

## Photochemical Study of [3<sub>3</sub>](1,3,5)Cyclophane and Emission Spectral Properties of [3<sub>n</sub>]Cyclophanes (n = 2–6)

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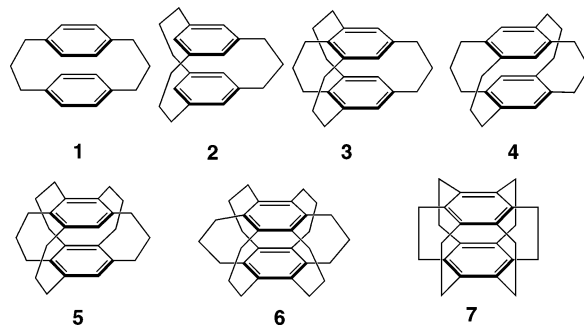
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**Abstract:** The photochemical reaction of [3<sub>3</sub>](1,3,5)cyclophane **2**, which is a photoprecursor for the formation of propella[3<sub>3</sub>]prismane **18**, was studied using a sterilizing lamp (254 nm). Upon photolysis in dry and wet CH<sub>2</sub>Cl<sub>2</sub> or MeOH in the presence of 2 mol/L aqueous HCl solution, the cyclophane **2** afforded novel cage compounds comprised of new skeletons, tetracyclo[6.3.1.0.2.7.0<sup>4,11</sup>]dodeca-5,9-diene **43**, hexacyclo[6.4.0.0.2.6.0.4.11.0.5.10<sup>9,12</sup>]dodecane **44**, and pentacyclo[6.4.0.0.2.6.0.4.11.0<sup>5,10</sup>]dodecane **45**. All of these products were confirmed by the X-ray structural analyses. A possible mechanism for the formation of these photoproducts via the hexaprismane derivative **18** is proposed. The photophysical properties in the excited state of the [3<sub>n</sub>]cyclophanes ([3<sub>n</sub>]CP, n = 2–6) were investigated by measuring the emission spectra and determining the quantum yields and lifetimes of the fluorescence. All [3<sub>n</sub>]CPs show excimeric fluorescence without a monomeric one. The lifetime of the excimer fluorescence becomes gradually longer with the increasing number of the trimethylene bridges. The [3<sub>n</sub>]CPs also shows excimeric phosphorescence spectra without vibrational structures for n = 2, 4, and 5, while phosphorescence is absent for n = 3 and 6. With an increase in symmetry of the benzene skeleton in the [3<sub>3</sub>]- and [3<sub>6</sub>]CPs, the probability of the radiation (phosphorescence) process from the lowest triplet state may drastically decrease.

### 1. Introduction

All members of the [3<sub>n</sub>]cyclophanes ([3<sub>n</sub>]CPs, n = 2–6) are available today<sup>2,3</sup> because of our efforts aimed at the synthesis of [3<sub>6</sub>](1,2,3,4,5,6)CP **6**, [3]superphane, with bridges longer, by one carbon unit, than that of [2<sub>6</sub>](1,2,3,4,5,6)CP (superphane) **7** by Boekelheide et al.<sup>4</sup> and Hopf et al. (Figure 1).<sup>5</sup> Elongation of the bridge causes the cyclophane structure to be increasingly



**Figure 1.** [3<sub>n</sub>]Cyclophanes (n = 2–6) **1–6** and superphane **7**.

strain-free and more flexible compared with the corresponding [2<sub>n</sub>]CP series. As a result, the [3<sub>n</sub>]CPs show much stronger

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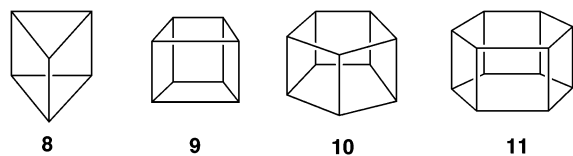


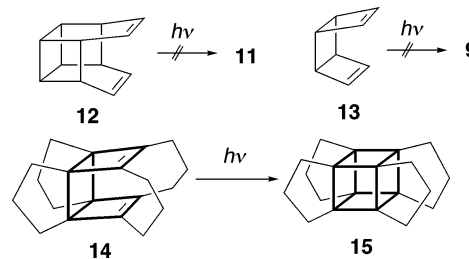
Figure 2. Prismane family.

$\pi$ -electron donating ability than the corresponding [2<sub>*n*</sub>]CPs.<sup>2,6</sup> We have already reported the synthetic methods of the [3<sub>*n*</sub>]CPs and their structural properties in solution<sup>2</sup> as well as in the solid state.<sup>6</sup> Our next subject to be solved in this field is the synthesis of propella[3<sub>*n*</sub>]prismanes via photochemical reaction of the [3<sub>*n*</sub>]CPs.<sup>7,8</sup>

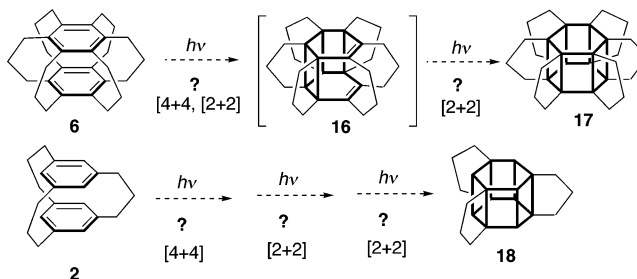
Prismanes constitute an infinite family of (CH)<sub>*n*</sub> polyhedra<sup>9</sup> that chemists find esthetically appealing because of their molecular regularity, many years of effort were needed before the first three members, prismane **8**,<sup>10</sup> cubane **9**,<sup>11</sup> and pentaprismane **10**,<sup>12</sup> could be successfully synthesized. Recently, attention has been focused on the challenging objective of constructing the higher prismanes, in particular, hexaprismane **11**. Many diverse synthetic strategies have been developed, and significant progress toward the synthesis of hexaprismane **11** has been made.<sup>13–16</sup> For example, synthesized secohexaprismane, in which only one C–C bond is missing from hexaprismane **11**.<sup>15</sup> However, **11** has eluded synthesis so far.

Pentacyclo[6.4.0.0.2.7.0.3.12.0.6.9]dodeca-4,10-diene **12**, an attractive and logical precursor, could not be photochemically converted to **11** (Scheme 1).<sup>17</sup> This result might have been anticipated because the related olefin, *syn*-tricyclo[4.2.0.0.2<sup>5</sup>]octa-3,7-diene **13** failed to give cubane **9** via [2+2]photocyclization.<sup>18</sup> However, the photochemical formation of propella[3<sub>4</sub>]prismane **15** from diene **14** is indicative that attaching trimethylene bridges

### Scheme 1. Intramolecular [2+2] Photochemical Reactions



### Scheme 2. Expected Photochemical Reactions



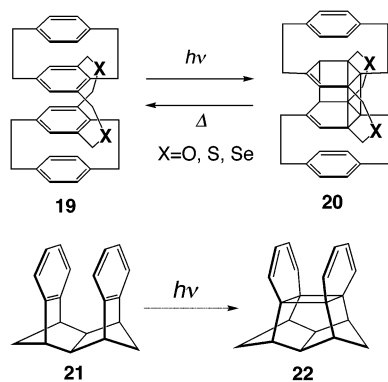
to the basic skeleton may enable [2+2] photocyclization leading to the prismane skeletons (Scheme 1).<sup>19</sup> These findings have been rationalized in terms of the order of the frontier molecular orbitals which are largely affected by through-bond interactions.<sup>20–23</sup> Moreover, on the basis of Frontier MO consideration, it was predicted that [3]superphane **6** would give the hexaprismane derivative **17** on irradiation.<sup>20</sup> It could be argued that three trimethylene bridges would be just as effective as six making the [3<sub>3</sub>]CP **2** a likely candidate for conversion to the triply bridged hexaprismane **18** (Scheme 2). Before putting this prediction to the test, we decided to first investigate the photochemical behavior of less substituted **2** with the aim of optimizing the reaction conditions. We now describe experiments with **2**,<sup>3a,24</sup> the lower homologue of **6**, which has the advantage of being available in large quantities.

