

Photoreaction of a 2,11-Diaza[3.3]paracyclophane Derivative: Formation of Octahedrane by Photochemical Dimerization of Benzene

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Photoreactions of the benzenes which are incorporated in a cyclophane have been of interest because their reaction modes reflect the intramolecular interactions of the aromatic chromophores in the cyclophane system. Prinzbach et al. reported the [6 + 6] photocycloaddition of benzenes,¹ and Misumi et al. investigated the photolysis of four-layered cyclophanes to demonstrate the formation of cage-like benzene dimers.² Recently, Shinmyozu et al. reported that, upon the photolysis of carbon-bridged cyclophanes, polycyclic products were formed through complex rearrangements.³

In contrast to the extensive studies on the photoreactions of carbon-bridged cyclophanes,^{1–4} those of the nitrogen-bridged cyclophanes are rather rare.^{5–7} However, it is worth noting that, in some cases, the nitrogen-bridged cyclophanes display different reactions than those of the corresponding carbon-bridged analogues or nonbridged chromophores.^{5–7} Thus, it would be of interest to reveal the photoreactions of the nitrogen-bridged cyclophane **1** in comparison to those of the carbon-bridged analogue **2**. Since very little experimental and theoretical studies on the reactions of the cyclophane **1** are available,⁸ we have investigated its photoreaction and describe now the results.

A solution of cyclophane **1** in benzene was irradiated at 300 nm for 36 h. The reaction mixture was repeatedly separated by preparative thin layer chromatography to afford photoproducts **3** and **4** in 33 and 3% yields, respectively, in addition to the unreacted cyclophane **1** (conversion 67%, Scheme 1). The photoproduct **3** possesses an octahedrane framework.

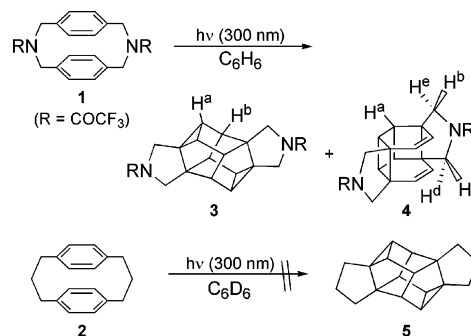
Octahedrane is the lowest homologue of polyhedrane, a (CH)_{2n} hydrocarbon family, and it has been attracted as a member of the benzene dimers.^{9,10} Although octahedrane itself has been prepared through a multistep synthetic process,¹⁰ it has not been photochemically constructed. Thus, the present photoreaction of cyclophane **1** provides a novel, one-step octahedrane synthesis via the photochemical dimerization of benzene.

The structure of the octahedrane **3** was established by an X-ray crystallographic analysis (Figure 1). The bond lengths of the cyclopropane moiety are about 1.50 Å, and the bond angles in the three-membered ring are almost 60°. These features are similar to those reported for octahedrane.^{10a}

In the ¹H NMR spectrum of the octahedrane **3**, the signal of the cyclopropyl hydrogen (H^a) appeared in the higher field (1.97 ppm) (Figure S1) corresponding to the characteristic high-field shift for cyclopropyl proton. The octahedrane-frame hydrogen (H^b) resonates at 3.35 ppm. Between H^a and H^b, no pronounced ¹H–¹H spin coupling was observed (Figure S1), although the dihedral angle H^a–C–H^b was close to 0°. This spectral feature is consistent with that reported for octahedrane.^{10a}

The structure of the cage product **4** has been confirmed by the NMR spectral data as well as an elemental analysis. The peak assigned to the cyclobutyl protons (H^b) appeared at 2.63 ppm. The olefinic protons resonate at 6.00 ppm (Figure S6). The signals of

Scheme 1. Photolyses of Cyclophanes **1** and **2**



the olefinic protons appeared as two singlets and a pair of doublets (AB pattern). These facts indicate that, due to the restricted rotation of the two amide moieties, two rotamers coexist for the structure of **4**; *syn*-**4** (C_s symmetrical) showed the two singlets, and the *anti*-**4** (C₂ symmetrical) displayed the AB signal (cf. Figure S8 and Chart S1). By means of phase-sensitive NOESY spectroscopy, exchanges (negative cross-peaks)¹¹ for the pairs of protons, H^b–H^c and H^d–H^e, were observed. Thus the *syn*-**4** and *anti*-**4** interconverted at room temperature.

Photolysis of carbon-bridged cyclophane **2** was investigated to clarify its photoreactivity in comparison to that of the diazacyclophane **1**. In contrast to the photoproperties of diazacyclophane **1**, cyclophane **2** was almost insensitive to the photoirradiation: When cyclophane **2** was exposed to 300 nm light in C₆D₆, it was found that 73% of the starting cyclophane **2** remained unreacted after 45 h and no appreciable product (namely, octahedrane **5**) was detected by ¹H NMR spectroscopy. Therefore, the nitrogen-containing bridges play an important role in displaying the unique photo-dimerization of the benzene chromophores in the cyclophane system **1** (Scheme 1).

