two [6:6] bonds of fullerene.

a Greek letter. Thus, lowercase Greek letters (α , β , and γ) are used to designate the relationship between a given standard bond and another [6:6]bond in a bond pair of the same hemisphere of C_{60} ; uppercase Greek letters A, B, and Γ) are used to denote the relationship concerning [6:6]bonds in a bond pair of the opposite hemisphere; the letters δ and ϵ are used to show relationships concerning equator bonds; and the letter ζ is used to describe a relationship concerning the bond at the south pole.

In terms of the membership criterion of topicity, the relationship between two [6:6]bonds in buckminsterfullerene is concluded to be homotopic.¹⁷ Such a homotopic relationship has been divided into two categories: *holotopic* and *hemitopic*, by considering whether it is concerned with a

homospheric orbit or with an enantiospheric orbit.¹⁹ Because the [6:6]bonds belong to a homospheric $I_h/(C_{2v})$ -orbit, each pairwise relationship in buckminsterfullerene bonds is ascribed to a holotopic case. The application of the topicity terms implies that each [6:6]bond of buckminsterfullerene is regarded as a proligand, which has been defined as a chemical or mathematical object that has chirality but no structure.²¹ Thus, a topicity term determines the pairwise relationship between a proligand and another proligand.

Since buckminsterfullerene has thirty [6:6]bonds, it has higher relationships than the pairwise relationships. The topicity terms are insufficient to describe such higher relationships. Suppose that a proligand pair (a bond pair in this context) is an object to be considered. Then, we consider the relationship between a proligand pair (bond pair) and another proligand pair (bond pair). In the light of this formulation, each proligand pair (bond pair) is considered to have structure.⁵³ It follows that achirality as a proligand pair is subdivided into several distinct categories. For further classification of achirality of proligand pairs, we propose locativity terms as follows:

pair as proligand	pair as proligand pair
achiral	mesolocate ... α, β, Γ
	equilocate ... ζ
	dialocate ... $\delta(\epsilon)$
chiral	semilocate ... A, B, γ

Since a bond pair (proligand pair) has a pairwise structure, the achirality of the bond pair can be discussed by taking into account pairwise relationship in every bond pair (not in buckminsterfullerene itself). When the α -bond is reversely selected as a standard, the original standard is in a mirror relationship to α , which is designated by the symbol with a tilde ($\tilde{\alpha}$). Such a bond pair is defined as being *mesolocate*.⁵⁴ In a similar way, β - and Γ -relationships are mesolocate ($\beta \leftrightarrow \tilde{\beta}$ and $\Gamma \leftrightarrow \tilde{\Gamma}$). Since the reverse of the ζ -relationship is also ζ , such a bond pair is defined as being *equilocate*. Since we have $\delta \leftrightarrow \epsilon$ ($\epsilon \leftrightarrow \delta$), such a bond pair is defined to be *dialocate*. The newly-formed terms (mesolocate, equilocate, and dialocate) are concerned with a homospheric CR as discussed later.

On the other hand, the γ -relationship is unchanged if the γ -bond is selected as an alternative standard. Such a bond pair is defined as being *semilocate*. It should be noted we have $\gamma \leftrightarrow \gamma$ and $\tilde{\gamma} \leftrightarrow \tilde{\gamma}$, which are superposed only by improper rotations. Since we have $A \leftrightarrow A$ ($\tilde{A} \leftrightarrow \tilde{A}$) and $B \leftrightarrow B$ ($\tilde{B} \leftrightarrow \tilde{B}$), these bond pairs are semilocate. Although the relationships represented by the Greek letters are applied only in fullerene chemistry, the locativity terms can generally be used in any other situations.

3.2. Stereochemical Nonequivalency in Mono- and Bisadducts. For the present purpose of discussing symmetry problems in addition reactions of the C_{60} -skeleton, we recognize them as desymmetrization of I_h symmetry. Hence, we will frequently refer to appropriate rows of Table 1 in the present section. In particular, we pay attention to the behavior of the $I_h/(C_{2v})$ -orbit of the [6:6]bonds as well as to that of the $I_h/(C_s)$ -orbit of the 60 atoms.

The coefficient of the term x in eq 27 indicates the existence of only one monoadduct. Then, each term x in eqs 5–24 is examined so as to reveal that the monoadduct

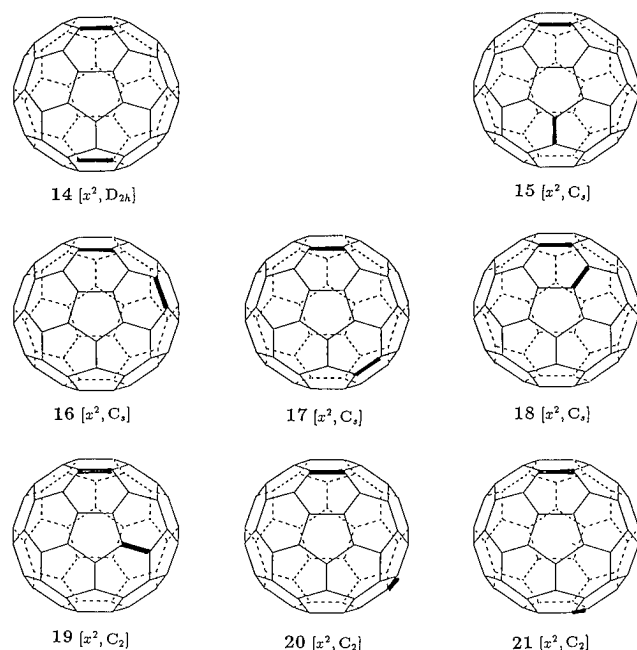


Figure 4. Bisadducts from C_{60} .

(13) has C_{2v} -symmetry. This conclusion is rationalized by the subduction appearing at the intersection of the I_h/C_{2v} -row and the C_{2v} -column in Table 1. It follows that any C_{2v} -adduct derived from C_{60} has six four-membered C_{2v}/C_1 -orbits, one two-membered C_{2v}/C_2 -orbit, one two-membered C_{2v}/C'_2 -orbit, and two one-membered C_{2v}/C_{2v} -orbits. Hence, a reagent molecule (addent) should occupy either one of the one-membered C_{2v}/C_{2v} -orbits in the monoadduct.

Eight bisadducts are possible in the light of the coefficient of the term x^2 of eq 27. Examination of the term x^2 in eqs 5–24 indicates that they are classified into one $[x^2, D_{2h}]$ -bisadduct (14), four $[x^2, C_s]$ -bisadducts (15–18), and three $[x^2, C_2]$ -bisadducts (19–21). Figure 4 schematically shows these bisadducts. Obviously, the bisadducts correspond to the relationships shown in Figure 3, except the ϵ -bond. It should be noted that, although the attack of a second reagent on the δ -bond gives the same bisadduct as the ϵ -attack, the attacking processes are different from each other. Since several bisadducts have been isolated and identified,^{55,28} the symmetrical properties of the unreacted double bonds (28 bonds) should be an interesting subject for further investigation.

The locativity in buckminsterfullerene can be related to the (a)chirality of bisadducts. Thus, two addents on the bonds of a mesolocative, equilocative, or dialocative relationship provide an achiral bisadduct, while two addents on the bonds of semilocative relation generate a chiral bisadduct. The three possibilities producing achiral bisadducts (mesolocative, equilocative, and dialocative relationships) can be differentiated if we consider further conversion of either one of the addents. First, a product (*e.g.*, 16) derived from a mesolocative relationship can be further converted into a chiral compound. For example, let the two addents of 16 be bis(ethoxycarbonyl)methylene groups. When either one is stereoselectively decarboxylated into a methylene group, the resulting adduct with a bis(ethoxycarbonyl)methylene and a methylene group is chiral, being antipodal with the adduct derived by the alternative decarboxylation.⁵⁶ Second, a compound with equilocative addents (*e.g.*, 14) gives the same achiral product even if either addent is converted; thus, the

adduct with a bis(ethoxycarbonyl)methylene and a methylene group is achiral if derived by either attack of the original bis(ethoxycarbonyl)methylenes of 14. Third, a compound with dialocative addents (*e.g.*, 15) gives distinct products in accord with either addent converted. Thus, the one product derived by decarboxylating the δ -bis(ethoxycarbonyl)methylene of 15 is different from the other derived by decarboxylating the ϵ -bis(ethoxycarbonyl)methylene of 15, although they are both achiral.⁵⁷

Symmetrical equivalence and nonequivalence of atoms (vertices) and bonds (edges) are fully characterized by such subduction as shown in Table 5. The $[x^2, D_{2h}]$ -bisadduct (14) is concluded to involve 30 edges (28 double bonds and two addition sites) that are classified into three eight-membered D_{2h}/C_1 -orbits, one two-membered D_{2h}/C_{2v} -orbit, one two-membered D_{2h}/C'_2 -orbit, and one two-membered D_{2h}/C''_2 -orbit (Table 5). Among them, two reagent molecules (addents) occupy the two-membered D_{2h}/C_{2v} -orbit. Note that the selection of the D_{2h}/C_{2v} -orbit is tentative, because the D_{2h}/C'_2 - and the D_{2h}/C''_2 -orbits are other possibilities for the addition sites. However, the conclusion is equivalent even if either one of the three possibilities is selected.