Benzene is very stable to photochemical reaction so that the photodimer of benzene has hardly been characterized except for a few examples, whereas the photodimer of condensed aromatics such as naphthalene and anthracene has been reported.<sup>25</sup> Misumi et al. first reported the novel photodimerization of benzene rings incorporated into *syn*-quadruple-layered di-hetera-cyclophane **19** and concluded that the photodimerization is affected by the face-to-face stacking of two fairly strained benzene rings, as well as the substituted positions of four bridges at the inner benzenes and that the outer benzene rings are required for an increase in thermal stability of the photoisomers **20** but not for photodimerization (Scheme 3).<sup>26</sup> Prinzbach et al. reported a second example of the photodimerization of benzene rings in a rigid polycyclic cage, the [6+6] photocyclization between two benzene rings in solution (**21** to **22**).<sup>27</sup> They

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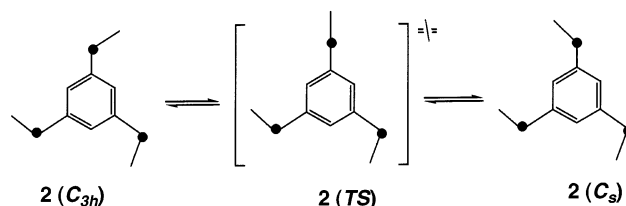
**Scheme 3.** Novel Photodimerizations of Benzene Rings in the *Syn*-Quadruple-Layered Diheterocyclophane **19** and **21**



proposed a synthetic route of the doubly birdcage-annelated hexaprismane derivatives via the [2+2] photocyclization.<sup>28</sup> Thus, a limited number of this type [2+2] photocyclization between two benzene rings has been reported so far. In our photochemical approach to the construction of propella[3<sub>n</sub>]prismanes, the [3<sub>n</sub>]-CPs ( $n = 3-6$ ), in which two benzene rings are completely stacked at 3.0–3.2 Å transannular distances, are used for the precursors.<sup>6a</sup>

The [3<sub>n</sub>]CPs are very useful chromophores for the study of the singlet and triplet excimer states.<sup>29</sup> An investigation of the excimeric states of aromatic compounds in intramolecular and intermolecular systems has been reported.<sup>25,29a</sup> The unique spectroscopic and photochemical properties of [2.2]metacyclophane and related compounds,<sup>30</sup> fluorene,<sup>31</sup> naphthalene derivatives,<sup>32,33</sup> and anthracene derivatives<sup>34</sup> with transannular  $\pi$ -electronic interaction have been extensively studied as benzene dimer models.<sup>35</sup> Fluorescence and phosphorescence from an excimer, a transient singlet and a triplet dimer formed by the association of electronically excited and unexcited molecules, have been observed for a number of aromatic hydrocarbons in liquid solution, pure liquid, and the crystalline state. However, only in the case of benzene, observation and definite conclusion have not been drawn because of the difficulty of its measure-

**Scheme 4.** Bridge Flipping Process and Two Stable Conformers ( $C_{3h}$  and  $C_s$ ) of [3<sub>3</sub>](1,3,5)Cyclophane **2**



ments except for gas-phase measurement. The [3<sub>n</sub>]CPs may elucidate this problem by behaving as a benzene dimer in the excited state due to their structural character, where the two benzene ring are completely stacked face to face by trimethylene chains. Furthermore, the [3<sub>n</sub>]CPs should show excimer emission efficiently rather than the [2<sub>n</sub>]CPs on the basis of a statistical rule known as Hirayama's  $n = 3$  rule.<sup>36</sup>

We wish to report here a photochemical study of [3<sub>3</sub>]CP **2** directed toward the synthesis of the first hexaprismane derivative, propella[3<sub>3</sub>]prismane **18**, and the emission spectral properties of the [3<sub>n</sub>]CPs ( $n = 2-6$ ) as fundamental information on the excited states.

## 2. Results and Discussion

The precursor of the photochemical reaction, [3<sub>3</sub>]CP **2**, was prepared by the TosMIC coupling method as previously reported.<sup>3a</sup> Two conformers having  $C_{3h}$  and  $C_s$  symmetries are observed in the <sup>1</sup>H NMR spectrum of 2,2,11,11,20,20-hexadeuterated **2** in CD<sub>2</sub>Cl<sub>2</sub>, and **2** ( $C_s$ ) is more stable than **2** ( $C_{3h}$ ) by 0.4 kcal/mol. The energy barrier for the bridge flipping process is 12.4 kcal/mol ( $T_c = -7$  °C) (Scheme 4),<sup>3a</sup> and the value is slightly higher than those of [3<sub>2</sub>](1,3)-<sup>37,38</sup> and [3<sub>2</sub>](1,4)-CPs.<sup>39,40</sup> The Density Functional calculations (B3LYP) estimated that the transition state **2** (*TS*) connecting the  $C_{3h}$  and the  $C_s$  conformers has only one flat bridge whose dihedral angle is calculated to be 180.0°, and one of three bridges can change its conformation independently without the influence of other bridges.<sup>41</sup> In the solid state, **2** takes the  $C_s$  conformation and the benzene rings are completely stacked with the transannular distance being 3.08–3.24 Å.<sup>6a</sup>

### 2.1. Photochemical Reaction of [3<sub>3</sub>](1,3,5)Cyclophane **2**.

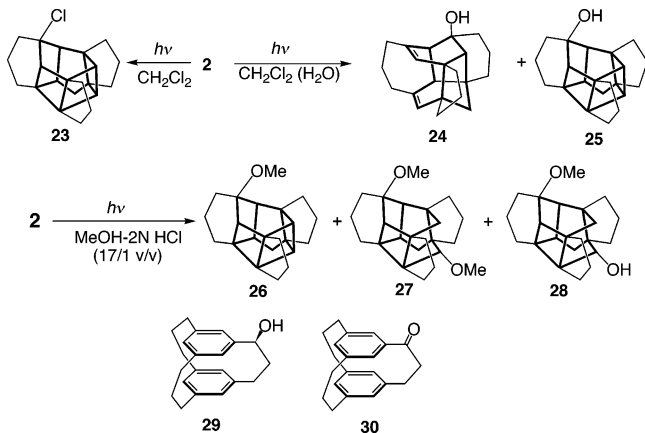
Irradiation of **2** by a sterilizing lamp ( $\lambda = 254$  nm) in cyclohexane, MeOH, or benzene left **2** intact, while causing some of the usual polymerization. However, two types of products were formed when CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent.<sup>7</sup> A dry CH<sub>2</sub>Cl<sub>2</sub> solution of **2** ( $4.90 \times 10^{-3}$  mol/L) in a quartz vessel

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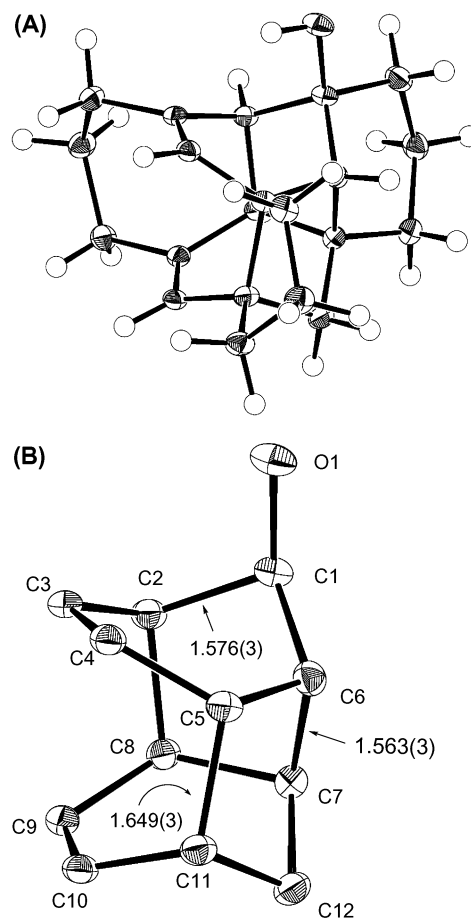
**Scheme 5.** Photochemical Reaction of [3<sub>3</sub>](1,3,5)Cyclophane **2** in Dry CH<sub>2</sub>Cl<sub>2</sub> or Wet CH<sub>2</sub>Cl<sub>2</sub> (upper) and in MeOH in the Presence of 2 mol/L Aqueous HCl (lower) under Sterilizing Lamp Irradiation



was irradiated by a sterilizing lamp for 2.5 h at room temperature under Ar. Separation of the reaction mixture by silica gel column chromatography with hexane afforded a new cage compound, the bridged hexacyclic chlorododecane **23** (5.3%) and the recovery of the starting compound **2** (40%) (Scheme 5). The structure of **23** was first proposed from the molecular formula, NMR data [the distortionless enhancement by polarization transfer (DEPT) spectrum and the <sup>1</sup>H-<sup>13</sup>C correlation spectroscopy], elemental analysis, and mass spectral data (FABMS: *m/z* = 311 [*M*<sup>+</sup> - 1]). Furthermore, the structure was confirmed by the fact that its <sup>1</sup>H- and <sup>13</sup>C NMR data are quite similar to those of the alcohol **25** with the same structure as described below.<sup>7a</sup>