Molecular orbital calculations of cyclophanes **1** and **2** were performed to provide an insight into the difference in their photoreactivities. Figure 2 shows the LUMO drawing calculated by the semiempirical AM1 method.¹² Ab initio DFT calculation at B3LYP/6-31+G(d)¹³ level of theory provided similar trends (Figure

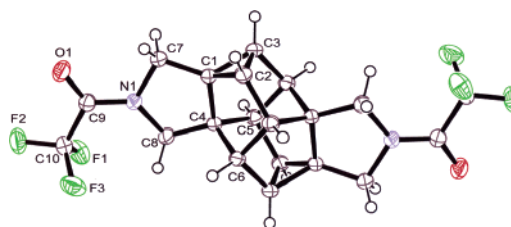


Figure 1. Molecular structure of octahedrane **3** observed at 173 K. Selected bond lengths (Å) and angles (°) of the cyclopropane moiety. C1–C2 1.503(2), C1–C3 1.499(2), C2–C3 1.519(2), C1–C4 1.5248(18), C3–C1–C2 60.78(10), C1–C2–C3 59.47(9), C1–C3–C2 59.76(9).

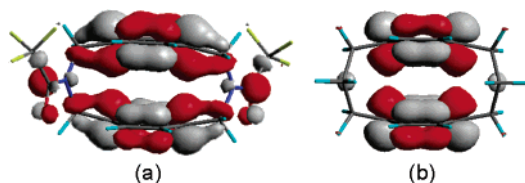
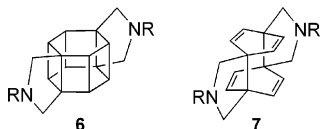


Figure 2. AM1-calculated LUMO figures of cyclophanes (a) **1** and (b) **2**.

Chart 1



S12). The LUMO of the cyclophanes consisted of an overlap of the LUMO of their *p*-xylene chromophores in an in-phase manner. For the diazacyclophane **1**, it is characteristic that the π -orbitals of the benzene rings delocalize to conjugate with the bridge C–N σ -bonds (Figure 2a). Such a through-bond interaction is not significant in the case of the carbon-bridged analogue **2** (Figure 2b). Thus, in the case of the diazacyclophane **1**, it is probable that the through-bond coupling between the π -orbitals of the benzene rings and the bridge C–N σ -bonds make the interaction of the benzene chromophores more significant in the excited state. It is also worth noting that bond distance of the C–N single bond is generally shorter than that of C–C single bond,¹⁴ thus, the two benzene rings are considered to locate closer in diazacyclophane **1** than in cyclophane **2**. Therefore, it is plausible that, by both the electronic and the steric factors, the interaction of the two benzenes more efficiently occurs in the case of diazacyclophane **1**, and consequently, the photodimerization of the benzene chromophores was more effective.

Cyclophanes **1** and **2** gave off broad fluorescence due to the excimer interaction,^{3a} and the emission profile was similar to each other [λ_{FL} 356 nm for **1** and 359 nm for **2** (Figure S13)], whereas diazacyclophane **1** displayed a blue-shifted absorption band (285 nm) compared to cyclophane **2** (294 nm) (Figure S13). Thus, Stokes shift was slightly larger for diazacyclophane **1** than for carbon-bridged analogue **2**, suggesting that the interaction between their benzene chromophores in the excited state was more significant for **1** than for **2**. These spectral features are consistent with the observed difference in the photoreactivity of the cyclophanes.

Considering the orbital interaction in the LUMO of cyclophane **1** (Figure 2a), the photochemical formation of a hexaprismane **6** and a [4 + 4] cycloadduct **7** (Chart 1) could be possible since the π -orbitals of the two benzene chromophores overlap entirely in an in-phase mode. However, for the photolysis of the cyclophane **1**, the octahedrane **3** was actually obtained as the main photoproduct instead of the expected products **6** and **7**. Octahedrane has been predicted to be the most stable among the (CH)₁₂ hydrocarbons, while hexaprismane has been noted as a highly strained framework.^{9,15} Therefore, the photoexcited cyclophane **1*** preferentially provided the much more stable octahedrane **3** rather than the unstable isomer **6**. Formation of [4 + 4] cycloadduct **7** was considered to be unfavorable due to thermal and photochemical lability of *p,p'*-dibenzene.^{16b,17}

It would be of additional interest to reveal whether the cage compound **4** undergoes a further photoreaction to afford a secondary product, such as hexaprismane **6**.¹⁵ Upon irradiation of the cage

compound **4** at 300 nm in C₆D₆, the formation of the cyclophane **1** was exclusively observed by ¹H NMR spectroscopy (data not shown). Thus, it has been disclosed that the cage compound **4** reverted to the aromatic components by photoexcitation. This phenomenon is consistent with reported photoreactions of related cage compounds, such as pentacyclo[6.4.0.0.2⁷0.3.120^{6,9}]dodeca-4,10-dienes.^{2,16}

In summary, upon photoexcitation, the nitrogen-bridged cyclophane **1** afforded the octahedrane **3**. To the best of our knowledge, this is the first photochemical octahedrane formation. In contrast, the carbon-bridged analogue **2** was almost photochemically inert. It is concluded that the photoreactivities of the [3.3]paracyclophane system could be modified by changing the bridge chains; that is, the novel photoreaction pathway of benzenes was opened by the nitrogen bridging.

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Supporting Information Available: Experimental procedures, NMR spectra of the photoproducts **3** and **4**, summary of the X-ray crystallographic studies for the octahedrane **3**, DFT calculation results, and absorption and fluorescence spectra of **1** and **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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