Since the 60 vertices (atoms) of C_{60} are governed by the CR I_h/C_s ,³⁵ the splitting pattern of equivalence classes of sites in the D_{2h} -derivative (14) is determined by the subduction: $I_h/C_s \downarrow D_{2h}$. By the inspection of the intersection of the I_h/C_s -row and the D_{2h} -column in Table 1, the vertices (atoms) of the $[x^2, D_{2h}]$ -bisadduct (14) split into nine categories, *i.e.*, six eight-membered D_{2h}/C_1 -orbits, one four-membered D_{2h}/C_s -orbit, one four-membered D_{2h}/C'_s -orbit, and one four-membered D_{2h}/C''_s -orbit. It follows that the four carbon atoms at the addition sites belong to the four-membered D_{2h}/C_s -orbit. In accord with the number of orbits ($6 + 1 + 1 + 1 = 9$), the 60 carbon atoms split into nine categories, which may be differentiated by ^{13}C NMR if no accidental degeneration occurs.

By examining the intersection of the I_h/C_{2v} -row and the C_s -column in Table 1 (*i.e.*, $I_h/C_{2v} \downarrow C_s$), the 30 edges (28 double bonds and two addition sites) in each of the four $[x^2, C_s]$ -bisadducts (15–18) are classified into 13 two-membered C_s/C_1 -orbits and four one-membered C_s/C_s -orbits. On the other hand, the 60 vertices are classified into 28 two-membered C_s/C_1 -orbits and four one-membered C_s/C_s -orbits by referring to the intersection of the I_h/C_s -row and the C_s -column in Table 1 (*i.e.*, $I_h/C_s \downarrow C_s$). Since the total number of orbits is calculated to be 32 ($= 28 + 4$), ^{13}C NMR of a C_s -bisadduct is expected to exhibit 32 distinct peaks, which are in accord with the data reported.⁵⁵ In particular, the bonds and atoms at the addition sites are governed by the following CRs.

objects	15	16	17	18
edges (bonds)	$2C_s/C_s$	C_s/C_1	C_s/C_1	C_s/C_1
vertices (atoms)	$C_s/C_1 + 2C_s/C_s$	$2C_s/C_1$	$2C_s/C_1$	$2C_s/C_1$

These data concerning (non)equivalency of edges (bonds) and vertices (atoms) are useful for the discussion of splitting patterns in NMR spectra.⁵⁸ For example, an isolated bisadduct, $C_{60}[\text{OsO}_4(4\text{-tert-butylpyridine})_2]_2$, has been reported to exhibit three 4-*tert*-butyl signals.⁵⁵ This result can be ascribed to a C_s -isomer which is expected to exhibit a

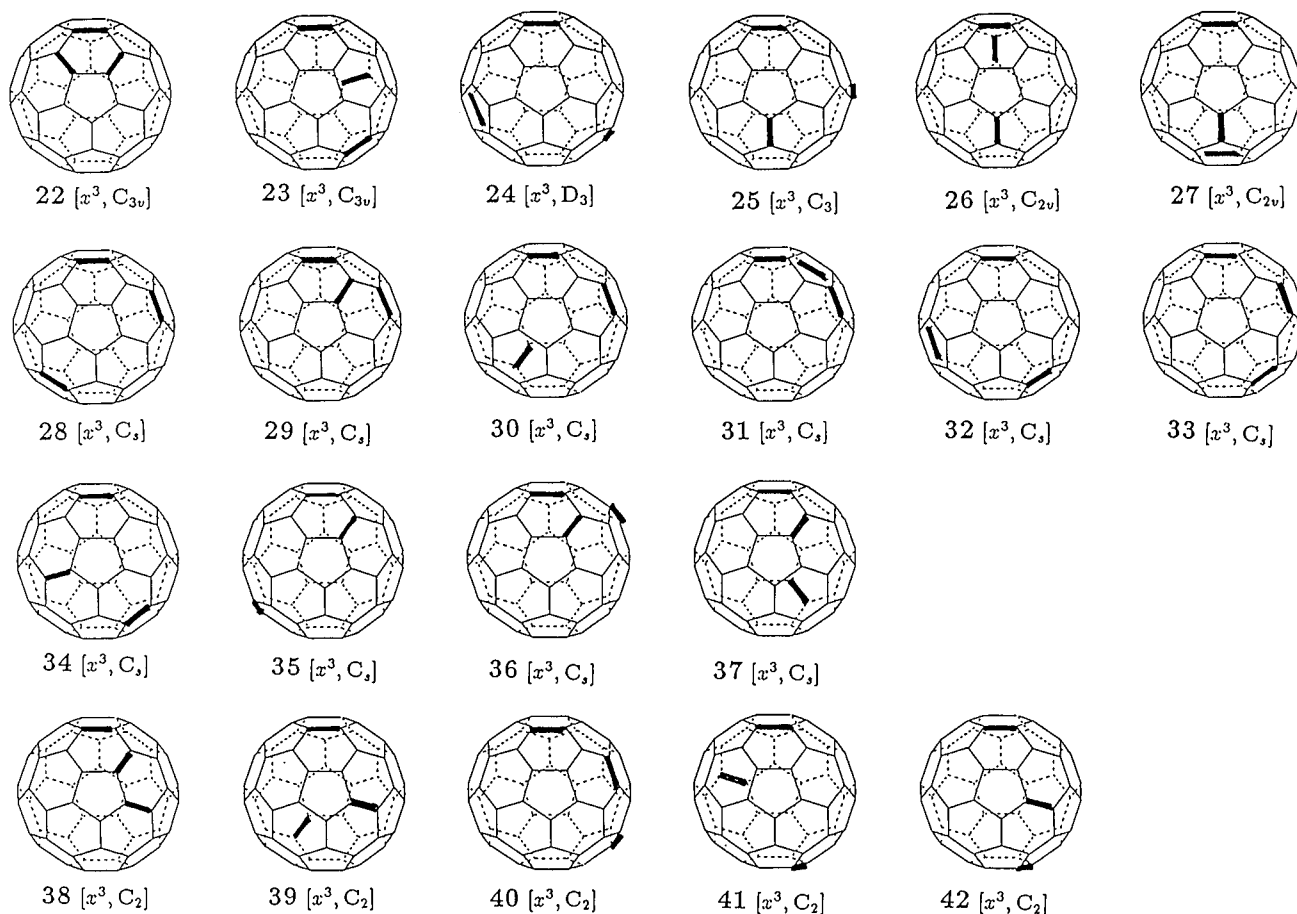


Figure 5. Trisadducts from C_{60} .

splitting pattern represented by $C_s/(C_1) + 2C_s/(C_s)$. The isomer is concluded to give the intensity ratio of 2:1:1, since we have $|C_s|/|C_1| = 2$ and $|C_s|/|C_s| = 1$.

The 30 edges in each of the three $[x^2, C_2]$ -bisadducts (**19**–**21**) are classified into 14 two-membered $C_2/(C_1)$ -orbits and two one-membered $C_2/(C_2)$ -orbits. This result is obtained from the subduction at the intersection of the $I_h/(C_{2v})$ -row and the C_2 -column in Table 1. On the other hand, the 60 vertices are classified into 30 two-membered $C_2/(C_1)$ -orbits by examining the intersection of $I_h/(C_s)$ -row and the C_2 -column in Table 1. The total number of orbits (30) predicts that ^{13}C NMR of a C_2 -bisadduct exhibits 30 distinct peaks with equal intensity; this conclusion is in accord with the data reported.⁵⁵ The bonds and atoms at the addition sites are governed by CRs as follows.

objects	19	20	21
edges (bonds)	$C_2/(C_1)$	$C_2/(C_1)$	$C_2/(C_1)$
vertices (atoms)	$2C_2/(C_1)$	$2C_1/(C_1)$	$2C_2/(C_1)$

3.3. Stereochemical Nonequivalency in Trisadducts.

Forty-six trisadducts are seen to be possible from an examination the coefficient of the term x^3 of eq 27. In light of the coefficient of x^3 in each of eqs 5–24, the trisadducts are classified into two $[x^3, C_{3v}]$ -trisadducts (**22** and **23**), one $[x^3, D_3]$ -trisadduct (**24**), one $[x^3, C_3]$ -trisadduct (**25**), two $[x^3, C_{2v}]$ -trisadducts (**26** and **27**), ten $[x^3, C_s]$ -trisadducts (**28** and **37**), five $[x^3, C_2]$ -trisadducts (**38** and **41**), and 25 $[x^3, C_1]$ -trisadducts. Figure 5 schematically shows the adducts other than the asymmetric ones. Two isolated trisadducts have

been reported to be the $[x^3, C_3]$ -adduct and the $[x^3, D_3]$ -adduct.²⁸

On the basis of the subduction data of Table 1, let us consider symmetrical properties of trisadducts with C_{3v} -, C_3 -, and D_3 -symmetry. By referring to the intersection of the $I_h/(C_{2v})$ -row and the C_{3v} -column in Table 1, the 30 edges (27 double bonds and three addition sites) in each of the $[x^3, C_{3v}]$ -trisadducts (**22** and **23**) are classified into three six-membered $C_{3v}/(C_1)$ -orbits and four three-membered $C_{3v}/(C_s)$ -orbits. The 60 vertices in **22** and **23** are, on the other hand, classified into eight six-membered $C_{3v}/(C_1)$ -orbits and four three-membered $C_{3v}/(C_s)$ -orbits by means of the intersection of the $I_h/(C_s)$ -row and the C_{3v} -column in Table 1. The total number of orbits ($8 + 4 = 12$) indicates that the ^{13}C NMR spectrum of a C_{3v} -trisadduct is expected to exhibit 12 distinct peaks.

