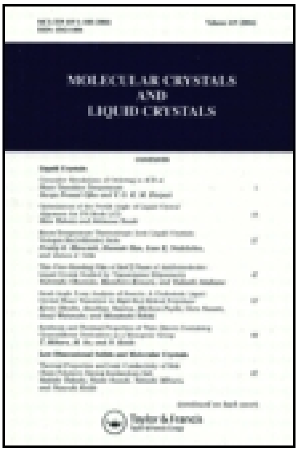

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Crystalline-State Reaction of a Syn-Tricyclo[4.2.0.0^{2,5}]Octane Derivative to a Cis, Cis-Cycloocta-1,5-Diene Derivative

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CRYSTALLINE-STATE REACTION OF A *SYN*-TRICYCLO[4.2.0.0^{2,5}]OCTANE DERIVATIVE TO A *CIS, CIS*-CYCLOOCTA-1,5-DIENE DERIVATIVE

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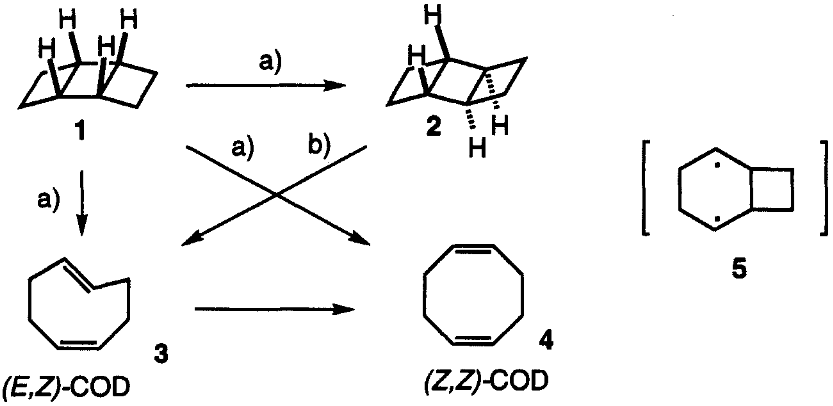
Abstract A *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative isomerized to a cycloocta-1,5-diene derivative on exposure to X-ray radiation keeping the single crystal structure. The two half-cylindrical molecules formed a cavity, in which three cyclohexanes used as recrystallization solvent were included. The single crystal obtained from a mixture of chloroform and ether was analyzed at -140 °C by X-ray crystallography, which confirmed the structure of *syn*-tricyclo[4.2.0.0^{2,5}]octane.

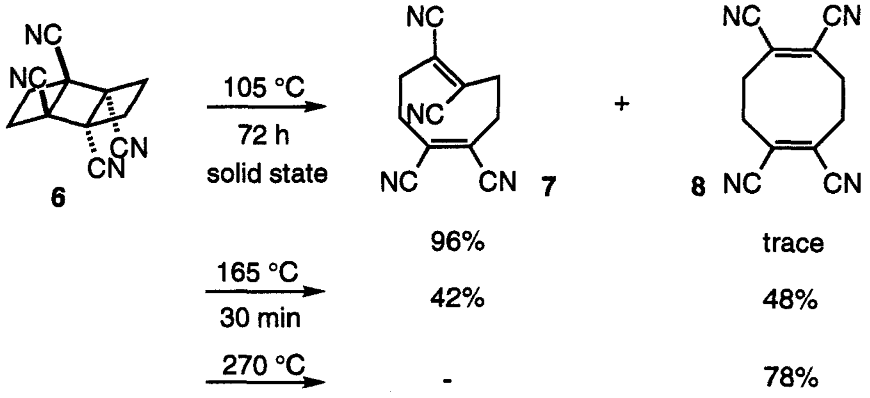
INTRODUCTION

The gas phase reactions of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octanes (**1**, **2**) have been studied to give (*E,Z*)- and (*Z,Z*)-cycloocta-1,5-dienes (**3**, **4**) as the major products.[1] From kinetic analyses, the bicyclo[4.2.0]octane-2,5-diyl biradical (**5**) was involved in a key intermediate.