Irradiation of **2** under the same conditions as before, while in a CH<sub>2</sub>Cl<sub>2</sub> solution saturated with water (1.45 × 10<sup>-2</sup> mol/L) for 2.5 h under Ar, followed by separation by column chromatography (SiO<sub>2</sub>, hexane:AcOEt, 10:1), gave, in addition to **2** (18%), two photoproducts. The <sup>1</sup>H- and <sup>13</sup>C NMR spectra of **25** are similar to those of **23**, suggesting that the two molecules have the same structure. The structure of the polycyclic olefin **24** was identified on the basis of the NMR data (<sup>1</sup>H- and <sup>13</sup>C NMR, DEPT spectrum), elemental analysis, mass spectral data (FABMS: *m/z* = 294 [*M*<sup>+</sup>]), and finally by X-ray structural analysis. The novel polycyclic diolefin **24** is composed of one cyclooctadiene, one cycloheptane, one cyclohexane, and two cyclohexene rings, which originate from the benzene rings, and three cyclopentanes (Figure 3A). The C3–C4 [1.340(3) Å] and C9–C10 [1.337(3) Å] bonds are double bonds. The upper and lower cyclohexenes are connected at three positions, C2–C8, C6–C7, and C5–C11 (Figure 3B). The upper cyclohexene ring takes the strained half-chair form of the cyclohexene [the dihedral angles of C2–C3–C4–C5 is -10.8(2)°]. To release this deviation, the bond lengths of C2–C8 [1.602(3) Å] and C5–C11 [1.649(3) Å] are abnormally long compared with the RHF/6-31G\* optimized C–C bond length (1.552 Å) of a cyclopentane. The crystal packing diagram of **24** is shown in Figure S1 in the Supporting Information, and the crystal data of **24** as well as those of other photoproducts **25**, **27**, **28**, and **31**, which will be mentioned hereafter, are summarized in Table S1 in the Supporting Information.

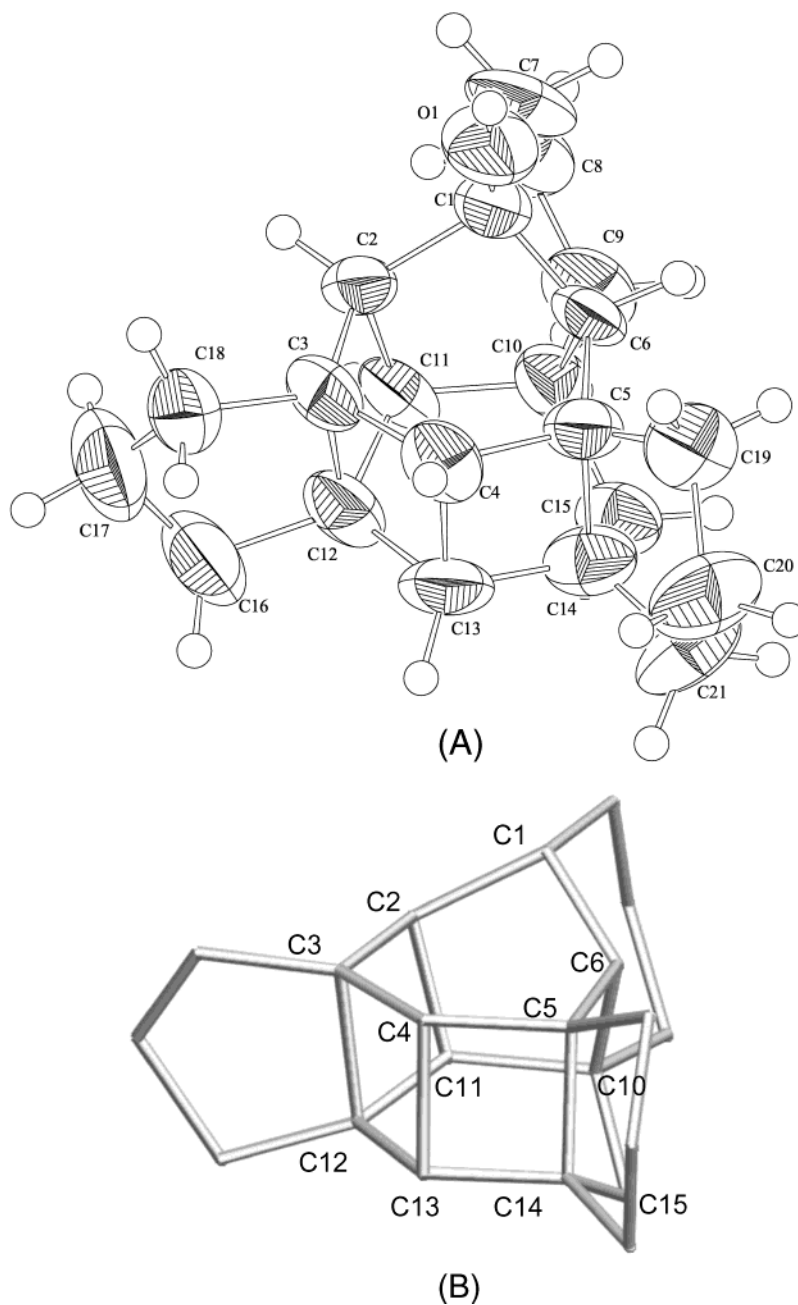
The structure of the cage compound **25** was determined by X-ray structural analysis (-170 °C) (Figure 4A). Compound **25** has the highest strain energy among the identified photo-



**Figure 3.** ORTEP drawings of the photoproduct **24** (-170 °C) (A) and its skeleton (B). Selected bond length (Å): C1–C2 1.543(3), C2–C3 1.521(3), C3–C4 1.340(3), C4–C5 1.515(3), C5–C6 1.563(3), C6–C7 1.538(3), C7–C8 1.576(3), C8–C9 1.524(3), C9–C10 1.337(3), C10–C11 1.497(3), C11–C12 1.546(3), C2–C8 1.602(3), C5–C11 1.649(3), C12–C7 1.538(3).

products because it has three consecutive cyclobutane rings. The skeleton of **25** is composed of the three consecutive cyclobutane rings and two cyclopentane rings. The cyclobutane rings are not square but are rectangular, and the magnitude of the deviation is significant in the central cyclobutane ring. The C3–C12 and C4–C13 bonds are significantly longer than other C–C bonds of the cyclobutane rings. However, a detailed discussion of the C–C bond lengths cannot be provided at the present stage because of the insufficient quality of the X-ray data. A more precise X-ray analysis of **25** is in progress. The central cyclobutane ring, therefore, is expected to be more reactive than the terminal rings, and in fact, the more strained central cyclobutane ring undergoes protonation in preference to the terminal rings as described later.

To reveal the photochemical reaction mechanism, the photolysis of **2** in acidic and basic conditions was examined. A CD<sub>3</sub>OD or CD<sub>3</sub>CN solution of **2** (2.71 × 10<sup>-2</sup> mol/L) containing 2 mol/L aqueous HCl solution (one drop) in a quartz NMR tube was irradiated with a sterilizing lamp for 2.5 h at room temperature under Ar, and the reaction was monitored by the <sup>1</sup>H NMR spectra. The reaction proceeded in acidic conditions, whereas the reaction in CD<sub>2</sub>Cl<sub>2</sub> in the presence of triethylamine did not proceed. Because the reaction afforded photoproducts only in CH<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>CN and CD<sub>3</sub>OD in the presence of HCl, the heavy atom effect on product formation was examined.



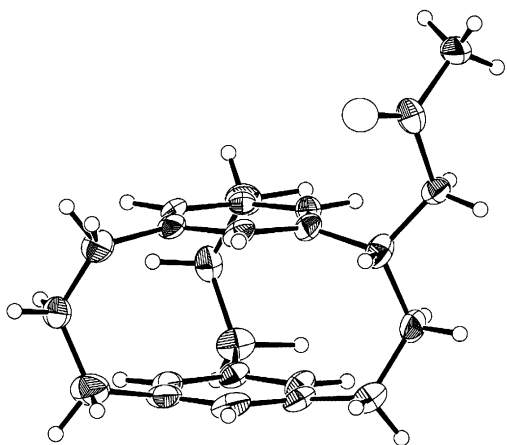
**Figure 4.** ORTEP drawings of the photoproduct **25** ( $-170\text{ }^{\circ}\text{C}$ ) (A) and its skeleton (B).