Since we have $I_h/(C_{2v}) \downarrow C_3 = 10C_3/(C_1)$ in Table 1, we can conclude that the 30 edges (27 double bonds and three addition sites) of the $[x^3, C_3]$ -trisadduct (**25**) are classified into ten three-membered $C_3/(C_1)$ -orbits. The 60 vertices are, on the other hand, classified into 20 three-membered $C_3/(C_1)$ -orbits, which is in accord with the subduction shown in Table 1, i.e., $I_h/(C_s) \downarrow C_3 = 20C_3/(C_1)$. The number of orbits predicts 20 distinct peaks with equal intensity in the ^{13}C NMR of a C_3 -trisadduct.

The symmetrical nature of $[x^3, D_3]$ -trisadduct (**24**) is also indicated from the data in the $I_h/(C_{2v})$ -row and the $I_h/(C_s)$ -row of Table 1. The 30 edges (27 double bonds and three addition sites) of the $[x^3, D_3]$ -trisadduct (**24**) are classified into four six-membered $D_3/(C_1)$ -orbits and two three-

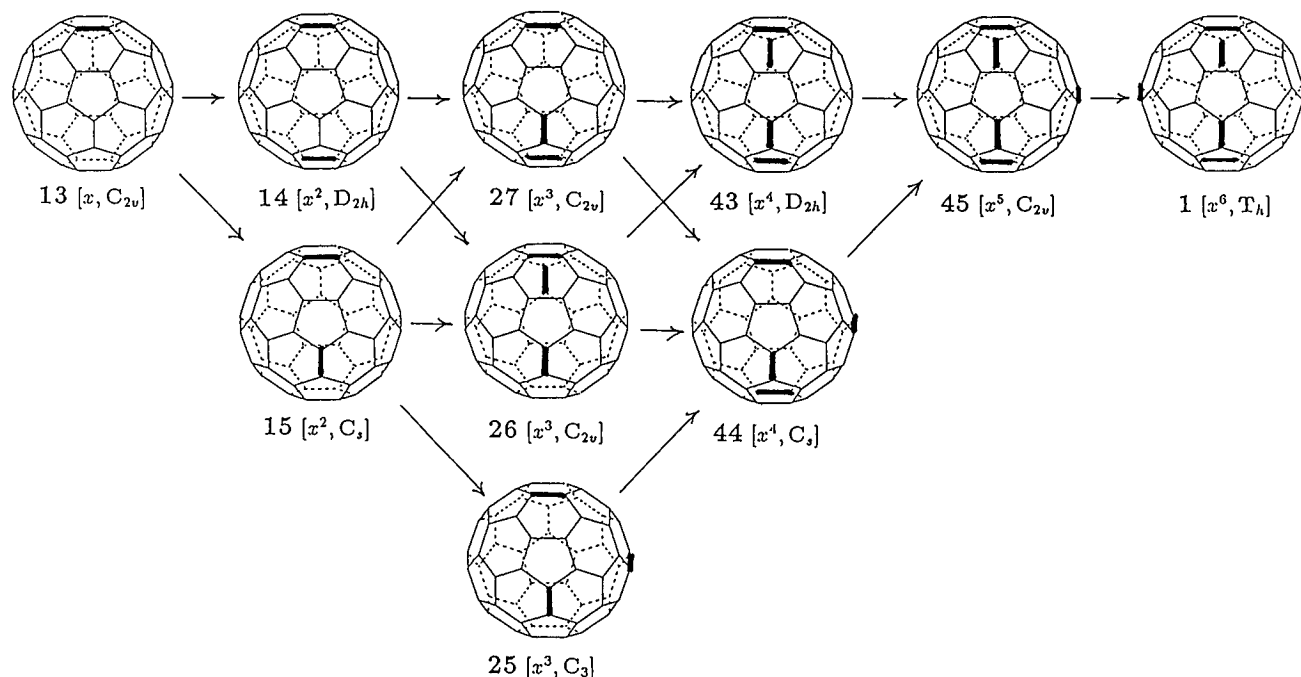


Figure 6. Possible routes to a T_h -hexakisadduct.

membered $D_3(C_2)$ -orbits, while the 60 vertices are classified into ten six-membered $D_3(C_1)$ -orbits, which predict the appearance of 10 distinct peaks in the ^{13}C NMR of a D_3 -trisadduct if no accidental degeneration occurs. In particular, the bonds and atoms at the addition sites are governed by the following CRs.

objects	22	23	24	25
edges (bonds)	$C_{3v}/(C_s)$	$C_{3v}/(C_s)$	$C_3/(C_1)$	$D_3/(C_2)$
vertices (atoms)	$C_{3v}/(C_1)$	$2C_{3v}/(C_s)$	$2C_3/(C_1)$	$D_3/(C_1)$

4. CHEMOSELECTIVE AND STERESELECTIVE CONVERSIONS

4.1. Possible Routes to T_h - and D_{3d} -Compounds via Successive Additions. This section deals with a systematic treatment of successive additions to double bonds of buckminsterfullerene in which a final polyadduct is given as a target. Such additions are referred to as bond-differentiating reactions, if chemo- or stereoselectivity emerges during the reactions. The present treatment enables us to enumerate all possibilities of chemoselective and stereoselective bond-differentiating reactions. Although the treatment is complex in nature and is not easy to solve generally, several cases such as T_h -adducts give rather simple results.

The term *chiral synthesis* is substituted for the term *asymmetric synthesis*, since the present treatment contains cases in which products are chiral but not asymmetric. The terms *enantioselective* and *diastereoselective* are replaced by the following terms in order to treat more general cases:

{	chemoselective achiral synthesis	(achiral-to-achiral synthesis)
	chemoselective chiral synthesis	(chiral-to-chiral synthesis)
	stereoselective chiral synthesis	(achiral-to-chiral synthesis)
	stereoselective achiral synthesis	(chiral-to-achiral synthesis)

The classification succeeds the one reported in Chapter 11 of ref 19, except for the last category. Note that stereose-

lective synthesis requires an appropriate chiral environment; otherwise, it results in the formation of racemic products. The term *enantioselective* is involved in the term *stereoselective chiral*, and the term *diastereoselective* is contained in the term *chemoselective chiral*.

Let us consider a T_h -adduct (**1**) in which six addends belong to the $T_h/(C_{2h})$ -orbit (Figure 6). Possible intermediates to this target compound can be regarded as molecules in which a given number of addends are deleted from the orbit. In other words, the symmetries of such intermediates should be the subgroups of T_h . Thus, the present problem is considered to be a combinatorial enumeration in which the six addends in the $T_h/(C_{2v})$ -orbit of the hexakisadduct (**1**) are reversely replaced by the original double bonds. Partial cycle indices (PCIs) for method II (eq 3) are calculated by starting from the USCI table (Table 4) and the inverse mark table (Table 3) of T_h point group. We introduce the inventory (eq 4) into each dummy variable of the PCIs. The following equations correspond to results with nonzero values.

$$\text{PCI}_{D_{2h}} = \frac{1}{3}s_2^3 - \frac{1}{3}s_6 = x^2 + x^4 \quad (28)$$

$$\text{PCI}_{C_{2v}} = \frac{1}{2}s_1^2s_2^2 - \frac{1}{2}s_2^3 = x + 2x^3 + x^5 \quad (29)$$

$$\text{PCI}_{C_3} = \frac{1}{2}s_3^2 - \frac{1}{2}s_2^3 - \frac{1}{2}s_6 + \frac{1}{2}s_6 = x^3 \quad (30)$$

$$\text{PCI}_{C_s} = \frac{1}{4}s_1^4s_2 - \frac{1}{2}s_1^2s_2^2 - \frac{1}{4}s_2^3 + \frac{1}{2}s_2^3 = x^2 + x^4 \quad (31)$$

Since the enumeration is itemized with respect to the numbers of addends as well as to symmetries, we obtain possible routes to the T_h -hexakisadduct (**1**), which are illustrated in Figure 6. It should be emphasized that other routes than listed in Figure 6 are concluded to be impossible if the starting molecule (**13**) and the target (**1**) are given.

