Benzene Derivatives with Achiral and Chiral Substituents and Relevant Derivatives Derived from D_{6h} Skeletons. Symmetry-Itemized Enumeration and Symmetry Characterization by the Unit-Subduced Cycle Index Approach

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The unit-subduced cycle index (USCI) approach is applied to the enumeration of isomers based on D_{6h} skeletons, where the inverses of a mark table and a USCI table are precalculated for the point group D_{6h}. Thus, benzene derivatives with achiral substituents are enumerated by using partial cycle indices (PCIs) in an itemized manner concerning the formulas and symmetries. The formulation of partial cycle indices with chirality fittingness (PCI-CFs) enables us to enumerate benzene derivatives with chiral and achiral substituents. The USCI approach is also applied to the enumeration of isomers derived from a coronene skeleton that also belongs to the point group D_{6h}. The PCIs (or PCI-CFs) of zero or nonzero expressions are discussed in terms of a selection rule for judging the existence of subsymmetries. The symmetries of the resulting derivatives are discussed in terms of sphericities.

1. INTRODUCTION

Permutation group theory has been widely applied to various chemical problems. In particular, Pólya's theorem[1] along with an equivalent counterpart known as Redfield's group-reduced distribution[2] has continuously been an important tool for chemical combinatorics, the details of which have been summarized in excellent reviews[3−6] and books.[7,8] An alternative approach to combinatorial enumeration is the Redfield−Read superposition theorem, which was originally established by Redfield,[2] rediscovered by Read,[9,10] and sophisticated as the *s*-function method.[11] Further mathematical aspects on the approach have been discussed extensively.[12−14] Its applicability to chemical problems was pointed out by Davidson.[15] A further approach has been reported by Ruch et al.,[16,17] where double-coset decompositions are applied to counting isomers. This approach has been extended to the enumeration of isomers with chiral ligands.[18] The double-coset method has been correlated to the Pólya cycle index method and de Bruijin's extension.[19] All of these methods aimed at the combinatorial enumeration of isomers with given formulas (or mathematically with given weights).

A more detailed enumeration of isomers has been desired as the next step, where formulas as well as symmetries will be taken into consideration. An effective formulation has been developed by Sheehan[20] for solving mathematical problems and later by Hässelbarth[21] for chemical applications, where tables of marks coming from Burnside[22] were used as key concepts. Redfield's long unpublished article[23] discussed a concept equivalent to mark tables, which has been interpreted from a modern mathematical point of view.[24] The same targets of enumeration have been accomplished by an alternative method developed by Brocas,[25] where double cosets were combined with framework groups originated by Pople.[26] The method reported by Mead[27] has used tables of marks and double cosets for isomer enumerations. A further method using marks of permutation groups has been reported by Lloyd.[28]

We have recently reported the importance of coset representations for isomer enumerations,[29] where we have proposed the subduction of coset representations that can be used in place of double cosets to discuss desymmetrization processes concerning the isomer enumerations.[30] Thereby, we have developed four relevant methods for accomplishing the more detailed enumeration of isomers, i.e., (1) a generating-function method using subduced cycle indices (SCIs) and mark tables,[29] (2) a generating-function method using partial cycle indices (PCIs),[31] (3) a method based on the elemental superposition,[32] and (4) a method based on the partial superposition,[32,31] which are collectively called "the unit-subduced cycle index (USCI) approach".[29,33]

One of the merits of the USCI approach is that the subduction of coset representations is at the same time a versatile tool to characterize the stereochemistries of organic and inorganic compounds.[34−36] Another merit is the capability of using precalculated tables of USCIs along with mark tables or their inverses. However, the latter merit may be inefficacious until we provide such requisites as precalculated USCI tables for every groups. Although several of the requisites were reported in our previous articles and collected in our book,[33] further data should be added to the collection to show the scope and limitations of the USCI approach. In particular, we have to give requisites for chemically important groups as preferentially as possible.

One such chemically important group is the point group D_{6h} assigned to a benzene nucleus, since the number of substitution isomers is a crucial key to conclude its hexagonal symmetry, as shown in typical textbooks on organic chemistry. This enumeration has once appeared in the original

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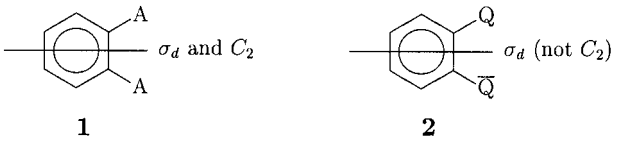
Chart 1



1 **2**

series of articles on Pólya's theorem,[37−39] has been repeatedly referred to as a representative example in many books,[40,6] and has been revisited in a recent article.[41] In the previous enumerations, the benzene nucleus was regarded as a regular hexagonal graph having an automorphism group D_6 of order 12. As long as achiral substituents (A) are taken into consideration, e.g., as in benzene derivative **1** (Chart 1), the use of D_6 for analyzing the *permutation properties* of the graph gave the same result as the use of the point group D_{6h}, to which the benzene nucleus belongs as a three-dimensional object. The use of D_6 is, however, insufficient to characterize the *three-dimensional properties* of the benzene nucleus. For example, another benzene derivative (**2**) having two antipodal substituents (Q and $\bar{Q}$) belongs to the point group C_s, which is a subgroup of D_{6h}. This cannot be characterized within the automorphism group D_6, since the effect of the reflection σ_d of D_{6h} is no longer the same as that of the rotation C_2. Moreover, the previous enumerations have taken no account of the symmetries of isomers, since they have been based on Pólya's theorem. Hence, it is meaningful to study the enumeration of benzene isomers in terms of the USCI approach by considering the point group D_{6h} and by taking the symmetries of the resulting isomers into account.

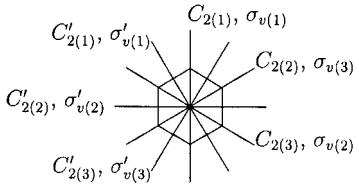


Figure 1. Several symmetry elements of D_{6h}.

As clarified in the introductory remarks, one of the targets of the present paper is to provide the inverse of the mark table and the USCI table for the point group D_{6h}. The other is subsymmetry-itemized enumeration based on benzene and other skeletons of D_{6h} symmetry, where the chiralities of the substituents are taken into consideration.

2. RESULTS

A. Coset Representations and Orbits. The collection of the subgroups of the point group D_{6h} is necessary to apply the USCI approach to a skeleton of D_{6h} symmetry. Table 1 shows distinct, up to conjugacy, subgroups of D_{6h}, where the elements (operations) of each subgroup are collected in parentheses. To avoid misunderstanding, several elements (operations) of D_{6h} are illustrated in Figure 1, which shows the symmetry elements (axes or plains) of D_{6h} other than the 6-fold axes perpendicular to the hexagon. The subgroups of D_{6h} are classified into two categories, i.e., chiral and achiral groups. The chirality of each subgroup is also shown in Table 1.

The subgroups of D_{6h} listed in Table 1 construct a nonredundant set of subgroups (SSG) for D_{6h}, i.e.,

Table 1. Subgroups of D_{6h}

subgroup	elements (operations)	chirality
C_1	$=\{I\}$	chiral
C_2	$=\{I, C_2\}$	chiral
C'_2	$=\{I, C_{2(1)}\}$	chiral
C''_2	$=\{I, C'_{2(1)}\}$	chiral
C_s	$=\{I, \sigma_{v(1)}\}$	achiral
C'_s	$=\{I, \sigma'_{v(1)}\}$	achiral
C''_s	$=\{I, \sigma_h\}$	achiral
C_i	$=\{I, i\}$	achiral
C_3	$=\{I, C_3, C_3^2\}$	chiral
D_2	$=\{I, C_2, C_{2(1)}, C'_{2(2)}\}$	chiral
C_{2v}	$=\{I, C_2, \sigma_{v(1)}, \sigma'_{v(2)}\}$	achiral
C'_{2v}	$=\{I, C_{2(1)}, \sigma_h, \sigma_{v(1)}\}$	achiral
C''_{2v}	$=\{I, C'_{2(1)}, \sigma_h, \sigma'_{v(1)}\}$	achiral
C_{2h}	$=\{I, C_2, \sigma_h, i\}$	achiral
C'_{2h}	$=\{I, C_{2(1)}, i, \sigma'_{v(2)}\}$	achiral
C''_{2h}	$=\{I, C'_{2(1)}, i, \sigma_{v(3)}\}$	achiral
C_6	$=\{I, C_6, C_3, C_2, C_3^2, C_6^5\}$	chiral
D_3	$=\{I, C_3, C_3^2, C_{2(1)}, C_{2(2)}, C_{2(3)}\}$	chiral
D'_3	$=\{I, C_3, C_3^2, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}\}$	chiral
C_{3v}	$=\{I, C_3, C_3^2, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}$	achiral
C'_{3v}	$=\{I, C_3, C_3^2, \sigma'_{v(1)}, \sigma'_{v(2)}, \sigma'_{v(3)}\}$	achiral
C_{3h}	$=\{I, C_3, C_3^2, \sigma_h, S_3, S_3^5\}$	achiral
C_{3i}	$=\{I, C_3, C_3^2, S_6, i, S_6^5\}$	achiral
D_{2h}	$=\{I, C_2, C_{2(1)}, C'_{2(2)}, \sigma_h, i, \sigma_{v(1)}, \sigma'_{v2}\}$	achiral
D_6	$=\{I, C_6, C_3, C_2, C_3^2, C_6^5, C_{2(1)}, C'_{2(1)}, C_{2(2)}, C'_{2(2)}, C_{2(3)}, C'_{2(3)}\}$	chiral
C_{6v}	$=\{I, C_6, C_3, C_2, C_3^2, C_6^5, \sigma_{v(1)}, \sigma'_{v(1)}, \sigma_{v(2)}, \sigma'_{v(2)}, \sigma_{v(3)}, \sigma'_{v(3)}\}$	achiral
C_{6h}	$=\{I, C_6, C_3, C_2, C_3^2, C_6^5, \hat{\sigma}_h, S_6, S_3, i, S_3^5, S_6^5\}$	achiral
D_{3h}	$=\{I, C_3, C_3^2, C_{2(1)}, C_{2(2)}, C_{2(3)}, \sigma_h, S_3, S_3^5, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}$	achiral
D'_{3h}	$=\{I, C_3, C_3^2, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}\sigma_h, S_3, S_3^5, \sigma'_{v(1)}, \sigma'_{v(2)}, \sigma'_{v(3)}\}$	achiral
D_{3d}	$=\{I, C_3, C_3^2, C_{2(1)}, C_{2(2)}, C_{2(3)}, S_6, i, S_6^5, \sigma'_{v(1)}, \sigma'_{v(2)}, \sigma'_{v(3)}\}$	achiral
D'_{3d}	$=\{I, C_3, C_3^2, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}, S_6, i, S_6^5, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}$	achiral
D_{6h}	$=\{I, C_6, C_3, C_2, C_3^2, C_6^5, C_{2(1)}, C'_{2(1)}, C_{2(2)}, C'_{2(2)}, C_{2(3)}, C'_{2(3)}, \sigma_h, S_6, S_3, i, S_3^5, S_6^5, \sigma_{v(1)}, \sigma'_{v(1)}, \sigma_{v(2)}, \sigma'_{v(2)}, \sigma_{v(3)}, \sigma'_{v(3)}\}$	achiral

$$\mathrm{SSG}_{D_{6h}} = \{C_1, C_2, C_2', C_2'', C_s, C_s', C_s'', C_i, C_3, D_2, C_{2v}, C_{2v}', C_{2v}'', C_{2h}, C_{2h}', C_{2h}'', C_6, D_3, D_3', C_{3v}, C_{3v}', C_{3h}, C_{3i}, D_{2h}, D_6, C_{6v}, C_{6h}, D_{3h}, D_{3h}', D_{3d}, D_{3d}', D_{6h}\} \quad (1)$$