However, the reaction in  $\text{CD}_3\text{OD}$  in the presence of EtI (5 or 10 mol %) gave no photoproducts. In the preparative scale of the reaction, a mixture of MeOH and 2 mol/L aqueous HCl solution (17:1 v/v) ( $1.02 \times 10^{-2}$  mol/L) of **2** was irradiated with a sterilizing lamp in a quartz vessel for 80 min at room temperature under Ar. Separation of the reaction mixture by recycle HPLC on GPC with  $\text{CHCl}_3$  afforded the recovered **2** (11%), the methoxy compound **26** (2.7%), as well as the dimethoxy and methoxy-hydroxy compounds **27** (11%) and **28** (5.9%) with a new caged skeleton. Prolonged irradiation gave the dimethoxy compound **27** as a major product (57%). Compound **26** has the same skeleton as **23** and **25**.

In degassed nonpolar solvents such as hexane, pentane, and cyclohexane, it was found that photoreaction did not appreciably proceed. On the other hand, in the presence of dissolved oxygen in the nonpolar solvents, trace amounts of the photoproducts

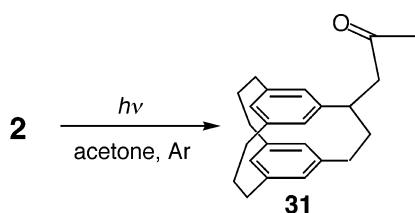
oxidized at the benzylic positions **29** and **30** (yield < 0.1%) were detected. The alcohol **29** was isolated from the reaction mixture and identified by the  $^1\text{H}$ - and  $^{13}\text{C}$  NMR (DEPT) spectra and mass spectrum. A question was raised regarding the source of this oxygen atom, oxygen gas in the solvent or singlet oxygen generated during the photoreaction. To answer this question, the reaction was conducted under the generation of singlet oxygen with 1,3-diphenyl-isobenzofuran known as a singlet oxygen monitor reagent. From this singlet oxygen reaction, the oxidized products (**29**, **30**) were obtained in a negligibly minute quantity. Therefore, it is concluded that the oxygen atom substituted at the benzylic position came from air, not from singlet oxygen.

Next, we tested the photosensitization of the  $[3_3]\text{CP}$  **2** ( $2.7 \times 10^{-2}$  mol/L) containing acetone as a sensitizer (2 mg). The solution containing acetone in a Pyrex NMR tube was irradiated



**Figure 5.** ORTEP drawing of 1-acetylmethyl [3<sub>3</sub>](1,3,5)cyclophane **31** (−170 °C).

**Scheme 6.** Photochemical Reaction of **2** in Acetone

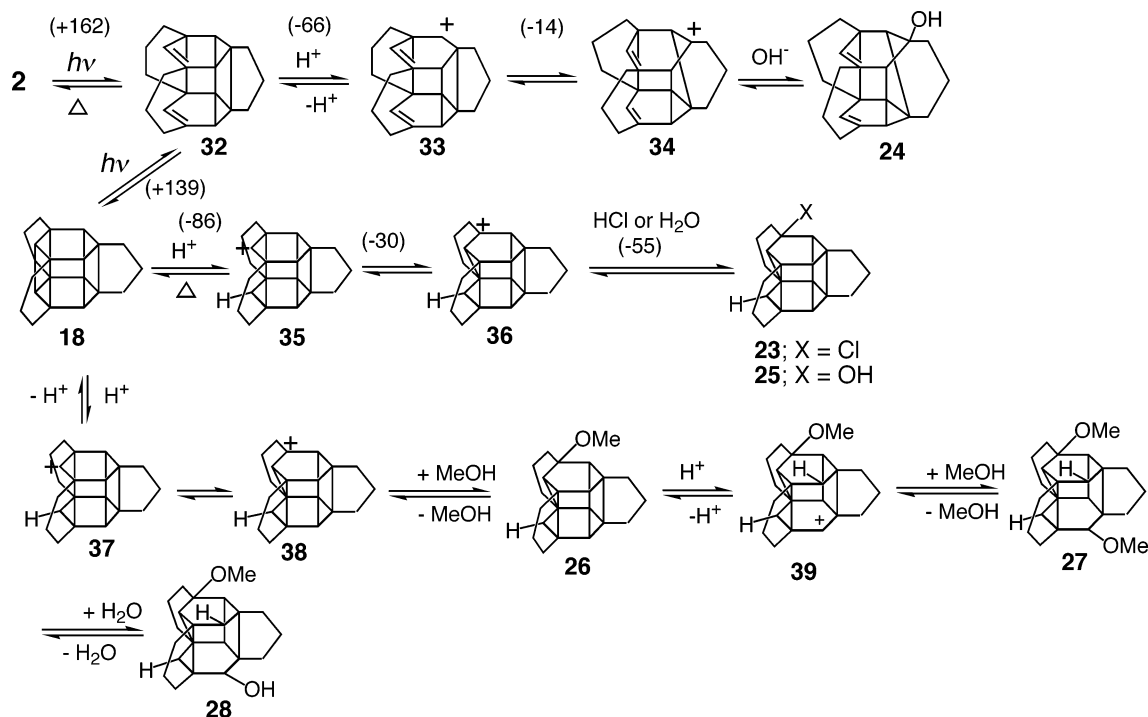


with a high-pressure Hg lamp (400 W) at room temperature under Ar, and the reaction was monitored by the <sup>1</sup>H NMR spectra. Irradiation of the benzene-*d*<sub>6</sub> solution of **2** for 26 h at room-temperature left **2** intact, whereas the irradiation of the CD<sub>3</sub>CN solution for 26 h at room temperature caused some of the usual polymerization. However, in the photochemical reaction of the acetone-*d*<sub>6</sub> solution, products which could be monitored by the <sup>1</sup>H NMR spectrum were observed. In the preparative scale reaction, an acetone solution (3.6 × 10<sup>−3</sup> mol/

L) of **2** was irradiated with a high-pressure Hg lamp for 6 h at room temperature. Separation of the reaction mixture by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> afforded **31** in a small quantity (Scheme 6). It is assumed that the irradiation of **2** formed a benzyl radical intermediate caused by abstraction of a hydrogen from a benzylic methylene group, which gave **31** by the reaction with acetone. The structure of **31** was identified as 1-acetylmethyl[3<sub>3</sub>]CP **31** by the mass spectrum, <sup>1</sup>H- and <sup>13</sup>C NMR spectra, and X-ray structural analysis (Figure 5). The role of acetone in this photochemical reaction is not clear at the present stage. The two benzene rings of **31** are completely stacked face to face similar to that of the [3<sub>3</sub>]CP **2**, but their transannular distances are slightly longer than those of **2**. The bridged carbon–carbon distance is 3.079–3.115 Å, whereas the unbridged carbon–carbon distance is 3.124–3.175 Å.

**2.2. Possible Photochemical Reaction Mechanism of [3<sub>3</sub>](1,3,5)Cyclophane.** There has been no conclusive evidence, but we speculated a reaction mechanism (protonation mechanism) as shown in Scheme 7. The [3<sub>3</sub>]CP **2** on irradiation in CH<sub>2</sub>Cl<sub>2</sub> first gives highly strained hexaprismane derivative **18**. However, protonation occurs at the unbridged carbon atom of a cyclobutane ring to give secondary carbocation **35**, which rearranges to the more stable tertiary carbocation **36**. Finally, **36** is intercepted by chloride or hydroxide ions to give the products **23** (X = Cl) or **25** (X = OH), respectively. One of the driving forces of a series of reactions may be the release of the steric energies. The formation of **24** can be explained by similar processes. Protonation at the unbridged cyclobutane carbon atom of the olefin **32** gives secondary carbocation **33**, which rearranges to the more stable tertiary carbocation **34**, and trapping the cation with water affords the olefin-alcohol **24**. The protons may be generated by the photolysis of CH<sub>2</sub>Cl<sub>2</sub>. In fact, the pH of the reaction mixture was ca. 2 after irradiation in the wet CH<sub>2</sub>Cl<sub>2</sub> solution.

**Scheme 7.** Expected Mechanism for the Formation of the Photoproducts **24–28**<sup>a</sup>



<sup>a</sup> The values (kcal/mol) denote the gain or release of steric energies estimated by MM3.

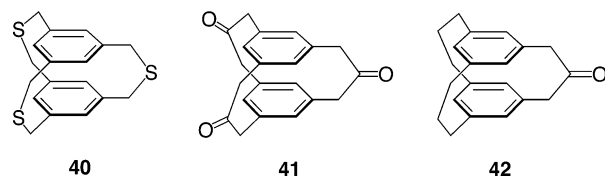


Figure 6.  $[3_3](1,3,5)$ cyclophanes 40–42.