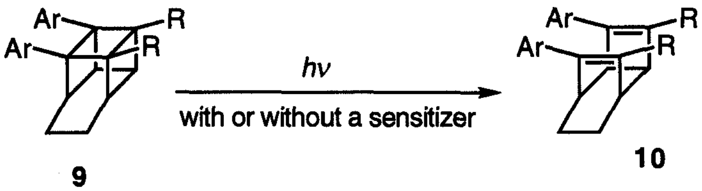


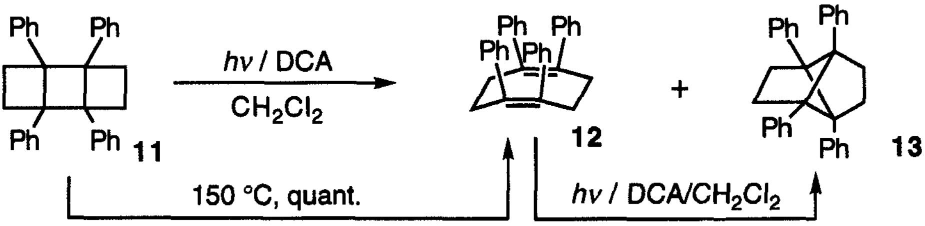
a) 117-146 °C, 1-10 Torr. b) 139-172 °C, 1-10 Torr.

The thermal reaction of *anti*-tetracyanotricyclo[4.2.0.0^{2,5}]octane (**6**) in the solid state at 105 °C gave (*E,Z*)-tetracyanocycloocta-1,5-diene (**7**) in 96% yield along with a trace amount of (*Z*,*Z*)-isomer **8**.[2] At 270 °C, only (*Z*,*Z*)-isomer was obtained in 78% yield. Then, (*E*,*Z*)-isomer is the primary product of the kinetically controlled [2+2] cycloreversion. Valence isomerization reactions of the arylated cage molecule **9** to diene **10** were observed upon irradiation with a 300 nm lamp. The homolytic cleavage to give a radical intermediate, which was stabilized by the aryl groups, was preferred.[3] Photosensitized isomerizations of **9** to **10** were also observed via an efficient cation-radical chain process in the presence of a quinone or a cyanoaromatic compound as a sensitizer.[4]



The irradiation of tetraphenyltricyclo[4.2.0.0^{2,5}]octane (**11**), whose stereochemistry was not specified, in the presence of 9,10-dicyanoanthracene (DCA) afforded (*Z*,*Z*)-tetraphenylcycloocta-1,5-diene (**12**) and tetraphenyltricyclo[3.3.0.0^{2,6}]octane (**13**),[5] while **11** was quantitatively converted at 150 °C into **12**.[6] The structure of **13** was elucidated by X-ray crystallographic analysis.

