

The method also provides for enumeration and identification of automorphic (locally isomorphic) atoms. The procedure is simple and fast enough for adaptation to microcomputer use.

ACKNOWLEDGMENT

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A Reasonable Triamantane Rearrangement Path Searched by the Selective Disource Propagation Algorithm[†]

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Triamantane rearrangement reactions reported by McKervery et al. are studied theoretically. A great many isomers must be considered to find rearrangement paths. A searching procedure by a graph-theoretical method and computational techniques along with force field calculations, "selective disource propagation algorithm", is developed to find a path efficiently. Several reasonable rearrangement paths with about 15 steps are found and are shown together with the structures of the isomers in these paths. These isomers and paths are expected to be experimentally verified.

INTRODUCTION

Some rearrangement reactions of the first member of the diamondoid hydrocarbons, adamantane, were studied graph theoretically by Whitlock and Siefken.¹ They studied relationships obtained by the 1,2 alkyl shift between 16 adamantane isomers. In addition to a graph-theoretical study of adamantane rearrangement reactions, Schleyer et al.² adopted empirical force field calculations to estimate rearrangement paths. They applied their method to rearrangement reactions of diamantane, the second member of the diamondoid hydrocarbons, and searched for rearrangement paths by computer.³ They generated more than 20 000 isomers of di-

amantane and found reasonable paths by calculating their strain energies. Ōsawa et al.⁴ searched rearrangement paths of tricycloundecane, a homologue of adamantane, by using the same method mentioned above. We were also interested in enumerating isomers⁵ of adamantane analogues and studying rearrangement relationships between them.⁶ McKervery et al.⁷ succeeded in synthesizing triamantane, the third member of the diamondoid hydrocarbon series,⁸ from the two elaborated pentacyclic hydrocarbons **1** and **2** through rearrangement reactions catalyzed by AlCl_3 (Figure 1). The rearrangement path in the synthesis had not yet been found experimentally. We were tempted by this report to use our path-finding algorithm, the disource propagation algorithm (DSPA),⁹ by which we succeeded in finding diamantane rearrangement paths efficiently. Soon after we started, we found that it is

[†] This work composes a part of Dr. Tanaka's thesis.

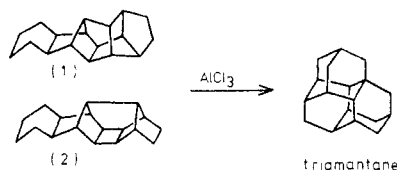


Figure 1. Triamantane is obtained through the rearrangement reaction of the two elaborated heptacyclic hydrocarbons $C_{18}H_{24}$ catalyzed by $AlCl_3$ (McKervey et al., 1976).

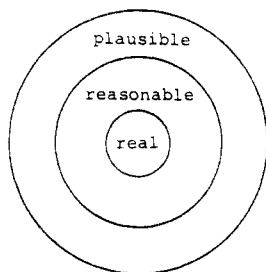
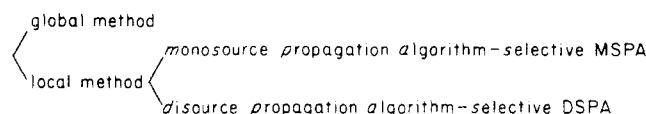


Figure 2. As the real set can be a subset of the reasonable set and the reasonable set can be subset of the plausible set, these relationships are shown by the concentric circles.

Chart I



necessary to make DSPA more powerful for the study of triamantane rearrangement paths, because in the triamantane rearrangement, both the number of isomers and paths involved are extraordinarily larger than in the diamantane rearrangement.¹⁰ Hereafter we shall use the following terms and definitions to clarify our discussion (see Figure 2). (a) **Real**: real isomers and paths are those that are experimentally verified. (b) **Reasonable**: reasonable isomers and paths are those that are obtained by a graph-theoretical method combined with empirical force field calculations. (c) **Plausible**: plausible isomers and paths are those that are obtained graph theoretically. (d) **Realizable**: realizable isomers and paths are those that are reasonable and are expected to be real.

Now, taking into account searching methods which have already been published and the present methods, we can systematize the searching methods as in Chart I. The global method is one to find the complete set of the plausible rearrangement relationships between the plausible isomers in the present study. The local method is one to find reasonable rearrangement relationships in a subset which is obtained by simultaneously deriving reasonable isomers and reasonable relationships by means of empirical force field calculations on the plausible isomers.