Let us next consider a D_{3d} -hexakisadduct (**7**) in which six addends attach to the $D_{3d}/(C_2)$ -orbit (Figure 7). The same

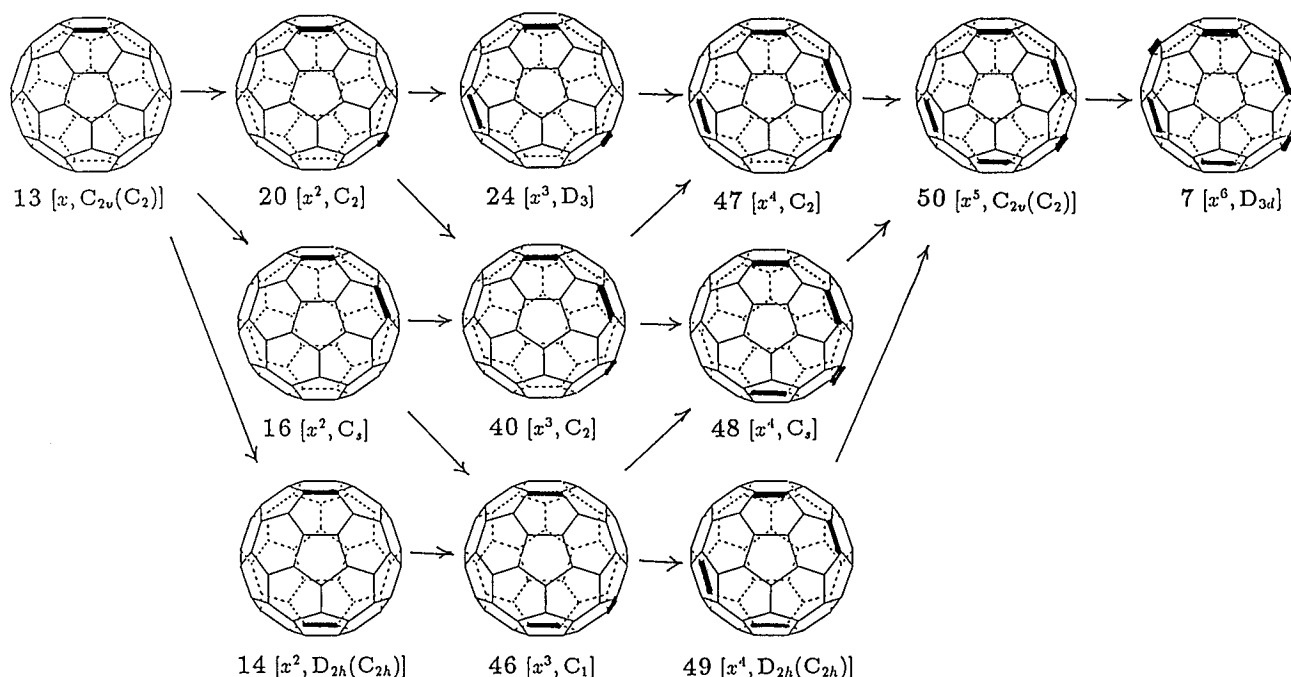


Figure 7. Possible routes to a D_{3d} -hexakisadduct.

methodology as above is applied to this case. Thus, we regard the present problem as a combinatorial enumeration in which the six addends in the $D_{3d}/(C_2)$ -orbit of the hexakisadduct (7) are reversely replaced by the original double bonds. Partial cycle indices (PCIs) for method II (eq 3) are calculated as follows, where the USCI table and the inverse mark table of the group D_{3h} ^{19,48} are used because D_{3d} is isomorphic to D_{3h} . We introduce the inventory (eq 4) into each dummy variable of the PCIs to obtain the following equations which contain nonzero values.

$$PCI_{D_3} = \frac{1}{2}s_3^2 - \frac{1}{2}s_6 = x^3 \quad (32)$$

$$PCI_{D_{2h}} = s_2s_4 - s_6 = x^2 + x^4 \quad (33)$$

$$PCI_{C_s} = \frac{1}{2}s_2^3 - \frac{1}{2}s_2s_4 - \frac{1}{2}s_6 + \frac{1}{2}s_6 = x^2 + x^4 \quad (34)$$

$$PCI_{C_2} = \frac{1}{2}s_1^2s_2^2 - \frac{1}{2}s_2s_4 - \frac{1}{2}s_3^2 + \frac{1}{2}s_6 = x + x^2 + x^3 + x^4 + x^5 \quad (35)$$

$$PCI_{C_1} = \frac{1}{12}s_1^6 - \frac{1}{4}s_1^2s_2^2 - \frac{1}{4}s_2^3 + \frac{1}{12}s_2^3 - \frac{1}{12}s_3^2 + \frac{1}{2}s_2s_4 + \frac{1}{4}s_3^2 + \frac{1}{4}s_6 + \frac{1}{12}s_6 - \frac{1}{2}s_6 = x^3 \quad (36)$$

The coefficient of each term x^k in the expanded equations (eqs 32–36) indicates the number of derivatives with a given symmetry in which k of the double bonds are attacked. Thus, we obtain possible routes to the D_{3d} -hexakisadduct (7) as illustrated in Figure 7. The C_{2v} -symmetry of the monoadduct (13) and the pentakisadduct (50) should be considered to be reduced into C_2 when we take account of the D_{3d} group. Likewise, the D_{2h} -symmetry of the bisadduct (14) and tetrakisadduct (49) should be considered to be reduced to C_{2h} within the D_{3d} group presumed.

Another D_{3d} -hexakisadduct (6) has six addends attached to the $D_{3d}/(C_s)$ -orbit (Figure 8). Possible routes to the adduct are combinatorially enumerated in a similar way. Partial cycle indices (PCIs) for method II (eq 3) are calculated by using the USCI table and the inverse mark table of the isomorphic group D_{3h} ^{19,48}. After introducing the inventory (eq 4) into each dummy variable of the PCIs, we obtain generating functions as follows, where results of zero values are omitted.

$$PCI_{C_{3v}} = \frac{1}{2}s_3^2 - \frac{1}{2}s_6 = x^3 \quad (37)$$

$$PCI_{C_{2h}} = s_2s_4 - s_6 = x^2 + x^4 \quad (38)$$

$$PCI_{C_s} = \frac{1}{2}s_1^2s_2^2 - \frac{1}{2}s_2s_4 - \frac{1}{2}s_3^2 + \frac{1}{2}s_6 = x + x^2 + x^3 + x^4 + x^5 \quad (39)$$

$$PCI_{C_2} = \frac{1}{2}s_2^3 - \frac{1}{2}s_2s_4 - \frac{1}{2}s_6 + \frac{1}{2}s_6 = x^2 + x^4 \quad (40)$$

$$PCI_{C_1} = \frac{1}{12}s_1^6 - \frac{1}{4}s_2^3 - \frac{1}{4}s_1^2s_2^2 + \frac{1}{12}s_2^3 - \frac{1}{12}s_3^2 + \frac{1}{2}s_2s_4 + \frac{1}{4}s_3^2 + \frac{1}{4}s_6 + \frac{1}{12}s_6 - \frac{1}{2}s_6 = x^3 \quad (41)$$

By examining the coefficient of each term of eqs 37–41, we obtain possible routes to the D_{3d} -hexakisadduct (6) as illustrated in Figure 8. In contrast to the counterparts in Figure 7, the C_{2v} -symmetry of the monoadduct (13) and the pentakisadduct (55) in Figure 8 should be considered to be reduced to C_s when we take account of the D_{3d} group. This difference stems from the different selections of the 3-fold axes. On the other hand, the D_{2h} -symmetry of the bisadduct (14) and tetrakisadduct (54) is also considered to be reduced to C_{2h} within the D_{3d} group presumed.

