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Photochromism of [2.n]Metacyclophan-1-ene Derivatives

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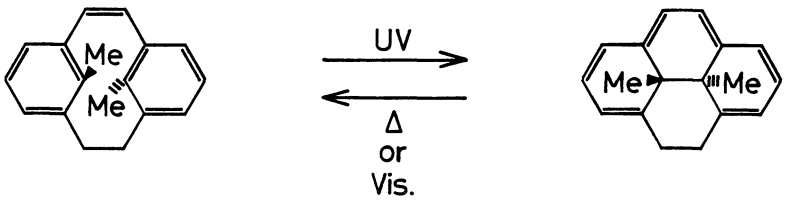
Photochromism of [2.n]metacyclophan-1-ene derivatives (n=2,3,4) was investigated. The reaction rates of the thermal decoloration were increased about thousand-fold with increasing of n by one.

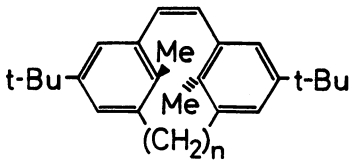
Recently, photochromic compounds which involve photochemical electrocyclic reactions such as fulgides and bisthienylethylenes have been interested because of their excellent fatigue resistance. [2.n]Metacyclophan-1-ene belongs to this type of photochromic compounds. The photochromism of [2.2]metacyclophan-1-ene has been reported; uncolored [2.2]metacyclophan-1-ene isomerizes to red meta-stable 4,5,10b,10c-tetrahydropyrene with irradiation of UV light, and the colored species returns back thermally or with irradiation of visible light to the original uncolored form.[1,2] The change of the length of methylene sequences in [2.2]meta-



cyclophan-1-ene, which serve to fix a "cis-stilbene structure", is expected to cause the alteration of the photochromic behaviors of [2.n]metacyclophan-1-enes. Recently, Yamato et al. reported the systematic syntheses of [2.n]metacyclophan-1-

ene derivatives.[3] In this letter, we, for the first time, report the photochromism of three [2.n]metacyclophan-1-enes (n=2,3,4). We found that every three compounds exhibited photochromism. The lifetimes of colored species, however, were markedly dependent on the length of bridged methylene chains.

The n-heptane solutions of three [2.n]metacyclophan-1-enes, 1-3,[3,4] were



1 : n=2
2 : n=3
3 : n=4

used. The spectra of the uncolored species of 1-3 were measured with a UV-visible spectrophotometer (Hitachi 330). The solutions of 1-3 in quartz cells were irradiated with UV light and the UV-visible spectra of the colored species were measured. The thermal decoloration reactions were followed by monitoring the absorbance changes at the wavelengths of the absorption peaks (λ_{max}) of the colored species in visible region after UV light irradiation. Quite different procedures and apparatus were adopted for the observation of the photochromic behaviors for 2 and 3 from the case of 1, because the lifetimes of the colored species were markedly short. For photo-coloration of 1, UV light from a 500 W Xe lamp (Ushio-Denki UXL-500D-O) equipped with a UV pass filter was used. The spectra of 1 after UV light irradiation was measured by use of a conventional spectrophotometer. The rate of the thermal decoloration of 1 was obtained from the variation of the absorbance at λ_{max} after UV light irradiation. In the cases of 2 and 3, 308 nm laser pulses from a XeCl excimer laser (Lambda Physik EMG-50E) were used for photo-coloration, and the spectra at 1 millisecond after the laser pulse irradiation were measured by using an optical multichannel detection system (Seki, & Co. Ltd). The variations of the absorbance at λ_{max} at room temperature after laser pulse irradiation were detected by using a monitor light from a halogen

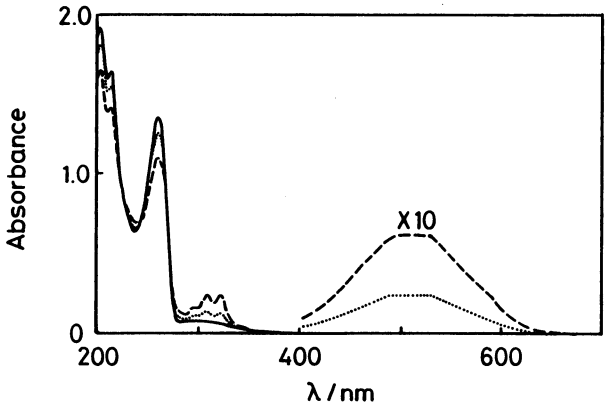


Fig. 1. Spectrum change of 1 in n-heptane with UV light irradiation;
———:before irradiation;
·····:after 5 s irradiation;
------:after 20 s irradiation.

lamp and a photomultiplier. Thus, the rates of thermal decoloration of 2 and 3 were obtained.