According to the SSG, we have the set of coset representations (SCR) as follows:

$$\mathrm{SCR}_{D_{6h}} = \{D_{6h}(/C_1), D_{6h}(/C_2), D_{6h}(/C_2'), D_{6h}(/C_2''), D_{6h}(/C_s), D_{6h}(/C_s'), D_{6h}(/C'_s), D_{6h}(/C_i), D_{6h}(/C_3), D_{6h}(/D_2), D_{6h}(/C_{2v}), D_{6h}(/C_{2v}'), D_{6h}(/C_{2v}''), D_{6h}(/C_{2h}), D_{6h}(/C_{2h}'), D_{6h}(/C_{2h}''), D_{6h}(/C_6), D_{6h}(/D_3), D_{6h}(/D_3'), D_{6h}(/C_{3v}), D_{6h}(/C_{3v}'), D_{6h}(/C_{3h}), D_{6h}(/C_{3i}), D_{6h}(/D_{2h}), D_{6h}(/D_6), D_{6h}(/C_{6v}), D_{6h}(/C_{6h}), D_{6h}(/D_{3h}), D_{6h}(/D_{3h}'), D_{6h}(/D_{3d}), D_{6h}(/D_{3d}'), D_{6h}(/D_{6h})\} \quad (2)$$

Each symbol $G(/G_i)$ consists of the global symmetry G (e.g., D_{6h} in this paper) and a local symmetry G_i (e.g., D_{3d}). The concrete form of each coset representation $G(/G_i)$ is given as a set of permutations,[33] though we do not show the permutations for the point group D_{6h} in this paper.

A mark for each coset representation in a subgroup can be obtained by counting invariant elements in all the permutations related to the subgroup.[33] We have reported the mark table of the pseudopoint group $\hat{D}_{6h}$ for counting cyclohexane isomers.[42] Since the D_{6h} is isomorphic to $\hat{D}_{6h}$, we are able to use the mark table as that of D_{6h}. In order to show the flexibility of the USCI approach, however, here we use the inverse of the mark table shown in Table 2.

A set of equivalent positions constructs an orbit, which is assigned to an appropriate coset representation. Thus, the six positions of a benzene nucleus construct an orbit. To determine the coset representation for the orbit, we first find the corresponding local symmetry, i.e., the largest subgroup that keeps one position of the orbit invariant. Obviously, the local symmetry of the vertex of the nucleus is concluded to be C_{2v}', since the vertex is fixed under every operation $\{I, C_{2(1)}, \sigma_h, \sigma_{v(1)}\}$ of C_{2v}'. In general, the local symmetries for every position of an orbit give a set of conjugate subgroups, either one of which (e.g., C_{2v}' in this case) can be selected as a representative to construct the SSG. It follows that the orbit is governed by the coset representation $D_{6h}(/C_{2v}')$.

The result obtained intuitively in the preceding paragraph is confirmed by a more mathematical treatment. First, we calculate a fixed-point vector (FPV) for the orbit of six vertexes, i.e.,

$$\mathrm{FPV} = (6, 0, 2, 0, 2, 0, 6, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) \quad (3)$$

where the numbers of fixed points in every subgroup are aligned in the order of the SSG. The FPV is multiplied by the inverse of the mark table (Table 2) to give

$$(\mathrm{FPV})M_{D_{6h}}{}^{-1} = (0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0) \quad (4)$$

where the symbol $M_{D_{6h}}{}^{-1}$ represents the inverse of the mark table (Table 2). The result gives $D_{6h}(/C_{2v}')$ as the coset representation to be obtained.

B. Subduction of Coset Representations. For counting benzene derivatives, here we calculate the subductions of the coset representation $D_{6h}(/C_{2v}')$ described in the preceding subsection. For example, the subduction of $D_{6h}(/C_{2v}')$ into C_{2v} can be carried out easily by means of the procedure described in section 9.2 of our previous book.[33] Thus, the 1st, 2nd, 5th, 6th, and 11th elements of the FPV (eq 3) are collected to give an FPV of the subduction, i.e., (6, 0, 2, 0, 0), since these elements correspond to the subgroups or conjugate ones of C_{2v} (see eq 1). The resulting FPV is multiplied by the inverse mark table of C_{2v} to give

$$(6, 0, 2, 0, 0)\begin{pmatrix} {}^1/_4 & 0 & 0 & 0 & 0 \\ -{}^1/_4 & {}^1/_2 & 0 & 0 & 0 \\ -{}^1/_4 & 0 & {}^1/_2 & 0 & 0 \\ -{}^1/_4 & 0 & 0 & {}^1/_2 & 0 \\ {}^1/_2 & -{}^1/_2 & -{}^1/_2 & -{}^1/_2 & 0 \end{pmatrix} = (1, 0, 1, 0, 0) \quad (5)$$

where the 5×5 matrix on the left-hand side is the inverse mark table of C_{2v}.[33] The row vector in the right-hand side corresponds to the subduction represented by $D_{6h}(/C_{2v}') \downarrow C_{2v} = C_{2v}(/C_1) + C_{2v}(/C_s)$. Since the coset representation $C_{2v}(/C_1)$ is enantiospheric,[35] it is characterized by a dummy variable of c_4 for a USCI with chirality fittingness (USCI-CF) (or s_4 for a USCI), where the subscript comes from the size of the relevant orbit ($|C_{2v}|/|C_1| = 4/1 = 4$).[33] On the other hand, the homospheric coset representation $C_{2v}(/C_s)$ (size: $|C_{2v}|/|C_s| = 4/2 = 2$) corresponds to a dummy variable of a_2 for a USCI-CF (or s_2 for USCI). Hence, we obtain the USCI-CF (a_2c_4) and the USCI (s_2s_4) for the subduction. These results are listed as eq 73 in Table 3. Other subductions can be calculated in similar ways and collected in Table 3. Each fraction in the column "sum" of Table 3 represents the summation of each row of the inverse mark table (Table 2), where the values other than the cyclic groups vanish into zero.

The same procedure as described above for the subduction of $D_{6h}(/C_{2v}')$ is applied to the other coset representations of D_{6h} to give the USCIs for every coset representation as well as for every subgroup. Therefore, we obtain the USCI table for D_{6h} (Table 4). Note that the data described above (eqs 63−94 in Table 3) appear in the row $D_{6h}(/C_{2v}')$.

C. Combinatorial Enumeration of Benzene Derivatives with Achiral Substituents. Let us count the benzene derivatives with achiral substituents only. As mentioned above, the six positions of a benzene nucleus are governed by the coset representation $D_{6h}(/C_{2v}')$. The $D_{6h}(/C_{2v}')$ row of the USCI table (Table 4) or, equivalently, the set of USCIs appearing in Table 3 (eqs 63−94) is formally multiplied by the inverse mark table (Table 2) to give PCIs. Note that the USCIs are used in place of the corresponding SCIs, since the latter are equal to the former in such a one-orbit case. The following list shows nonzero PCIs. The PCIs for the remaining subgroups are omitted, since they are calculated to be equal to zero.

$$\mathrm{PCI}(C_s''; s_d) = \frac{1}{12}s_1^6 - \frac{1}{3}s_2^3 - \frac{1}{4}s_1^2s_2^2 + \frac{1}{6}s_3^2 + \frac{1}{2}s_2s_4 - \frac{1}{6}s_6 \quad (6)$$

$$\mathrm{PCI}(C_{2v}'; s_d) = \frac{1}{2}s_1^2s_2^2 - \frac{1}{2}s_3^2 - \frac{1}{2}s_2s_4 + \frac{1}{2}s_6 \quad (7)$$

$$\mathrm{PCI}(C_{2v}''; s_d) = \frac{1}{2}s_2^3 - \frac{1}{2}s_2s_4 \quad (8)$$

$$\mathrm{PCI}(C_{2h}; s_d) = \frac{1}{6}s_2^3 - \frac{1}{2}s_2s_4 + \frac{1}{3}s_6 \quad (9)$$

$$\mathrm{PCI}(D_{2h}; s_d) = s_2s_4 - s_6 \quad (10)$$

$$\mathrm{PCI}(D_{3h}; s_d) = \frac{1}{2}s_3^2 - \frac{1}{2}s_6 \quad (11)$$

$$\mathrm{PCI}(D_{6h}; s_d) = s_6 \quad (12)$$

Let us consider a set of achiral substituents of six kinds (X, Y, Z, V, W, and implicitly H). Suppose that six substituents selected from the set are placed on the D_{6h}-($/C_{2v}'$) orbit to give a derivative of molecular formula $C_6H_iX_jY_kZ_lV_mW_n$, where the subscripts are nonnegative integers satisfying $i + j + k + l + m + n = 6$. Our target is to count the number of derivatives with a given formula $C_6H_iX_jY_kZ_lV_mW_n$ along with a given symmetry. In order to use the second method of the USCI approach, we adopt the following inventory for the present enumeration:

$$s_d = 1 + x^d + y^d + z^d + v^d + w^d \quad (13)$$

where each small letter corresponds to a substituent of its capital letter (except H). The inventory is introduced into eqs 6−12. The generating functions are expanded and the coefficients of the terms $1^ix^jy^kz^lv^mw^n$ (represented as [*i*,*j*,*k*,*l*,*m*,*n*]) are collected to give Table 5. The symbol [*i*,*j*,*k*,*l*,*m*,*n*] ($i \geq j \geq k \geq l \geq m \geq n$) denotes the molecular formulas $C_6H_iX_jY_kZ_lV_mW_n$, $C_6H_jX_kY_lZ_mV_nW_i$, $C_6H_kX_lY_mZ_nV_iW_j$, etc., since the corresponding terms $1^ix^jy^kz^lv^mw^n$, $1^jx^ky^lz^mv^nw^i$, $1^kx^ly^mz^nv^iw^j$, etc., have the same coefficient. Each column of Table 5 is concerned with subsymmetry and each row with the term [*i*,*j*,*k*,*l*,*m*,*n*]. It should be noted that the number for each subsymmetry other than the ones listed in Table 5 is equal to zero.

The total number of isomers with a given formula can be calculated by using a cycle index, which is obtained for the present case by using the USCIs and the sums listed in eqs 63 to eq 94 in the light of the USCI approach.[43]

$$\mathrm{CI}(D_{6h}; s_d) = \frac{1}{12}s_1^6 + \frac{1}{3}s_2^3 + \frac{1}{4}s_1^2s_2^2 + \frac{1}{6}s_3^2 + \frac{1}{6}s^6 \quad (14)$$

Such a CI as eq 14 obtained by the USCI approach is equivalent to the counterpart obtained by using the Pólya−Redfield theorem, as we have proven generally.[43] The equivalent CI was obtained by the Pólya−Redfield theorem on the basis of the automorphism group D_6.[40,6] After the introduction of the inventory (eq 13) into the CI (eq 14), the expansion of the resulting polynomial gives a generating function, in which the coefficients of the respective terms represent the total numbers we aim at. These values are listed in the rightmost column of Table 5. They are equal to those obtained by the summations of every row.

