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# A GRAPH THEORETICAL DERIVATION OF THE ISOMERS OF TRICYCLIC HYDROCARBONS

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The isomers of tricyclic hydrocarbons $C_nH_{2n-4}$ having neither side chains nor multiple bonds have been classified into 12 classes from a graph theoretical point of view. We have also found an algorithm for deriving all the structures and the numbers of the isomers, and as an example, we show all the skeletons and the indices of the isomers in the class for $C_{10}H_{16}$ to which Adamantane belongs.

Extensive works on syntheses and rearrangements of tricyclic hydrocarbons have been done[1], but little knowledge seems to have been obtained about the structures and the numbers of isomers. We have systematically studied their structures by a graph theoretical approach.

We express the structures of isomers of $C_nH_{2n-4}$ by (n,n+2) graphs, where n is the number of vertices which correspond to carbon atoms and n+2 is the number of edges which correspond to carbon-carbon bonds. By remembering the theorem: the number of independent cycles in a (n,m) graph is equal to m-n+1, we see that there are 3 independent cycles in a (n,n+2) graph. Denoting by $\phi$,v,u,and k the numbers of vertices in a (n,n+2) graph whose degrees are equal to 1,2,3, and 4 respectively (see Table I), we obtain

$$1\phi + 2v + 3u + 4k = 2(n+2) \qquad (1)$$

$$\phi + v + u + k = n \qquad (2)$$

$$\phi \geq 0,\ v \geq 0,\ u \geq 0,\ k \geq 0 \qquad (3)$$

From (1) and (2) the equation

$$u + 2k = 4 + \phi \qquad (4)$$

holds. All the possible (n,n+2) graphs corresponding to carbon frameworks, in general, should satisfy (2),(3),and (4).

Hereafter we shall consider $C_nH_{2n-4}$ under the following conditions:

(i) without multiple bonds,

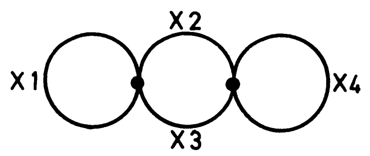
(ii) without side chains.

Since (ii) means

$$\phi = 0, \qquad (5)$$

we obtain all the integral solutions ($\phi$,v,u,k) for a given n as shown in Table II.

Fig.1




Thus we can classify the (n,n+2) graphs in question into 3 classes (see the (k,u) column in Table III). And we introduce θ, the number of self-cycles in a graph, where a self-cycle means the cycle which has only one vertex of degree 3 or 4. Then the above 3 classes are classified by θ into 2,4,and 4 minor classes respectively (see the θ column in Table III). Moreover we introduce $\Sigma$ , the total number of vertices of degree 3 and/or 4 which belong to independent cycles in a graph. Then the 5th and 10th classes mentioned above are divided by $\Sigma$ into two minor classes respectively (see the $\Sigma$ column in Table III). Thus we finally obtain 12 classes for the (n,n+2) graphs under condition (ii).

In order to derive all the structures in each class, we construct an index which expresses a manner of assigning vertices of degree 2 to each edge of a graph.

In the case of the 1st class we assign labels x1,x2,x3,and x4 to each edge of a graph (see Fig. 1), and for convenience, by x1,x2,x3,and x4 we also express the numbers of vertices on each edge. We impose the conditions

$$x1 \geq x4\ ,\ x2 \geq x3 \qquad (6)$$

in order to avoid repetition caused by symmetry, and from (i) we obtain

$$x4 \geq 2\ ,\ x2 \geq 1\ . \qquad (7)$$

Since the total number of vertices is equal to v, from Table II

$$x1 + x2 + x3 + x4 = n-2 \qquad (8)$$

holds for a given n.

We define the index of a graph in the 1st class as denoting the 4-tuple of integers (x1,x2,x3,x4) such that x1,x2,x3,and x4 satisfy (6),(7) and (8).

In the case of the 12th class we assign labels x1,x2,x3,x4,x5,and x6 to each edge of a graph (see Fig 2). Since in this case Condition (i) is automatically satisfied, we are only concerned with the conditions which prohibit repetition caused by symmetry. We finally obtained the following:

$$x1 \geq x2,\ x3,\ x4,\ x5,\ x6\ , \qquad (9)$$

$$x2 \geq x3,\ x5,\ x6\ , \qquad (10)$$

$$x1 = x2 \Longrightarrow x4 \geq x6\ , \qquad (11)$$

$$x1 = x3 \Longrightarrow x4 \geq x5 \geq x6\ , \qquad (12)$$

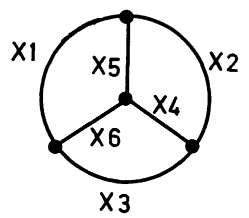
$$x1 = x4 \Longrightarrow x3 \geq x5\ , \qquad (13)$$

$$x2 = x3 \Longrightarrow x5 \geq x6\ , \qquad (14)$$

$$x2 = x5 \Longrightarrow x3 \geq x6\ , \qquad (15)$$

$$x2 = x6 \Longrightarrow x3 \geq x5\ . \qquad (16)$$

Fig. 2




And from Table II

$$x1 + x2 + x3 + x4 + x5 + x6 = n-4 \qquad (17)$$

holds for a given n.

