

CYCLOPHANES CONTAINING NITROGEN ATOMS IN THE BRIDGED CHAINS.
 PHOTOCHROMISM OF N,N'-BIS(ARYLSULFONYL)-2,11-DIAZA[3.3]-
 PARACYCLO(9,10)ANTHRACENOPHANES¹⁾

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Diaza[3.3]paracyclo(9,10)anthracenophane derivatives were synthesized under the high dilution conditions. These cyclophanes showed reproducible photochromism both in solution and solid.

Photochromism of layered cyclophanes with anthracene nucleus has been reported by some investigators.²⁻⁵⁾ Cyclophanes containing nitrogen atoms in the bridged chains (azacyclophanes) have been actively studied from the viewpoint of properties of clathrate compounds,⁶⁻⁸⁾ but little attention has been paid to their photochromic behaviors. Azacyclophanes with N-H bond could easily lead to various derivatives and polymers by use of their active hydrogens. Therefore, layered azacyclophanes of photochromic property are useful as starting materials for the syntheses of various photochromic substances.

In this paper we wish to report the syntheses and the photochromic behaviors of layered diazaparacycloanthracenophanes^{9,10)} 1a and 1b (Fig. 1).

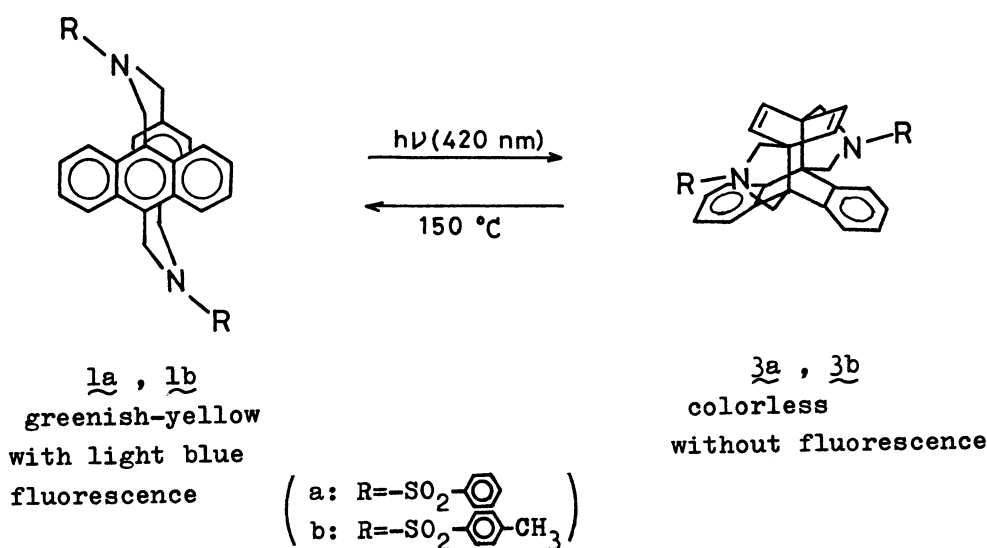


Fig. 1. Structure and photochromism of 1a and 1b.

1a was synthesized by high dilution coupling reaction between 9,10-bis(chloromethyl)anthracene and disodium salt of p-bis(N-phenylsulfonylaminomethyl)benzene (2a) in N,N-dimethylformamide at 90 °C under nitrogen atmosphere.¹¹⁾ Synthesis of 1b was attempted in a similar manner as above, by the use of disodium salt of p-bis(N-p-tolylsulfonylaminomethyl)benzene instead of that of 2a. Crude products were purified by use of a Preparative Liquid Chromatograph Model LC-08 (Japan Analytical Industry Co., Ltd.) and then recrystallized from ethanol. 1a: greenish-yellow crystals (yield 61%), mp 256.0–256.5 °C (decomp), M⁺, 618. 1b: greenish-yellow crystals (yield 55%), M⁺, 646. These cyclophanes gave satisfactory elemental analyses.

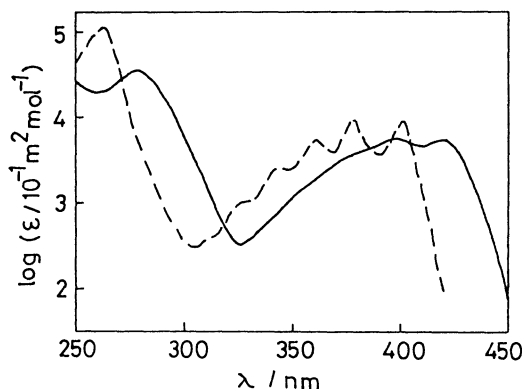


Fig. 2. Electronic spectra of 1a (—) and 9,10-dimethylantracene (---) in chloroform.

