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ADAMANTANE ISOMERS WITH GIVEN SYMMETRIES. SYSTEMATIC ENUMERATION BY UNIT SUBDUCED CYCLE INDICES

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Tricyclic isomers of adamantane ($C_{10}H_{16}$) are characterized by polymethylene indices (PMIs) and molecular symmetry. The PMI is a partition denoted as $[1^{m_1}, 2^{m_2}, \ldots, 6^{m_6}]$ ($m_1 + 2m_2 + \ldots + 6m_6 = 6$), in which each integer is the length of a polymethylene unit and the power (m_r) denotes the number of the units. The isomers are then enumerated by starting from tetrahedrane (T_d) and cyclobutadiene (D_{2h}) as parent skeletons, in which the edges are considered to be substituted by polymethylenes. From the tetrahedrane skeleton, there emerge 32 isomers, which are classified in terms of PMIs and subsymmetries of T_d. The cyclobutadiene skeleton yields 89 isomers classifed by PMIs and subsymmetries of D_{2h}. Isomer enumerations are also discussed regarding noradamantane and homoadamantane.

* * *

Adamantane rearrangements have long been investigated, since Schleyer's discovery on the rearrangement of tetrahydrocyclopentadiene to adamantane.[1] Whitlock and Siefken studied the mechanisms of such reactions by constructing a rearrangement graph, which contains various tricyclodecane intermediates.[2] Molecular mechanics provided a method of calculating the stabilities of the intermediates.[3,4] Various precursors and intermediates for adamantane were reported and the relationship regarding them was discussed in terms of "adamantaneland".[4] Recently, a renaissance on the adamantane chemistry led to more detailed information on the isomeric intermediates and on the mechanisms of the rearrangements.[5-7]

In order to clarify the mechanisms, enumerations of potential intermediates are necessary. Computational and graph-theoretical investigations[4,8] enumerated isomers of adamantane. They were, however, concerned only with their constitutions but not with their configurations. In other words, the enumerations regarded the isomers as two-dimentional objects or as chemical graphs. Moreover, the symmetries of the isomers have attracted little attention of chemists, because there exist no effective methods for enumerating molecular symmetries.

We have reported a method of enumeration based on unit subduced cycle indices (USCIs) that are derived from the subduction of coset representations.[9] This method allows us to enumerate chemical structures as three-dimensional objects. In the continuation of this work, the present paper deals with an enumeration of adamantane isomers as three-dimensional objects. That is to say, this considers the symmetries or stereochemistries of the isomers. For the purpose of applying the method to adamantane isomers, we should construct tables of USCIs for T_d and D_{2h} point groups, the construction of which is the other subject of the present paper (see ref. 9).

Enumeration of Tricyclodecanes With T_d or Its Subsymmetry.

Let us consider tetrahedrane (1) of T_d as a parent skeleton. Tricyclodecanes and their homologs are derived by substitution of polymethylenes on the edges of the tetrahedrane skeleton (1).

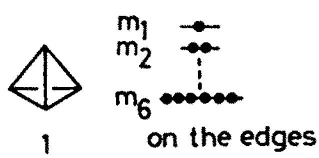

Figure 1. Derivation of Adamantane Isomers by Substitution of Polymethylenes on the Edges of a Tetrahedrane Skeleton (1).

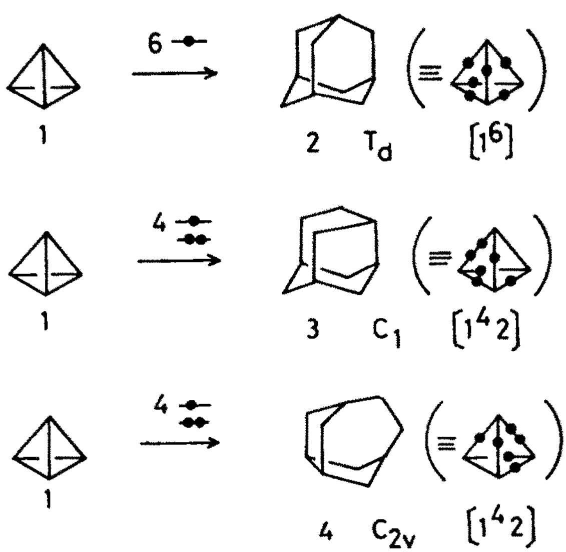

Figure 2. Polymethylene Indices (PMI) and Subsymmetries of Td in Several Isomers of Adamantane

If we consider m_1 methylenes, m_2 ethylenes, ... and m_6 hexamethylenes to be such substituents (Fig. 1), the resulting tricycloalkane has a molecular formula of $(CH)_4(CH_2)_m$, where

$$m_1 + 2m_2 + \ldots, + 6m_6 = m. \qquad (1)$$

The integer m is equal to 6 when we consider the isomers of adamantane. It should be noted that this methodology takes account of their configurations, but not of their conformations. The partition of m is denoted as $[1^{m_1}\ 2^{m_2}\ \ldots\ 6^{m_6}]$, which is called a polymethylene index (PMI) in the present paper. Since the PMIs indicate the modes of substitution, they are capable of characterizing the resulting isomers. For example, adamantane (2), which is derived by the substituteion of 6 methylenes on the 6 edges of 1, is chracterized by the PMI $[1^6]$. Similarly, protoadamnantane (3) and its isomer (4) have the same PMI $[1^4 2]$.

Alternatively, the adamnatane isomers can also be classified in terms of their symmetries. Since the present skeleton has T_d symmetry, the isomers have the subsymmetries of T_d. Figure 2 shows that adamantane (2) of $[1^6]$ has T_d symmetry, protoadamanetane (3) has C_1 symmetry, and the isomer (4) has C_{2v} symmetry.

The above discussions indicate that our target is an enumeration with respect not only to PMIs but also to symmetries. The present method of enumerations contains the following steps.

Table 1. Mark Table of T_d

i \ j	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	24	0	0	0	0	0	0	0	0	0	0
$T_d(/C_2)$	12	4	0	0	0	0	0	0	0	0	0
$T_d(/C_s)$	12	0	2	0	0	0	0	0	0	0	0
$T_d(/C_3)$	8	0	0	2	0	0	0	0	0	0	0
$T_d(/S_4)$	6	2	0	0	2	0	0	0	0	0	0
$T_d(/D_2)$	6	6	0	0	0	6	0	0	0	0	0
$T_d(/C_{2v})$	6	2	2	0	0	0	2	0	0	0	0
$T_d(/C_{3v})$	4	0	2	1	0	0	0	1	0	0	0
$T_d(/D_{2d})$	3	3	1	0	1	3	1	0	1	0	0
$T_d(/T)$	2	2	0	2	0	2	0	0	0	2	0
$T_d(/T_d)$	1	1	1	1	1	1	1	1	1	1	1

Step 1 is classification of the edges of a parent skeleton into orbits and determination of coset representations. The six edges of the skeleton (1) construct an orbit that is subject to a coset representaion, $T_d(/C_{2v})$.[10] This symbol denotes a coset representation (CR) obtained by the coset decomposition of T_d by C_{2v}. This step requires the mark table of T_d (Table 1).[11] When we examine the skeleton (1) and count fixed edges regarding every subgroup, we obtain a fixed-point vector,[12], i.e., (6 2 2 0 0 0 2 0 0 0