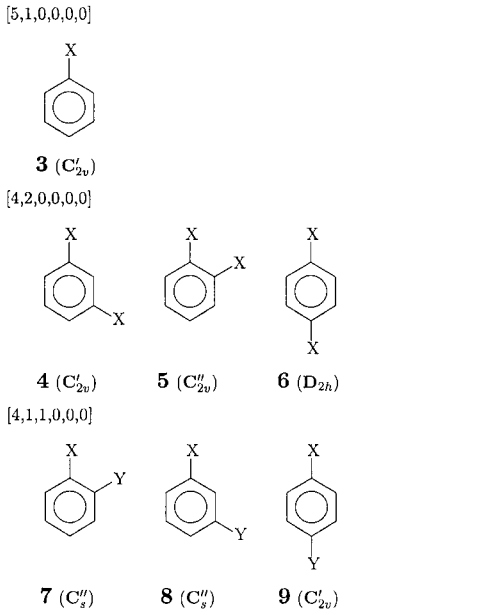


Figure 2. Mono- and disubstituted benzene derivatives with achiral substituents.

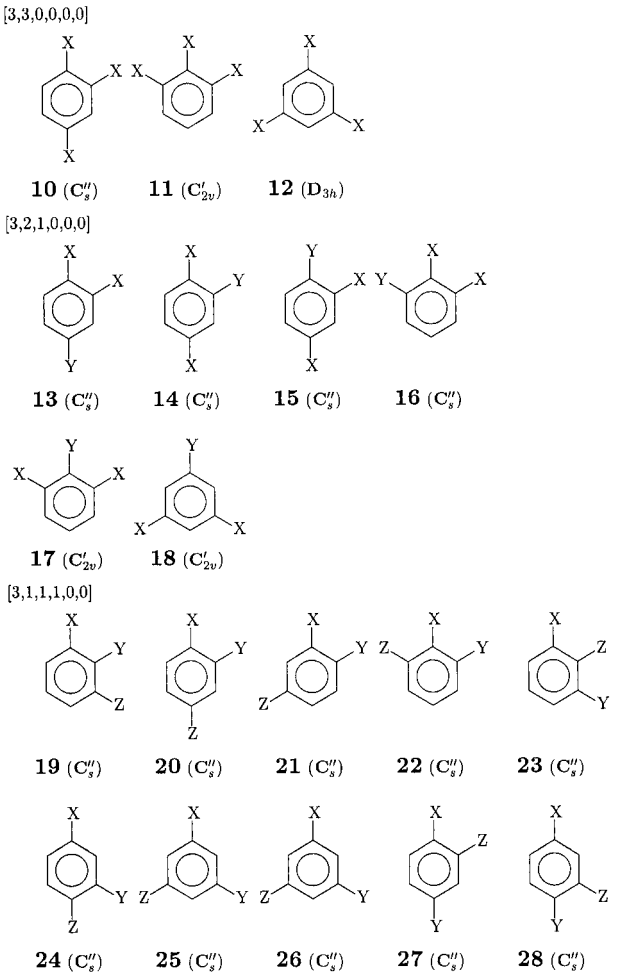


Figure 3. Trisubstituted benzene derivatives with achiral substituents.

For exemplifying the results collected in Table 5, Figure 2 depicts mono- and disubstituted benzene derivatives with achiral substituents. Their numbers are listed in the [5,1,0,0,0,0], [4,2,0,0,0,0], and [4,1,1,0,0,0] rows of Table 5, where each row is itemized with respect to symmetry.

Table 2. Inverse Mark Table for D_{6h}

	$\downarrow C_1 \times {}^1/_{24}$	$\downarrow C_2$	$\downarrow C_2'$	$\downarrow C_2''$	$\downarrow C_2$	$\downarrow C_s'$	$\downarrow C_s''$	$\downarrow C_i$	$\downarrow C_3$	$\downarrow D_2$	$\downarrow C_{2v}$	$\downarrow C_{2v}'$	$\downarrow C_{2v}''$	$\downarrow C_{2h}$	$\downarrow C_{2h}'$	$\downarrow C_{2h}''$
$D_{6h}(/C_1)$	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2)$	−1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2')$	−3	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2'')$	−3	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s)$	−3	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s')$	−3	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s'')$	−1	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_i)$	−1	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0
$D_{6h}(/C_3)$	−1	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0
$D_{6h}(/D_2)$	6	−6	−6	−6	0	0	0	0	0	12	0	0	0	0	0	0
$D_{6h}(/C_{2v})$	6	−6	0	0	−6	−6	0	0	0	0	12	0	0	0	0	0
$D_{6h}(/C_{2v}')$	6	0	−6	0	−6	0	−6	0	0	0	0	12	0	0	0	0
$D_{6h}(/C_{2v}'')$	6	0	0	−6	0	−6	−6	0	0	0	0	0	12	0	0	0
$D_{6h}(/C_{2h})$	2	−2	0	0	0	0	−2	−2	0	0	0	0	0	4	0	0
$D_{6h}(/C_{2h}')$	6	0	−6	0	0	−6	0	−6	0	0	0	0	0	0	12	0
$D_{6h}(/C_{2h}'')$	6	0	0	−6	−6	0	0	−6	0	0	0	0	0	0	0	12
$D_{6h}(/C_6)$	1	−2	0	0	0	0	0	0	−3	0	0	0	0	0	0	
$D_{6h}(/D_3)$	3	0	−6	0	0	0	0	0	−3	0	0	0	0	0	0	0
$D_{6h}(/D_3')$	3	0	0	−6	0	0	0	0	−3	0	0	0	0	0	0	0
$D_{6h}(/C_{3v})$	3	0	0	0	−6	0	0	0	−3	0	0	0	0	0	0	0
$D_{6h}(/C_{3v}')$	3	0	0	0	0	−6	0	0	−3	0	0	0	0	0	0	0
$D_{6h}(/C_{3h})$	1	0	0	0	0	0	−2	0	−3	0	0	0	0	0	0	0
$D_{6h}(/C_{3i})$	1	0	0	0	0	0	0	−2	−3	0	0	0	0	0	0	0
$D_{6h}(/D_{2h})$	−24	12	12	12	12	12	12	12	0	−12	−12	−12	−12	−12	−12	−12
$D_{6h}(/D_6)$	−6	6	6	6	0	0	0	0	6	−12	0	0	0	0	0	0
$D_{6h}(/C_{6v})$	−6	6	0	0	6	6	0	0	6	0	−12	0	0	0	0	0
$D_{6h}(/C_{6h})$	−2	2	0	0	0	0	2	2	6	0	0	0	0	−4	0	0
$D_{6h}(/D_{3h})$	−6	0	6	0	6	0	6	0	6	0	0	−12	0	0	0	0
$D_{6h}(/D_{3h}')$	−6	0	0	6	0	6	6	0	6	0	0	0	−12	0	0	0
$D_{6h}(/D_{3d})$	−6	0	6	0	0	6	0	6	6	0	0	0	0	0	−12	0
$D_{6h}(/D_{3d}')$	−6	0	0	6	6	0	0	6	6	0	0	0	0	0	0	−12
$D_{6h}(/D_{6h})$	24	−12	−12	−12	−12	−12	−12	−12	−24	12	12	12	12	12	12	12

	$\downarrow C_6 \times {}^1/_{24}$	$\downarrow D_3$	$\downarrow D_3'$	$\downarrow C_{3v}$	$\downarrow C_{3v}'$	$\downarrow C_{3h}$	$\downarrow C_{3i}$	$\downarrow D_{2h}$	$\downarrow D_6$	$\downarrow C_{6v}$	$\downarrow C_{6h}$	$\downarrow D_{3h}$	$\downarrow D_{3h}'$	$\downarrow D_{3d}$	$\downarrow D_{3d}'$	$\downarrow D_{6h}$
$D_{6h}(/C_1)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_2'')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_s'')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_i)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_3)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/D_2)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2v})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2v}')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2v}'')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2h})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2h}')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{2h}'')$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_6)$	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/D_3)$	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/D_3')$	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{3v})$	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{3v}')$	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{3h})$	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0
$D_{6h}(/C_{3i})$	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0
$D_{6h}(/D_{2h})$	0	0	0	0	0	0	0	24	0	0	0	0	0	0	0	0
$D_{6h}(/D_6)$	−6	−6	−6	0	0	0	0	0	12	0	0	0	0	0	0	0
$D_{6h}(/C_{6v})$	−6	0	0	−6	−6	0	0	0	0	12	0	0	0	0	0	0
$D_{6h}(/C_{6h})$	−6	0	0	0	0	−6	−6	0	0	0	12	0	0	0	0	0
$D_{6h}(/D_{3h})$	0	−6	0	−6	0	−6	0	0	0	0	0	12	0	0	0	0
$D_{6h}(/D_{3h}')$	0	0	−6	0	−6	−6	0	0	0	0	0	0	12	0	0	0
$D_{6h}(/D_{3d})$	0	−6	0	0	−6	0	−6	0	0	0	0	0	0	12	0	0
$D_{6h}(/D_{3d}')$	0	0	−6	−6	0	0	−6	0	0	0	0	0	0	0	12	0
$D_{6h}(/D_{6h})$	12	12	12	12	12	12	12	−24	−12	−12	−12	−12	−12	−12	−12	24

Figure 3 shows trisubstituted benzene derivatives with achiral substituents. The isomer numbers are confirmed by the comparison between Table 5 and Figure 3. Thus, the [3,3,0,0,0,0] row of Table 5 indicates that there exist one C_s'' isomer, one C_{2v}' isomer, and one D_{3h} isomer. The [3,2,1,0,0,0] row of Table 5 predicts the existence of 4 C_s'' isomers and 2 C_{2v}' isomers, while the [3,1,1,1,0,0] row shows the existence of 10 C_s'' isomers.