There was a possibility that **25** might be formed from **24** via [2+2] photocyclization. To examine the suggested process, a  $\text{CD}_2\text{Cl}_2$  solution of **24** ( $2.38 \times 10^{-5}$  mol/L) containing water (1  $\mu\text{L}$ ) in a quartz NMR tube was irradiated with a sterilizing lamp for 1.5 h at room temperature under Ar. The reaction was monitored by the  $^1\text{H}$  NMR spectra. With a decrease in the signal intensity of **24**, the signals due to the cyclophane **2** began to appear after 30 min, and the signal intensities increased. This result suggests that the photochemical conversion between **2** and **24** is reversible. However, after 45 min, both signal intensities due to **2** and **24** were decreased, and finally the  $^1\text{H}$  NMR spectrum for photoproduct(s) with no aromatic or olefinic protons appeared. Thus, the olefin **24** may convert to **25** via the cyclophane **2**. The direct conversion of **24** to **25** is unlikely, but the process via the cyclophane **2** is plausible.

The photochemical reaction of **2** did proceed in MeOH in the presence of a proton source to give **26** as was the case in  $\text{CH}_2\text{Cl}_2$ . Subsequent protonation to the unbridged carbon atom of the central bicyclo[2.2.0]hexane skeleton of **26** from the upper side may give the secondary carbocation **39**, which is intercepted by MeOH or  $\text{H}_2\text{O}$  to give the products **27** and **28**, respectively. This interception of the secondary carbocation occurred in the preferable lower side because the steric hindrance of the methoxy group and the repulsion of the lone pair on the oxygen atoms between the flag-pole bond arise if the interception occurs on the upper side. In this reaction, we were unable to isolate and characterize the highly strained propella[ $3_3$ ]prismane **18**, a possible intermediate, because **18** may be protonated under acidic conditions. Therefore, we studied the neutral reaction conditions using a photosensitizer. An alternative single electron transfer (SET) mechanism is also considered, and the details are described in Scheme S1 in the Supporting Information. However, this mechanism is unlikely based on the experimental results.

We investigated the photochemical reaction also in the solid state with the hope of obtaining propella[ $3_3$ ]prismane **18** because protonation of the caged photoproducts would be eliminated in the solid state. A  $\text{CH}_2\text{Cl}_2$  solution of **2** (30 mg) in a quartz test tube was evaporated to dryness in vacuo with a rotary evaporator. The resulting thin film around the wall of the test tube was irradiated with a sterilizing lamp for 6 h at room temperature under Ar. However, no apparent change was observed in the crystal color and forms, and the  $^1\text{H}$  NMR spectrum showed complete recovery of **2**. Photolysis of 2,11,20-trithia[ $3_3$ ]CP **40**, triketone **41**, and monoketone **42** were also studied, but no reaction was observed (Figure 6).

**2.3. Photophysical Properties of  $[3_n]$ Cyclophanes ( $n = 2-6$ ).** To investigate the photophysical properties of the  $[3_n]$ -CPs ( $n = 2-6$ ), absorption and emission spectra were measured. Figure 7 shows the absorption, fluorescence and phosphorescence spectra of the  $[3_n]$ CPs ( $n = 2-6$ ).<sup>42</sup> Absorption spectra were measured in degassed cyclohexane at 295 K. The absorption band at around  $35\,000-40\,000\text{ cm}^{-1}$  and a much lower

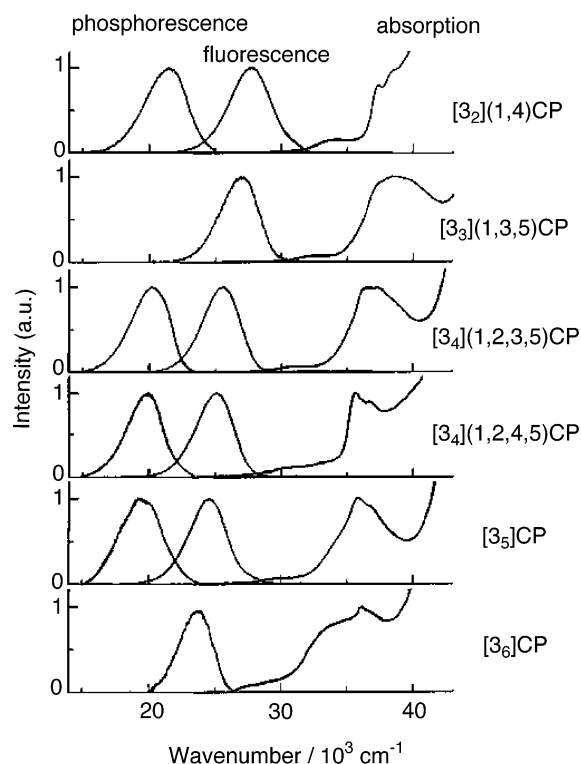


Figure 7. Absorption, fluorescence and phosphorescence spectra of  $[3_n]$ -cyclophanes ( $n = 2-6$ ). Absorption and fluorescence spectra of the cyclophanes were obtained in degassed cyclohexane at 295 K. Phosphorescence spectra were obtained in degassed methylcyclohexane/isopentane (3:1 v/v) at 77 K.

intensity band in the region of  $30\,000\text{ cm}^{-1}$  are observed in all cyclophanes. The former band corresponding to the “cyclophane band” gradually shifts to a smaller wavenumber region with an increase in the number of trimethylene bridges. In the photochemical reaction, the excited state was generated by irradiating this band with a sterilizing lamp. The weak absorption band is due to the transannular  $\pi-\pi^*$  interaction between the two benzene rings as a benzene dimer in the ground state.<sup>43</sup> The appearance of this band is a characteristic phenomenon in the  $[3_n]$ CPs, whereas the  $[2_n]$ CPs ( $n = 2-6$ ) and their derivatives do not show this band.

The fluorescence spectra of the  $[3_n]$ CPs ( $n = 2-6$ ) were measured in cyclohexane at 295 K with a Hitachi F-4010 fluorescence spectrophotometer. All cyclophanes show broad fluorescence bands without vibrational structures in the region of  $20\,000-30\,000\text{ cm}^{-1}$  due to the excimer interaction.<sup>43</sup> It was confirmed that the fluorescence excitation spectra of the  $[3_n]$ -CPs agreed well with the corresponding absorption spectra. The excimeric fluorescence band shifts to a smaller wavenumber with the increasing number of the trimethylene bridges. The maximum wavelengths for the absorption and emission spectra of the  $[3_n]$ CPs are listed in Table 1.

The quantum yield ( $\Phi_f$ ) of the fluorescence was determined by comparing the correct fluorescence spectrum of the  $[3_n]$ CP with that of mesitylene in cyclohexane, which is reported to

(42) One of the reviewers suggested that Figure 7 should report the absorption coefficients of all compounds. But the low solubility of the higher members of  $[3_n]$ CPs, especially  $[3_6]$ CP, in cyclohexane inhibited the determination of the absorption coefficients. Absorption spectra of  $[3_n]$ CPs in  $\text{CHCl}_3$  were already reported in ref 2b.

(43) Birks, J. B. *Photophysics of Aromatic Compounds*; John Wiley & Sons: New York, 1970.



**Table 1.** Maximum Wavelengths of Absorption and Emission Spectra of the [3<sub>n</sub>]cyclophanes (*n* = 2–6)

compound	$\lambda_{\text{max}}/\text{nm}^{\text{a}}$	$\lambda_{\text{max}}^{\text{fluo}}/\text{nm}^{\text{a}}$	$\lambda_{\text{max}}^{\text{phos}}/\text{nm}^{\text{b}}$
[3 <sub>2</sub> ]CP <b>1</b>	267	360	470
[3 <sub>3</sub> ]CP <b>2</b>	258	370	
[3 <sub>4</sub> ](1,2,3,5)CP <b>3</b>	270	390	495
[3 <sub>4</sub> ](1,2,4,5)CP <b>4</b>	280	400	500
[3 <sub>5</sub> ]CP <b>5</b>	280	405	515
[3 <sub>6</sub> ]CP <b>6</b>	275	420	

<sup>a</sup> In cyclohexane at 295 K. <sup>b</sup> In a mixture of methylcyclohexane/isopentane (3:1 v/v) at 77 K.

have a  $\Phi_{\text{f}}$  value of 0.088.<sup>44</sup> The rates ( $k_{\text{f}}$ ) of the fluorescence were obtained by eq 1.

$$k_{\text{f}} = \Phi_{\text{f}}\tau_{\text{f}}^{-1} \quad (1)$$

The lifetimes ( $\tau_{\text{f}}$ ) of the [3<sub>n</sub>]CPs were determined by time-correlated single photon counting with an Edingburg FL-900 fluorescence photometer. It is interesting that the lifetime ( $\tau_{\text{f}}$ ) becomes gradually longer with an increase in the number of trimethylene bridges. The quantum yields of the [3<sub>n</sub>]CPs are considerably smaller than that of mesitylene as a reference compound. The deactivation process from the singlet state to other states via intersystem crossing or internal conversion, singlet or triplet reactions may occur much more rapidly than in mesitylene. For example, the total quantum yield of the [3<sub>3</sub>]CP **2** during the photochemical reaction was estimated to be ca. 10<sup>-4</sup>.