The D_3 -triadduct (24) appears in Figure 7, while the C_{3v} -triadduct (23) appears in Figure 8. Among the eight

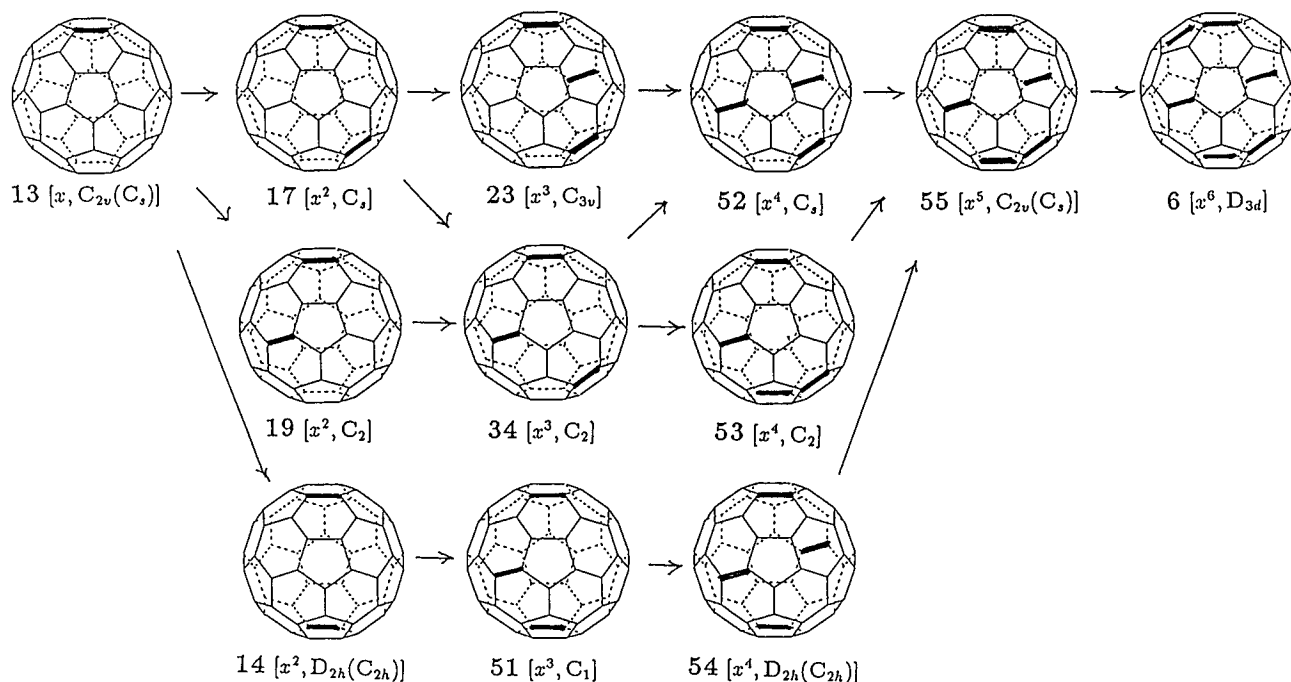


Figure 8. Possible routes to a D_{3d} -hexakisadduct.

bisadducts, the possible routes shown in Figures 6–8 contain the one D_{2h} -bisadduct (**14**), the three C_s -bisadducts (**15**, **16**, and **17**), and the two C_2 -bisadducts (**19** and **20**) but does not involve **18** and **21**.

It should be noted that the method described in this section can be applied to cases in which all the addends in a final product belong to the same orbit, as illustrated in the example enumerations. This limitation, however, is not crucial, when we consider an appropriate supergroup in which further addition makes nonequivalent addends equivalent. The routes shown in Figures 6–8 have a mirror plane with respect to the possible conversions. This fact corresponds to the symmetry of the coefficients appearing in the generating functions (eqs 28–31 and 37–41).

4.2. Bond-Differentiating Reactions in Mono- and Bisadducts. Since equivalent bonds (edges) of a skeleton (such as C_{60}) belong to an orbit governed by a CR $G/(G_i)$ as described in the preceding sections, we can consider the sphericity of such an orbit of bonds.^{17,19} Thus, there are three cases: enantiospheric (G is an achiral group and G_i is a chiral group), homospheric (both G and G_i is achiral), and hemispheric (both G and G_i is chiral). The theorem described in ref 17 (referred to as theorem I) is generally applied to any enantiospheric orbits of any objects: *An enantiospheric orbit is capable of separating into hemispheric orbits of the same length under a chiral environment, whether the change is reversible or irreversible.* The resulting two hemispheric orbits come from the two halves of the original enantiospheric orbit, which cannot be superposed under any proper rotations but are capable of being superposed upon each other under an improper rotation.

Theorem I also holds for orbits of bonds. Hence, we define a *bond-differentiating (stereoselective) chiral reaction* as a reaction in which an achiral compound with at least one enantiospheric orbit of bonds is converted into a chiral product, where the two halves of the orbit are totally or partly differentiated in an appropriate environment (such as in the

action of a chiral reagent). The adjective “stereoselective” may be omitted if no serious confusion emerges. In the present discussion, we presume that such a chiral reagent attacks *each bond*. This means that there is not direct method of chiral induction in C_{60} , because the $I_h/(C_{2v})$ -orbit of the 30 double bonds of C_{60} is homospheric. However, achiral monoadducts or higher intermediates are capable of participating in such bond-differentiating chiral reactions if they have an enantiospheric orbit of bonds (in other words, if they are prochiral).

The C_{2v} -monoadduct (**13**) has enantiospheric orbits, *i.e.*, six four-membered $C_{2v}/(C_1)$ -orbits, where two categories of $C_{2v}/(C_1)$ -orbits are differentiated in terms of further addition reactions. The one corresponds to γ , A, and B and the other to α , β , and Γ . Although the symbols for designating the locativity are also used here in slightly different meaning, there may emerge no confusion. With respect to the first category, attack on the orbits concerning γ , A, and B creates C_2 -bisadducts, **19**, **20**, and **21**. The second category of the orbits concerning α , β , and Γ generate achiral bisadducts (**16**–**18**). This category, however, does not represent a counterexample to the sphericity concept, because it creates a new symmetry element other than the original ones of **13**. The sphericity concept is effective so that chiral products are generated if the second addend is different from the first one. As an example, we refer to asymmetric bisosmylation of C_{60} reported by Hawkins.³² If we presume such successive additions as above, the chiral induction step in the bisosmylation is concluded to be the second step of a monoadduct into a bisadduct.

Let us regard chiral formation of trisadducts as simultaneous bisaddition to the monoadduct **13**, where the full part of the four bonds of the four-membered $C_{2v}/(C_1)$ -orbit participates in the reaction. A simultaneous chiral attack on the orbits concerning γ and its hemitopic position $\tilde{\gamma}$ produces a C_2 -adduct (**42**). In a similar way, a simultaneous chiral attack on the orbits concerning A and its hemitopic position \tilde{A} produces a C_2 -adduct (**39**). An attack on the orbits

concerning B and its hemitopic position \tilde{B} generates a D_3 -adduct (**24**).

Let us consider chiral formation from the second category of the $C_{2v}/(C_1)$ -orbits (the orbits concerning α , β , and Γ), where chiral trisadducts are generated. Thus, attack on the orbits concerning α , β , and Γ creates C_2 -trisadducts, **38**, **40**, and **41**, respectively. Alternatively, the C_2 -trisadducts (**38**, **40**, and **41**) can be regarded as the chiral attack of the enantiospheric $C_s/(C_1)$ -orbits of the C_s -bisadducts **18**, **16**, and **17**, which are in turn generated by the attack on the orbits concerning α , β , and Γ . It should be emphasized that, in both of the possibilities, a chiral induction step involves an enantiospheric orbit.

The C_{2v} -monoadduct (**13**) has homospheric orbits, *i.e.*, one two-membered $C_{2v}/(C_s)$ -orbit (δ), one two-membered $C_{2v}/(C_s')$ -orbit (ϵ), and two one-membered $C_{2v}/(C_s')$ -orbits (ζ and the bond with an addent). These orbits are inactive to chiral induction.

Trisadducts can be alternatively generated from monoaddition to bisadducts, if the latter are isolated. Let us consider possibilities of chiral reactions in such monoadditions. In particular, chiral synthesis of a C_3 -trisadduct (**25**) is an example to be examined. The precursor should be the bisadduct (**15**) of C_s -symmetry (Figure 6). Table 5 indicates that **15** has 13 $C_s/(C_1)$ -orbits and four $C_s/(C_s)$ -orbits, where each of the $C_s/(C_1)$ -orbits is a clue for chiral synthesis. Since the 13 $C_s/(C_1)$ -orbits are energetically different, some of them are preferably attacked by a third addent. Although the determination of such preferable orbits requires experiments or quantum-chemical calculation, a C_3 -trisadduct, if isolated under a chiral environment, is anticipated to be optical active (**25** or its antipode). Note that **25** contains three anti-clockwise δ -relations (or three clockwise ϵ -relations), while the antipode contains three clockwise δ -relations (or three anti-clockwise ϵ -relations).

The trisadduct of D_3 -symmetry (**24**) can be generated from the bisadduct of C_2 -symmetry (**20**). The bisadduct (**20**) has 14 $C_2/(C_1)$ -orbits and two $C_2/(C_2)$ -orbits, as shown in Table 5. Since **20** is chiral, any synthesis is a *chemoselective chiral synthesis*, if it occurs preferably. Among possibilities to give trisadducts, **24** is generated by monoaddition to the specific one of the $C_2/(C_2)$ -orbits, where additional chiral environments are unnecessary.