"Selective" means to perform empirical force field calculations on the plausible isomers to select suitable isomers for search paths. The method by Whitlock et al. is categorized into a global one. Schleyer's method as applied to diamantane is categorized into one of SMSPA. As MSPA is used for up to only 5000 isomers of diamantane, we devised DSPA. However, as mentioned above, we had to make DSPA more powerful for the triamantane rearrangements, which involve 30 000 isomers, and have at last succeeded in constructing SDSPA.

I. Selective Disource Propagation Algorithm (SDSPA).

Definitions: $p(a,b)$, a path between an isomer a and an isomer b ; $R(a,b)$, the set of the plausible shortest paths between an isomer a and an isomer b ; V , The set of reasonable subpaths which are worthwhile being searched to find a reasonable rearrangement path.

Algorithm. (1) The set of the plausible shortest paths between a starting isomer S and a target isomer T , $R(S,T)$ is obtained by DSPA. (2) For each path $p(S,T)$ in $R(S,T)$ do as follows: store into the set V reasonable subpaths which survive against the procedure CHECK. (3) If reasonable path $p(S,T)$ is in V , then go to step 8. (4) Apply the CHECK to one-step paths from S and store the survived paths in V . (5) Select a path $p(S,g)$ from V and one-step paths $p(g,g+1)$ if necessary and calculate $R(g,T)$ by DSPA. (6) For each path $p(g,T)$ in $R(g,T)$ do as follows: store into V the reasonable subpaths which survive against the CHECK. (7) If a reasonable path $p(S,T)$ is not in V , then go to step 5. (8) End.

Procedure CHECK.¹¹ (1) Input a path $p(l,n)$. (2) Check the strain energy and the possibility of bond shift of the isomers in the path $p(l,n)$. (3) Store the unreasonable part $p(j,j+1)$. (4) Return the reasonable part $p(l,j)$, $j \leq n$, of the path $p(l,n)$. (5) End.

II. Selective Monosource Propagation Algorithm (SMSPA).

Definition: $n(g)$ is a set of the nearest-neighbor isomers which are obtained from an isomer g by a 1,2 edge shift.

Algorithm. (1) Store into the set V a path $p(S,S)$ from the starting isomer S ; we introduce the path of zero length for algorithmic convenience. (2) Choose a path $p(S,g)$ from V . (3) Enumerate the nearest isomers of the isomer g and construct a set $n(g)$ from them. (4) Test the strain energy and the possibility of bond shift from g for each isomer in $n(g)$ by CHECK. (5) Exclude isomers from $n(g)$ which are unreasonable. (6) Store into V a reasonable path $p(S,r)$ which is composed of $p(S,g)$ and a one-step path $p(g,r)$ where r is an isomer in $n(g)$. (7) If a reasonable path $p(S,T)$ between S and a target isomer T is not in V , then go to step 2. (8) End.

RESULTS

As mentioned in the Introduction, McKervey et al., experimentally obtained triamantane from two pentacyclic hydrocarbons (Figure 1) through rearrangement reactions, but the rearrangement paths have never been known.

In order to predict theoretical rearrangement paths, we have used our SDSPA and succeeded in finding several reasonable rearrangement paths, which are shown in Figure 5, by imposing the following conditions on the rearrangement reaction: (1) the reaction proceeds via 1,2-bond shifts; (2) the isomers have (a) no side chains, (b) neither three- and/or four-membered rings, and (c) no more than one quaternary carbon. We have used Morgan labeling¹² for identification of the isomers because it gives a uniquely labeled graph and is a suitable algorithm for a computer. But it is inconvenient for us to study relationships between isomers by using only such machine-oriented labels. We have introduced an intelligible notation of an isomer which corresponds to its unique label. For example, in "Si-&&" or "Ti-&&", Si is a set of isomers which are generated by performing a 1,2 shift the i th consecutive time on an isomer S and are called the i th generation. "&&" is a serial number of an isomer in the Si generation which is allotted randomly. "Ti-&&" is generated in the same way as "Si-&&". S0 and T0 are used instead of S0-1 and T0-1 if both generations have only one isomer.