Table 2. The Inverse of the Mark Table of T_d

i \ j	$T_d(/C_1)$	$T_d(/C_2)$	$T_d(/C_s)$	$T_d(/C_3)$	$T_d(/S_4)$	$T_d(/D_2)$	$T_d(/C_{2v})$	$T_d(/C_{3v})$	$T_d(/D_{2d})$	$T_d(/T)$	$T_d(/T_d)$	$\sum_i \bar{m}_{ji}$
C_1	1/24	0	0	0	0	0	0	0	0	0	0	1/24
C_2	-1/8	1/4	0	0	0	0	0	0	0	0	0	1/8
C_s	-1/4	0	1/2	0	0	0	0	0	0	0	0	1/4
C_3	-1/6	0	0	1/2	0	0	0	0	0	0	0	1/3
S_4	0	-1/4	0	0	1/2	0	0	0	0	0	0	1/4
D_2	1/12	-1/4	0	0	0	1/6	0	0	0	0	0	0
C_{2v}	1/4	-1/4	-1/2	0	0	0	1/2	0	0	0	0	0
C_{3v}	1/2	0	-1	-1/2	0	0	0	1	0	0	0	0
D_{2d}	0	1/2	0	0	-1/2	-1/2	-1/2	0	1	0	0	0
T	1/6	0	0	-1/2	0	-1/6	0	0	0	1/2	0	0
T_d	-1/2	0	1	1/2	0	1/2	0	-1	-1	-1/2	1	0

0), whose elements are the number of fixed edges. This vector is identical to the $T_d(/C_{2v})$ row of Table 1. Hence, we arrive at the assignment of the six edges. Alternatively, the vector is multiplied by the inverse of the mark table (Table 2). Then we obtain a vector, (0 0 0 0 0 0 1 0 0 0 0), which shows the appearance of $T_d(/C_{2v})$.

Step 2 is construction of a subduced cycle index (SCI) from unit subduced cycle indices (USCIs). We have preestimated USCIs for T_d symmetry as shown in Table 3.[13] Using the $T_d(/C_{2v})$ row of this table, we obtain an SCI for every subsymmetry. Note that, in this case, the SCI is equal to the USCI, because there emerges only one orbit.[14]

Step 3 is introduction of a figure inventory into the SCI. For the purpose of maniputlating this case, we introduce a figure inventory,

$$s_k = 1 + x_1^k + x_2^k + \dots + x_6^k, \qquad (2)$$

into the above SCIs. Thereby, we obtain fixed-point-counting polynomials. The variable x_r is concerened with the substitution of $(CH_2)_r$. Hence, the term $x_1^{m_1}x_2^{m_2}\dots x_6^{m_6}$ corresponds to the PMI $[1^{m_1}\ 2^{m_2}\ \dots\ 6^{m_6}]$.

$$s_1^6 = (1 + x_1 + \dots + x_6)^6 \quad \text{for } C_1; \qquad (3a)$$

$$s_1^2s_2^2 = (1 + x_1 + \dots + x_6)^2(1 + x_1^2 + \dots + x_6^2)^2 \quad \text{for } C_2; \qquad (3b)$$

$$s_1^2s_2^2 = (1 + x_1 + \dots + x_6)^2(1 + x_1^2 + \dots + x_6^2)^2 \quad \text{for } C_s; \qquad (3c)$$

$$s_3^2 = (1 + x_1^3 + \dots + x_6^3)^2 \quad \text{for } C_3; \qquad (3d)$$

$$s_2s_4 = (1 + x_1^2 + \dots + x_6^2)(1 + x_1^4 + \dots + x_6^4) \quad \text{for } S_4; \qquad (3e)$$

$$s_3^2 = (1 + x_1^3 + \dots + x_6^3)^2 \quad \text{for } C_3; \qquad (3f)$$

$$s_2s_4 = (1 + x_1^2 + \dots + x_6^2)(1 + x_1^4 + \dots + x_6^4) \quad \text{for } S_4; \qquad (3g)$$

$$s_2^3 = (1 + x_1^2 + \dots + x_6^2)^3 \quad \text{for } D_2; \qquad (3h)$$

$$s_1^2s_4 = (1 + x_1 + \dots + x_6)^2(1 + x_1^4 + \dots + x_6^4) \quad \text{for } C_{2v}; \qquad (3i)$$

$$s_3^2 = (1 + x_1^3 + \dots + x_6^3)^2 \quad \text{for } C_{3v}; \qquad (3j)$$

Table 3. Unit Subduced Cycle Indices for $\mathbf{T_d}$

i \ j	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	s_1^{24} (b_1^{24})	s_2^{12} (b_2^{12})	s_2^{12} (c_2^{12})	s_3^8 (b_3^8)	s_4^6 (c_4^6)	s_4^6 (b_4^6)	s_4^6 (c_4^6)	s_6^4 (c_4^6)	s_8^3 (c_8^3)	s_{12}^2 (b_{12}^2)	s_{24} (c_{24})
$T_d(/C_2)$	s_1^{12} (b_1^{12})	$s_1^4s_2^4$ $(b_1^4b_2^4)$	s_2^6 (c_2^6)	s_3^4 (b_3^4)	$s_2^2s_4^2$ $(c_2^2c_4^2)$	s_2^6 (b_2^6)	$s_2^2s_4^2$ $(c_2^2c_4^2)$	s_6^2 (c_6^2)	s_4^3 (c_4^3)	s_6^2 (b_6^2)	s_{12} (c_{12})
$T_d(/C_s)$	s_1^{12} (b_1^{12})	s_2^6 (b_2^6)	$s_1^2s_2^5$ $(a_1^2c_2^5)$	s_3^4 (b_3^4)	s_4^3 (c_4^3)	s_4^3 (b_4^3)	$s_2^2s_4^2$ $(a_2^2c_4^2)$	$s_3^2s_6$ $(a_3^2b_6)$	s_4s_8 (a_4c_8)	s_{12} (b_{12})	s_{12} (a_{12})
$T_d(/C_3)$	s_1^8 (b_1^8)	s_2^4 (b_2^4)	s_2^4 (c_2^4)	$s_1^2s_3^2$ $(b_1^2b_3^2)$	s_4^2 (c_4^2)	s_4^2 (b_4^2)	s_4^2 (c_4^2)	s_2s_6 (c_2c_6)	s_8 (c_8)	s_4^2 (b_4^2)	s_8 (c_8)
$T_d(/S_4)$	s_1^6 (b_1^6)	$s_1^2s_2^2$ $(b_1^2b_2^2)$	s_2^3 (c_2^3)	s_2^3 (b_3^2)	$s_1^2s_4$ $(a_1^2c_4)$	s_2^3 (b_2^3)	s_2s_4 (c_2c_4)	s_6 (c_6)	s_2s_4 (a_2c_4)	s_6 (b_6)	s_6 (a_6)
$T_d(/D_2)$	s_1^6 (b_1^6)	s_1^6 (b_1^6)	s_2^3 (c_2^3)	s_3^2 (b_3^2)	s_2^3 (c_2^3)	s_1^6 (b_1^6)	s_2^3 (c_2^3)	s_6 (c_6)	s_2^3 (c_2^3)	s_3^2 (b_3^2)	s_6 (c_6)
$T_d(/C_{2v})$	s_1^6 (b_1^6)	$s_1^2s_2^2$ $(b_1^2b_2^2)$	$s_1^2s_2^2$ $(a_1^2c_2^2)$	s_3^2 (b_3^2)	s_2s_4 (c_2c_4)	s_2^3 (b_2^3)	$s_1^2s_4$ $(a_1^2c_4)$	s_3^2 (a_3^2)	s_2s_4 (a_2c_4)	s_6 (b_6)	s_6 (a_6)
$T_d(/C_{3v})$	s_1^4 (b_1^4)	s_2^2 (b_2^2)	$s_1^2s_2$ $(a_1^2c_2)$	s_1s_3 (b_1b_3)	s_4 (c_4)	s_4 (b_4)	s_2^2 (a_2^2)	s_1s_3 (a_1a_3)	s_4 (a_4)	s_4 (b_4)	s_4 (a_4)
$T_d(/D_{2d})$	s_1^3 (b_1^3)	s_1^3 (b_1^3)	s_1s_2 (a_1c_2)	s_3 (b_3)	s_1s_2 (a_1c_2)	s_1^3 (b_1^3)	s_1s_2 (a_1c_2)	s_3 (a_3)	s_1s_2 (a_1c_2)	s_3 (b_3)	s_3 (a_3)
$T_d(/T)$	s_1^2 (b_1^2)	s_1^2 (b_1^2)	s_2 (c_2)	s_1^2 (b_1^2)	s_2 (a_2)	s_1^2 (b_1^2)	s_2 (c_2)	s_2 (c_2)	s_2 (b_2)	s_1^2 (b_1^2)	s_2 (c_2)
$T_d(/T_d)$	s_1 (b_1)	s_1 (b_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)	s_1 (a_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)
$\sum_{i} \bar{m}_{ji}$	1/24	1/8	1/4	1/3	1/4	0	0	0	0	0	0