Table 3. Subductions of $D_{6h}(/C'_{2v})$

subduction	USCI	USCI-CF	sum	eq
$D_{6h}(/C'_{2v})\downarrow C_1 = 6C_1(/C_1)$	s_1^6	b_1^6	$^1/_{24}$	63
$D_{6h}(/C'_{2v})\downarrow C_2 = 3C_2(/C_1)$	s_2^3	b_2^3	$^1/_{24}$	64
$D_{6h}(/C'_{2v})\downarrow C'_2 = 2C'_2(/C_1) + 2C'_2(/C'_2)$	$s_1^2s_2^2$	$b_1^2b_2^2$	$^1/_8$	65
$D_{6h}(/C'_{2v})\downarrow C''_2 = 3C''_2(/C_1)$	s_2^3	b_2^3	$^1/_8$	66
$D_{6h}(/C'_{2v})\downarrow C_s = 2C_s(/C_1) + 2C_s(/C_s)$	$s_1^2s_2^2$	$a_1^2c_2^2$	$^1/_8$	67
$D_{6h}(/C'_{2v})\downarrow C'_s = 3C'_s(/C_1)$	s_2^3	c_2^3	$^1/_8$	68
$D_{6h}(/C'_{2v})\downarrow C''_s = 6C''_s(/C''_s)$	s_1^6	a_1^6	$^1/_{24}$	69
$D_{6h}(/C'_{2v})\downarrow C_i = 2C_i(/C_1)$	s_2^3	c_2^3	$^1/_{24}$	70
$D_{6h}(/C'_{2v})\downarrow C_3 = 2C_3(/C_1)$	s_3^2	b_3^2	$^1/_{12}$	71
$D_{6h}(/C'_{2v})\downarrow D_2 = D_2(/C_1) + D_2(/C'_2)$	s_2s_4	b_2b_4	0	72
$D_{6h}(/C'_{2v})\downarrow C_{2v} = C_{2v}(/C_1) + C_{2v}(/C_s)$	s_2s_4	a_2c_4	0	73
$D_{6h}(/C'_{2v})\downarrow C'_{2v} = 2C'_{2v}(/C_s) + 2C'_{2v}(/C_{2v})$	$s_1^2s_2^2$	$a_1^2a_2^2$	0	74
$D_{6h}(/C'_{2v})\downarrow C''_{2v} = 3C''_{2v}(/C'_s)$	s_2^3	a_2^3	0	75
$D_{6h}(/C'_{2v})\downarrow C_{2h} = 3C_{2h}(/C_s)$	s_2^3	a_2^3	0	76
$D_{6h}(/C'_{2v})\downarrow C'_{2h} = C'_{2h}(/C_1) + C'_{2h}(/C_2)$	s_2s_4	c_2c_4	0	77
$D_{6h}(/C'_{2v})\downarrow C''_{2h} = C''_{2h}(/C_1) + C''_{2h}(/C_s)$	s_2s_4	a_2c_4	0	78
$D_{6h}(/C'_{2v})\downarrow C_6 = C_6(/C_1)$	s_6	b_6	$^1/_{12}$	79
$D_{6h}(/C'_{2v})\downarrow D_3 = 2D_3(/C_2)$	s_3^2	b_3^2	0	80
$D_{6h}(/C'_{2v})\downarrow D'_3 = D'_3(/C_1)$	s_6	b_6	0	81
$D_{6h}(/C'_{2v})\downarrow C_{3v} = 2C_{3v}(/C_s)$	s_3^2	a_3^2	0	82
$D_{6h}(/C'_{2v})\downarrow C'_{3v} = 2C'_{3v}(/C_1)$	s_6	c_6	0	83
$D_{6h}(/C'_{2v})\downarrow C_{3h} = 2C_{3h}(/C_s)$	s_3^2	a_3^2	$^1/_{12}$	84
$D_{6h}(/C'_{2v})\downarrow C_{3i} = C_{3i}(/C_1)$	s_6	c_6	$^1/_{12}$	85
$D_{6h}(/C'_{2v})\downarrow D_{2h} = D_{2h}(/C''_s) + D_{2h}(/C'_{2v})$	s_2s_4	a_2a_4	0	86
$D_{6h}(/C'_{2v})\downarrow D_6 = D_6(/C'_2)$	s_6	b_6	0	87
$D_{6h}(/C'_{2v})\downarrow C_{6v} = C_{6v}(/C_s)$	s_6	a_6	0	88
$D_{6h}(/C'_{2v})\downarrow C_{6h} = C_{6h}(/C_s)$	s_6	a_6	0	89
$D_{6h}(/C'_{2v})\downarrow D_{3h} = 2D_{3h}(/C_{2v})$	s_3^2	a_3^2	0	90
$D_{6h}(/C'_{2v})\downarrow D'_{3h} = D_{3h}(/C'_s)$	s_6	a_6	0	91
$D_{6h}(/C'_{2v})\downarrow D_{3d} = D_{3d}(/C_2)$	s_6	c_6	0	92
$D_{6h}(/C'_{2v})\downarrow D'_{3d} = D'_{3d}(/C_s)$	s_6	a_6	0	93
$D_{6h}(/C'_{2v})\downarrow D_{6h} = 2D_{6h}(/C'_{2v})$	s_6	a_6	0	94

D. Combinatorial Enumeration of Benzene Derivatives with Chiral and Achiral Substituents. Let us next count benzene derivatives with achiral and chiral substituents. In this purpose, the generating-function method using partial cycle indices (method 2 described above) is extended to be capable of treating chiral substituents along with achiral ones. Although a mathematical proof is not described here, it is obtained in the same line as a previous derivation for achiral substituents only.[31]

As mentioned above, the six positions of a benzene nucleus are governed by the coset representation $D_{6h}(/C'_{2v})$. In place of the USCIs listed in eqs 63−94, the use of the USCI-CFs listed in the same equations gives PCI-CFs for their respective subgroups as follows:

$$\text{PCI-CF}(C_1; a_d, b_d, c_d) = \frac{1}{24}b_1^6 - \frac{1}{24}a_1^6 - \frac{1}{6}b_2^3 - \frac{1}{6}c_2^3 + \frac{1}{3}a_2^3 - \frac{1}{8}b_1^2b_2^2 - \frac{1}{8}a_1^2c_2^2 + \frac{1}{4}a_1^2a_2^2 + \frac{1}{12}b_3^2 - \frac{1}{12}a_3^2 + \frac{1}{4}b_2b_4 + \frac{1}{2}a_2c_4 + \frac{1}{4}c_2c_4 - a_2a_4 - \frac{1}{12}b_6 - \frac{1}{12}c_6 + \frac{1}{6}a_6 \quad (15)$$

$$\text{PCI-CF}(C_2; a_d, b_d, c_d) = \frac{1}{12}b_2^3 - \frac{1}{12}a_2^3 - \frac{1}{4}b_2b_4 - \frac{1}{4}a_2c_4 + \frac{1}{2}a_2a_4 + \frac{1}{6}b_6 - \frac{1}{6}a_6 \quad (16)$$

$$\text{PCI-CF}(C'_2; a_d, b_d, c_d) = \frac{1}{4}b_1^2b_2^2 - \frac{1}{6}a_1^2a_2^2 - \frac{1}{4}b_3^2 + \frac{1}{4}a_3^2 - \frac{1}{4}b_2b_4 - \frac{1}{4}c_2c_4 + \frac{1}{2}a_2a_4 + \frac{1}{4}b_6 + \frac{1}{4}c_6 - \frac{1}{2}a_6 \quad (17)$$

$$\text{PCI-CF}(C''_2; a_d, b_d, c_d) = \frac{1}{4}b_2^3 - \frac{1}{4}a_2^3 - \frac{1}{4}b_2b_4 - \frac{1}{4}a_2c_4 + \frac{1}{2}a_2a_4 \quad (18)$$

$$\text{PCI-CF}(C_s; a_d, b_d, c_d) = \frac{1}{4}a_1^2c_2^2 - \frac{1}{4}a_1^2a_2^2 - \frac{1}{2}a_2c_4 + \frac{1}{2}a_2a_4 \quad (19)$$

$$\text{PCI-CF}(C'_s; a_d, b_d, c_d) = \frac{1}{4}c_2^3 - \frac{1}{4}a_2^3 - \frac{1}{4}a_2c_4 - \frac{1}{4}c_2c_4 + \frac{1}{2}a_2a_4 \quad (20)$$

$$\text{PCI-CF}(C''_s; a_d, b_d, c_d) = \frac{1}{12}a_1^6 - \frac{1}{3}a_2^3 - \frac{1}{4}a_1^2a_2^2 + \frac{1}{6}a_3^2 + \frac{1}{2}a_2a_4 - \frac{1}{6}a_6 \quad (21)$$

$$\text{PCI-CF}(C_i; a_d, b_d, c_d) = \frac{1}{12}c_2^3 - \frac{1}{12}a_2^3 - \frac{1}{4}a_2c_4 - \frac{1}{4}c_2c_4 + \frac{1}{2}a_2a_4 + \frac{1}{6}c_6 - \frac{1}{6}a_6 \quad (22)$$

$$\text{PCI-CF}(C_3; a_d, b_d, cd) = 0 \quad (23)$$

$$\text{PCI-CF}(D_2; a_d, b_d, c_d) = \frac{1}{2}b_2b_4 - \frac{1}{2}a_2a_4 - \frac{1}{2}b_6 + \frac{1}{2}a_6 \quad (24)$$

$$\text{PCI-CF}(C_{2v}; a_d, b_d, c_d) = \frac{1}{2}a_2c_4 - \frac{1}{2}a_2a_4 \quad (25)$$

$$\text{PCI-CF}(C'_{2v}; a_d, b_d, c_d) = \frac{1}{2}a_1^2a_2^2 - \frac{1}{2}a_3^2 - \frac{1}{2}a_2a_4 + \frac{1}{2}a_6 \quad (26)$$

$$\text{PCI-CF}(C''_{2v}; a_d, b_d, c_d) = \frac{1}{2}a_2^3 - \frac{1}{2}a_2a_4 \quad (27)$$

$$\text{PCI-CF}(C_{2h}; a_d, b_d, c_d) = \frac{1}{6}a_2^3 - \frac{1}{2}a_2a_4 + \frac{1}{3}a_6 \quad (28)$$

$$\text{PCI-CF}(C'_{2h}; a_d, b_d, c_d) = \frac{1}{2}c_2c_4 - \frac{1}{2}a_2a_4 - \frac{1}{2}c_6 + \frac{1}{2}a_6 \quad (29)$$

$$\text{PCI-CF}(C''_{2h}; a_d, b_d, c_d) = \frac{1}{2}a_2c_4 - \frac{1}{2}a_2a_4 \quad (30)$$

$$\text{PCI-CF}(C_6; a_d, b_d, c_d) = 0 \quad (31)$$

$$\text{PCI-CF}(D_3; a_d, b_d, c_d) = \frac{1}{4}b_3^2 - \frac{1}{4}a_3^2 - \frac{1}{4}b_6 - \frac{1}{4}c_6 + \frac{1}{2}a_6 \quad (32)$$

$$\text{PCI-CF}(D'_3; a_d, b_d, c_d) = 0 \quad (33)$$

$$\text{PCI-CF}(C_{3v}; a_d, b_d, c_d) = 0 \quad (34)$$

$$\text{PCI-CF}(C'_{3v}; a_d, b_d, c_d) = 0 \quad (35)$$

$$\text{PCI-CF}(C_{3h}; a_d, b_d, c_d) = 0 \quad (36)$$

$$\text{PCI-CF}(C_{3i}; a_d, b_d, c_d) = 0 \quad (37)$$

$$\text{PCI-CF}(D_{2h}; a_d, b_d, c_d) = a_2a_4 - a_6 \quad (38)$$

$$\text{PCI-CF}(D_6; a_d, b_d, c_d) = \frac{1}{2}b_6 - \frac{1}{2}a_6 \quad (39)$$

$$\text{PCI-CF}(C_{6v}; a_d, b_d, c_d) = 0 \quad (40)$$

$$\text{PCI-CF}(C_{6h}; a_d, b_d, c_d) = 0 \quad (41)$$

$$\text{PCI-CF}(D_{3h}; a_d, b_d, c_d) = \frac{1}{2}a_3^2 - \frac{1}{2}a_6 \quad (42)$$

$$\text{PCI-CF}(D'_{3h}; a_d, b_d, c_d) = 0 \quad (43)$$

$$\text{PCI-CF}(D_{3d}; a_d, b_d, c_d) = \frac{1}{2}c_6 - \frac{1}{2}a_6 \quad (44)$$

$$\text{PCI-CF}(D'_{3d}; a_d, b_d, c_d) = 0 \quad (45)$$

$$\text{PCI-CF}(D_{6h}; a_d, b_d, c_d) = a_6 \quad (46)$$

Let us consider a set of achiral substituents of four kinds (X, Y, Z, and implicitly H) and two chiral substituents of opposite chiralities (Q and $\bar{Q}$). Suppose that six substituents selected from the set are placed on the $D_{6h}(/C'_{2v})$ orbit to give a derivative of the molecular formulas $C_6H_iX_jY_kZ_lQ_m\bar{Q}_n$, where the subscripts are nonnegative integers satisfying $i + j + k + l + m + n = 6$. The number of derivatives with a given formula $C_6H_iX_jY_kZ_lQ_m\bar{Q}_n$ along with a given symmetry is obtained by using PCI-CFs (eqs 15−46). For this purpose, we adopt the following inventories with chirality fittingness (sphericity),

$$a_d = 1 + x^d + y^d + z^d \quad (47)$$

$$b_d = 1 + x^d + y^d + z^d + q^d + \bar{q}^d \quad (48)$$

$$c_d = 1 + x^d + y^d + z^d + 2(q^d\bar{q}^d)^{d/2} \quad (49)$$

where each small letter corresponds to a substituent of its capital letter (except H). Note that a homospheric orbit (ascribed to a_d) takes achiral substituents only, a hemispheric orbit (to b_d) accommodates achiral or chiral substituents, and an enantiospheric orbit (to c_d) carries chiral substituents in a pairwise manner.[33]