Let us explain our finding process in detail. Table I shows the result of the number of plausible isomers generated by applying DSPA to the triamantane rearrangement from the isomer **I** in Figure 1 as the starting isomer to triamantane as the target isomer.

Four successive 1,2 shifts from both sources gave two isomers which commonly belong to the fourth generation S4 and T4 and which represent plausible shortest paths of eight steps (Figure 3).

Among the plausible shortest paths, the path $S0 \rightarrow S1-4$ survived to the procedure CHECK as a reasonable subpath.

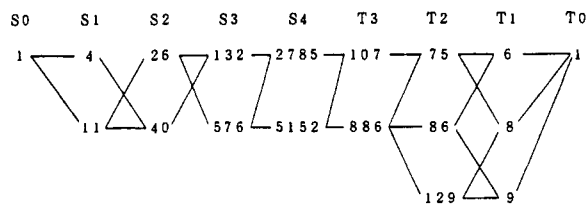


Figure 3. Plausible shortest paths by DSPA. Di sources are S0-1 (1 in Figure 1) and T0-1 (triamantane).

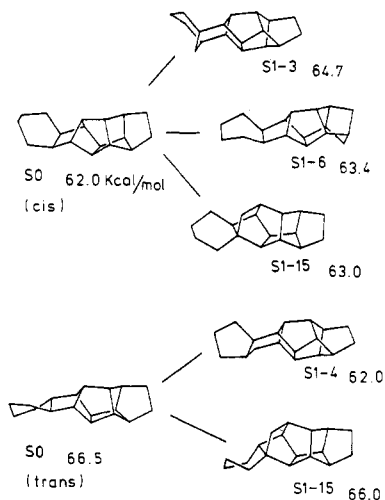


Figure 4. Reasonable one-step paths from two starting isomers, one with cis condensation and the other with trans condensation.

Then the strain energy of the 21 isomers in the S1 generation was calculated, after which the subpaths $S0 \rightarrow S1-3$, $S0 \rightarrow S1-6$, and $S0 \rightarrow S1-15$ survived and were stored in the set V (Figure 4). When DSPA was applied to each terminal isomer of these subpaths and T0 as the two sources, the two subpaths

Table 1. Numbers of Plausible Isomers by DSPA when the Isomer 1 in Figure 1 and Triamantane Are Adopted as the Disources

starting from 1		starting from triamantane	
generation	no.	generation	no.
S0		T0	
S1	21	T1	10
S2	147	T2	204
S3	989	T3	2543
S4	5943	T4	23069
total	7101		25827

Table II. Numbers of Plausible and Reasonable Isomers

	generation			
isomer	T0	T1	T2	T3
plausible	1	10	204	2543
reasonable	1	6	58 ^a (7)	60 ^b

^a The reasonable isomers in T2 are obtained by SMSPA from T1 to T2 by setting the higher energy value below 50 kcal/mol.

^b The reasonable isomers in T3 are obtained by SMSPA from seven isomers in T2 (≤ 45 kcal/mol) to T3.

S0 \rightarrow S1-15 \rightarrow S2-43 \rightarrow S3-417 and S0 \rightarrow S1-15 \rightarrow S2-43 \rightarrow S3-104 were selected as the reasonable subpaths (Figure 5). The latter path has proceeded to a local minima, and the searching flow came to a deadlock. The former path was stretched to S3-417 \rightarrow S4-940 \rightarrow T4-4653 \rightarrow T3-107. But plausible paths from T3-107 to T0 through isomers of the T3, T2, and T1 generations were not estimated as reasonable, so we had to get back from T3-107 to isomers of T4 generation. The outline of this process is shown in Figure 6. Then unreasonable paths and isomers in the T3 generation were selected from T0 by using SMSPA (Table II). They were adopted as the targets for the subpath searching from the S side.