$$s_2s_4 = (1 + x_1^2 + \ldots + x_6^2)(1 + x_1^4 + \ldots + x_6^4) \quad \text{for } \mathbf{D}_{2d}; \quad (3k)$$
$$s_6 = 1 + x_1^6 + \ldots + x_6^6 \quad \text{for } \mathbf{T}; \quad (3l) \text{ and}$$
$$s_6 = 1 + x_1^6 + \ldots + x_6^6 \quad \text{for } \mathbf{T}_d. \quad (3m)$$

We expand these equations and then collect terms of the same power. Table 4 lists the resulting coefficients of the index terms ($x_1^{m_1}x_2^{m_2}\ldots x_6^{m_6}$), where $m_1 + 2m_2 + \ldots + 6m_6 = 6$. These partitions of the integer 6 correpond to adamantane isomers.

In Step 4, Table 4 is regarded as a matrix, which is then multiplied by the inverse of the mark table for $\mathbf{T}_d$ (Table 2). The resulting matrix is found in Table 5, in which each row is concerned with an index term (or PMI) and each column corresponds to a subsymmetry; and their intersection is the number of adamantane isomers with the PMI and the subsymmetry.

Figure 3 depicts the 32 isomers enumerated in Table 5. Each of the isomers is accompanied with its PMI and its symmetry. There emerge no isomers belonging to $\mathbf{C}_3$, $\mathbf{S}_4$ or $\mathbf{T}$ symmetry. The total number (32) is equal to the value obtained by Balaban.[15] However, the present result provides more detailed information on the symmetry of the isomers, which has never been discussed. Thus, we are able to conclude that there emerge 16 chiral isomers, among which the 12 isomers are assymetric ($\mathbf{C}_1$), the three belong to $\mathbf{C}_2$ and the one is a $\mathbf{D}_2$ isomer.

The enumeration of noradamantane isomers is accomplished in a similar way. The terms at issue are x_1^5, $x_1^3x_2$, $x_1^2x_3$, $x_1x_2^2$, x_1x_4, x_2x_3, and x_5 in eqs. 3a-3m. The results are found in Table 6. There emerge 18 isomers in all. Figure 4 illustrates these isomers.

The numbers of homoadamantane isomers are calculated and collected in Table 7, which totally contains 47 isomers.[16]

If we use an alternative figure inventory,

$$s_k = 1 + x^k + x^{2k} + \ldots + x^{6k}, \quad (4)$$

in place of eq. 2, we can obtain a summarized result. Note that the corresponding generating functions regarding eq. 4 are those in which the variables (x_r) of eqs. 3a-3m are replaced by x^r. Table 8 collects the coefficients of the terms x^r ($r = 0$ to 8). Table 8 regarded as a matrix is multiplied by Table 2 to afford Table 9; the terms (x^7, x^6, and x^5) indicate the isomers of homoadamantane, adamantane, and noradamantane, respectively. Hence, the row for x^6 (adamantane isomers) is equal to the bottom of Table 5, which is obtained by summing up each column. Similarly, the rows for x^7 (homoadamantane isomers) and x^5 (noradamantane isomers) in Table 9 are identical with the bottoms of Tables 6 and 7.

The total number of isomers with the index term (x^r) is calculated in the form of a generating function. We again use the $\mathbf{T}_d(/\mathbf{C}_{2v})$ row of Table 1. Additionally, we utilize the factors collected at the bottom of Table 3. These factors have been obtained by summing up the respective rows of the inverse of a mark table (Table 2). We thereby obtain a cycle index (ZI),

$$\begin{aligned} ZI(\mathbf{T}_d; s_k) &= (1/24)s_1^6 + (1/8)s_1^2s_2^2 + (1/4)s_1^2s_2^2 + (1/3)s_3^2 + (1/4)s_2s_4 \\ &= (1/24)(s_1^6 + 9s_1^2s_2^2 + 8s_3^2 + 6s_2s_4). \end{aligned} \quad (5)$$

Table 4. Coefficients Appearing in Eq. 3

Index term	PMI	Coefficients for										
		C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
x_1^6	$[1^6]$	1	1	1	1	1	1	1	1	1	1	1
$x_1^4x_2$	$[1^42]$	30	2	2	0	0	0	2	0	0	0	0
$x_1^3x_3$	$[1^33]$	60	4	4	0	0	0	0	0	0	0	0
$x_1^2x_2^2$	$[1^22^2]$	90	6	6	0	0	6	0	0	0	0	0
$x_1^2x_4$	$[1^24]$	60	4	4	0	0	0	0	0	0	0	0
$x_1x_2x_3$	$[123]$	120	0	0	0	0	0	0	0	0	0	0
x_1x5	$[15]$	30	2	2	0	0	0	2	0	0	0	0
x_2^3	$[2^3]$	20	4	4	2	0	0	0	2	0	0	0
x_2x_4	$[24]$	30	2	2	0	0	0	2	0	0	0	0
x_3^2	$[3^2]$	15	3	3	0	1	3	1	0	1	0	0
x_6	$[6]$	6	2	2	0	0	0	2	0	0	0	0

Table 5. Number of Adamantane Isomers ($C_{10}H_{16}$)