The inventories (eqs 47−49) are introduced into each of the PCI-CFs (eqs 15−46). The resulting equations are expanded to give generating functions, in which the coefficients of the terms $1^i x^j y^k z^l q^m q^n$ (represented as $[i,j,k,l;m,n]$) represent the numbers to be obtained (Table 6). The symbol $[i,j,k,l;m,n]$ ($i \geq j \geq k \geq l$ and $m \geq n$) is used in place of the molecular formulas $C_6H_iX_jY_kZ_lQ_m\bar{Q}_n$, $C_6H_jX_kY_lZ_iQ_m\bar{Q}_n$, $C_6H_kX_lY_iZ_jQ_m\bar{Q}_n$, etc., since the corresponding terms $1^i x^j y^k z^l q^m \bar{q}^n$, $1^j x^k y^l z^i q^m \bar{q}^n$, $1^k x^l y^i z^j q^m \bar{q}^n$, etc., give the same coefficient. It should be noted that the number of isomers with $m = n$ (achiral or chiral) appears directly as the coefficient of the corresponding term. On the other hand, each isomer having $1^i x^j y^k z^l q^m \bar{q}^n$ ($m \neq n$) has its enantiomer having $1^i x^j y^k z^l q^n \bar{q}^m$. Since such a pair of enentiomers is counted as a single isomer in the present enumeration, the coefficients of these terms are summed to give the number of isomers with $1^i x^j y^k z^l q^m \bar{q}^n$ (or $1^i x^j y^k z^l q^n \bar{q}^m$).

The total number of isomers with a given formula can be calculated by using a cycle index with chirality fittingness (CI-CF), which is obtained for the present case by using the USCI-CFs and the sums listed in eqs 15−46 in light of the USCI approach.[43]

$$\text{CI-CF}(D_{6h}; a_d, b_d, c_d) = \frac{1}{24}b_1^6 + \frac{1}{24}a_1^6 + \frac{1}{6}b_2^3 + \frac{1}{6}c_2^3 + \frac{1}{8}b_1^2b_2^2 + \frac{1}{8}a_1^2c_2^2 + \frac{1}{12}b_3^2 + \frac{1}{12}a_3^2 + \frac{1}{12}b_6 + \frac{1}{12}c_6 \quad (50)$$

The introduction of the inventories (eqs 47−49) into eq 50 and the expansion of the resulting polynomial give a generating function in which the coefficients of the respective terms represent the total numbers we aim at. The same treatment as described above for PCI-CFs is necessary to obtain correct results for enantiomeric pairs. These values are listed in the rightmost column of Table 6, where these values are equal to those obtained by the summation of every row.

Figure 4 depicts several chiral benzene derivatives with achiral and chiral substituents for exemplifying the numbers appearing in the [0,0,0,0;4,2], [1,0,0,0;4,1], [2,0,0,0;4,0], and [1,1,0,0;4,0] rows of Table 6. Since each of these isomers are chiral, an arbitrary enantiomer is depicted in Figure 4.

Figure 5 depicts [2,0,0,0;2,2] derivatives with achiral and chiral substituents. Among them, the achiral deivatives (**44**−**48**) are so-called meso forms, since chiral substituents and the same number of their enantiomeric ones compensate the chirality intramolecularly.

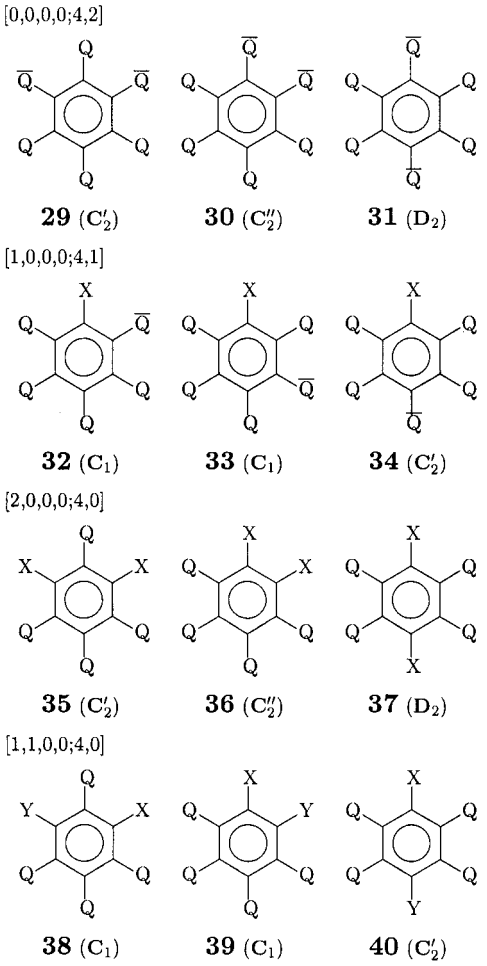


Figure 4. Several chiral benzene derivatives with achiral and chiral substituents.

Table 4. USCI Table for D_{6h}

	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_2'$	$\downarrow C_2''$	$\downarrow C_s$	$\downarrow C_s'$	$\downarrow C_s''$	$\downarrow C_i$	$\downarrow C_3$	$\downarrow D_2$	$\downarrow C_{2v}$	$\downarrow C_{2v}'$	$\downarrow C_{2v}''$	$\downarrow C_{2h}$	$\downarrow C_{2h}'$	$\downarrow C_{2h}''$
$D_{6h}(/C_1)$	s_1^{24}	s_2^{12}	s_2^{12}	s_2^{12}	s_2^{12}	s_2^{12}	s_2^{12}	s_2^{12}	s_3^8	s_4^6	s_4^6	s_4^6	s_4^6	s_4^6	s_4^6	s_4^6
$D_{6h}(/C_2)$	s_1^{12}	s_1^{12}	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_3^4	s_2^6	s_2^6	s_4^3	s_4^3	s_2^6	s_4^3	s_4^3
$D_{6h}(/C_2')$	s_1^{12}	s_2^6	$s_1^4s_2^4$	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_3^4	$s_2^2s_4^2$	s_4^3	$s_2^2s_4^2$	s_4^3	s_4^3	$s_2^2s_4^2$	s_4^3
$D_{6h}(/C_2'')$	s_1^{12}	s_2^6	s_2^6	$s_1^4s_2^4$	s_2^6	s_2^6	s_2^6	s_2^6	s_3^4	$s_2^2s_4^2$	s_4^3	s_4^3	$s_2^2s_4^2$	s_4^3	s_4^3	$s_2^2s_4^2$
$D_{6h}(/C_s)$	s_1^{12}	s_2^6	s_2^6	s_2^6	$s_1^4s_2^4$	s_2^6	s_2^6	s_2^6	s_3^4	s_4^3	$s_2^2s_4^2$	$s_2^2s_4^2$	s_4^3	s_4^3	s_4^3	$s_2^2s_4^2$
$D_{6h}(/C_s')$	s_1^{12}	s_2^6	s_2^6	s_2^6	s_2^6	$s_1^4s_2^4$	s_2^6	s_2^6	s_3^4	s_4^3	$s_2^2s_4^2$	s_4^3	$s_2^2s_4^2$	s_4^3	$s_2^2s_4^2$	s_4^3
$D_{6h}(/C_s'')$	s_1^{12}	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_1^{12}	s_2^6	s_3^4	s_4^3	s_4^3	s_2^6	s_2^6	s_2^6	s_4^3	s_4^3
$D_{6h}(/C_i)$	s_1^{12}	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_2^6	s_1^{12}	s_3^4	s_4^3	s_4^3	s_4^3	s_4^3	s_2^6	s_2^6	s_2^6
$D_{6h}(/C_3)$	s_1^8	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_1^8	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2
$D_{6h}(/D_2)$	s_1^6	s_1^6	$s_1^2s_2^2$	$s_1^2s_2^2$	s_2^3	s_2^3	s_2^3	s_2^3	s_3^2	$s_1^2s_2^2$	s_2^3	s_2s_4	s_2s_4	s_2^3	s_2s_4	s_2s_4
$D_{6h}(/C_{2v})$	s_1^6	s_1^6	s_2^3	s_2^3	$s_1^2s_2^2$	$s_1^2s_2^2$	s_2^3	s_2^3	s_3^2	s_2^3	$s_1^2s_2^2$	s_2s_4	s_2s_4	s_2^3	s_2s_4	s_2s_4
$D_{6h}(/C_{2v}')$	s_1^6	s_2^3	$s_1^2s_2^2$	s_2^3	$s_1^2s_2^2$	s_2^3	s_1^6	s_2^3	s_3^2	s_2s_4	s_2s_4	$s_1^2s_2^2$	s_2^3	s_2^3	s_2s_4	s_2s_4
$D_{6h}(/C_{2v}'')$	s_1^6	s_2^3	s_2^3	$s_1^2s_2^2$	s_2^3	$s_1^2s_2^2$	s_1^6	s_2^3	s_3^2	s_2s_4	s_2s_4	s_2^3	$s_1^2s_2^2$	s_2^3	s_2s_4	s_2s_4
$D_{6h}(/C_{2h})$	s_1^6	s_1^6	s_2^3	s_2^3	s_2^3	s_2^3	s_1^6	s_1^6	s_3^2	s_2^3	s_2^3	s_2^3	s_2^3	s_1^6	s_2^3	s_2^3
$D_{6h}(/C_{2h}')$	s_1^6	s_2^3	$s_1^2s_2^2$	s_2^3	s_2^3	$s_1^2s_2^2$	s_2^3	s_1^6	s_3^2	s_2s_4	s_2s_4	s_2s_4	s_2s_4	s_2^3	$s_1^2s_2^2$	s_2^3
$D_{6h}(/C_{2h}'')$	s_1^6	s_2^3	s_2^3	$s_1^2s_2^2$	$s_1^2s_2^2$	s_2^3	s_2^3	s_1^6	s_3^2	s_2s_4	s_2s_4	s_2s_4	s_2s_4	s_2^3	s_2^3	$s_1^2s_2^2$
$D_{6h}(/C_6)$	s_1^4	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_4	s_4	s_2^2	s_4	s_4
$D_{6h}(/D_3)$	s_1^4	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_4	s_2^2	s_4	s_4	s_2^2	s_4
$D_{6h}(/D_3')$	s_1^4	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_4	s_4	s_2^2	s_4	s_4	s_2^2
$D_{6h}(/C_{3v})$	s_1^4	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_1^4	s_4	s_2^2	s_2^2	s_4	s_4	s_4	s_2^2
$D_{6h}(/C_{3v}')$	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_1^4	s_4	s_2^2	s_4	s_2^2	s_4	s_2^2	s_4
$D_{6h}(/C_{3h})$	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_1^4	s_4	s_4	s_2^2	s_2^2	s_2^2	s_4	s_4
$D_{6h}(/C_{3i})$	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_1^4	s_4	s_4	s_4	s_4	s_2^2	s_2^2	s_2^2
$D_{6h}(/D_{2h})$	s_1^3	s_1^3	s_1s_2	s_1s_2	s_1s_2	s_1s_2	s_1^3	s_1^3	s_3	s_1s_2	s_1s_2	s_1s_2	s_1s_2	s_1^3	s_1s_2	s_1s_2
$D_{6h}(/D_6)$	s_1^2	s_1^2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2
$D_{6h}(/C_{6v})$	s_1^2	s_1^2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2
$D_{6h}(/C_{6h})$	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_1^2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2
$D_{6h}(/D_{3h})$	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2
$D_{6h}(/D_{3h}')$	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_1^2	s_2	s_1^2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2
$D_{6h}(/D_{3d})$	s_1^2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2
$D_{6h}(/D_{3d}')$	s_1^2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_1^2
$D_{6h}(/D_{6h})$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1