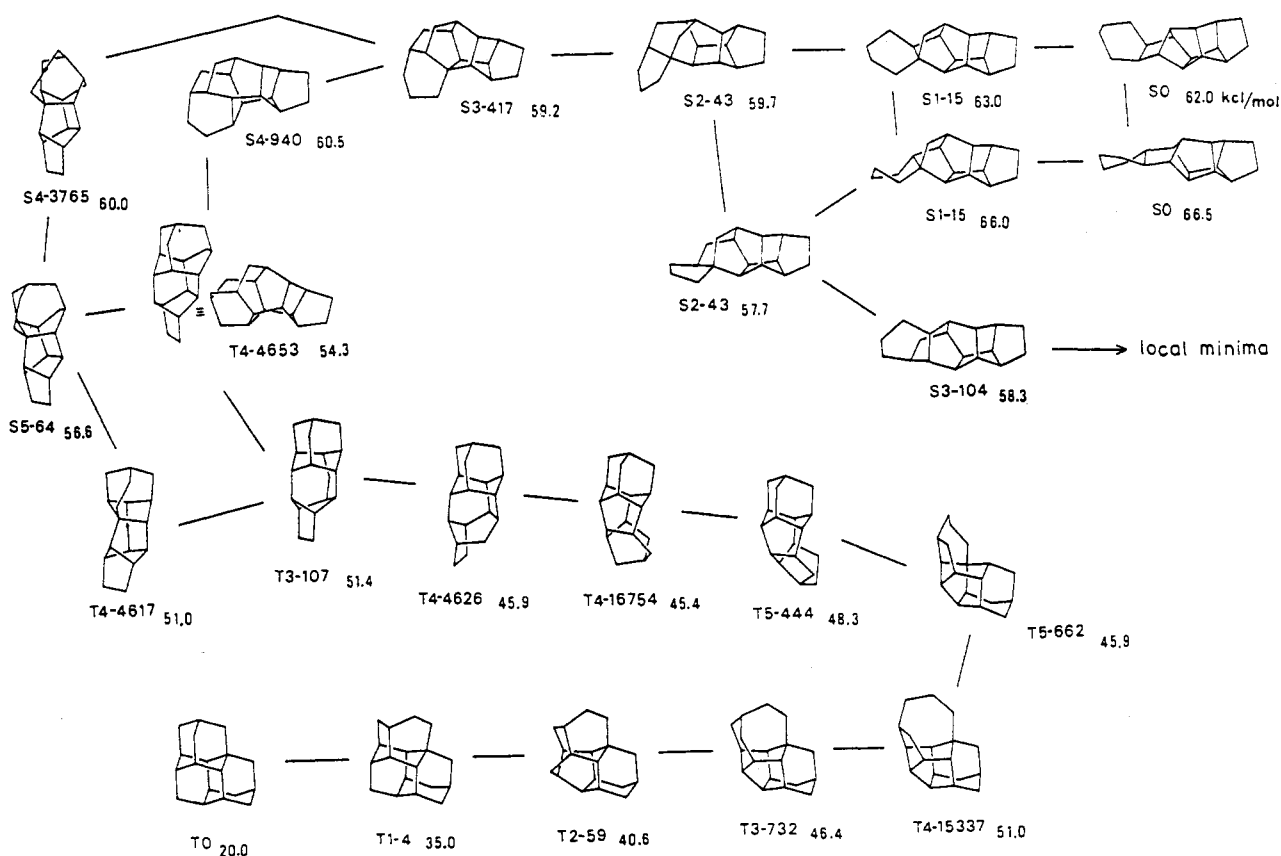


Figure 5. Part of the reasonable paths in triamantane rearrangement obtained by SDSPA from the elaborated starting isomer. The structures are drawn by a plotter according to the converged strain energy.

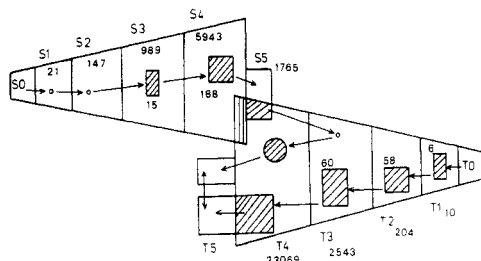


Figure 6. Outline of the searching process in the triamantane rearrangement. Squares with oblique lines and neighboring figures show the amount of reasonable isomers calculated in the search. The overlap between S4 and T4 means the existence of the shortest paths with eight steps. Along with those paths we applied SDSPA and got the reasonable paths from S0 to the upper circle in T3. Next, SMSPA was operated to T0 and calculated the paths from T0 to T3. And we applied SDSPA between T3-107 in the circle and 60 isomers in T3 from T0 as both sources.