Idex term	PMI	Number of Adamantane Isomers of											Total for PMI
		C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	
x_1^6	$[1^6]$	0	0	0	0	0	0	0	0	0	0	1	1
$x_1^4x_2$	$[1^42]$	1	0	0	0	0	0	1	0	0	0	0	2
$x_1^3x_3$	$[1^33]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1^2x_2^2$	$[1^22^2]$	2	0	3	0	0	1	0	0	0	0	0	6
$x_1^2x_4$	$[1^24]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1x_2x_3$	$[123]$	5	0	0	0	0	0	0	0	0	0	0	5
x_1x5	$[15]$	1	0	0	0	0	0	1	0	0	0	0	2
x_2^3	$[2^3]$	0	1	0	0	0	0	0	2	0	0	0	3
x_2x_4	$[24]$	1	0	0	0	0	0	1	0	0	0	0	2
x_3^2	$[3^2]$	0	0	1	0	0	0	0	0	1	0	0	2
x_6	$[6]$	0	0	0	0	0	0	1	0	0	0	0	1
Total		12	3	8	0	0	1	4	2	1	0	1	32

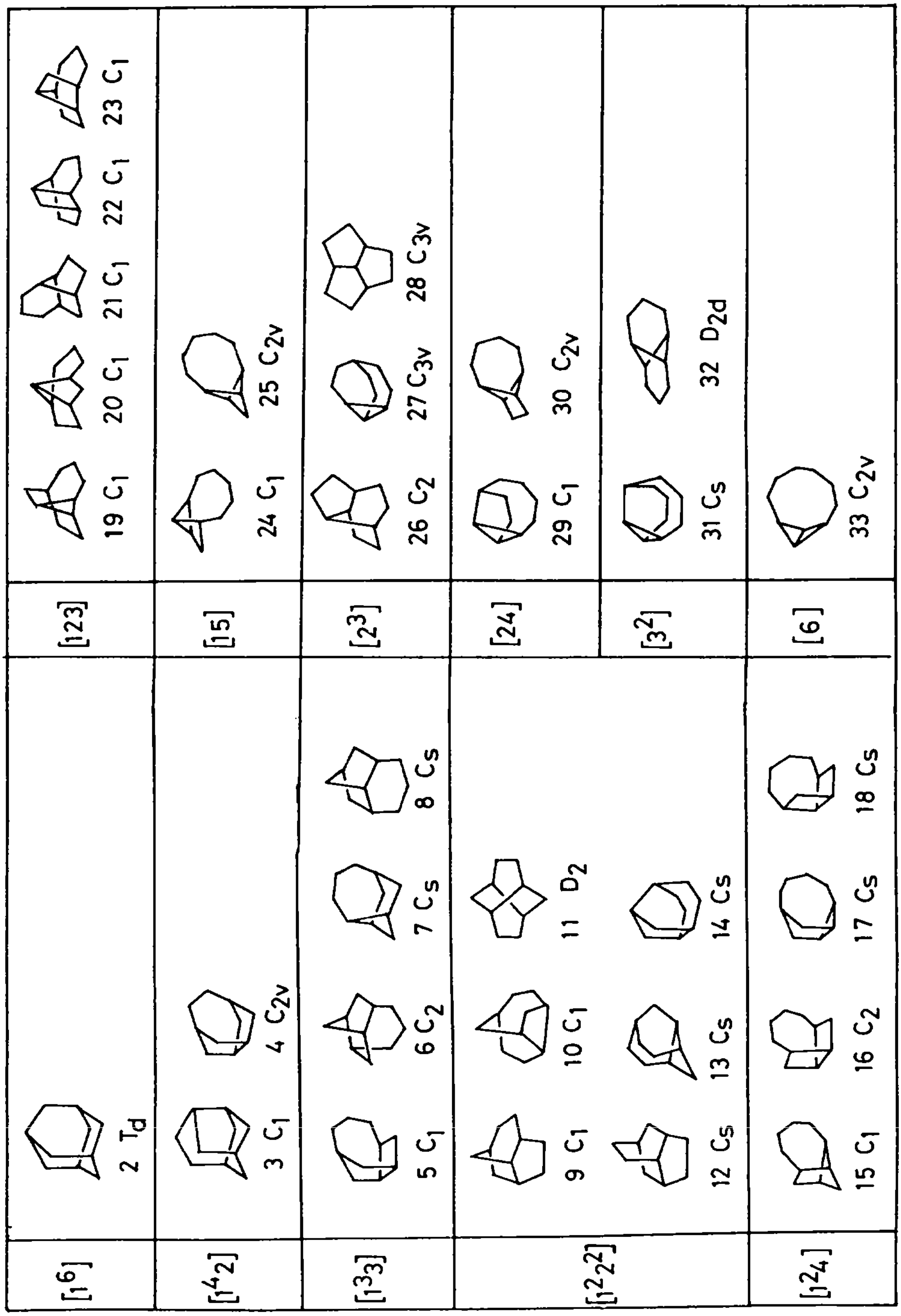
[1^6]
2 Td
[123]
19 C1
20 C1
21 C1
22 C1
23 C1
[1^4 2]
3 C1
4 C2v
[15]
24 C1
25 C2v
[1^3 3]
5 C1
6 C2
7 Cs
8 Cs
[2^3]
26 C2
27 C3v
28 C3v
[1^2 2^2]
9 C1
10 C1
11 D2
12 Cs
13 Cs
14 Cs
[24]
29 C1
30 C2v
[3^2]
31 Cs
32 D2d
[1^2 4]
15 C1
16 C2
17 Cs
18 Cs
[6]
33 C2v

Fig. 3

Table 6. Number of Noradamantane Isomers (C_9H_{14})

Idex term	PMI	Number of Noradamantane Isomers of											Total for PMI
		C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	
x_1^5	$[1^5]$	0	0	0	0	0	0	1	0	0	0	0	1
$x_1^3x_2$	$[1^32]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1^2x_3$	$[1^23]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1x_2^2$	$[12^2]$	1	1	2	0	0	0	0	0	0	0	0	4
x_1x_4	[14]	1	0	0	0	0	0	1	0	0	0	0	2
x_2x_3	[23]	1	0	0	0	0	0	1	0	0	0	0	2
x_5	[5]	0	0	0	0	0	0	1	0	0	0	0	1
Total		5	3	6	0	0	0	4	0	0	0	0	18

