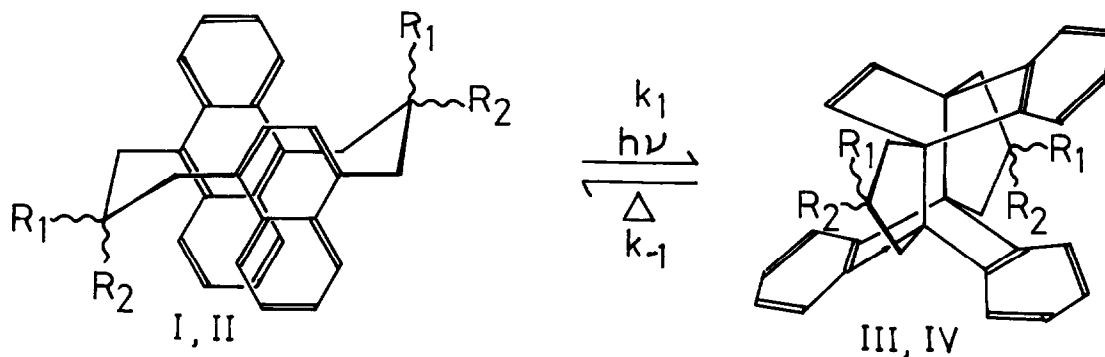


PHOTOISOMERIZATION AND THERMAL REVERSION OF  
 [3.3] (1,4)NAPHTHALENO (9,10)ANTHRACENOPHANE DERIVATIVES

Shigeo Tazuke\* and Hiroyuki Watanabe  
 Research Laboratory of Resources Utilization,  
 Tokyo Institute of Technology,  
 4259 Nagatsuta, Midori-ku, Yokohama, Japan 227

*Summary: All compounds (I and II) photoisomerized to III and IV with  $\phi=0.3$  both in air and nitrogen while thermal reversion of III was 40 times slower than that of IV indicative of strained structure of I as judged by UV and NMR spectroscopy.*

In a series of study on photoreactions of anthracene derivatives<sup>1-3</sup> we are interested in anthracene containing cyclophanes. Since photodimerization of anthracene derivatives brings about large changes in absorption spectrum and refractive index, and furthermore the thermal reversion is a facile reaction, anthracene derivatives could be candidates for reversible image recording materials. A drawback is their sensitivity to photochemical oxygenation via singlet state pathway in competition with photodimerization. The key concept for fast photodimerization is to reduce molecular motions necessary for the bimolecular process. If two chromophores are in fixed positions by means of cyclophane formation, the excited chromophore is destined to react with its partner. However, the mode of reaction depends on the ring size of cyclophane and the aromatic positions which are bridged by alkyl chains.<sup>4</sup> [2.2] (9,10)Anthracenophane is easily photoisomerized to give anthracene photodimer structure. Due to the



I, III:  $R_1 = R_2 = -COOC_2H_5$ , II, IV:  $R_1 = H$ ,  $R_2 = -COO(n-C_4H_9)$

strained ring, the isomerized form gives rise in part to ring opening polymerization on heating and therefore thermal reversion is not clean.<sup>5</sup> [2.2](1,4)-Anthracenophane exists in both anti- and syn-forms, the latter alone being photoactive.<sup>6</sup> Based on these information we examined the title cyclophanes having different substituents on the methylene chain. These [3.3] mixed cyclophanes are expected to be less strained than the [2.2] analogues and the relevant anthracenophanes. Our initial intention of introducing substituents is to ensure good solubility in matrix of image recording system. Now we found strong substituent effects on the rate of reaction.

Absorption spectra of I and II are shown in Fig. 1. Spectra of other alkyl esters of II are identical to that of II. Number of substituents on the 2 and 15 positions seem to influence interchromophore interaction. Determining factors for absorption spectra of cyclophanes are the amount of chromophore overlapping, the distortion of planar aromatic groups, and the separation between two aromatic groups. Since there is no differentiation of syn and anti forms in the present systems, the first factor is probably same for these two compounds. It has been concluded that the non-planarity effect can not explain the large red shift observed for cyclophanes in general.<sup>7,8</sup> The spectral difference between I and II resembles that between anti [2.2](1,4)- and anti [3.3](1,4)naphthalenophanes<sup>9</sup>, indicating that the present spectral difference is attributable to the difference in interchromophore separation. It is unexpected to find such clear influence of substituents when the skeletons of cyclophane are identical.