	$\downarrow C_6$	$\downarrow D_3$	$\downarrow D_3'$	$\downarrow C_{3v}$	$\downarrow C_{3v}'$	$\downarrow C_{3h}$	$\downarrow C_{3i}$	$\downarrow D_{2h}$	$\downarrow D_6$	$\downarrow C_{6v}$	$\downarrow C_{6h}$	$\downarrow D_{3h}$	$\downarrow D_{3h}'$	$\downarrow D_{3d}$	$\downarrow D_{3d}'$	$\downarrow D_{6h}$
$D_{6h}(/C_1)$	s_6^4	s_6^4	s_6^4	s_6^4	s_6^4	s_6^4	s_6^4	s_8^3	s_{12}^2	s_{12}^2	s_{12}^2	s_{12}^2	s_{12}^2	s_{12}^2	s_{12}^2	s_{24}
$D_{6h}(/C_2)$	s_3^4	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_4^3	s_6^2	s_6^2	s_6^2	s_{12}	s_{12}	s_{12}	s_{12}	s_{12}
$D_{6h}(/C_2')$	s_6^2	s_3^4	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_4s_8	s_6^2	s_{12}	s_{12}	s_6^2	s_{12}	s_6^2	s_{12}	s_{12}
$D_{6h}(/C_2'')$	s_6^2	s_6^2	s_3^4	s_6^2	s_6^2	s_6^2	s_6^2	s_4s_8	s_6^2	s_{12}	s_{12}	s_{12}	s_6^2	s_{12}	s_6^2	s_{12}
$D_{6h}(/C_s)$	s_6^2	s_6^2	s_6^2	s_3^4	s_6^2	s_6^2	s_6^2	s_4s_8	s_{12}	s_6^2	s_{12}	s_6^2	s_{12}	s_{12}	s_6^2	s_{12}
$D_{6h}(/C_s')$	s_6^2	s_6^2	s_6^2	s_6^2	s_3^4	s_6^2	s_6^2	s_4s_8	s_{12}	s_6^2	s_{12}	s_{12}	s_6^2	s_6^2	s_6^2	s_{12}
$D_{6h}(/C_s'')$	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_3^4	s_6^2	s_4^3	s_{12}	s_{12}	s_6^2	s_6^2	s_6^2	s_6^2	s_{12}	s_{12}
$D_{6h}(/C_i)$	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_6^2	s_3^4	s_4^3	s_{12}	s_{12}	s_6^2	s_{12}	s_{12}	s_6^2	s_6^2	s_{12}
$D_{6h}(/C_3)$	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_2^4	s_8	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_8
$D_{6h}(/D_2)$	s_3^2	s_3^2	s_3^2	s_6	s_6	s_6	s_6	s_2s_4	s_3^2	s_6	s_6	s_6	s_6	s_6	s_6	s_6
$D_{6h}(/C_{2v})$	s_3^2	s_6	s_6	s_3^2	s_3^2	s_6	s_6	s_2s_4	s_6	s_3^2	s_6	s_6	s_6	s_6	s_6	s_6
$D_{6h}(/C_{2v}')$	s_6	s_3^2	s_6	s_3^2	s_6	s_3^2	s_6	s_2s_4	s_6	s_6	s_6	s_3^2	s_6	s_6	s_6	s_6
$D_{6h}(/C_{2v}'')$	s_6	s_6	s_3^2	s_6	s_3^2	s_3^2	s_6	s_2s_4	s_6	s_6	s_6	s_6	s_3^2	s_6	s_6	s_6
$D_{6h}(/C_{2h})$	s_3^2	s_6	s_6	s_6	s_6	s_3^2	s_3^2	s_2^3	s_6	s_6	s_3^2	s_6	s_6	s_6	s_6	s_6
$D_{6h}(/C_{2h}')$	s_6	s_3^2	s_6	s_6	s_3^2	s_6	s_3^2	s_2s_4	s_6	s_6	s_6	s_6	s_6	s_3^2	s_6	s_6
$D_{6h}(/C_{2h}'')$	s_6	s_6	s_3^2	s_3^2	s_6	s_6	s_3^2	s_2s_4	s_6	s_6	s_6	s_6	s_6	s_6	s_3^2	s_6
$D_{6h}(/C_6)$	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_4	s_2^2	s_2^2	s_2^2	s_4	s_4	s_4	s_4	s_4
$D_{6h}(/D_3)$	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_4	s_2^2	s_4	s_4	s_2^2	s_4	s_2^2	s_4	s_4
$D_{6h}(/D_3')$	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_2^2	s_4	s_2^2	s_4	s_4	s_4	s_2^2	s_4	s_2^2	s_4
$D_{6h}(/C_{3v})$	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_2^2	s_4	s_4	s_2^2	s_4	s_2^2	s_4	s_4	s_2^2	s_4
$D_{6h}(/C_{3v}')$	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_2^2	s_4	s_4	s_2^2	s_4	s_4	s_2^2	s_2^2	s_4	s_4
$D_{6h}(/C_{3h})$	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_2^2	s_4	s_4	s_4	s_2^2	s_2^2	s_2^2	s_4	s_4	s_4
$D_{6h}(/C_{3i})$	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_2^2	s_1^4	s_4	s_4	s_4	s_2^2	s_4	s_4	s_2^2	s_2^2	s_4
$D_{6h}(/D_{2h})$	s_3	s_3	s_3	s_3	s_3	s_3	s_3	s_1s_2	s_3	s_3	s_3	s_3	s_3	s_3	s_3	s_3

Table 4 (Continued)

	$\downarrow C_6$	$\downarrow D_3$	$\downarrow D'_3$	$\downarrow C_{3v}$	$\downarrow C'_{3v}$	$\downarrow C_{3h}$	$\downarrow C_{3i}$	$\downarrow D_{2h}$	$\downarrow D_6$	$\downarrow C_{6v}$	$\downarrow C_{6h}$	$\downarrow D_{3h}$	$\downarrow D'_{3h}$	$\downarrow D_{3d}$	$\downarrow D'_{3d}$	$\downarrow D_{6h}$
$D_{6h}(/D_6)$	s_1^2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_2
$D_{6h}(/C_{6v})$	s_1^2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2
$D_{6h}(/C_{6h})$	s_1^2	s_2	s_2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2
$D_{6h}(/D_{3h})$	s_2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2
$D_{6h}(/D'_{3h})$	s_2	s_2	s_1^2	s_2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2	s_2
$D_{6h}(/D_{3d})$	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2	s_2
$D_{6h}(/D'_{3d})$	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2
$D_{6h}(/D_{6h})$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1

Table 5. Benzene Derivatives with Achiral Substituents

	C''_s	C'_{2v}	C''_{2v}	C_{2h}	D_{2h}	D_{3h}	D_{6h}	total
[6,0,0,0,0,0]	0	0	0	0	0	0	1	1
[5,1,0,0,0,0]	0	1	0	0	0	0	0	1
[4,2,0,0,0,0]	0	1	1	0	1	0	0	3
[4,1,1,0,0,0]	2	1	0	0	0	0	0	3
[3,3,0,0,0,0]	1	1	0	0	0	1	0	3
[3,2,1,0,0,0]	4	2	0	0	0	0	0	6
[3,1,1,1,0,0]	10	0	0	0	0	0	0	10
[2,2,2,0,0,0]	4	3	3	1	0	0	0	11
[2,2,1,1,0,0]	14	2	0	0	0	0	0	16
[2,1,1,1,1,0]	30	0	0	0	0	0	0	30
[1,1,1,1,1,1]	60	0	0	0	0	0	0	60

E. Combinatorial Enumeration of Coronene Derivatives with Achiral Substituents. The orbit of the 12 substitution positions of coronene is assigned to the coset representation $D_{6h}(/C''_s)$. The $D_{6h}(/C''_s)$ row of the USCI table (Table 4) is formally multiplied by the inverse mark table (Table 2) and gives PCIs as follows:

$$\mathrm{PCI}(C''_s; s_d) = \frac{1}{12}s_1^{12} - \frac{7}{12}s_2^6 - \frac{1}{12}s_3^4 + \frac{1}{2}s_4^3 + \frac{7}{12}s_6^2 - \frac{1}{2}s_{12} \quad (51)$$

$$\mathrm{PCI}(C'_{2v}; s_d) = \frac{1}{2}s_2^6 - \frac{1}{2}s_4^3 - \frac{1}{2}s_6^2 + \frac{1}{2}s_{12} \quad (52)$$

$$\mathrm{PCI}(C''_{2v}; s_d) = \frac{1}{2}s_2^6 - \frac{1}{2}s_4^3 - \frac{1}{2}s_6^2 + \frac{1}{2}s_{12} \quad (53)$$

$$\mathrm{PCI}(C_{2h}; s_d) = \frac{1}{6}s_2^6 - \frac{1}{2}s_4^3 - \frac{1}{6}s_6^2 + \frac{1}{2}s_{12} \quad (54)$$

$$\mathrm{PCI}(C_{3h}; s_d) = \frac{1}{4}s_3^4 - \frac{9}{12}s_6^2 + \frac{1}{2}s_{12} \quad (55)$$

$$\mathrm{PCI}(D_{2h}; sd) = s_4^3 - s_{12} \quad (56)$$

$$\mathrm{PCI}(C_{6h}; s_d) = \frac{1}{2}s_6^2 - \frac{1}{2}s_{12} \quad (57)$$

$$\mathrm{PCI}(D_{3h}; s_d) = \frac{1}{2}s_6^2 - \frac{1}{2}s_{12} \quad (58)$$

$$\mathrm{PCI}(D'_{3h}; s_d) = \frac{1}{2}s_6^2 - \frac{1}{2}s_{12} \quad (59)$$

$$\mathrm{PCI}(D_{6h}; s_d) = s_{12} \quad (60)$$

The PCIs of the remaining subgroups are omitted in the above list, since they are calculated to be equal to zero.