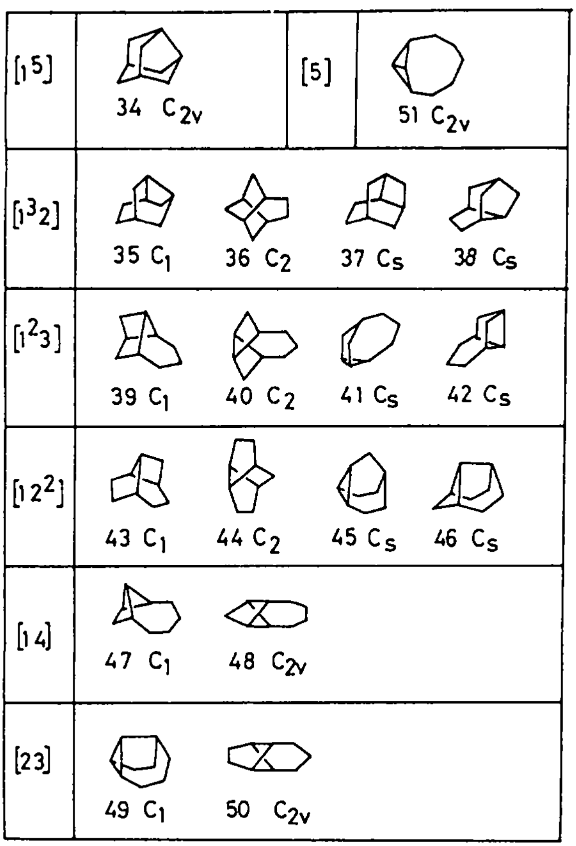

Fig. 4

Table 7. Number of Homoadamantane Isomers ($C_{11}H_{18}$)

Idex term	PMI	Number of Homoadamantane Isomers of											Total for PMI
		C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	
$x_1^5x_2$	$[1^52]$	0	0	0	0	0	0	1	0	0	0	0	1
$x_1^4x_3$	$[1^43]$	1	0	0	0	0	0	1	0	0	0	0	2
$x_1^3x_2^2$	$[1^32^2]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1^3x_4$	$[1^34]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1^2x_2x_3$	$[1^223]$	6	1	2	0	0	0	0	0	0	0	0	9
$x_1^2x_5$	$[1^25]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1x_2^3$	$[12^3]$	1	1	2	0	0	0	0	0	0	0	0	4
$x_1x_3x_4$	$[124]$	5	0	0	0	0	0	0	0	0	0	0	5
$x_1x_3^2$	$[13^2]$	1	1	2	0	0	0	0	0	0	0	0	4
x_1x_6	$[16]$	1	0	0	0	0	0	1	0	0	0	0	2
$x_2^2x_3$	$[2^23]$	1	1	2	0	0	0	0	0	0	0	0	4
x_2x_5	$[25]$	1	0	0	0	0	0	1	0	0	0	0	2
x_3x_4	$[34]$	1	0	0	0	0	0	1	0	0	0	0	2
Total		21	7	14	0	0	0	5	0	0	0	0	47

Table 8. Coefficients Derived By the Figure Inventory (Eq. 4)[a]

Index term[b]	Coefficients for										
	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
x^8	1251	51	51	0	3	15	11	0	3	0	0
x^7	786	38	38	0	0	0	10	0	0	0	0
x^6	462	30	30	3	2	10	10	3	2	1	1
x^5	252	20	20	0	0	0	8	0	0	0	0
x^4	126	14	14	0	2	6	6	0	2	0	0
x^3	56	8	8	2	0	0	4	2	0	0	0
x^2	21	5	5	0	1	3	3	0	1	0	0
x	6	2	2	0	0	0	2	0	0	0	0
1	1	1	1	1	1	1	1	1	1	1	1

[a] The coefficients of the term x^m are obtained by introducing the figure inventory (eq. 4) into the SCIs (eq. 3). [b] The index term (x^7) corresponds to homoadamantane isomers. The term (x^6) corresponds to adamantane isomers. The term (x^5) is concerned with noradamantane isomers.

Table 9. Numbers of Isomers of Bishomoadamantane, Homoadamantane, Adamantane, Noradamantane, and Lower Homologs[a]

Index term[b]	Number of Isomers for											Total number
	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	
x^8	37	7	20	0	0	1	4	0	3	0	0	72
x^7	21	7	14	0	0	0	5	0	0	0	0	47
x^6	12	3	8	0	0	1	4	2	1	0	1	32
x^5	5	3	6	0	0	0	4	0	0	0	0	18
x^4	2	1	4	0	0	0	2	0	2	0	0	11
x^3	1	1	0	0	0	0	2	2	0	0	0	6
x^2	0	0	1	0	0	0	1	0	1	0	0	3
x	0	0	0	0	0	0	1	0	0	0	0	1
1	0	0	0	0	0	0	0	0	0	0	1	1

[a] The coefficients of the term x^m are obtained by introducing the figure inventory (eq. 4) into the SCIs (eq. 3). [b] The index term (x^7) corresponds to homoadamantane isomers. The term (x^6) corresponds to adamantane isomers. The term (x^5) is concerned with noradamantane isomers.

Table 10. Unit Subduced Cycle Indices for D_{2h} Group.

	C_1	C_2	C_2'	C_2''	C_s	C_s'	C_s''	C_i	C_{2v}	C_{2v}'	C_{2v}''	C_{2h}	C_{2h}'	C_{2h}''	D_2	D_{2h}
$D_{2h}(/C_1)$	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_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_4^2	s_8
$D_{2h}(/C_2)$	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_2^2	s_4	s_4	s_2^2	s_4	s_4	s_2^2	s_4
$D_{2h}(/C_2')$	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_4	s_2^2	s_4	s_4	s_2^2	s_4	s_2^2	s_4
$D_{2h}(/C_2'')$	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_2^2	s_4	s_2^2	s_4	s_4	s_2^2	s_2^2	s_4
$D_{2h}(/C_s)$	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_2^2	s_2^2	s_4	s_4	s_4	s_2^2	s_4	s_4
$D2_h(/C_s')$	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_2^2	s_4	s_2^2	s_4	s_2^2	s_4	s_4	s_4
$D_{2h}(/C_s'')$	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_2^2	s_2^2	s_4	s_4	s_4	s_4
$D_{2h}(/C_i)$	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_4	s_4	s_4	s_2^2	s_2^2	s_2^2	s_4	s_4
$D_{2h}(/C_{2v})$	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_2	s_2	s_2	s_2	s_2	s_2
$D_{2h}(/C_{2v}')$	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_1^2	s_2	s_2
$D_{2h}(/C_{2v}'')$	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_1^2	s_2	s_2	s_2	s_2	s_2
$D_{2h}(/C_{2h})$	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_1^2	s_2	s_2	s_2	s_2
$D_{2h}(/C_{2h}')$	s_1^2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2
$D_{2h}(/C_{2h}'')$	s_1^2	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_1^2	s_2	s_2
$D_{2h}(/D_2)$	s_1^2	s_1^2	s_1^2	s_1^2	s_2	s_2	s_2	s_2	s_2	s_2	s_2	s_2	s_2	s_2	s_1^2	s_2
$D_{2h}(/D_{2h})$	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
Factor	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8	0	0	0	0	0	0	0	0

This ZI can be proved to be identical to that derived alternatively by Pólya's theorem.[17] Introduction of eq. 4 into eq. 5 affords a generating function,

$$G(x) = ZI(T_d;\ 1 + x^k + x^{2k} + \ldots + x^{6k})$$
$$= (1 + x^{36}) + (x + x^{35}) + 3(x^2 + x^{34}) + 6(x^3 + x^{33}) + 11(x^4 + x^{32}) + 18(x^5 + x^{31}) + 32(x^6 + x^{30}) + 47(x^7 + x^{29}) + 72(x^8 + x^{28}) + 102(x^9 + x^{27}) + 140(x^{10} + x^{26}) + 182(x^{11} + x^{25}) + 235(x^{12} + x^{24}) + 282(x^{13} + x^{23}) + 334(x^{14} + x^{22}) + 378(x^{15} + x^{21}) + 414(x^{16} + x^{20}) + 434(x^{17} + x^{19}) + 447x^{18}. \quad (6)$$

The coefficients of the terms x^r ($r = 0$ to 8) in eq. 6 are equal to the values of the rightmost column of Table 9, which are obtained by summing up the respective rows.