After this process, the reasonable paths with six steps by SDSPA between T3-107 and 60 reasonable isomers in T3 were found. Thus several reasonable paths with 15 steps were eventually obtained as shown in Figure 5. We searched other isomers and paths by SMSPA on the basis of those paths and got some reasonable paths where lengths were longer than those already found. One of them is the path that branches from S3-417 and goes to S3-3675 \rightarrow S5-64 \rightarrow T4-4617 and reaches T3-107 (Figure 5).

The neighbors of the target site are shown in more detail. The isomer T3-733 in Figure 7 has an icesan structure with a strain energy lower than that of its neighbor isomers. So it is expected that this isomer could be isolated as an intermediate of this triamantane rearrangement from **1** under mild catalytic conditions such as, for example, with methanesulfonic acid. Figure 8 shows reasonable isomers and their strain energies in T1 generation. These results suggest the existence of other reasonable paths.

SMSPA and SDSPA were programmed by using FORTRAN for a MELCOM COSMO 700 computer. Graphs were represented by an "edge table" as the list of edges¹³ and

were stored after being converted into the form of a bit matrix of five words. The computing time to find the first shortest paths was about 10 h. Strain energies of about 300 plausible isomers were calculated by using Imai's and Allinger's programs for empirical force field calculations.¹⁴ This took about 100 h.

DISCUSSION

(A) Review from our Viewpoint. As mentioned above, we systematized several path-finding algorithms, which are effective for reducing the number of isomers produced in rearrangement paths of adamantane, diamantane, and triamantane. Now, from our standpoint, we shall review searching algorithms used for particular studies. Whitlock and Siefken studied rearrangement paths of adamantane between 16 isomers by the global method. Ōsawa et al. applied the global method to rearrangement paths of tricycloundecane in which 69 plausible isomers were produced, and interrelations between them were obtained by 1,2 shifts. In diamantane rearrangement, more than 5000 plausible isomers would be produced by this method, so we considered it unsuitable.

We formulated MSPA and DSPA as local methods and tried to evaluate these methods by applying them to known paths obtained by Schleyer et al. For these paths, about 1000 plausible isomers were produced in the case of MSPA, while about 100 plausible isomers were produced in the case of DSPA. Schleyer et al. tentatively enumerated 20000 plausible isomers and used the "pruning" algorithm, which is categorized as SMSPA, to find reasonable paths. They did not disclose the number of isomers to which their force field calculation was applied. We suppose that they had to calculate many reasonable isomers and branches of paths because of local energy minima and had to choose realizable paths of diamantane rearrangement solely on the basis of chemical intuition.

In the triamantane rearrangement, it is impossible by using DSPA to practically find reasonable isomers and paths, since about 30000 plausible isomers are generated by DSPA. Thus, in the next section, we shall show why it becomes impossible