Phosphorescence spectra were measured in methylcyclohexane-isopentane (3:1 v/v, MP) glass at 77 K using a mechanical chopper incorporated in a Hitachi F-4010 fluorescence spectrometer. The maximum wavelengths of the phosphorescence observed are listed in Table 1. With the [3<sub>n</sub>]CPs for *n* = 2, 4, and 5, broad phosphorescence spectra without vibrational structures are seen in the region of 15 000–25 000 cm<sup>-1</sup>, which are considered to originate from the triplet excimer state of the cyclophanes as a benzene dimer. On the other hand, quite interestingly, phosphorescence from [3<sub>3</sub>]CP **2** and [3<sub>6</sub>]CP **6** was not observed at all with the Hitachi F-4010 fluorescence spectrometer.

These observations suggest that the molecular distortion, transannular strain, and distances of the two benzene rings stacked face to face are significant factors, as was suggested by the study of the triplet excimer of naphthalenophane.<sup>45,46</sup> Aromatic triplet excimers play an important role and show an attractive character. Lim and co-workers reported the molecular triplet excimer of naphthalene derivatives in solution.<sup>29</sup> It is reported that the face-to-face stacking of two fairly strained benzene rings of the cyclophanes and a sandwich-pair or parallel conformation of the tethered chromophores are favored for singlet excimers. In contrast to the singlet excimer, a triplet excimer prefers an L-shaped arrangement.<sup>29</sup> In the case of the [3<sub>n</sub>]CPs, two benzene rings are completely stacked with each other, but a slight conformational change has to take place in the excited state when *n* = 2, 4, and 5 but not for the *n* = 3 and 6. Table 3 shows the distances of two benzene rings of the [3<sub>n</sub>]-

**Table 2.** Quantum Yields ( $\Phi_{\text{f}}$ ), Lifetimes of Fluorescence ( $\tau_{\text{f}}$ ), Rate Constants for Fluorescence ( $k_{\text{f}}$ ) in the Degassed Cyclohexane Solution of Mesitylene and [3<sub>n</sub>]cyclophanes (*n* = 2–6) Obtained at 295 K, and the Lifetime of Phosphorescence ( $\tau_{\text{p}}$ ) in a Mixture of Methylcyclohexane and Isopentane (3:1 v/v) at 77 K

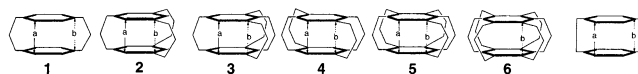
compounds	$\Phi_{\text{f}}^{\text{a}}$	$\tau_{\text{f}}/\text{ns}$	$k_{\text{f}}/10^5 \text{ s}^{-1}$	$\tau_{\text{p}}/\text{s}$
mesitylene	0.088 <sup>c</sup>	37.3	23.6	6.3
[3 <sub>2</sub> ](1, 4)CP: <b>1</b>	0.012	30.3	4.0	6.0
[3 <sub>3</sub> ](1, 3, 5)CP: <b>2</b>	0.013	31.5	4.1	<sup>d</sup>
[3 <sub>4</sub> ](1, 2, 3, 5)CP: <b>3</b>	0.019	62.3	3.0	1.7
[3 <sub>4</sub> ](1, 2, 4, 5)CP: <b>4</b>	0.020	67.8	3.0	3.4
[3 <sub>5</sub> ]CP: <b>5</b>	0.014	116	1.2	1.2
[3 <sub>6</sub> ]CP: <b>6</b>	0.004	160	0.25	<sup>d</sup>

<sup>a</sup> Errors  $\pm$  0.001. <sup>b</sup> Determined by the equation,  $k_{\text{f}} = \Phi_{\text{f}}\tau_{\text{f}}^{-1}$ . <sup>c</sup> Data from *J. Phys. Chem.* **1972**, 76, 3566. <sup>d</sup> No detection.

**Table 3.** Transannular Distances of Benzene Rings of [3<sub>n</sub>]cyclophanes (*n* = 2–6).

	a (Å)	b (Å)	$\Delta$ (a – b)
[2 <sub>2</sub> ](1,4)CP <sup>c</sup>	3.09	2.78	0.31
[3 <sub>2</sub> ](1,4) CP <b>1</b>	3.30	3.14	0.16
[3 <sub>3</sub> ](1,3,5) CP <b>2</b>	3.14	3.09	0.05
[3 <sub>4</sub> ](1,2,3,5) CP <b>3</b>	3.20	2.98–3.12	0.22–0.08
[3 <sub>4</sub> ](1,2,4,5) CP <b>4</b>	3.24	3.03	0.17
[3 <sub>5</sub> ](1,2,3,4,5) CP <b>5</b>	3.24	2.93–3.07	0.31–0.17
[3 <sub>6</sub> ](1,2,3,4,5,6) CP <b>6</b>	–	2.93	–

<sup>a</sup>Distances of unbridged carbon atoms. <sup>b</sup>Distances of bridged carbon atoms:  $\Delta$  (a – b) indicates the difference between a and b. <sup>c</sup> Data from *J. Am. Chem. Soc.* **1954**, 76, 6132.



CPs (*n* = 2–6) obtained by X-ray structural analyses.<sup>6a</sup> The transannular distances between two benzene rings of unbridged carbons (a) and bridged carbons (b), as well as the difference between them ( $\Delta$ ), are summarized. The benzene ring is more distorted in the [3<sub>n</sub>]CPs (*n* = 2,<sup>47</sup> 4, 5) than in the [3<sub>n</sub>]CPs (*n* = 3, 6) in the ground state. This is the reason the [3<sub>3</sub>]- and [3<sub>6</sub>]-CPs do not show triplet excimer phosphorescence. The order of the lifetime ( $\tau_{\text{p}}$ ) is similar to that of mesitylene, suggesting that the electronic structure of the excited triplet state is similar to that of mesitylene.

### 3. Conclusions

Irradiation of **2** with a sterilizing lamp in solutions of dry and wet CH<sub>2</sub>Cl<sub>2</sub> gave prismane derivatives, the bishomopentaprismyl chloride **23**, its hydroxy analogue **25**, and the triply bridged hexacyclic dienol **24**. We speculated a protonation mechanism. Irradiation of **2** would give highly strained hexaprismane derivative **18**, which undergoes protonation of a cyclobutane ring to give a carbocation species. Interception of the carbocation gives photoproducts. This reaction proceeds in acidic conditions; photolysis of **2** in MeOH/2 mol/L aqueous HCl (17:1 v/v) with a sterilizing lamp afforded the new polycyclic caged dimethoxy and methoxy-hydroxy compounds **27** and **28** with a novel pentacyclo[6.4.0.0.<sup>3,7</sup>0.<sup>4,11</sup>0<sup>5,10</sup>]dodecane skeleton **45**, in addition to methyl ether **26** with bishomopentaprismane **44**. Because isolation and characterization of the highly strained **18** are expected to be impossible under acidic conditions, we examined neutral reaction conditions. The reaction of **2** in

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(45) East, A. L. L.; Lim, E. C. *J. Chem. Phys.* **2000**, 113, 8981–8994.

(46) Yamaji, M.; Tsukada, H.; Nishimura, J.; Shizuka, H.; Tobita, S. *Chem. Phys. Lett.* **2002**, 357, 137–142.

(47) (a) Gantzel, P. K.; Trueblood, K. N. *Acta Cryst.* **1965**, 18, 958–968.



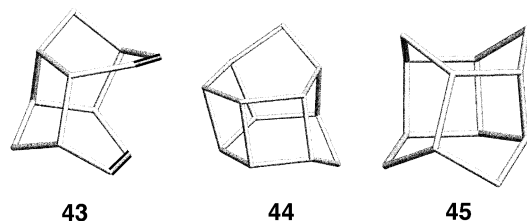


Figure 8. Skeletons of the new cage compounds.

acetone did not afford cage compounds except for the 1-acetylmethyl[3<sub>3</sub>]CP **31**.