Enumeration of Tricyclodecanes with D_{2h} or Its Subsymmetry.

Let us work out cyclobutadiene (**52**) as a parent skeleton (Fig. 5). In order to derive stereoisomers, we consider the cyclobutadiene to be a D_{2h} body whose double bond is regarded as a double arc perpendicular to the molecular plane. Thus the skeleton (**52**) has 6 edges. We then place methylenes on the edges in a similar way as described in the previous section. The present enumeration requires a table of USCIs (Table 10) and the inverse of a mark table (Table 11) for D_{2h} symmetry.

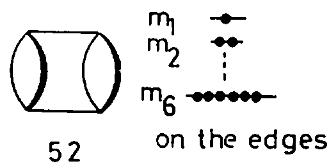

Figure 5. Cyclobutadiene as a D_{2h} skeleton

The six edges are classified into two orbits, which are subject to $D_{2h}(/C_s)$ and $D_{2h}(/C_{2v}")$.[18] The SCIs for the skeleton (**52**) are constructed from USCIs of Table 10 as follows.

$(s_1^2)(s_1^4)$	for C_1;	(6a)
$(s_2)(s_2^2)$	for C_2, C_2', C_i, C_{2v}, C_{2v}', and $C_{2h}"$;	(6b)
$(s_1^2)(s_2^2)$	for $C_2"$, C_s, and $C_s"$;	(6c)
$(s_2)(s_1^4)$	for C_s;	(6d)
$(s_1^2)(s_4)$	for $C_{2v}"$;	(6e) and
$(s_2)(s_4)$	for C_{2h}, C_{2h}', D_2, and D_{2h};	(6f)

in which each USCI in the first parentheses comes from the $D_{2h}(/C_{2v}")$ row of Table 10 and each USCI in the second parentheses stems from the $D_{2h}(/C_s)$ row.

The introduction of a figure inventory (eq. 2) and the subsequent expansion of the

Table 11. The Inverse of the Mark Table for D_{2h} Group.

	D_{2h} $(/C_1)$	D_{2h} $(/C_2)$	D_{2h} $(/C_2')$	D_{2h} $(/C_2'')$	D_{2h} $(/C_s)$	D_{2h} $(/C_s')$	D_{2h} $(/C_s'')$	D_{2h} $(/C_i)$	D_{2h} $(/C_{2v})$	D_{2h} $(/C_{2v}')$	D_{2h} $(/C_{2v}'')$	D_{2h} $(/C_{2h})$	D_{2h} $(/C_{2h}')$	D_{2h} $(/C_{2h}'')$	D_{2h} $(/D_2)$	D_{2h} $(/D_{2h})$	Factor[a]
C_1	1/8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1/8
C_2	-1/8	1/4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1/8
C_2'	-1/8	0	1/4	0	0	0	0	0	0	0	0	0	0	0	0	0	1/8
C_2''	-1/8	0	0	1/4	0	0	0	0	0	0	0	0	0	0	0	0	1/8
C_s	-1/8	0	0	0	1/4	0	0	0	0	0	0	0	0	0	0	0	1/8
C_s'	-1/8	0	0	0	0	1/4	0	0	0	0	0	0	0	0	0	0	1/8
C_s''	-1/8	0	0	0	0	0	1/4	0	0	0	0	0	0	0	0	0	1/8
C_i	-1/8	0	0	0	0	0	0	1/4	0	0	0	0	0	0	0	0	1/8
C_{2v}	1/4	-1/4	0	0	-1/4	-1/4	0	0	1/2	0	0	0	0	0	0	0	0
C_{2v}'	1/4	0	-1/4	0	-1/4	0	-1/4	0	0	1/2	0	0	0	0	0	0	0
C_{2v}''	1/4	0	0	-1/4	0	-1/4	-1/4	0	0	0	1/2	0	0	0	0	0	0
C_{2h}	1/4	-1/4	0	0	0	0	-1/4	-1/4	0	0	0	1/2	0	0	0	0	0
C_{2h}'	1/4	0	-1/4	0	0	-1/4	0	-1/4	0	0	0	0	1/2	0	0	0	0
C_{2h}''	1/4	0	0	-1/4	-1/4	0	0	-1/4	0	0	0	0	0	1/2	0	0	0
D_2	1/4	-1/4	-1/4	-1/4	0	0	0	0	0	0	0	0	0	0	1/2	0	0
D_{2h}	-1	1/2	1/2	1/2	1/2	1/2	1/2	1/2	-1/2	-1/2	-1/2	-1/2	-1/2	-1/2	-1/2	1	0

[a]Factor = $\sum_i \bar{m}_{ji}$ (the sum of each row)

SCIs afford generating functions, in which the coefficients of the term $(x_1^{m_1}x_2^{m_2}\ldots x_6^{m_6})$ indicates the number of fixed points. Table 12 collects the coefficients that correspond to the partition, $m_1 + 2m_2 + \ldots + 6m_6 = 6$.

Table 12 is multiplied by the inverse of the mark table for D_{2h} (Table 11).[19] The resulting matrix is shown in Table 13, in which the number of isomers is found at the intersection of a subsymmetry column and a PMI row.

Figure 6 illustrates all the isomers shown in Table 13. There appear 89 isomers. Stereoisomers are linked by a bracket, if they have the same subsymmetry.[20] Endo- and exo-tetrahydrodicyclopentadienes, which are Schleyer's precursors of adamantane, appear as C_s isomers in the [123] series. There are several stereoisomers that belong to different subsymmetry. The C_{2v} and C_{2h}'' isomers in the $[1^22^2]$ series are examples of such cases. For example, a syn-form (**94**) belongs to C_{2v} symmetry and anti-form (**95**) has C_{2h}'' symmetry.

In order to obtain a summarized result, we introduce the other figure inventory (eq. 4) into the SCIs (eqs. 6). The resulting generating functions afford the numbers of fixed points as the coefficients of the terms $(1, x, x^2, \ldots, x^8)$, which are collected in the form of a matrix. This matrix is multiplied by the inverse (Table 11) to give Table 14. This table contains the number of isomers having the respective subsymmetries. For the adamantane series, the x^6 row of Table 14 shows the numbers, which are equal to those listed at the bottom of Table 13.

This skeleton ($D_{2h}(/C_s)$ and $D_{2h}(/C_{2v}'')$) provides a cycle index in terms of the data of Table 10, i.e.,

$$ZI(D_{2h};\, s_k) = (1/8)(s_1^6 + 3s_2^3 + 3s_1^2s_2^2 + s_1^4s_2). \qquad (7)$$

Introduction of eq. 4 into eq. 7 affords a generating function,

$$\begin{aligned} G(x) &= ZI(D_{2h};\, 1 + x^k + \ldots + x^{6k}) \\ &= x^{36} + 2x^{35} + \ldots + 216x^8 + 137x^7 + 89x^6 + 49x^5 + 29x^4 + \\ &\quad 13x^3 + 7x^2 + 2x + 1. \qquad (8) \end{aligned}$$

The coefficient of x^6 in eq. 8 is 89, which is equal to the sum obtained from Table 13 or 14.