The spectrum change of 1 with UV light irradiation is shown in Fig. 1. The absorption of the colored species appeared in a 400-650 nm region after UV light irradiation. After heating the solution for 15 min at 60 °C, the original spectrum was restored. Fig. 2 shows the spectra of 2 and 3 at 1 millisecond after laser pulse irradiation. The spectra of colored species of 2 and 3 were very similar to that of 1, except for their fast fading rates. From the observation of repeated coloration-decoloration cycles, the photochromism of [2.3] and [2.4]metacyclophan-1-ene was confirmed.

The spectra of 1, 2, and 3 in uncolored forms are compared in Fig. 3. The absorption peaks of the uncolored species shifted to shorter wavelength with the increase of the number of methylene chains n, approaching to that of cis-stilbene which had no bridged methylene.[5] On the other hand, the peaks of colored species tended to shift to longer wavelengths with increasing n. The long methylene bridge brings about the molecular strain in the colored species and causes the twist of the π conjugated bonds. Twisting of conjugated bonds or double bonds raises the energy level of the ground state and

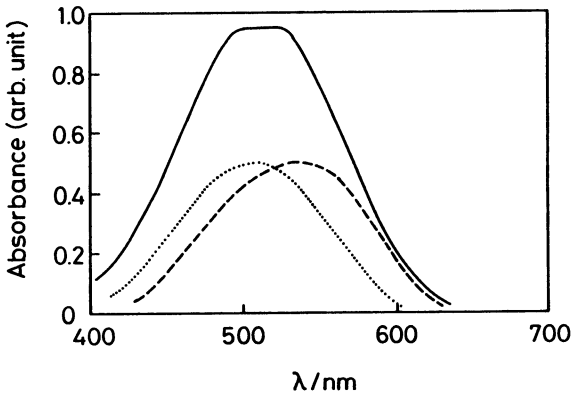


Fig. 2. Spectra of colored species in n-heptane.
———:1; ·····:2; ------:3.

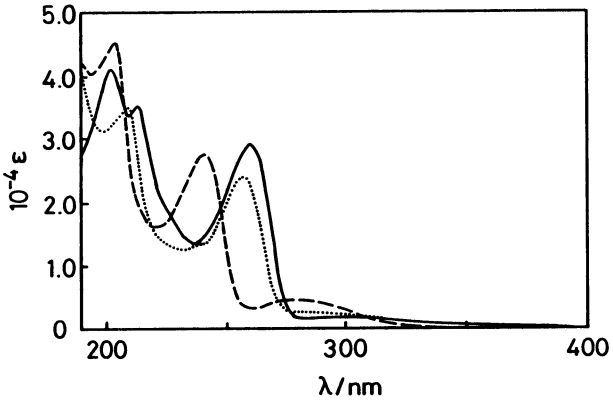


Fig. 3. Spectra of uncolored species in n-heptane.
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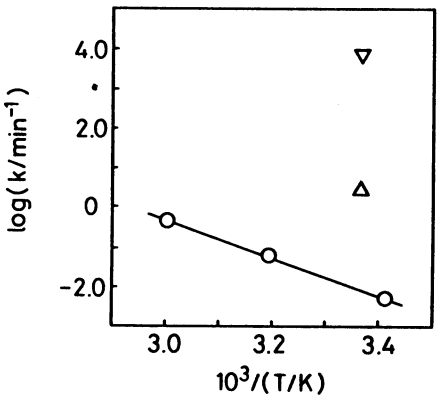

Fig. 4. Arrhenius plots of thermal decoloration.
○:1; △:2; ▽:3.

stabilizes the excited state.[6] Therefore, the absorption peak shifts to longer wavelength.

The Arrhenius plots of the thermal decoloration reactions of 1-3 are shown in Fig. 4. The reaction rates increased about thousand-fold with increasing of n by only one. The strong dependence of the decoloration rate on the bridged methylene length should be explained in terms of molecular strain in the colored species, which was mentioned above. The presence of large molecular strain causes fast thermal decolorations. Also in the interconversion between uncolored cis-stilbenes and colored 4a,4b-dihydrophenanthrenes, very similar observation has been reported; the colored species with a large molecular strain, which possessed a long wavelength absorption, exhibited very fast thermal decoloration.[7]

In summary, we reported new series of photochromic compounds, [2.n]metacyclophan-1-enes. The length of the methylene bridge in the compounds was found to govern both the thermal stability and the peak wavelength of colored species. These findings, we believe, is helpful for the molecular design of new photochromic compounds which show the photochemical electrocyclic reactions.

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