Let us consider a set of achiral substituents of 3 kinds (X, Y, and implicitly H), from which 12 substituents are selected and placed on the $D_{6h}(/C''_s)$ orbit to give a derivative of the formulas $C_{24}H_iX_jY_k$. The subscripts are nonnegative integers

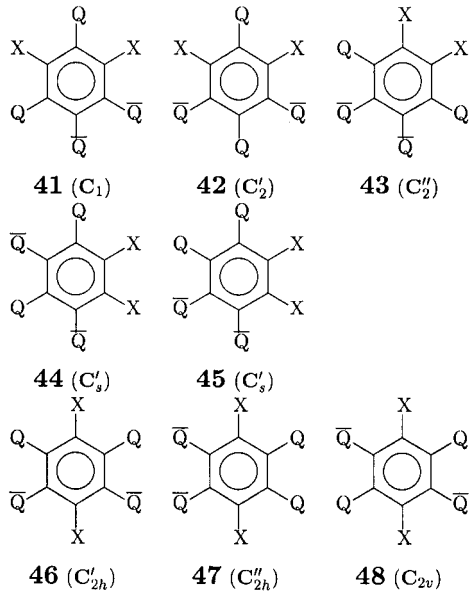


Figure 5. [2,0,0,0;2,2] benzene derivatives with achiral and chiral substituents.

satisfying $i + j + k = 12$. Our problem is to count the number of derivatives with a given formula $C_{24}H_iX_jY_k$ and a given symmetry. The second method of the USCI approach is applied to this problem by adopting the following inventory:

$$s_d = 1 + x^d + y^d \quad (61)$$

where each small letter corresponds to the substituent of its capital letter (except H). The inventory is introduced into eqs 51−60. The resulting equations are expanded to give generating functions. The coefficients of the terms $1^i x^j y^k$ (represented as $[i,j,k]$) in each equation are collected to give the corresponding column of Table 7, where i, j, and k run from 0 to 12, satisfying $i + j + k = 12$ and $i \geq j \geq k$. Note that the number of each subsymmetry other than the ones listed in Table 7 is equal to zero.

The total number of isomers with a given formula can be calculated by using a cycle index, which is obtained by adding all the equations (eqs 51−59).[43]

$$\mathrm{CI}(D_{6h}; s_d) = \frac{1}{12}s_1^{12} + \frac{7}{12}s_2^6 + \frac{1}{6}s_3^4 + \frac{1}{6}s_6^2 \quad (62)$$

The equivalent CI was obtained by the Pólya−Redfield theorem on the basis of the automorphism group D_6.[44] The introduction of the inventory (eq 61) and the expansion of the resulting polynomial give a generating function. The

Table 6. Benzene Derivatives with Chiral and Achiral Substituents

	C_1	C_2	C_2'	C_2''	C_s	C_s'	C_i	D_2	C_{2v}	C_{2h}'	C_{2h}''	D_3	D_6	D_{3d}	total
[0,0,0,0;6,0]	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1
[0,0,0,0;5,1]	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1
[1,0,0,0;5,0]	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1
[0,0,0,0;4,2]	0	0	1	1	0	0	0	1	0	0	0	0	0	0	3
[1,0,0,0;4,1]	2	0	1	0	0	0	0	0	0	0	0	0	0	0	3
[2,0,0,0;4,0]	0	0	1	1	0	0	0	1	0	0	0	0	0	0	3
[1,1,0,0;4,0]	2	0	1	0	0	0	0	0	0	0	0	0	0	0	3
[0,0,0,0;3,3]	0	0	0	0	0	1	0	0	0	1	0	0	0	1	3
[1,0,0,0;3,2]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[2,0,0,0;3,1]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[1,1,0,0;3,1]	10	0	0	0	0	0	0	0	0	0	0	0	0	0	10
[3,0,0,0;3,0]	1	0	1	0	0	0	0	0	0	0	0	1	0	0	3
[2,1,0,0;3,0]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[1,1,1,0;3,0]	10	0	0	0	0	0	0	0	0	0	0	0	0	0	10
[2,0,0,0;2,2]	1	0	1	1	0	2	0	0	1	1	1	0	0	0	8
[1,1,0,0;2,2]	6	0	1	0	2	0	0	0	0	0	0	0	0	0	9
[3,0,0,0;2,1]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[2,1,0,0;2,1]	14	0	2	0	0	0	0	0	0	0	0	0	0	0	16
[1,1,1,0;2,1]	30	0	0	0	0	0	0	0	0	0	0	0	0	0	30
[4,0,0,0;2,0]	0	0	1	1	0	0	0	1	0	0	0	0	0	0	3
[3,1,0,0;2,0]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[2,2,0,0;2,0]	4	1	3	3	0	0	0	0	0	0	0	0	0	0	11
[2,1,1,0;2,0]	14	0	2	0	0	0	0	0	0	0	0	0	0	0	16
[1,1,1,1;2,0]	30	0	0	0	0	0	0	0	0	0	0	0	0	0	30
[4,0,0,0;1,1]	0	0	0	0	1	1	0	0	0	1	0	0	0	0	3
[3,1,0,0;1,1]	4	0	0	0	2	0	0	0	0	0	0	0	0	0	6
[2,2,0,0;1,1]	4	0	1	0	2	3	1	0	0	0	0	0	0	0	11
[2,1,1,0;1,1]	14	0	0	0	2	0	0	0	0	0	0	0	0	0	16
[1,1,1,1;1,1]	30	0	0	0	0	0	0	0	0	0	0	0	0	0	30
[5,0,0,0;1,0]	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1
[4,1,0,0;1,0]	2	0	1	0	0	0	0	0	0	0	0	0	0	0	3
[3,2,0,0;1,0]	4	0	2	0	0	0	0	0	0	0	0	0	0	0	6
[3,1,1,0;1,0]	10	0	0	0	0	0	0	0	0	0	0	0	0	0	10
[2,2,1,0;1,0]	14	0	2	0	0	0	0	0	0	0	0	0	0	0	16
[2,1,1,1;1,0]	30	0	0	0	0	0	0	0	0	0	0	0	0	0	30

Table 7. Coronene Derivatives with Achiral Substituents

	C_s''	C_{2v}'	C_{2v}''	C_{2h}	C_{3h}	D_{2h}	C_{6h}	D_{3h}	D_{3h}'	D_{6h}	total
[12,0,0]	0	0	0	0	0	0	0	0	0	1	1
[11,0,0]	1	0	0	0	0	0	0	0	0	0	1
[10,2,0]	2	3	3	1	0	0	0	0	0	0	9
[10,1,1]	11	0	0	0	0	0	0	0	0	0	11
[9,3,0]	18	0	0	0	1	0	0	0	0	0	19
[9,2,1]	55	0	0	0	0	0	0	0	0	0	55
[8,4,0]	34	6	6	1	0	3	0	0	0	0	50
[8,3,1]	165	0	0	0	0	0	0	0	0	0	165
[8,2,2]	230	15	15	5	0	0	0	0	0	0	265
[7,5,0]	66	0	0	0	0	0	0	0	0	0	66
[7,4,1]	330	0	0	0	0	0	0	0	0	0	330
[7,3,2]	660	0	0	0	0	0	0	0	0	0	660
[6,6,0]	66	9	9	3	0	0	1	1	1	0	90
[6,5,1]	462	0	0	0	0	0	0	0	0	0	462
[6,4,2]	1120	30	30	10	0	0	0	0	0	0	1190
[6,3,3]	1539	0	0	0	3	0	0	0	0	0	1542
[5,5,2]	1386	0	0	0	0	0	0	0	0	0	1386
[5,4,3]	2310	0	0	0	0	0	0	0	0	0	2310
[4,4,4]	2838	42	42	12	0	6	0	0	0	0	2940

coefficients of the respective terms in the generating function represent the total numbers of coronene derivatives which are equal to those obtained by the summation of every row. These values are listed in the rightmost column of Table 7.

Figure 6 depicts [10,2,0] coronene derivatives with achiral substituents for exemplifying the results collected in the [10,2,0] row of Table 7. Thus, a total of nine isomers (two C_s''isomers, one C_{2h} isomer, three C_{2v}' isomers, and three C_{2v}'' isomers) are illustrated.

Figure 7 depicts C_{3h} coronene derivatives with achiral substituents for exemplifying the results collected in the C_{3h} column of Table 7. Thus, one [9,3.0] isomer and three [6,3,3] isomers are presented.

3. DISCUSSION

A. Effect of Achiral and Chiral Substituents on Global Symmetries. Let us first examine the case in which only achiral substituents are taken into consideration. Equations 6−12 show the nonzero PCIs for the seven subgroups of D_{6h}. On the other hand, the remaining 25 subgroups have PCIs of zero value. The latter result can be explained by inspection of the USCIs listed in eqs 63−94 in light of "the selection rule for judging the existence of subsymmetries" (theorem 3 of ref 34). Thereby, we have seven sets of subgroups having the same cycle structures:

s_1^6: C_1, C_s''

s_2^3: C_2'', C_s', C_{2v}''

s_2^3: C_2, C_i, C_{2h}

$s_1^2 s_2^2$: C_2', C_s, C_{2v}'

s_3^2: $C_3, D_3, C_{3v}, C_{3h}, D_{3h}$

$s_2 s_4$: $D_2, C_{2v}, C_{2h}', C_{2h}'', D_{2h}$

s_6: $C_6, D_3', C_{3v}', C_{3i}, D_6, C_{6v}, C_{6h}, D_{3h}', D_{3d}, D_{3d}', D_{6h}$

Note that the variable s_2^3 corresponds to the two series of group−subgroup relationships. These equations show that

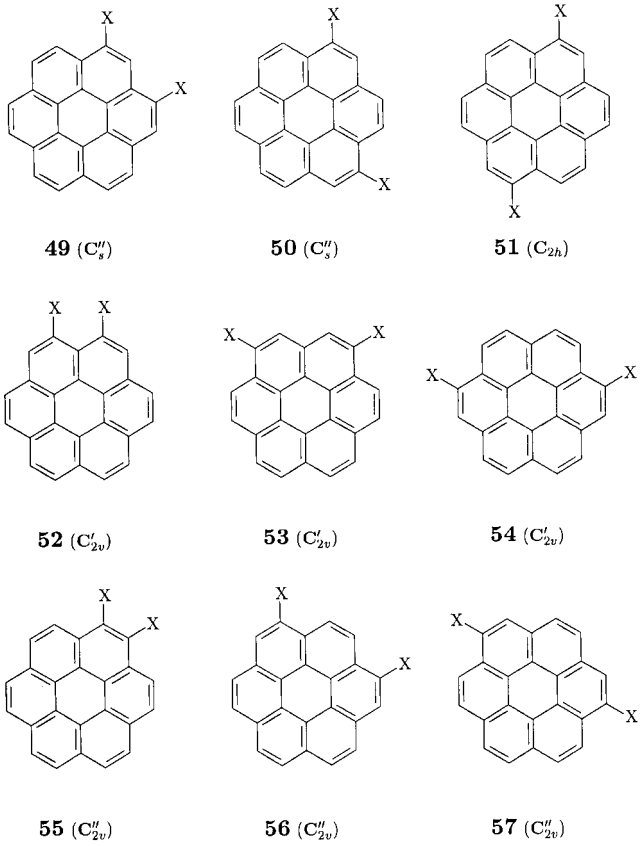


Figure 6. [10,2,0] coronene derivatives with achiral substituents.