Conclusion.

Tricyclic isomers of adamantane are enumerated by starting from tetrahedrane (T_d) and cyclobutadiene (D_{2h}). The method of enumeration is based on unit subduced cycle indices, which are derived from the subduction of coset representations. The enumeration is concerned with polymethylene indices (PMIs) as well as subsymmetries of the two point groups. For example, adamantane itself is chracterized by the PMI $[1^6]$ and T_d symmetry. There emerge 32 isomers from the tetrahedrane skeleton and 89 isomers from the cyclobutadiene skeleton.

Table 12. Coefficients of the Terms from Eqs. 2 and 4.

Index Term	PMI	Coefficient of the Index Term C_1	C_2	C_2'	C_2''	C_s	C_s'	C_s''	C_i	C_{2v}	C_{2v}'	C_{2v}''	C_{2h}	C_{2h}'	C_{2h}''	D_2	D_{2h}
x_1^6	$[1^6]$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$x_1^4x_2$	$[1^42]$	30	0	0	2	12	2	2	0	0	0	2	0	0	0	0	0
$x_1^3x_3$	$[1^33]$	60	0	0	4	26	4	4	0	0	0	0	0	0	0	0	0
$x_1^2x_2^2$	$[1^22^2]$	90	6	6	6	18	6	6	6	6	6	0	0	0	6	0	0
$x_1^2x_4$	$[1^24]$	60	0	0	4	26	4	4	0	0	0	0	0	0	0	0	0
$x_1x_2x_3$	[123]	120	0	0	0	24	0	0	0	0	0	0	0	0	0	0	0
x_1x5	[15]	30	0	0	2	12	2	2	0	0	0	2	0	0	0	0	0
x_2^3	$[2^3]$	20	0	0	0	4	8	4	4	0	0	0	0	0	0	0	0
x_2x_4	[24]	30	0	0	2	12	2	2	0	0	0	2	0	0	0	0	0
x_3^2	$[3^2]$	15	3	3	3	7	3	3	3	3	3	1	1	1	3	1	1
x_6	[6]	6	0	0	2	4	2	2	0	0	2	0	0	0	0	0	0

Table 13. Number of Adamantane Isomers ($C_{10}H_{16}$) Based on the Skeleton (52)

Index Term	PMI	Number of Isomers C_1	C_2	C_2'	C_2''	C_s	C_s'	C_s''	C_i	C_{2v}	C_{2v}'	C_{2v}''	C_{2h}	C_{2h}'	C_{2h}''	D_2	D_{2h}
x_1^6	$[1^6]$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
$x_1^4x_2$	$[1^42]$	2	0	0	0	3	0	0	0	0	0	1	0	0	0	0	0
$x_1^3x_3$	$[1^33]$	4	0	0	1	4	1	1	0	0	0	0	0	0	0	0	0
$x_1^2x_2^2$	$[1^22^2]$	9	0	0	0	0	0	0	0	3	3	0	0	0	3	0	0
$x_1^2x_4$	$[1^24]$	4	0	0	1	4	1	1	0	0	0	0	0	0	0	0	0
$x_1x_2x_3$	[123]	12	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0
x_1x5	[15]	2	0	0	0	3	0	0	0	0	0	1	0	0	0	0	0
x_2^3	$[2^3]$	0	0	0	1	2	1	1	0	0	0	0	0	0	0	0	0
x_2x_4	[24]	2	0	0	0	3	0	0	0	0	0	1	0	0	0	0	0
x_3^2	$[3^2]$	1	0	0	0	0	0	0	0	1	1	0	0	0	1	0	1
x_6	[6]	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0
Total		36	0	0	3	26	3	3	0	4	4	4	0	0	4	0	2

Table 14. Number of C_4 to C_{12} Isomers Based on the Skeleton (52)

Index Term[a]	C_1	C_2	C_2'	C_2''	C_s	C_s'	C_s''	C_i	C_{2v}	C_{2v}'	C_{2v}''	C_{2h}	C_{2h}'	C_{2h}''	D_2	D_{2h}	Total
x^8	110	0	0	7	60	7	7	0	6	6	4	0	0	6	0	3	216
x^7	62	0	0	7	49	7	7	0	0	0	5	0	0	0	0	0	137
x^6	36	0	0	3	26	3	3	0	4	4	4	0	0	4	0	2	89
x^5	16	0	0	3	20	3	3	0	0	0	4	0	0	0	0	0	49
x^4	8	0	0	1	8	1	1	0	2	2	2	0	0	2	0	2	29
x^3	2	0	0	1	6	1	1	0	0	0	2	0	0	0	0	0	13
x^2	1	0	0	0	1	0	0	0	1	1	1	0	0	1	0	1	7
x	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	2
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1

[a] The term (x^m) corresponds to a compound having m methylenes. Thus, adamantane isomers are found in the row of m = 6.