Then we define the index of a graph in the 12th class as denoting the 6-tuple of integers (x1,x2,x3,x4,x5,x6) such that x1,x2,x3,x4,x5,and x6 satisfy (9) through (17).

In a similar way we can construct the indices for other classes. As seen above one structure of isomers can be expressed by this index, and we can easily write a corresponding skeleton from it.

Thus our problem is reduced to obtaining all the r-tuples of integers which satisfy the conditions for each class, where r is determined for the class in question, and as seen from the above description it is easy to construct an algorithm to realize our method.

We have implemented the program *ISOMER* for MELCOM 1101. As one of the results which we have obtained by using ISOMER, we show all the skeletons and the indices of the isomers in the 12th class for $C_{10}H_{16}$ to which adamantane belongs (see Table IV).

DISCUSSION: Sasaki group[2] and Hosoya group[3] studied structures of isomers of chain, monocyclic, and bicyclic hydrocarbons under certain conditions. Whitlock et al.[4] studied rearrangements among the isomers of tricyclic hydrocarbon $C_{10}H_{16}$ and in course of his work described a classification of the isomers of $C_{10}H_{16}$ under the similar conditions to ours. They showed 10 classes which are contained in our 12 classes, but they did not describe its derivation and failed in to find the 9th class of our classification. Balaban[5] studied the structures of isomers of $C_{2p}H_{2p}$ (p = 2,3,4,and 5) under condition (ii). He derived empirically the results by hand, and it seems that it is difficult to apply his method in case $p > 5$. Lederberg[6] studied a system for computer construction, enumeration and notation of organic molecules as tree structures and cyclic graphs. He attained to many fruitful results, but he did not completely classify the members of a set of hydrocarbons $C_nH_{f(n)}$ , where $f(n)$ is a particular function of n. Thus our work is characterized as follows: (1) the isomers of $C_nH_{2n-4}$ is completely classified, (2) the index denoting each structure of isomers in each class is introduced, and (3) the program ISOMER has been implemented, by which we can obtain all the indices for an arbitrary n.

## References


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Table I. Modes of bonds.

| | | | | |
|---|---|---|---|---|
| Mode | C<br>C—C*—C<br>C | C<br>C—C*—H<br>C | C<br>H—C*—H<br>C | C<br>H—C*—H<br>H |
| Degree | 4 | 3 | 2 | 1 |
| | k | u | v | ø |

Table II. The integral solutions

| ø | k | u | v |
|---|---|---|---|
| 0 | 0 | 4 | n-4 |
| 0 | 1 | 2 | n-3 |
| 0 | 2 | 0 | n-2 |