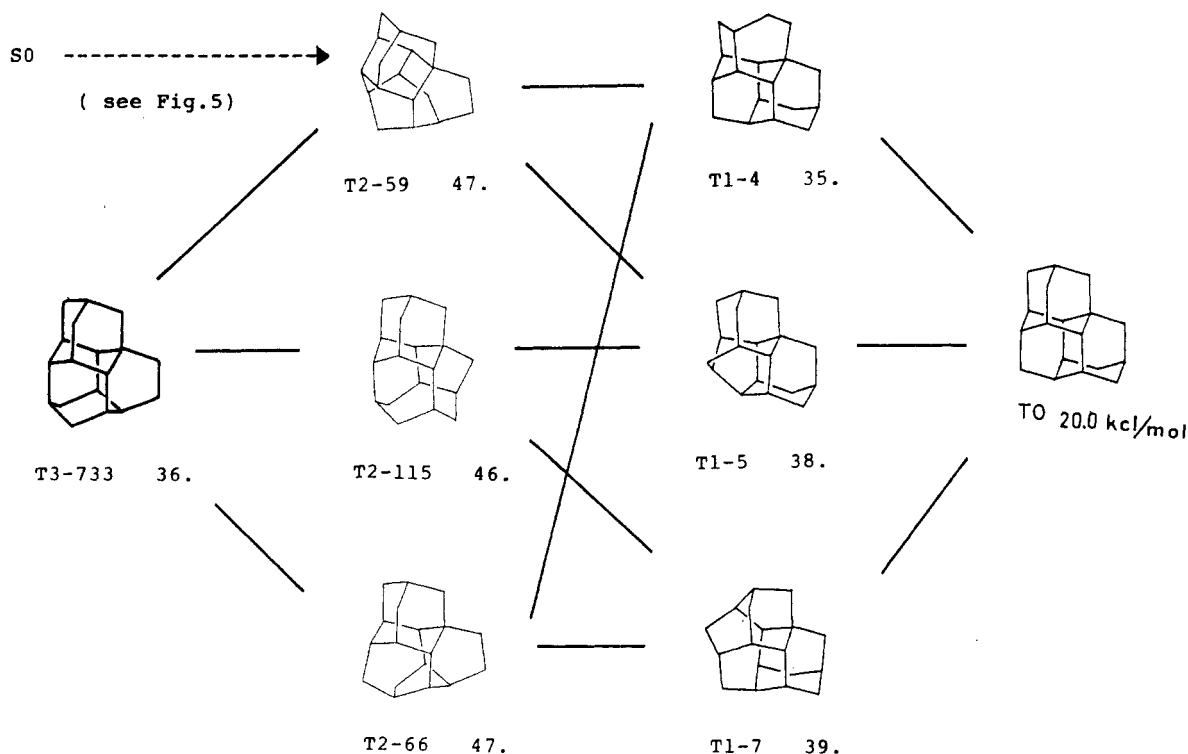


Figure 7. Rearrangement relationships between triamantane and the isomer T3-733 with an icesan structure.

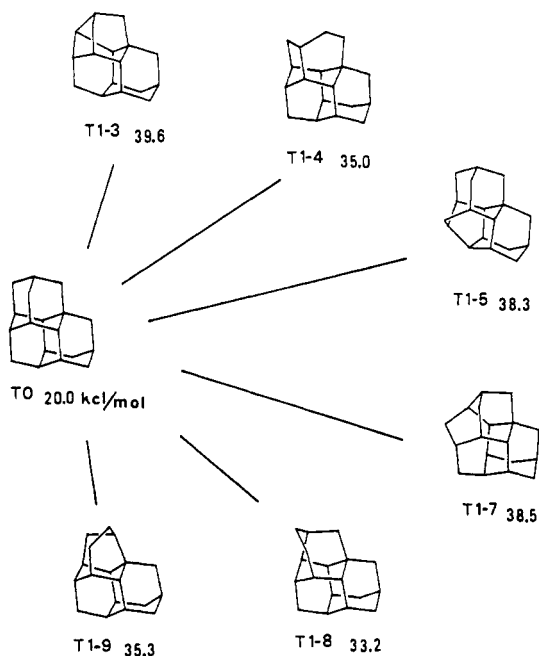


Figure 8. Reasonable one step paths from triamantane.

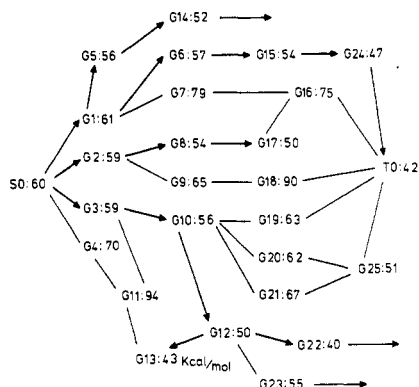


Figure 9. Hypothetical map for an illustration of the difference between SDSPA and SMSPA.

to use SMSPA for the triamantane rearrangement and why it is necessary to devise a new method which we call SDSPA.

(B) Comparison SMSPA with SDSPA. Let us consider a hypothetical rearrangement map (Figure 9) in order to make clear a difference between SDSPA and SMSPA including the pruning method.