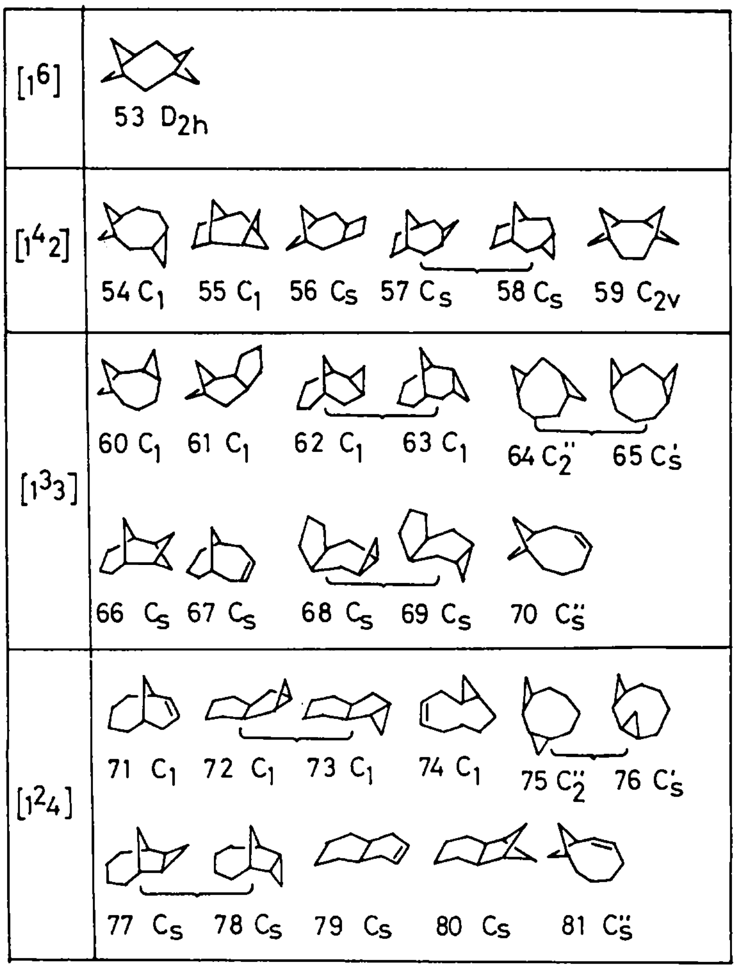

Fig. 6

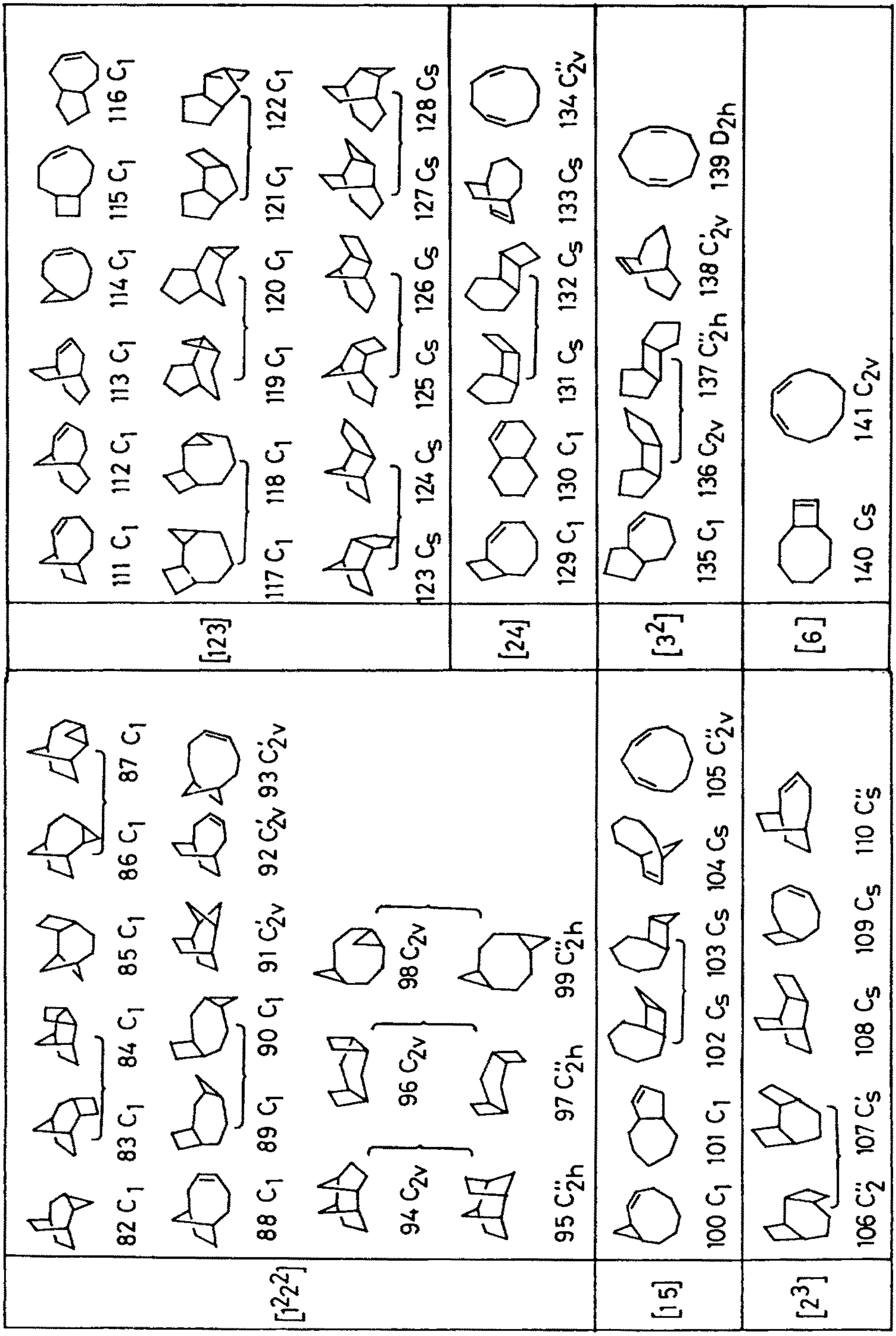

Fig. 6 (continued)

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10 The coset representations (CRs) for $\mathbf{T}_d$ point group are $\{\mathbf{T}_d(/C_1)$, $\mathbf{T}_d(/C_2)$, $\mathbf{T}_d(/C_s)$, $\mathbf{T}_d(/C_3)$, $\mathbf{T}_d(/S_4)$, $\mathbf{T}_d(/D_2)$, $\mathbf{T}_d(/C_{2v})$, $\mathbf{T}_d(/C_{3v})$, $\mathbf{T}_d(/D_{2d})$, $\mathbf{T}_d(/T)$, and $\mathbf{T}_d(/T_d)\}$ in all. These symbols of CRs are designed for characterization of molecular symmetry. See ref. 9. For the assignment of such a CR to an orbit, see W. Burnside, Theory of Groups of Finite Order (2nd ed), Cambridge Unive. Press, Cambridge (1911). For application of a mark table, see W. Hässelbarth, Theor. Chim. Acta, 67, 339 (1985); and C. A. Mead, J. Am. Chem. Soc., 109, 2130 (1987).

11 Table 1 was constructed by examining the concrete coset representations of the $\mathbf{T}_d$ symmetry, which were, in turn, obtained from the corresponding multiplication table. The detailed procedure will be reported elsewhere.

12 We refer to all of the positions or of edges as "points", in an abstract fashion.

13 For the construction of the table of USCIs, see ref. 9.

14 Mathematical foundations will be reported elsewhere.

15 Balaban's enumeration is concerned only with constitution of isomers, because he considered the tetrahedrane skeleton to be a graph. See ref. 8.

16 The present enumeration takes no account of heptamethylene units.

17 For the proof, see ref. 9.

18 The CRs for $\mathbf{D}_{2h}$ are $\{\mathbf{D}_{2h}(/C_1)$, $\mathbf{D}_{2h}(/C)$, $\mathbf{D}_{2h}(/C_2')$, $\mathbf{D}_{2h}(/C_2'')$, $\mathbf{D}_{2h}(/C_s)$, $\mathbf{D}_{2h}(/C_s')$, $\mathbf{D}_{2h}(/C_s'')$, $\mathbf{D}_{2h}(/C_i)$, $\mathbf{D}_{2h}(/C_{2v})$, $\mathbf{D}_{2h}(/C_{2v}')$, $\mathbf{D}_{2h}(/C_{2v}'')$, $\mathbf{D}_{2h}(/C_{2h})$, $\mathbf{D}_{2h}(/C_{2h}')$, $\mathbf{D}_{2h}(/C_{2h}'')$, $\mathbf{D}_{2h}(/D_2)$, and $\mathbf{D}_{2h}(/D_{2h})\}$, in all.

19 The inverse of a mark table for $\mathbf{D}_{2h}$ was obtained by a coset decomposition of $\mathbf{D}_{2h}$.

20 Balaban's enumeration took no account of stereoisomerism.[8] Hence, it yielded the total number of 66 for this series.