Although we have not yet succeeded in the isolation of propella[3<sub>3</sub>]prismane **18**, we expected that **18** would be generated via the excited singlet state after irradiation of [3<sub>2</sub>]CP **2**. Further investigations of the photochemical reaction conditions via the excited singlet state of **2**, as well as modifications of the structure of **2** in order to stabilize the hexaprismane skeleton, may lead to the isolation of the hexaprismane derivatives. The photochemical reaction of [3<sub>6</sub>]CP **6** and fluorinated [3<sub>3</sub>](1,3,5)-CPs are in progress, and the results will be reported soon. The photochemical reactions in the present work provide useful one-step synthetic methods leading to new polycyclic cage compounds with novel skeletons **43–45** from the [3<sub>3</sub>]CP **2** (Figure 8).

All of the [3<sub>*n*</sub>]CPs (*n* = 2–6) show excimeric fluorescence without monomer fluorescence. The lifetime gradually becomes longer with an increase in the number of the bridges. The phosphorescence from the [3<sub>*n*</sub>]CPs is also observed when *n* = 2, 4, and 5, although it is absent for *n* = 3 and 6. To clarify this phenomenon in more detail, a transient absorption spectral study of the [3<sub>*n*</sub>]CPs (*n* = 2–6) is in progress, and the results will be reported elsewhere.

#### 4. Experimental Section

**General Procedures.** Melting points were measured on a Yanako MP-S3 micro melting point apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on JEOL JNM-GX 270 and AL-300 spectrometers. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (TMS) in CDCl<sub>3</sub> unless otherwise noted. Mass spectra (EIMS ionization voltage 70 eV) and fast atom bombardment mass spectra (FAB-MAS *m*-nitrobenzyl alcohol) were obtained with a JEOL JMS-SX/SX 102A mass spectrometer. Gas chromatograph mass spectrometer was measured on a SHIMADZU GCMS-QP5050A. Electronic spectra were recorded on a Hitachi U-3500 spectrometer. Infrared data were obtained on a Hitachi Nicolet I-5040 FT-IR spectrometer. Elemental analyses were performed by the Service Centre of the Elemental Analysis of Organic Compound affiliated with the Faculty of Science, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on Silica gel 60 F<sub>254</sub> Merk and Merk Aluminumoxide 60 GF<sub>254</sub> neutral (TypeE). Column chromatography was performed on Merk Silica gel 60 (40–63 μm).

All solvents and reagents were of reagent quality, purchased commercially, and used without further purification, except as noted below. Aldrich anhydrous CH<sub>2</sub>Cl<sub>2</sub> (99.8%) was used for photochemical reaction. MeOH was distilled from magnesium methoxide and acetone was distilled from CaSO<sub>4</sub>.

As a light source of the photochemical reactions, we used TOSHIBA-GL sterilizing lamps (10 W × 7) in place of a low-pressure Hg lamp.

Absorption and emission spectra were measured with a U-best V-550 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrometer, respectively. The samples for emission measurements were degassed on a high vacuum line by freeze–pump–thaw cycles. It was confirmed that the excitation spectra of emission from the employed

cyclophanes agreed well with the corresponding absorption spectra. The absolute fluorescence quantum yield was determined by comparing the corrected fluorescence spectra of cyclophanes with that of mesitylene in cyclohexane which is known to have a fluorescence quantum yield of 0.088.<sup>44</sup> The fluorescence lifetime was determined by single-photon counting method with a FL-900 CDT spectrophotometer (Edinburgh Analytical Instruments, UK).

**X-ray Crystallographic Study.** The X-ray structural analyses were obtained with a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα λ = 0.71070 Å radiation and rotating anode generator. The crystal structure was solved by the direct method [SIR88]<sup>48</sup> (**24**, **31**) [SHELXS86]<sup>49</sup> (**25**), and [SIR92]<sup>50</sup> (**27**, **28**), and refined by the full-matrix least-squares methods.<sup>51</sup> The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were isotropically. All computations were performed using the teXsan package.<sup>52</sup> The computations were performed with MM3(92)<sup>53</sup> and the Gaussian 94 program<sup>54</sup> graphically facilitated by Insight II from Ryoka Systems, Inc., on Silicon Graphics Octane.

**Photochemical Reaction of [3<sub>3</sub>](1,3,5)Cyclophane **2**. (1) Photolysis of **2** in Dry CH<sub>2</sub>Cl<sub>2</sub>.** A dry CH<sub>2</sub>Cl<sub>2</sub> solution (650 mL) of **2** (880 mg, 3.29 mmol) in a quartz vessel was irradiated with sterilizing lamps (10 W × 7) under Ar for 150 min at room temperature. After removal of the solvent under reduced pressure, the residue was separated by SiO<sub>2</sub> column chromatography (hexane) to give bishomo-prismyl chloride **23** (53.1 mg, 5.2%) and the recovery of the starting **2** (352 mg, 40%). **23**: mp 68.5–70.0 °C; <sup>1</sup>H NMR δ 1.23 (d, *J* = 11.9 Hz, 1H), 1.47 (d, *J* = 11.9 Hz, 1H), 1.41–1.73 (m, 11H), 1.64 (s, 1H), 1.82–2.09 (m, 7H), 2.07 (s, 2H), 2.14 (d, *J* = 6.3 Hz, 1H), 2.40 (d, *J* = 6.3 Hz, 1H); <sup>13</sup>C NMR (DEPT) δ 21.2 (sec.), 30.2 (sec.), 31.1 (sec.), 36.2 (sec.), 37.4 (two sec.), 38.6 (sec.), 39.7 (tert.), 40.1 (sec.), 40.7 (sec.), 42.1 (sec.), 43.0 (quat.), 45.8 (quat.), 47.2 (tert.), 49.5 (tert.), 53.9 (tert.), 55.8 (quat.), 58.2 (quat.), 59.7 (quat.), 65.8 (tert.), 74.5 ppm (quat.); MS (FAB, *m/z*) 311 [M<sup>+</sup>-H]. Anal. Calcd for C<sub>21</sub>H<sub>25</sub>Cl: C, 80.62; H, 8.05%. Found: C, 80.42; H, 8.04%.

**(2) Photolysis of **2** in Wet CH<sub>2</sub>Cl<sub>2</sub>.** A water-saturated CH<sub>2</sub>Cl<sub>2</sub> solution (200 mL) of **2** (800 mg, 2.89 mmol) in a quartz vessel was irradiated with sterilizing lamps (10 W × 7) under Ar for 150 min at room temperature. After removal of the solvent under reduced pressure, the residue was separated by SiO<sub>2</sub> column chromatography (hexane/AcOEt, 10:1) to afford polycyclic olefinic compound **24** (144 mg, 17%, *R<sub>f</sub>* = 0.30), polycyclic hydroxy dodecane **25** (47 mg, 5.4%, *R<sub>f</sub>* = 0.18), and the recovery of the starting **2** (143 mg, 18%). **24**: colorless crystals (toluene), mp 115.5–119.0 °C; <sup>1</sup>H NMR δ 1.34 (t, *J* = 1.6 Hz, 1H), 1.18–2.05 (m, 14H), 1.43 (d, *J* = 2.64 Hz, 2H), 2.15–2.48 (m, 4H), 2.33 (dd, *J* = 7.59 Hz, 1H), 2.53 (dd, *J* = 7.59 Hz, 1H), 2.79 (s, 1H), 5.12 (s, 1H), 5.60 (s, 1H); <sup>13</sup>C NMR (DEPT) δ 20.3 (sec.), 26.3 (sec.) 28.2 (sec.), 33.8 (sec.), 33.9 (sec.), 34.4 (sec.), 35.4 (sec.), 35.7 (sec.),

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39.1 (sec.), 42.8 (sec.), 51.8 (quat.), 52.2 (tert.), 54.8 (tert.), 61.5 (quat.), 64.5 (quat.), 67.0 (tert.), 75.5 (quat.), 136.0 (olefinic), 139.3 (olefinic), 141.3 (olefinic), 144.1 ppm (olefinic); MS (FAB, *m/z*) 294 [M<sup>+</sup>]. Anal. Calcd for C<sub>21</sub>H<sub>26</sub>O·1/4H<sub>2</sub>O: C, 84.37; H, 8.85%. Found: C, 84.49; H, 8.85%. **25**: colorless crystals (toluene), mp 69–71 °C; <sup>1</sup>H NMR δ 1.20 (d, *J* = 12.0 Hz, 1H), 1.28 (s, 1H), 1.35 (s, 1H), 1.41 (d, *J* = 12.0 Hz, 1H), 1.44–1.71 (m, 13H), 1.78–1.81 (m, 1H), 1.88–1.94 (m, 2H), 1.99–2.02 (m, 2H), 2.04 (d, *J* = 6.5 Hz, 1H), 2.06 (s, 2H), 2.14 (d, *J* = 6.5 Hz, 1H); <sup>13</sup>C NMR (DEPT) δ 19.5 (sec.), 29.4 (sec.), 30.4 (sec.), 35.4 (sec.), 36.4 (sec.), 36.8 (sec.), 37.8 (two sec.), 38.3 (tert.), 39.3 (sec.), 40.1 (sec.), 43.1 (quat.), 43.3 (quat.), 46.0 (tert.), 47.1 (tert.), 50.8 (tert.), 55.8 (quat.), 56.0 (quat.), 58.5 (quat.), 62.7 (tert.), 77.0 (quat.); MS (FAB, *m/z*) 294 [M<sup>+</sup>]. Anal. Calcd for C<sub>21</sub>H<sub>26</sub>O·1/2H<sub>2</sub>O: C, 83.12; H, 8.97%. Found: C, 83.16; H, 8.94%.