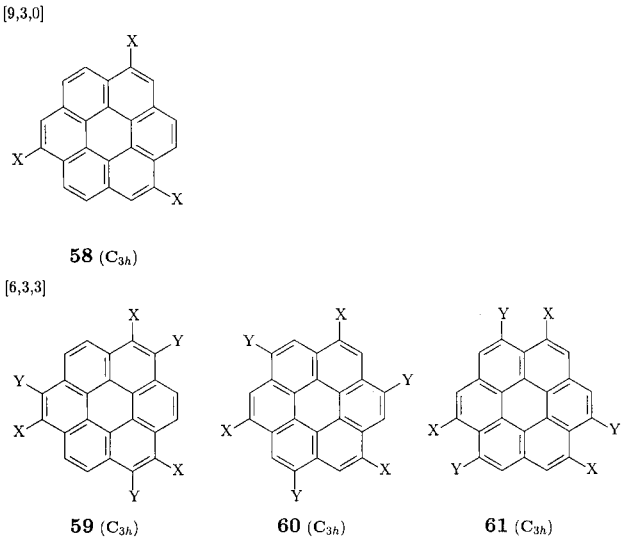


Figure 7. C_{3h} coronene derivatives with achiral substituents.

the subgroup appearing at the rightmost position of every row (i.e., C_s'', C_{2v}'', C_{2h}, C_{2v}', D_{3h}, D_{2h}, or D_{6h}) contains the other subgroups (up to conjugacy) appearing in the row at issue. This means that the substitution with achiral substituents for the $D_{6h}(/C_{2v}')$ orbit yields a derivative of C_s'', C_{2v}'', C_{2h}, C_{2v}', D_{3h}, D_{2h}, or D_{6h} symmetry. The other subgroups are concealed by the respective supergroups. This qualitative examination is verified by the derivation of partial cycle indices (PCIs), where the PCIs corresponding to the available symmetries are nonzero, while the remaining PCIs vanish to zero.

Let us next examine the case in which both achiral and chiral substituents are taken into consideration. Eleven

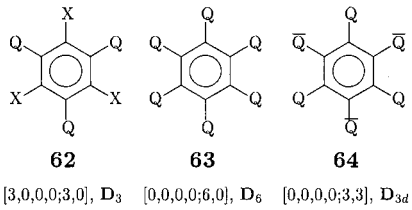


Figure 8. Benzene derivatives with chiral and achiral Substituents.

subgroups appear having a PCI-CF of value zero in eqs 15−46. These zero values can be explained by the inspection of the USCI-CFs listed in eqs 63−94. We have five sets of subgroups having he same cycle structures with chirality fittingness:

b_3^2: C_3, D_3

a_3^2: C_{3v}, C_{3h}, D_{3h}

b_6: C_6, D_3', D_6

c_6: C_{3v}', C_{3i}, D_{3d}

a_6: $C_{6v}, C_{6h}, D_{3h}', D_{3d}', D_{6h}$

Note that these variables correspond to s_3^2 and s_6 listed earlier. The subgroup appearing at the rightmost position of every row (i.e., D_3, D_{3h}, D_6, D_{3d}, or D_{6h}) covers the other subgroups (up to conjugacy). Hence, the latter covered subgroups give the PCIs of zero.

The discussion for the two cases can be extended into general cases. As a result, the selection rule for judging the existence of subsymmetries (theorem 3 of ref 34) is modified as follows:

Theorem 1. *Let us consider a molecule of G_i summetry by starting from a skeleton of G symmetry. The molecule of G_i summetry can exist if the corresponding PCI (or PCI-CF) is nonzero.*

The comparison between the PCIs (eqs 6−12) and PCI-CFs (eqs 15−46) indicates the effect of achiral and chiral substituents on the global symmetries of the benzene derivatives. The variable s_3^2 for the PCIs corresponds to the variable b_3^2 ascribed to chiral subgroups through the PCI-CFs as well as to the variable a_3^2 ascribed to achiral subgroups. This means that the D_3 derivatives of benzene are absent if achiral substituents are taken into consideration but appear if achiral and chiral substituents are considered. An example (**62**) is illustrated in Figure 8.

On the other hand, the variable s_6 for the PCIs corresponds to the variables b_6, c_6, and a_6 for PCI-CFs. The variable b_6 is ascribed to a chiral subgroup so that the D_6 derivatives of benzene are absent if achiral substituents are taken into consideration but appear if achiral and chiral substituents are considered as shown in Figure 8. The variable c_6 is ascribed to a prochiral (also achiral) subgroup, which indicates the existence of a D_{3d} molecule, as shown in Figure 8. The variable a_6 is ascribed to an achiral subgroup, which is in the same situation as the case where only achiral substituents are taken into account.

B. Sphericities. As shown in our previous book,[33] an orbit governed by a coset representation $G(/G_i)$ is classified into one of three categories: homospheric orbit for an achiral G

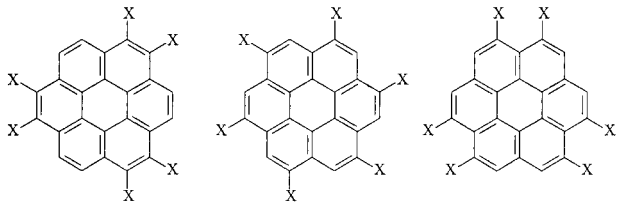


Figure 9. [6,6,0] coronene derivatives with achiral substituents.

and an achiral G_i, enantiospheric orbit for an achiral G and a chiral G_i, and hemispheric orbit for a chiral G and a chiral G_i. The enumeration of isomers is considered to be a kind of desymmetrization, which is strictly controlled by the sphericity of each orbit. This fact is referred to as "chirality fittingness", since the control by the sphericity is regarded as the capability of accommodating chiral or achiral substituents.[35] For example, a homospheric orbit takes achiral subsituents only in order to keep the achirality due to the G group.

For illustrating a homospheric orbit, we first examine the subduction represented by eq 90. Thus, two orbits governed by the homospheric $D_{3h}(/C_{2v})$ are generated. Since we have $|D_{3h}|/|C_{2v}| = 12/4 = 3$, each of the orbits accommodates three achiral substituents. An example (**12** as a [3,3,0,0,0,0] D_{3h} isomer) is illustrated in Figure 3, where three X's and three H's construct respective orbits governed by $D_{3h}(/C_{2v})$.

The subduction represented by eq 92 shows that the resulting orbit is governed by $D_{3d}(/C_2)$, which is enantiospheric. Note that the local symmetry C_2 appearing in $D_{3d}(/C_2)$ corresponds to the C'_2 subgroup of D_{6h}. The orbit of six positions governed by $D_{3d}(/C_2)$ is able to accommodate three Q's and three $\bar{Q}$'s, giving the D_{3d} molecule (**64** as a [0,0,0,0;3,3] D_{3d} isomer) shown in Figure 8. Thus, the set of three Q's and three $\bar{Q}$'s constructs a six-membered orbit governed by $D_{3d}(/C_2)$. It should be noted that the chiral group Q should have a symmetry superior to the local symmetry C_2 of the orbit. If the symmetry of Q is C_1 (asymmetric), the global symmetry is restricted to C_{3v}.

Derivative **2** belongs to C'_s symmetry, which comes from the subduction represented by eq 68. The three two-membered orbits are enantiospheric, since they are ascribed to the coset representation $C'_s(/C_1)$. One of the orbits accommodates Q and $\bar{Q}$ to produce the disubstituted derivative (**2**). Each of the remaining orbits is occupied by two hydrogens, which are enantiotopic to each other.

For exemplifying a hemispheric orbit, let us consider the subduction represented by eq 80. The resulting two $D_3(/C_2)$ orbits are three-membered ($|D_3|/|C_2| = 6/2 = 3$), and each accommodates a set of three chiral substituents or a set of three achiral substituents. An example (**62** as a [3,0,0,0;3,0] D_3 isomer) is illustrated in Figure 8, where three Q's (chiral) and three X's (achiral) are used as substituents. The same symmetry can be realized by using three Q's (chiral) and three R's (chiral) as substituents, though the present enumeration takes no account of this case.

C. Coronenes versus Benzenes. The inspection of the USCIs listed in the $D_{6h}(/C'_s)$ row of the USCI table (Table 4) gives 10 sets of subgroups having the same cycle structures:

$$s_1^{12}: \quad C_1, C''_s$$

$$s_2^6: \quad C'_2, C_s, C'_{2v}$$

$$s_2^6: \quad C''_2, C'_s, C''_{2v}$$

$$s_2^6: \quad C_2, C_i, C_{2h}$$

$$s_3^4: \quad C_3, C_{3h}$$

$$s_4^3: \quad D_2, C_{2v}, C'_{2h}, C''_{2h}, D_{2h}$$

$$s_6^2: \quad C_6, C_{3i}, C_{6h}$$

$$s_6^2: \quad D_3, C_{3v}, D_{3h}$$

$$s_6^2: \quad D'_3, C'_{3v}, D'_{3h}$$

$$s_1^2: \quad D_6, C_{6v}, D_{3d}, D'_{3d}, D_{6h}$$

where their group−subgroup relationships are taken into consideration. Note that the variable s_2^6 corresponds to three sets of subgroups and the variable s_6^2 is associated with three sets of subgroups. These equations show that the subgroup appearing at the rightmost position of every row is realized as a molecule and, as a result, conceals the other subgroups (up to conjugacy) in the row at issue. Hence, these concealed subgroups give the SCIs of zero value.

A comparison between the PCIs for the benzene derivatives and those for the coronene derivatives shows that C_{3h}, C_{6h}, and D'_{3h} additionally appear for the coronene derivatives. The C_{3h} derivatives of coronene are depicted in Figure 7. When we place X = Y in Figure 7, we obtain a C_{6h} and a D'_{3h} derivative along with a D_{3h} derivative, as shown in Figure 9. From the viewpoint of symmetry, the D_{3h} derivative of coronene shown in Figure 9 is obviously related to 1,3,5-trisubstituted benzene (D_{3h}) shown in Figure 3. On the other hand, the remaining derivatives shown in Figure 9 cannot find the counterparts of benzene derivatives.

4. CONCLUSIONS

Benzene derivatives with achiral and chiral substituents are enumerated by means of the unit-subduced cycle index (USCI) approach. Thus, partial cycle indices with and without chirality fittingness (PCI-CFs and PCIs) are calculated by using the precalculated inverse of the mark table and the USCI table for the point group D_{6h} and are applied to the enumeration of the benzene derivatives. The USCI approach is also applied to the enumeration of coronene derivatives. The symmetries of the resulting derivatives are discussed in terms of sphericities. Although the present paper deals with a limited number of examples, the inverse mark table (Table 2) and the USCI table (Table 4) can be applied to the enumeration based on any skeletons of D_{6h} symmetry.

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