NMR Spectroscopy (360MHz in CDCl<sub>3</sub>) supports the results of absorption spectroscopy. Although the details are subjects of a separate publication, the protons at the 2 and 3 positions of naphthalene absorbed at  $\delta=5.55$  and 5.93 ppm for I and II, respectively, indicating stronger ring current effect for I than for II as a result of closer approach of anthracene group to naphthalene group in I. On the other hand, such substituent effects almost disappear after photoisomerization as judged by <sup>1</sup>H NMR spectroscopy.

The difference in ring strain is expected to affect photoisomerization and thermal reversion processes. Quantum efficiency( $\phi$ ) of photoisomerization is however nearly identical for I and II as given in Table I.

Table I Photoisomerization and thermal reversion of I and II in anisole

	$\phi$ in N <sub>2</sub>	$\phi$ in air	k <sub>-1</sub> at 130°C(s <sup>-1</sup> )	E <sub>-1</sub> (kJ/mol)
I	0.31	0.32	1.13x10 <sup>-5</sup>	147
II	0.28	0.26	4.88x10 <sup>-4</sup>	111

Irradiation wavelength: 426.5 nm for I, 430 nm for II

Closer approach of chromophores in I results in marginal difference in  $\phi$ . As initially expected, photoisomerization is not disturbed by air. Both I and II are non-fluorescent suggesting photoisomerization as well as non-radiative process are extremely rapid. Contrary to photoisomerization, thermal reversion process of IV is more facile than that of III. The rate constant at 130°C is about 40 times faster for IV than for III. Temperature dependence of the rate constant for IV shown in Fig. 2 is lower than that for III by 36kJ/mol. While photoisomerization is an activation energy free process, the activation energy of thermal reversion process would reflect the energy differences between I and III, and II and IV. Apparently, the strain in I is responsible for large activation energy of the III  $\rightarrow$  I thermal reversion process.

This series of compounds are promising candidates for highly sensitive reversible photochromic materials. Besides optical density measurement, refractive index measurement would be a more sensitive detection method. For example, the difference in molar refractance between I and III is determined as 0.0136 in THF. Since refractance difference of  $10^{-6}$  is measurable, less than 0.1% reaction of 1 M solution of I could be detected. Furthermore, photoisomerization of I in poly(methyl methacrylate) matrix proceeds with  $\phi=0.34$  either above or below the glass transition temperature of matrix resin. This is the manifestation that the present photoisomerization accompanies very little volume change.

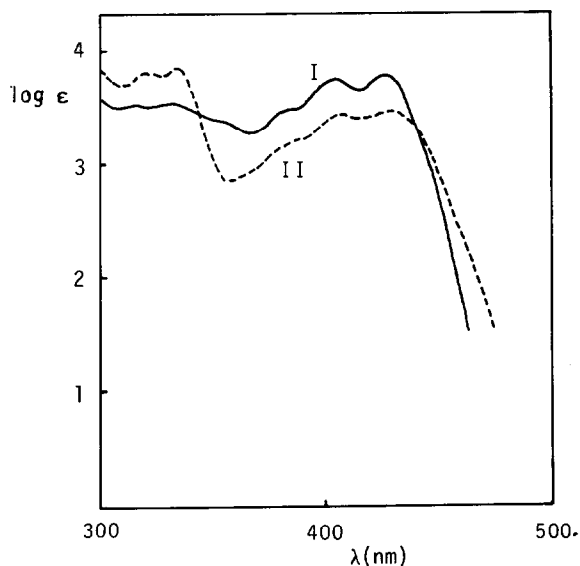


Figure 1. Absorption spectra of the cyclophanes in anisole.