4.3. Chirogenic Sites in a Homospheric Orbit. In the preceding sections, the formation of the bisadducts has been explained in terms of successive additions. It can be alternatively explained by a direct bisaddition, in which two addents simultaneously attack different double bonds. Although it requires experimental studies to determine which mechanism is working, discussion of symmetrical properties of the latter mechanism is desirable to obtain a guideline for further investigation.

Suppose that a pair of two-bonds is a reaction site which undergoes simultaneous addition of two addents. Although the bond pair can be specified by means of the locativity terms defined above, it is alternatively regarded as an object which is transformed under the action of each symmetry of the group I_h . Thus, every symmetry operation of I_h acts on a pair of a standard bond and an α -bond (called an α -pair) so as to generate a set of pairs which constructs an $I_h/(C_s)$ -orbit. On the other hand, a set of γ -pairs is governed by the CR, $I_h/(C_2)$. In a similar way, we obtain the following correspondence.

$$\alpha\text{-pair} \leftrightarrow I_h/(C_s) \quad A\text{-pair} \leftrightarrow I_h/(C_2)$$

$$\beta\text{-pair} \leftrightarrow I_h/(C_s) \quad B\text{-pair} \leftrightarrow I_h/(C_2)$$

$$\gamma\text{-pair} \leftrightarrow I_h/(C_2) \quad \Gamma\text{-pair} \leftrightarrow I_h/(C_s)$$

$$\delta\text{-pair} (\epsilon\text{-pair}) \leftrightarrow I_h/(C_s) \quad \zeta\text{-pair} \leftrightarrow I_h/(D_{2h})$$

Since the semilocal relationships in C_{60} correspond to γ -, A-, and B-pairs, they are associated with the enantiospheric CR $I_h/(C_2)$. For example, the γ -relationship corresponds to one-half of the $I_h/(C_2)$ -orbit, while the $\tilde{\gamma}$ -relationship corresponds to the other half. In other words, the γ -, A-, and B-pair have their antipodal counterparts, *i.e.*, $\tilde{\gamma}$ -, \tilde{A} -, and \tilde{B} -pair. Theorem I teaches that, if simultaneous attack of two addents is postulated, each pair (γ -, A-, or B-pair) is energetically differentiated from its antipodal pair ($\tilde{\gamma}$ -, \tilde{A} -, or \tilde{B} -pair) under a chiral environment. It follows that either an optically active adduct (**19**, **20**, or **21**) or its antipode is generated according to energetical preference. Since the resulting bisadducts belong to C_2 -symmetry, the original pairs are called C_2 -chirogenic sites in homospheric orbits.

On the other hand, α -, β -, and Γ -pairs (corresponding mesolocal relationships) are associated with the homospheric CR $I_h/(C_s)$. When simultaneous attack of two addents are postulated, such a bis-attack on each pair (α -, β -, or Γ -pair) generates a bisadduct belonging to C_s -symmetry (**16**, **17**, or **18**) even under a chiral environment. In a similar way, a δ -pair (equal to ϵ -pair) generates a bisadduct (**15**) of C_s -symmetry, and a ζ -pair produces a bisadduct (**14**) belonging to D_{2h} -symmetry. These pairs are called *achirogenic sites* in homospheric orbits.

It is worthwhile to mention the difference between enantiospheric orbits and homospheric ones in their capability of generating chirogenic and achirogenic sites. Corollary 2 of ref 18 indicates that each G_i -ligand in an enantiospheric $G/(G_i)$ orbit is a G_i -chirogenic site. Theorem 7 of ref 18 shows that each of the two halves (*i.e.*, hemitopic halves) of an enantiospheric $G/(G_i)$ orbit is a G^{max} -chirogenic site, where G^{max} is the maximal chiral subgroup of G . The combination of the two propositions teaches us that an appropriate site in either hemitopic half of an enantiospheric $G/(G_i)$ orbit is a chirogenic site. On the other hand, an appropriate site in a homospheric orbit is chirogenic or achirogenic. Although the present discussion deals only with a pair in a homospheric orbit, it can be extended to a wider site in a homospheric orbit.

5. FURTHER DERIVATIVES OF A T_H -DERIVATIVE

5.1. Enumeration Starting From a T_h -Derivative. The hexakisadduct (**1**) with T_h -symmetry has been preferably formed as one of the multiply-substituted derivatives of buckminsterfullerene.^{25,31} Since such T_h -compounds as **1** have been rarely observed, the symmetrical nature of equivalent positions (bonds or atoms) remains undiscussed. Further addition reactions are potential routes providing new compounds with subsymmetries of T_h , which are here enumerated combinatorially.

We start from a hexakisadduct (**1**), in which the 30 bonds of buckminsterfullerene are partitioned into a 24-membered $T_h/(C_1)$ -orbit and a six-membered $T_h/(C_{2v})$ -orbit as shown by

Table 6. USCIs of T_h

	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_3$	$\downarrow C_i$	$\downarrow C_3$	$\downarrow C_{2v}$	$\downarrow C_{2h}$	$\downarrow D_2$	$\downarrow C_{3i}$	$\downarrow D_{2h}$	$\downarrow T$	$\downarrow T_h$	sum
$T_h(C_1)$	s_1^{24}	s_2^{12}	s_2^{12}	s_2^{12}	s_3^8	s_4^6	s_4^6	s_4^6	s_6^4	s_8^3	s_{12}^2	s_{24}	$\frac{1}{24}$
$T_h(C_2)$	s_1^{12}	$s_1^4 s_2^4$	s_2^6	s_2^6	s_3^4	$s_2^2 s_4^2$	$s_2^2 s_4^2$	s_2^6	s_6^2	s_4^3	s_6^2	s_{12}	$\frac{1}{8}$
$T_h(C_3)$	s_1^{12}	s_2^6	$s_1^4 s_2^4$	s_2^6	s_3^4	$s_2^2 s_4^2$	$s_2^2 s_4^2$	s_4^3	s_6^2	s_4^3	s_{12}	s_{12}	$\frac{1}{8}$
$T_h(C_i)$	s_1^{12}	s_2^6	s_2^6	s_1^{12}	s_3^4	s_4^3	s_2^6	s_4^3	s_3^4	s_4^3	s_{12}	s_{12}	$\frac{1}{24}$
$T_h(C_3)$	s_1^8	s_2^4	s_2^4	s_2^4	$s_1^2 s_3^2$	s_4^2	s_4^2	s_4^2	$s_2 s_6$	s_8	s_8	s_8	$\frac{1}{3}$
$T_h(C_{2v})$	s_1^6	$s_1^2 s_2^2$	$s_1^4 s_2^2$	s_2^3	s_3^2	$s_1^2 s_2^2$	s_3^2	s_3^2	s_6	s_2^3	s_6	s_6	0
$T_h(C_{2h})$	s_1^6	$s_1^2 s_2^2$	$s_1^2 s_2^2$	s_1^6	s_3^2	s_3^2	$s_1^2 s_2^2$	s_3^2	s_3^2	s_2^3	s_6	s_6	0
$T_h(D_2)$	s_1^6	s_1^6	s_2^3	s_2^3	s_3^2	s_2^3	s_2^3	s_1^6	s_6	s_2^3	s_3^2	s_6	0
$T_h(C_{3i})$	s_1^4	s_2^2	s_2^2	s_1^4	$s_1 s_3$	s_4	s_2^2	s_4	$s_1 s_3$	s_4	s_4	s_4	$\frac{1}{3}$
$T_h(D_{2h})$	s_1^3	s_1^3	s_1^3	s_1^3	s_3	s_1^3	s_1^3	s_1^3	s_3	s_1^3	s_3	s_3	0
$T_h(T)$	s_1^2	s_1^2	s_2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	0
$T_h(T_h)$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	0

the corresponding subduction (Table 5). Since the six edges in the latter orbit are already attacked, the $T_h(C_1)$ -orbit is taken into consideration.