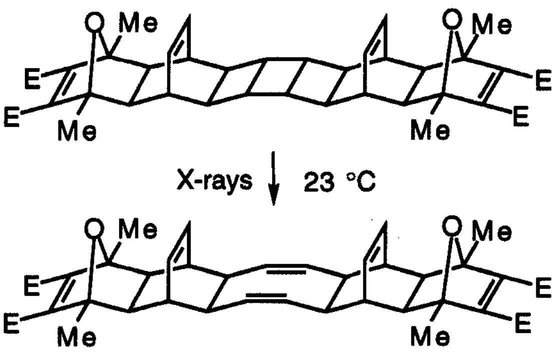




RESULTS AND DISCUSSION

Recently, we found the cleavage of the central four membered ring of a *syn*-tricyclo-[4.2.0.$0^{2,5}$]octane derivative (**14**) during the X-ray crystallographic analysis.[7] When the single crystal **14A**, obtained from a mixture of cyclohexane and chloroform, was irradiated by Cu Kα line at room temperature, the intensity of one of the monitoring reflections for data collection gradually decreased. After 6 h, the intensity of the reflection became nearly constant to make it possible to collect three-dimensional intensity data, where the cell parameters were a=15.953 (4), b=10.543 (1), and c=26.181 (3) Å with β=95.66 (1)° and V=4382.2 Å^3. However, no apparent change of the crystal was observed during the period. This means that a chemical change occurred without disrupting the single crystalline state. The final molecular structure was a cycloocta-1,5-diene derivative (**15A**) as shown in Figure 1. Indeed, the ^{1}H NMR spectrum of the sample recovered from the X ray work was identical with that of authentic **15**. The cell dimensions after exposure to the X-ray were a=15.950 (5), b=10.543 (2), and c=26.370 (6) Å with β=95.72 (2)°. The change in the cell dimensions throughout the X ray irradiation was certainly as small as less than 1%.

The X ray analysis of a single crystal **15B**, which was obtained by recrystallization from a mixed solution of cyclohexane and chloroform, was independently carried out to get the same conclusion; the cell dimensions were a=15.968 (2), b=19.548 (1), and c=26.406 (2) Å with β=95.72 (2)Å, being slightly larger than those of **15A**. This indicates that the **15A** formed by the single crystalline state reaction from **14A** has a strain to minimize the molecular motion within the lattice. It is noteworthy that the crystal structures of **15A** and **15B** possessed a unique feature; both **15A** and **15B** prepared by recrystallization from a mixture of cyclohexane and chloroform provided a spherical space to include cyclohexanes in the circular column formed by two hemicylindrical molecules as shown in Figure 2.



14

15

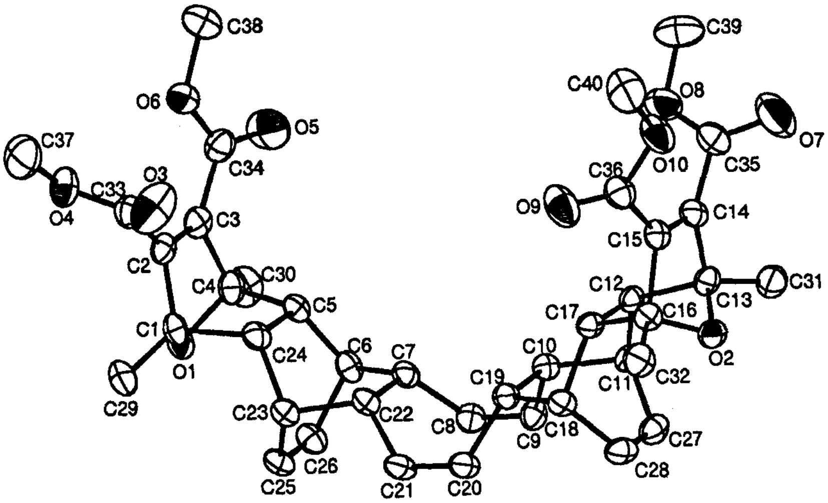


FIGURE 1 ORTEP drawing of the cycloocta-1,5-diene derivative **15A** from **14A**.