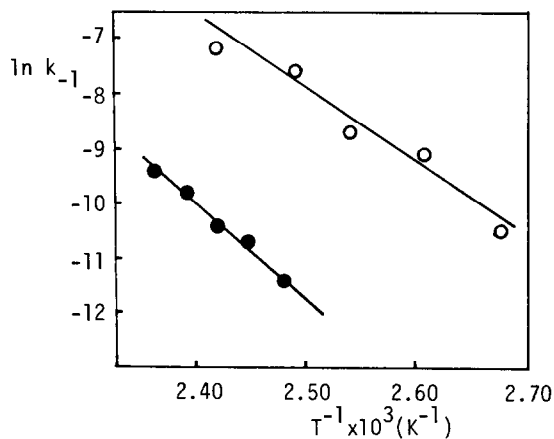
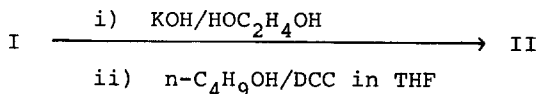


Figure 2. Temperature dependence of thermal reversion process of III (●) and IV (○) in anisole.

## Experimental

Materials: Tetraethyl [3.3] (1,7)naphthaleno(9,10)anthracenophane-2,2,15,15-tetracarboxylate(I) was prepared according to literature<sup>10</sup>.

Di(n-butyl) [3.3] (1,4)naphthaleno(9,10)anthracenophane-2,15-dicarboxylate (II) was derived from I as follows. Crude II was purified on a silica gel column



(elutant:  $\text{CHCl}_3$ ) and then recrystallized twice from benzene/n-hexane. Y=11%. M.p. 182.5-4.5°C. I.R.(KBr)  $1725\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ). NMR: agreed. E.A.(%) Found(Calcd) C 81.89(81.88), H7.20(7.21).

Photoreaction: The sample solution in anisole was prepared in a 1 cm spectroscopic cell so that the absorbance at the irradiation wavelength was about 2. The solution was purged with nitrogen for 25 min for reactions under anaerobic condition. The sample solution was then irradiated with a 500 W Xenon lamp (Ushio) monochromatized by a H-20 monochrometer(Jobin-Yvon). The incident light intensity was determined by an optical power detector(United Detector Tech. Inc., Type-21A) calibrated for a chemical actinometer. Decrease in absorbance was periodically monitored by a Shimadzu UV-200 spectrometer during photoirradiation. Thermal reversion reaction: After completion of photoisomerization, thermal reversion reaction was followed spectroscopically in a thermostatted oil bath. Thermal reversion was shown to follow unimolecular reaction kinetics.

## References:

- 1) S. Tazuke and F. Banba, J. Polym. Sci., Polym. Chem. Ed., 14, 2463(1976)
- 2) S. Tazuke and N. Hayashi, J. Polym. Sci., Polym. Chem. Ed., 16, 2729(1976)
- 3) S. Tazuke and T. Tanabe, Macromolecules, 12, 853(1979)
- 4) Y. Sakata, J. Syn. Org. Chem. Japan, 38(2), 164(1980)
- 5) J. H. Golden, J. Chem. Soc., 3741(1961)
- 6) A. Inada, T. Toyoda, T. Otsubo, and S. Misumi, Tetrahedron Lett., 725(1973)
- 7) N. L. Allinger, J. T. Sprague, and T. Liljefors, J. Am. Chem. Soc., 96, 5100 (1974)
- 8) M. Yoshinaga, T. Otsubo, Y. Sakata, S. Misumi, Bull. Chem. Soc., Japan, 52, 3759(1979)
- 9) A. Iwama, T. Toyoda, M. Yoshida, T. Otsubo, Y. Sakata, and S. Misumi, Bull. Chem. Soc., Japan, 51, 2988(1978)
- 10) T. Shinmyozu, T. Inazu, and T. Yoshino, Chem. Lett., 405(1978)

## Acknowledgements:

The authors are indebted very much to Professor T. Inazu for the detailed information on the synthesis of I under extremely high dilution condition.

{Received in Japan 7 September 1981}