(I) An Exposition of SMSPA Including the Pruning Method (Figure 10). (1) g_1, g_2, g_3 , and g_4 are obtained from S_0 as elements of $n(S_0)$, but g_4 is judged to be unreasonable. Therefore, $S_0 \rightarrow g_1$, $S_0 \rightarrow g_2$, and $S_0 \rightarrow g_3$ are stored in the set V , and $S_0 \rightarrow g_4$ is pruned. (2) $S_0 \rightarrow g_3$ is chosen, and g_{10} and g_{11} are obtained from g_3 , but g_{11} is judged to be unreasonable. Therefore, $g_3 \rightarrow g_{10}$ is stored in V , and $g_3 \rightarrow g_{11}$ is pruned. $V = [S_0 \rightarrow g_1, S_0 \rightarrow g_2, S_0 \rightarrow g_3 \rightarrow g_{10}]$. (3) Consecutively, $S_0 \rightarrow g_3 \rightarrow g_{10}$ is chosen, g_{19}, g_{20}, g_{21} , and g_{12} are obtained from g_{10} as elements of $n(g_{10})$, but g_{19}, g_{20} , and g_{21} are judged to be unreasonable. Then V becomes $[S_0 \rightarrow g_1, S_0 \rightarrow g_2, S_0 \rightarrow g_3 \rightarrow g_{10} \rightarrow g_{12}]$. (4) $n(g_{12}) = [g_{13}, g_{22}, g_{23}]$ is obtained but g_{23} is judged to be unreasonable. Then V becomes $[S_0 \rightarrow g_1, S_0 \rightarrow g_2, S_0 \rightarrow g_3 \rightarrow g_{10} \rightarrow g_{12} \rightarrow g_{13}, S_0 \rightarrow g_3 \rightarrow g_{10} \rightarrow g_{12} \rightarrow g_{22}]$.

In this way unreasonable branches were pruned, and the paths were stored in V . However, at this stage we might not be able to reach the target T_0 , since V might not contain a subpath of a successful path.

(II) An Exposition of SDSPA (Figure 11). (1) By DSPA, three plausible shortest paths from a starting isomer S_0 to a

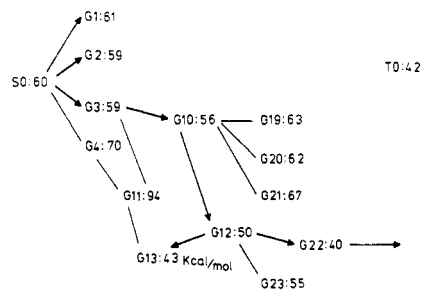


Figure 10. Part of the rearrangement map (Figure 9) illustrates that SMSPA does not guarantee whether a path proceeds to the target or to a local minima.

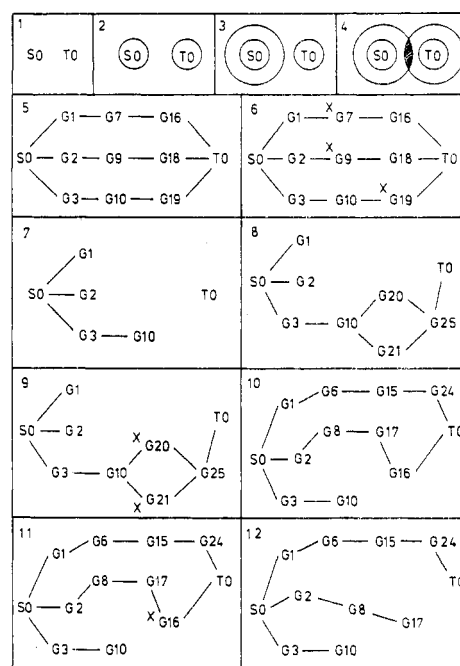


Figure 11. Twelve scenes illustrate in stepwise manner how a reasonable path is found by SDSPA in Figure 9, avoiding the calculation of paths to the local minima.