The USCI table (Table 6) for T_h point group is obtained from the data of Table 4. Partial cycle indices (PCIs) for method II (eq 3) are calculated by starting from the USCI table (Table 6) and the inverse mark table (Table 3) of T_h point group. To memorize the process of PCI construction, suppose that an SCI (multiplied rows of such a USCI table as Table 6) is multiplied by an inverse mark table (Table 4), where both are regarded as matrices. For example, we have PCI_{C_i} as follows.

$$\begin{aligned}
 PCI_{C_i} &= (s_1^{12}, s_2^6, s_2^6, s_1^{12}, s_3^4, s_3^4, s_2^6, s_2^6, s_3^4, s_3^4, s_{12}^3, s_{12}^3) \times \\
 &\quad \left(0, 0, 0, \frac{1}{12}, 0, 0, -\frac{1}{4}, 0, -\frac{1}{3}, \frac{1}{6}, 0, \frac{1}{3}\right)^T \\
 &= \frac{1}{12}s_2^{12} - \frac{1}{4}s_4^6 - \frac{1}{3}s_6^4 + \frac{1}{6}s_8^3 + \frac{1}{3}s_{24}
 \end{aligned}$$

Then, we introduce the inventory (eq 4) into each dummy variable of the PCIs, giving the following generating functions.

$$PCI_T = \frac{1}{2}s_{14}^2 - \frac{1}{2}s_{24} = x^{12} \quad (42)$$

$$PCI_{D_{2h}} = \frac{1}{3}s_8^3 - \frac{1}{3}s_{24} = x^8 + x^{16} \quad (43)$$

$$PCI_{C_{3i}} = \frac{1}{3}s_6^4 - \frac{1}{3}s_{24} = 4x^6 + 6x^{12} + 4x^{18} \quad (44)$$

$$\begin{aligned}
 PCI_{D_2} &= \frac{1}{6}s_4^6 - \frac{1}{6}s_8^3 - \frac{1}{6}s_{12}^2 + \frac{1}{6}s_{42} = x^4 + 2x^8 + 3x^{12} + \dots \\
 &\quad (45)
 \end{aligned}$$

$$PCI_{C_{2h}} = \frac{1}{2}s_4^6 - \frac{1}{2}s_8^3 = 3x^4 + 6x^8 + 10x^{12} + \dots \quad (46)$$

$$PCI_{C_{2v}} = \frac{1}{2}s_4^6 - \frac{1}{2}s_8^3 = 3x^4 + 6x^8 + 10x^{12} + \dots \quad (47)$$

$$\begin{aligned}
 PCI_{C_3} &= \frac{1}{2}s_3^8 - \frac{1}{2}s_6^4 - \frac{1}{2}s_{12}^2 + \frac{1}{2}s_{24} = 4x^3 + 12x^6 + \\
 &\quad 28x^9 + 31x^{12} + \dots \quad (48)
 \end{aligned}$$

$$\begin{aligned}
 PCI_{C_i} &= \frac{1}{12}s_2^{12} - \frac{1}{4}s_4^6 - \frac{1}{3}s_6^4 + \frac{1}{6}s_8^3 + \frac{1}{3}s_{24} \\
 &= x^2 + 4x^4 + 17x^6 + 38x^8 + 66x^{10} + 70x^{12} + \dots \quad (49)
 \end{aligned}$$

$$\begin{aligned}
 PCI_{C_s} &= \frac{1}{4}s_2^{12} - \frac{1}{2}s_4^6 - \frac{1}{4}s_6^4 + \frac{1}{2}s_8^3 \\
 &= 3x^2 + 12x^4 + 55x^6 + 114x^8 + 198x^{10} + 216x^{12} + \dots \\
 &\quad (50)
 \end{aligned}$$

$$\begin{aligned}
 PCI_{C_2} &= \frac{1}{4}s_2^{12} - \frac{1}{4}s_4^6 - \frac{1}{4}s_6^4 - \frac{1}{4}s_8^3 + \frac{1}{2}s_8^3 \\
 &= 3x^2 + 12x^4 + 55x^6 + 114x^8 + 198x^{10} + 216x^{12} + \dots \\
 &\quad (51)
 \end{aligned}$$

$$\begin{aligned}
 PCI_{C_1} &= \frac{1}{24}s_1^{24} - \frac{1}{8}s_2^{12} - \frac{1}{8}s_2^{12} - \frac{1}{24}s_2^{12} - \frac{1}{6}s_3^8 + \frac{1}{12}s_4^6 + \\
 &\quad \frac{1}{4}s_4^6 + \frac{1}{4}s_4^6 + \frac{1}{6}s_6^4 - \frac{1}{3}s_8^3 + \frac{1}{6}s_{12}^2 - \frac{1}{6}s_{24} \\
 &= x + 8x^2 + 83x^3 + 427x^4 + 1771x^5 + 5540x^6 + \\
 &\quad 14421x^7 + 30508x^8 + 54470x^9 + 81488x^{10} + \\
 &\quad 104006x^{11} + 112405x^{12} + \dots \quad (52)
 \end{aligned}$$

The coefficient of each term x^k in the expanded equations (eqs 42–52) indicates the number of derivatives with a given symmetry in which k of the double bonds are attacked.

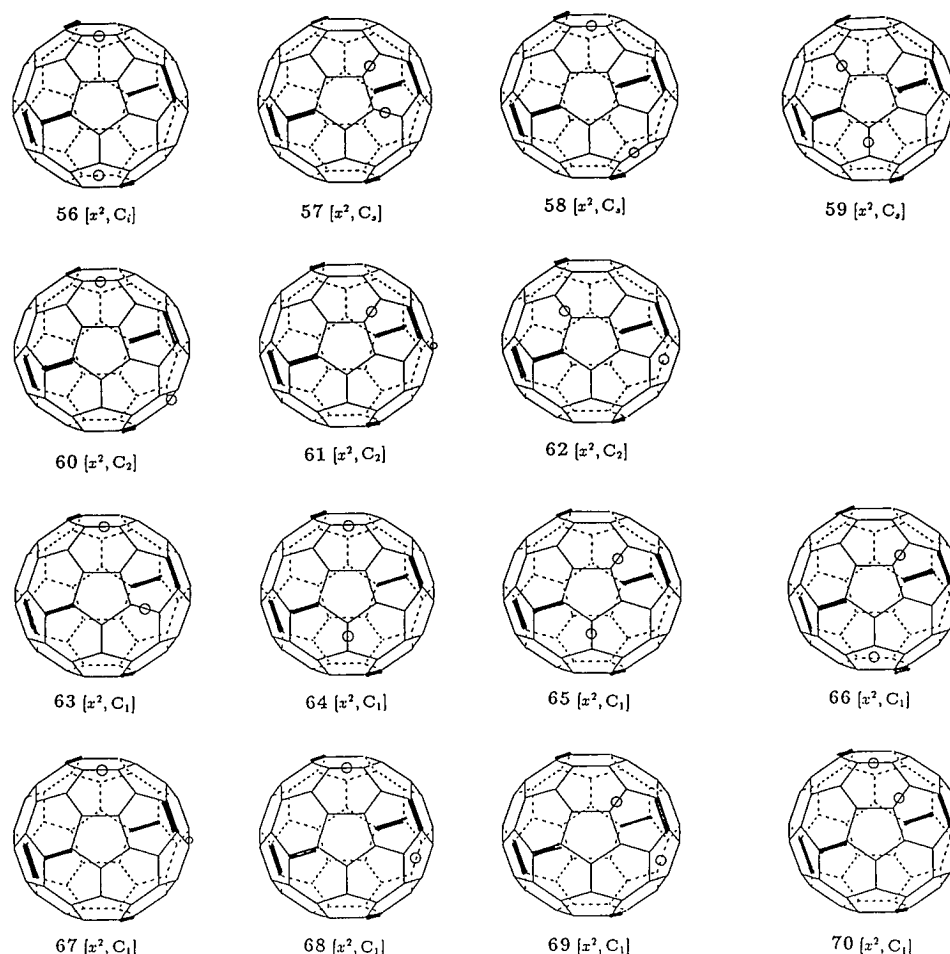


Figure 9. Bisadducts derived from a T_h -hexakisadduct.

The CI (eq 26) for T_h are calculated by the matrix-like multiplication of the USCIs of the first row and the sum of the rightmost column appearing in Table 4. By introducing the inventory (eq 4) into the resulting CI, we have the following generating function, where the coefficient of each monomial indicates the corresponding total number without consideration of subsymmetry.

$$\begin{aligned}
 \text{CI} &= (1/24)s_1^{24} + (1/8)s_2^{12} + (1/8)s_2^{12} + (1/24)s_2^{12} + \\
 &\quad (1/3)s_3^8 + (1/3)s_6^4 \\
 &= 1 + x + 15x^2 + 87x^3 + 462x^4 + 1771x^5 + 5683x^6 + \\
 &\quad 14421x^7 \\
 &\quad + 30789x^8 + 54498x^9 + 81950x^{10} + 104006x^{11} + \\
 &\quad 112968x^{12} \quad (53)
 \end{aligned}$$

5.2. Bond-Differentiating Reactions of a T_h -Derivative.

The coefficient of the term x^2 in eq 53 is 15, which indicates the number of bisadducts. Note that the number of addends (the prefix "bis" in bisadducts) is the one which takes no account of the six original addends. The bisadducts are classified by inspection of eqs 42–52 into one C_i - (56), three C_s - (57–59), three C_2 - (60–62), and eight C_1 -derivatives (63–70). These adducts are illustrated in Figure 9, in which six boldfaced bonds denote the original attacked ones and two bonds with a small circle designate newly-attached ones.