**(3) Photolysis of 2 in a Mixture of MeOH and 2 mol/L Aqueous HCl (17:1, v/v).** A MeOH-2 mol/L HCl (17:1, v/v) solution (270 mL) of **2** (760 mg, 2.74 mmol) in a quartz vessel was irradiated with sterilizing lamps (10 W × 7) under Ar for 80 min at room temperature while monitoring the reaction by the <sup>1</sup>H NMR spectra in every 20 min. After removal of the solvent under reduced pressure, the residue was separated by recycle HPLC on GPC with CHCl<sub>3</sub> to afford polycyclic methoxy compound **26** (23 mg, 2.7%), polycyclic dimethoxy compound **27** (100 mg, 11%), and polycyclic methoxyhydroxy compound **28** along with the recovery of the starting **2** (80 mg, 11%). **26**: colorless oil. <sup>1</sup>H NMR δ 1.12 (d, *J* = 11 Hz, 1H), 1.23 (s, 1H), 2.17 (d, *J* = 11 Hz, 1H), 1.41–2.06 (m, 26H), 3.17 (s, 3H); <sup>13</sup>C NMR (DEPT) δ 19.9 (sec.), 30.1 (sec.), 30.9 (sec.), 33.4 (sec.), 36.2 (sec.), 37.0 (sec.), 37.1 (sec.), 37.3 (sec.), 38.4 (sec.), 39.8 (sec.), 39.8 (tert.), 40.8 (sec.), 43.7 (quat.), 44.4 (quat.), 46.6 (tert.), 47.6 (quat.), 49.2 (quat.), 51.2 (tert.), 56.1 (quat.), 57.0 (quat.), 59.0 (quat.), 61.3 (prim.), 81.9 (quat.); HRMS (FAB, *m/z*) obsd. 308.2144 [M<sup>+</sup>], calcd for 308.4637. **27**: mp 56–57 °C; <sup>1</sup>H NMR δ 1.03 (d, *J* = 13 Hz, 1H), 1.16 (d, *J* = 11 Hz, 1H), 1.26–1.78 (m, 20H), 1.90 (d, *J* = 11 Hz, 1H), 2.03 (d, *J* = 5.7 Hz, 1H), 2.26 (d, *J* = 13 Hz, 1H), 2.83 (s, 1H), 3.16 (s, 3H), 3.35 (s, 3H); <sup>13</sup>C NMR (DEPT) δ 19.9 (sec.), 25.0 (sec.), 26.1 (sec.), 32.1 (sec.), 34.0 (sec.), 35.4 (sec.), 36.5 (sec.), 36.6 (sec.), 37.4 (sec.), 37.9 (sec.), 40.9 (sec.), 45.1 (tert.), 45.3 (tert.), 48.2 (quat.), 49.2 (quat.), 51.0 (tert.), 51.9 (quat.), 56.4 (quat.), 57.3 (quat.), 59.4 (prim.), 65.0 (prim.), 86.2 (quat.), 89.6 ppm (tert.). GC-MS (EI, *m/z*) 340 [M<sup>+</sup>]. Anal. Calcd for C<sub>23</sub>H<sub>32</sub>O<sub>2</sub>·1/8H<sub>2</sub>O: C, 80.63; H, 9.39%. Found: C, 80.65; H, 9.33%. **28**: mp 138–139 °C; <sup>1</sup>H NMR δ 1.10 (d, *J* = 13 Hz, 1H), 1.19 (d, *J* = 12 Hz, 1H), 1.27–1.73 (m, 21H), 1.93 (d, *J* = 12 Hz, 1H), 2.07 (d, *J* = 4.2 Hz, 1H), 2.25 (d, *J* = 13 Hz, 1H), 3.18 (s, 3H), 3.32 (s, 1H); <sup>13</sup>C NMR (DEPT) δ 19.9 (sec.), 25.4 (sec.), 26.1 (sec.), 31.4 (sec.), 34.0 (sec.), 35.0 (sec.), 35.4 (sec.), 36.1 (sec.), 37.4 (two, sec.), 41.5 (sec.), 45.1 (tert.), 45.3 (tert.), 47.7 (quat.), 49.5 (quat.), 51.0 (tert.), 52.2 (quat.), 56.0 (quat.), 57.6 (quat.), 64.5 (prim.), 79.3 (tert.), 86.2 ppm (quat.). GC-MS (EI, *m/z*) 326 [M<sup>+</sup>]. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>O<sub>2</sub>·1/2H<sub>2</sub>O: C, 79.83; H, 9.28%. Found: C, 79.78; H, 9.13%.

**(4) Photolysis of 2 in Nonpolar Solvents.** A dry hexane solution (500 mL) of **2** (700 mg, 2.52 mmol) in a quartz apparatus was irradiated with sterilizing lamps (10 W × 7) with continuous oxygen gas bubbling for 25 min at room temperature. The solvent was removed under reduced pressure, the residue was separated by PTLC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>), and then by HPLC (C18, MeOH). Very small amounts of **29** and **30** were isolated and identified by <sup>1</sup>H NMR and GC-MS. The yields of these compounds depend on the amount of dissolved oxygen in solution; **29** (0.8–1%) and **30** (0.6–0.7%). Irradiation of **2** (700 mg, 2.52 mmol) in acetone with high-pressure Hg lamp for 1 h gave the compounds **29** (2.7%) and **30** (1.2%) after the similar separation and purification procedure described above. **29**: yellow oil. <sup>1</sup>H NMR δ 7.01 (s, 1H), 6.78 (s, 2H), 6.65 (s, 1H), 6.37 (s, 2H), 2.54–3.12 (m, 16H); MS (FAB, *m/z*) 292 [M<sup>+</sup>-H]. Anal. Calcd for C<sub>21</sub>H<sub>24</sub>O: 1.5H<sub>2</sub>O, C, 78.96, H, 8.52%. Found: C, 78.81, H, 8.28%. **30**: yellow oil. <sup>1</sup>H NMR δ 6.79 (s, 1H), 6.68 (s, 1H), 6.57 (s, 1H), 6.51 (s, 1H), 6.45 (s, 1H), 6.28 (s, 1H), 4.62 (s, 1H), 2.62–2.87 (m, 10H), 2.10–2.22 (m, 6H); MS (FAB, *m/z*) 291 [M<sup>+</sup>]. Anal. Calcd for C<sub>21</sub>H<sub>22</sub>O: 0.65MeOH, C, 83.55; H, 7.97%. Found: C, 83.62; H, 8.01%.

**(5) Photolysis of 2 in Acetone.** A solution of **2** (400 mg, 1.45 mmol) in acetone (400 mL) was irradiated with a high-pressure Hg lamp (400 W) under argon for 14 h at room temperature while monitoring the reaction by <sup>1</sup>H NMR. After removal of the solvent under reduced pressure, the residue was purified by recycle HPLC on GPC type with CH<sub>2</sub>Cl<sub>2</sub> to afford 1-acetyl[3<sub>3</sub>](1,3,5)cyclophane **31** (5 mg, 1.1%) along with the recovery of the starting material (114 mg, 29%). **31**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.01 (s, -COMe, 3H), 2.19 (m), 2.68–2.74 (m), 3.00 (m), 6.39 (s, aromatic), 6.48–6.49 (m), 6.54–6.56 (m) <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 28.6, 28.8, 28.8, 30.0, 34.8, 36.8, 36.4, 36.5, 60.8, 127, 128, 130, 132, 133, 138, 140, 141, 141, 142, 208 ppm. MS (FAB, *m/z*) 332 [M<sup>+</sup>]. Anal. Calcd for C<sub>24</sub>H<sub>28</sub>O·0.05 benzene: C, 86.76; H, 8.48%. Found: C, 86.75; H, 8.52%.

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**Supporting Information Available:** The alternative mechanism of single electron transfer (Scheme S1), crystal packing diagrams of compounds **24** and **31** (Figures S1, S2), and a summary of the crystallographic data and refinement details (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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