target isomer T_0 with four steps are obtained (no. 1-5). (2) The strain energies of the isomers derived from S_0 are calculated (no. 6). (a) In the path $S_0 \rightarrow g_1 \rightarrow g_7 \rightarrow g_{16} \rightarrow T_0$, the subpath $\rightarrow g_7 \rightarrow g_{16} \rightarrow$ is cut away, since the energy of g_7 is higher than that of g_1 . (b) In the paths $S_0 \rightarrow g_2 \rightarrow g_9 \rightarrow g_{18} \rightarrow T_0$ and $S_0 \rightarrow g_3 \rightarrow g_{10} \rightarrow g_{19} \rightarrow T_0$, the subpaths $\rightarrow g_9 \rightarrow g_{18} \rightarrow$ and $\rightarrow g_{10} \rightarrow g_{19} \rightarrow$ are cut away, respectively, for the same reason as in a (no. 6 and 7). (3) In the path $S_0 \rightarrow g_3 \rightarrow g_{10}$, the shortest paths from g_{10} to T_0 are obtained by DSPA (no. 8). (4) The energies of isomers in the path $g_{10} \rightarrow T_0$ are calculated (no. 9). (5) As the energies of g_{20} and g_{21} are higher than that of g_{10} , the subpaths $\rightarrow g_{20} \rightarrow g_{25} \rightarrow$ and $\rightarrow g_{21} \rightarrow g_{25} \rightarrow$ are cut away (no. 10). (6) The subpaths $S_0 \rightarrow g_1$ and $S_0 \rightarrow g_2$ are examined in a similar way, and the two plausible shortest paths with five steps are obtained (no. 10). (7) In the path $\rightarrow g_2 \rightarrow g_8 \rightarrow g_{17} \rightarrow g_{16} \rightarrow$, the energy of g_{16} is much too high, and the subpath $g_{17} \rightarrow g_{16} \rightarrow$ is cut away (no. 11). (8) The strain energies of the isomers in the path $S_0 \rightarrow g_1 \rightarrow g_6 \rightarrow g_{15} \rightarrow g_{24} \rightarrow T_0$ are all reasonable, and this path is chosen to be a reasonable path which may be a realizable one (no. 12).

A reasonable subpath obtained by SMSPA is searched along with the energy level of the intermediates, but it is neither graph theoretically nor energetically guaranteed to reach the target. In the above example (Figure 10) the path from g_{22} to T_0 might be eventually found. However, many fruitless calculations must be carried out. In SDSPA, the plausible shortest paths are first obtained by DSPA, a reasonable path

to reach the target is searched along the plausible paths, and then the energies of the isomers in them are calculated. Therefore, it is very efficient to find a reasonable path to reach the target. The biggest difference between SMSPA and SDSPA is in the selection of a plausible shortest subpath to reach the target before force field calculations. In SDSPA, a plausible shortest subpath by DSPA gives a criterion for selection of an isomer as a candidate, but in SMSPA, there is no such facility.

The plausible shortest paths are not necessarily the realizable paths. It can be considered as an imagined straight line drawn between two cities on a driver's map. However, one cannot drive straight to the destination but must usually drive by choosing a road near the straight line as a reasonable path from one city to the another city. The distinction is clear between SDSPA and the pruning method, in which the concept of the shortest path does not exist.

CONCLUSION

Whitlock and Siefken introduced graphs in the treatment of adamantane rearrangement. Schleyer et al. and Ōsawa et al. showed the importance of investigation by empirical force field calculations in studying more diamondoid hydrocarbon rearrangements. We studied a more powerful method to find a rearrangement path of triamantane. In this paper we have shown the importance of information obtained by graph-theoretical investigation in finding rearrangement paths and have developed a path-finding algorithm, SDSPA, which could remarkably reduce the number of empirical force field calculations on the basis of this information.

We have classified isomers and paths appearing in diamondoid hydrocarbon rearrangements to evaluate the efficiency and to evaluate the ability of the method to predict the real paths. We have established a suitable terminology for the isomers and paths and could systematize the searching methods which had already been published, including our present methods.

When the number of isomers to be considered in a rearrangement reaction becomes large, SMSPA as used by the Schleyer group and by the Ōsawa group needs many tries and error calculations to select a branch to the target isomers, as the steps of searching proceed. In this case, we find that the shortest path by DSPA becomes a very important factor in efficiently finding a direction and a path to reach the target isomer.¹⁵⁻¹⁷ Also, the shortest path shows the lower limit of steps by which a starting isomer can be rearranged into a target one by 1,2 shifts. This provides us with an early indication of the amount of difficulty involved in finding reasonable paths.

We have succeeded in developing SDSPA and have showed that this method is very efficient for triamantane rearrangement. We have obtained reasonable paths with about 15 steps (shown in Figure 5) for the triamantane rearrangement. We expect that our theoretical prediction will stimulate an effort toward the detection of intermediates and will be accurate in determining which are isolable and which are unstable.

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Registry No. Triamantane, 13349-10-5.

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