The locativity terms proposed above can be used for classification of sites in the hemitopic and enantiotopic

relationships. However, they provide no additional discriminative results in the hemitopic and enantiotopic cases. Thus, the bond pair concerning the newly-attached bonds of an achiral bisadduct (56–59) is mesolocate, and the corresponding pairwise relationship is enantiotopic. In general, an enantiotopic relationship is associated with a mesolocate case. On the other hand, the bond pair concerning the newly-attached bonds of a chiral bisadduct (60–70) is semilocate, and the corresponding pairwise relationship is also hemitopic. Generally speaking, a hemitopic relationship is associated with a semilocate case.

Since the 24 bonds of **1** belong to the enantiospheric T_h -(C_1)-orbit, they are separated into two halves, each having 12 bonds under a chiral environment. As shown in eqs 42–52, only one monoadduct is derived from **1** and belongs to C_1 -symmetry. Under a chiral environment, the monoadduct is formed chirally by attacking a bond contained in either half of the T_h -(C_1)-orbit. Each of the 23 unreacted double bonds in the monoadduct belongs to a distinct one-membered C_1 -(C_1)-orbit, the successive attack of an addend is essentially chemoselective (diastereoselective).

6. CONCLUSION

Chemoselective and stereoselective conversions in high-symmetry molecules such as buckminsterfullerene are discussed in order to prevent confusion that may occur by the inspection without group-theoretical consideration:

1. The subduction tables of I_h - and T_h -groups are presented.

2. In order to obtain a perspective on a variety of fullerene derivatives, they are combinatorially enumerated with respect to symmetries and molecular formulas.

3. The symmetrical properties of the derivatives are discussed in terms of the sphericity concept.

4. Bond-differentiating reactions are formulated by using the enumerated derivatives as examples. Then, possible routes are discussed to obtain derivatives of several sub-symmetries (T_h and D_{3d}) of I_h .

5. The bond-differentiating reactions are classified into four categories, i.e., chemoselective achiral, chemoselective chiral, stereoselective chiral, and stereoselective achiral.

6. Chirogenic sites in a homospheric orbit are examined to show the possibility of direct chiral reactions. The terms *mesolocative*, *equilocative*, *dialocative*, and *semilocative* are proposed to characterize bond pairs in a homospheric orbit.

REFERENCES AND NOTES

- (1) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York-London, 1962.
- (2) Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice-Hall: Englewood Cliffs, 1971.
- (3) Mulzer, J.; Altenbach, H.-J.; Braun, M.; Krohn, K.; Reissig, H.-U. *Organic Synthesis Highlights*; VCH: Weinheim, 1991.
- (4) Prelog, V. *Helv. Chim. Acta* **1953**, *36*, 308–319.
- (5) Cram, D. J.; Elhafez, F. A. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–5835.
- (6) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1.
- (7) Mislow, K. *Bull. Soc. Chim. Belg.* **1977**, *85*, 595.
- (8) Hanson, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731.
- (9) Hirschmann, H.; Hanson, K. R. *J. Org. Chem.* **1971**, *36*, 3293.
- (10) Nakazaki, M. *Shape and Symmetry of Organic Molecules (Bunshi no Katachi to Taisho)*; Nankodo: Tokyo, 1965.
- (11) Izumi, Y. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 871–881.
- (12) Mislow, K.; Siegel, J. J. *Am. Chem. Soc.* **1984**, *106*, 3319.
- (13) McCasland, G. E. *A New General System for the Naming of Stereoisomers*; Chemical Abstracts Service: Columbus, OH, 1953.
- (14) Prelog, V.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 567.
- (15) O'loane, J. K. *Chem. Rev.* **1980**, *80*, 41.
- (16) Eliel, E. L. *Top. Curr. Chem.* **1982**, *105*, 1.
- (17) Fujita, S. *J. Am. Chem. Soc.* **1990**, *112*, 3390–3397.
- (18) Fujita, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3313–3323.
- (19) Fujita, S. *Symmetry and Combinatorial Enumeration in Chemistry*; Springer-Verlag: Berlin-Heidelberg, 1991.
- (20) Fujita, S. *Tetrahedron* **1990**, *46*, 5943–5954.
- (21) Fujita, S. *Tetrahedron* **1991**, *47*, 31–46.
- (22) Fujita, S. *J. Chem. Inf. Comput. Sci.* **1992**, *32*, 354–363.
- (23) Fujita, S. *Polyhedron* **1993**, *12*, 95–110.
- (24) For the *re/si*-nomenclature, see ref 8.
- (25) Fagan, P. J.; Calarese, J. C.; Malone, B. J. *Am. Chem. Soc.* **1991**, *113*, 9408–9409.
- (26) Wudl, F. *Accts. Chem. Res.* **1992**, *25*, 106–112.
- (27) Taylor, R.; Walton, R. M. *Nature* **1993**, *363*, 685–693.
- (28) Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437–438.
- (29) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138–1141.
- (30) Henderson, C. C.; Rohlfang, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786–788.
- (31) Hirsch, A.; Lamparth, I.; Gösser, T.; Karfunkel, H. R. *J. Am. Chem. Soc.* **1994**, *116*, 9385–9386.
- (32) Hawkins, J. M.; Meyer, A.; Nambu, M. *J. Am. Chem. Soc.* **1993**, *115*, 9844–9845.
- (33) Fujita, S. *Theor. Chim. Acta* **1989**, *76*, 247–268.
- (34) Fujita, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 315–327.
- (35) Fujita, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3215–3223.
- (36) Table 1 of ref 35 contains misprints. Edges [6:6] of **1** should be corrected to be edges [5:6] and edges [5:6] of **1** should be corrected to be edges [6:6]. The [6:6] edges in the right column of page 3216 and the [5:6] edges in the left column of page 3217 should be corrected into [5:6] edges and [6:6] edges, respectively.
- (37) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243–255.
- (38) Fujita, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2759–2769. Table 5 contains a misprint. The value 6 at the intersection of the [8.7.5]-row and the C_3 column should be corrected into zero. However, the total value 832592 remains unaffected and correct, since we have $830212 + 2380 = 832592$.
- (39) Pólya, G. *Acta Math.* **1937**, *68*, 145–254.
- (40) Pólya, G.; Read, R. C. *Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds*; Springer-Verlag: New York, 1987.
- (41) For reviews on chemical applications of the Pólya-Redfield theorem, see: Rouvray, D. H. *Chem. Soc. Rev.* **1974**, *3*, 355. *Chemical Applications of Graph Theory*; Balaban, A. T. Ed.; Academic: London, 1976. Balasubramanian, K. *Chem. Rev.* **1985**, *85*, 599.
- (42) Hosoya, H. *Gendai-Kagaku* **1987**, *201*, 38.
- (43) Balasubramanian, K. *J. Phys. Chem.* **1993**, *97*, 6990–6998; *Chem. Phys. Lett.* **1995**, *237*, 229–238.
- (44) Hässelbarth, W. *Theor. Chim. Acta* **1985**, *67*, 339–367.
- (45) Mead, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2130–2137.
- (46) Brocas, J. *J. Am. Chem. Soc.* **1986**, *108*, 1135–1145.
- (47) Lloyd, E. K. *J. Math. Chem.* **1992**, *11*, 207–222.
- (48) Fujita, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1876–1883.
- (49) Fujita, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2270–2275.
- (50) Fujita, S. *Theor. Chim. Acta* **1992**, *82*, 473–498.
- (51) Fujita, S. *J. Math. Chem.* **1993**, *12*, 173–195.
- (52) Fujita, S. *J. Math. Chem.* **1990**, *5*, 99–120.
- (53) A prolignand pair can be regarded as a prolignand in an abstract fashion. From this standpoint, such a prolignand is reversely considered to have an inner structure. This is an alternative way to treat higher relationships.
- (54) A prolignand pair (bond pair) is considered to be composed of two prolignands selected from S, T, P, and \bar{P} , where S and T are achiral prolignands, and P and \bar{P} are chiral prolignands with inverse chirality. Then, we have three types of achiral segments, S–S, S–T, and P– \bar{P} , which correspond to the terms equilocative, dialocative and mesolocative, respectively.
- (55) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Bunz, U.; Nunlist, R.; Ball, G. E.; Ebbesen, T. W.; Tanigaki, K. *J. Am. Chem. Soc.* **1992**, *114*, 7954–7955.
- (56) This selection can be alternatively expressed by sphericity, because the two bis(ethoxycarbonyl)methylene groups construct an enantiospheric $C_s/(C_1)$ -orbit in **16**. Although the locativity terms are convenient to communicate stereochemical relationships, elaborate consideration should be based on the sphericity concept to avoid undesired confusion.
- (57) The two bis(ethoxycarbonyl)methylene groups of **15** belong to distinct one-membered homospheric $C_s/(C_s)$ -orbits. Since they are energetically different from each other, the decarboxylation is a chemoselective achiral process.
- (58) Fujita, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 439–449.

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