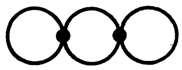
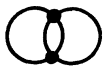
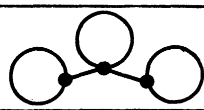
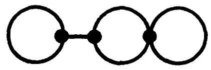
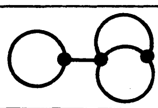
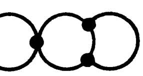
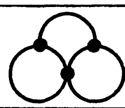
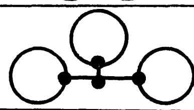
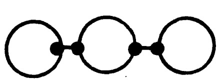
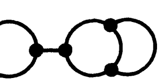
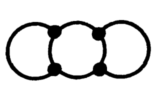
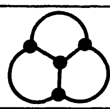
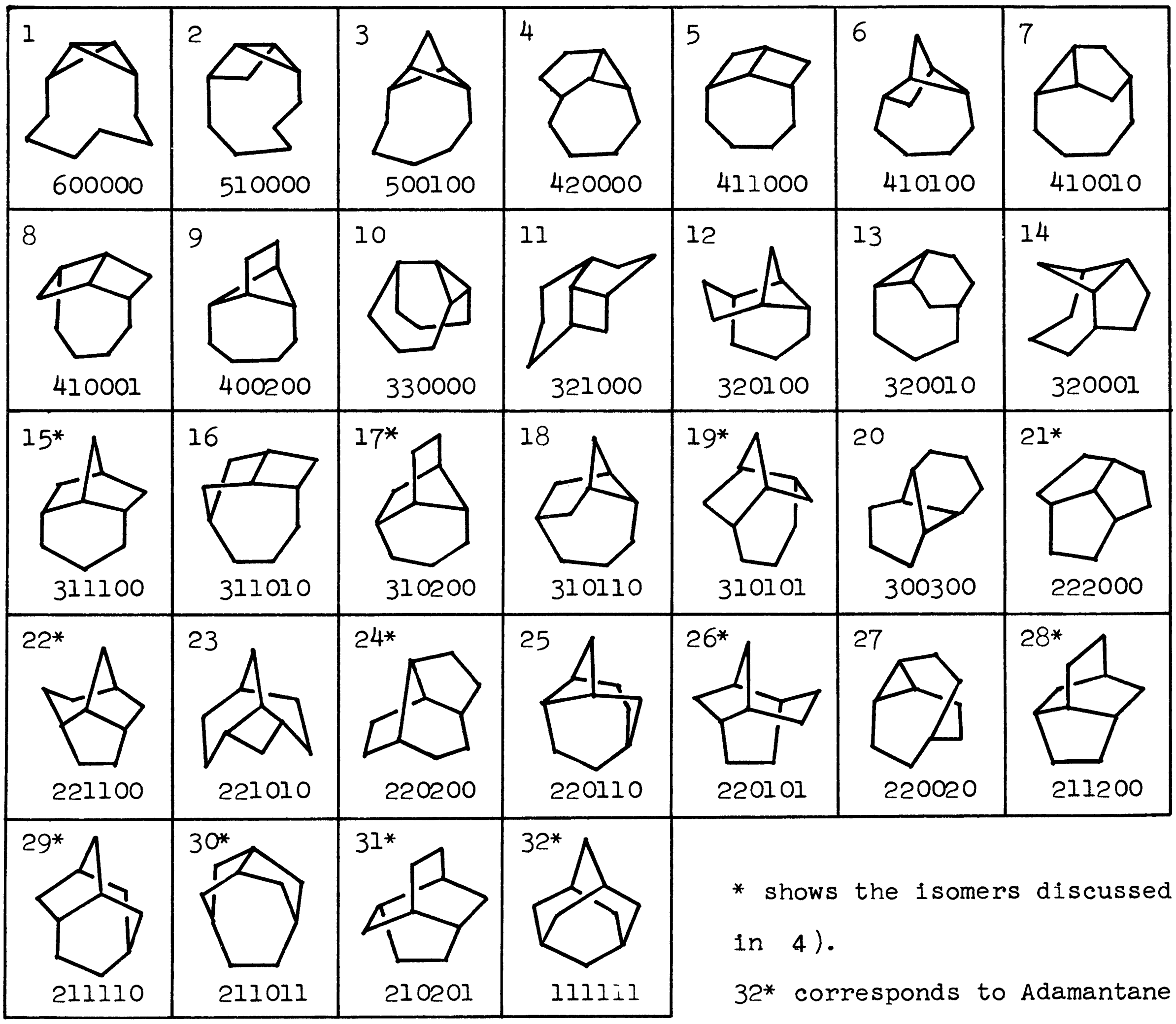
| Hydrocarbon | | Graph | | ø | | k , u | | θ | Σ | Class | No |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_nH_{2n-4}$ | ⟶ | (n,n+2) | ⟶ | 0 | ⟶ | 2 , 0 | ⟶ | 2 | ⟶ 4 |  | 1 |
| | | | | | | | | 0 | ⟶ 6 |  | 2 |
| | | | | | | 1 , 2 | ⟶ | 3 | ⟶ 3 |  | 3 |
| | | | | | | | | 2 | ⟶ 4 |  | 4 |
| | | | | | | | | 1 | ⟶ 5 |  | 5 |
| | | | | | | | | | 6 |  | 6 |
| | | | | | | | | 0 | ⟶ 7 |  | 7 |
| | | | | | | 0 , 4 | ⟶ | 3 | ⟶ 3 |  | 8 |
| | | | | | | | | 2 | ⟶ 4 |  | 9 |
| | | | | | | | | 1 | ⟶ 6 |  | 10 |
| | | | | | | | | 0 | ⟶ 8 |  | 11 |
| | | | | | | | | | 9 |  | 12 |

Table III. Process for finding classes.

Table IV. The skeletons and indices of the isomers of $C_{10}H_{16}$ in the 12th class.




* shows the isomers discussed in 4).

32* corresponds to Adamantane.

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