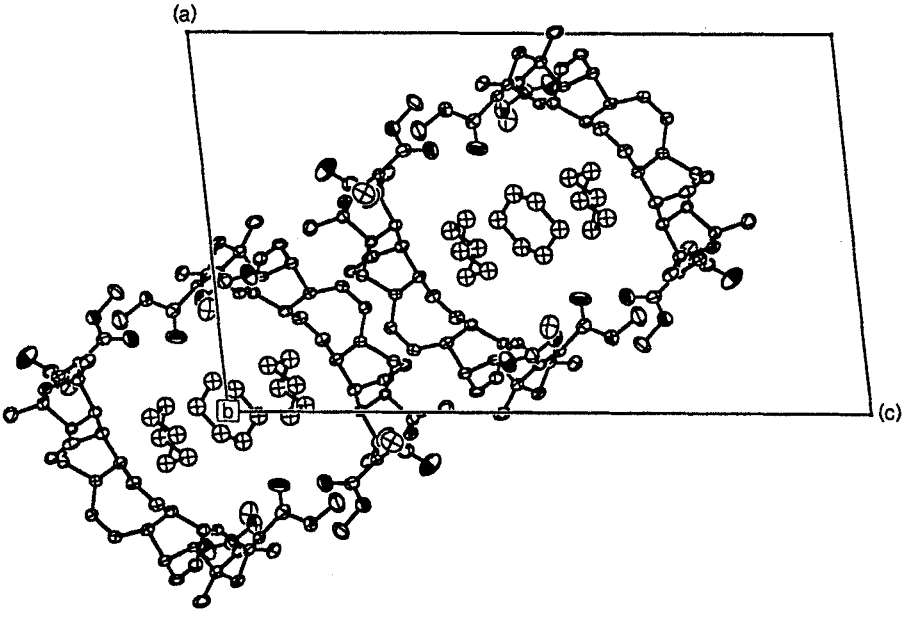


FIGURE 2 ORTEP drawing of the cycloocta-1,5-diene derivative **15B**.

A single crystal **14B**, obtained from a mixture of chloroform and ether, was analyzed at room temperature to determine the crystal structure using Cu Kα radiation. Again, the central four membered ring was cleaved. In this case, two hemi-cylindrical molecules did not form a cavity. They faced each other with a slip of the half of the molecular length to reduce the molecular volume as shown in Figure 3. The cell dimensions of **14B** at the initial stage were a=8.372(2), b=25.297 (4), and c=17.156 (4) Å with β=98.78 (2)° and V=3591 (1) $Å^3$, whereas those of the final stage were a=8.338 (2), b=25.765 (4), and c=17.341 (5) Å with β=102.35 (2)° and V=3639 (2) $Å^3$. The angle β changed largely.

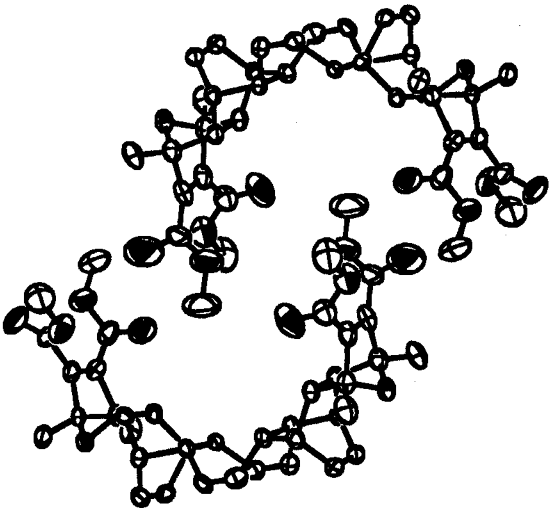


FIGURE 3 ORTEP drawing of the cycloocta-1,5-diene derivative from **14B**.

When a single crystal of **14B** was analyzed at -140 °C, the cell dimensions were a=8.317 (3), b=25.090 (2), and c=17.058 (3) Å with β=98.41 (2)° and V=3521 (2) $Å^3$. The crystal had a *syn*-tricyclo[4.2.0.0^{2,5}]octane structure. The central cyclobutane ring had been retained.

Consequently, it is clear that **14** had a *syn*-tricyclo[4.2.0.0^{2,5}]octane structure and that the X-ray radiation induced a cleavage of the bonds of the central four membered ring to give **15** within a single crystal lattice. It has been reported that structural investigations on *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octane derivatives are very rare.[8] Then, it may be interpreted that the deformation of the crystal lattice caused by the structural change of crystalline **14** into crystalline **15** could be negligible since the reaction occurred in the center of the molecule and the bulky substituents would keep the intermolecular distance approximately constant during the reaction. Relaxation of the local stress generated in the crystal should occur with minimal atomic and molecular rearrangement.

Acknowledgement

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