In electronic spectra the longest wavelength band of 1a¹²⁾ shows the broadening and red shift compared with that of 9,10-dimethylantracene (Fig. 2). NMR spectrum of 1a¹²⁾ shows the Ha proton as situated just above the faced nucleus by comparison with the NMR spectrum of a reference compound 2a (Fig. 3). These data support the layered structures of 1a and 1b.

1a and 1b showed photochromism¹²⁾ as in Fig. 1. Photo-irradiation of 1a and 1b at 420 nm in chloroform, a KBr pellet, or a Nujol-mull not only resulted in a change of color but also fluorescence with formation of 3a¹³⁾ and 3b. The initial greenish-yellow color became colorless, and the light blue fluorescence was completely lost. However, the phenomenon was reverted when the photo-products (3a and 3b) were heated¹⁴⁾ at 150 °C for 30 min in the dark.

Figure 4 and 5 show the reversible changes of the absorbance of 1b and of

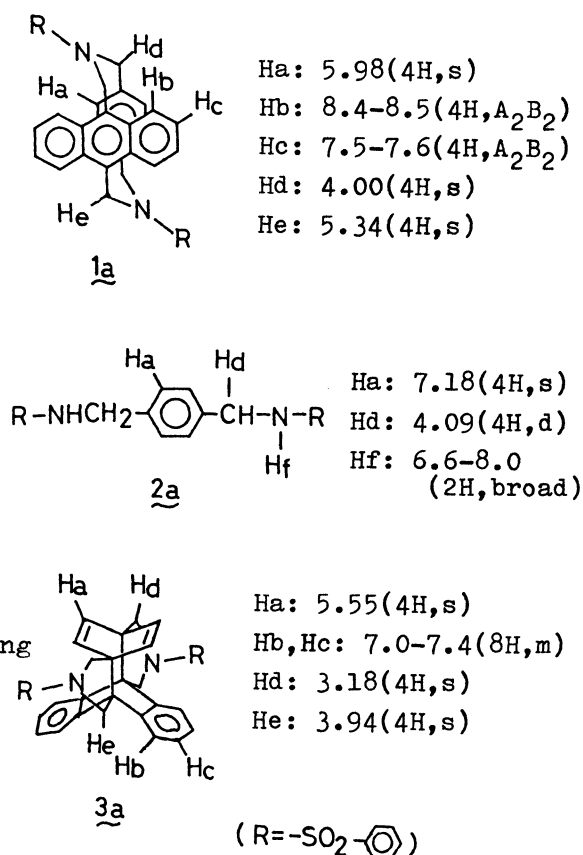


Fig. 3. NMR spectra (δ value) in CDCl₃ or (CD₃)₂CO.

the IR spectra of la, respectively, by repetition of photo-thermal cycles.

The kinetic analysis on the decay curve of lb in Fig. 4 suggested that 3b is formed through a unimolecular reaction process.

The reaction quantum yields were determined to be 0.116, 0.088, and 0.054 in chloroform under nitrogen, air, and oxygen atmosphere, respectively. These yields clearly show that the photo-cyclization was affected by oxygen.

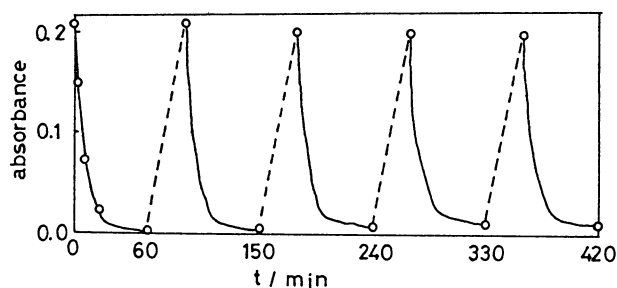


Fig. 4. Reproducibility of absorbance change of lb at 419 nm in chloroform by irradiation(—) at 420 nm under aerobic atmosphere, followed by heating(-->) at 150 °C.

On the other hand, Tazuke and Watanabe reported⁵⁾ that [3.3](1,4)naphthalenoanthracenophanes underwent the photo-cyclization in ca. 0.3 of quantum yields and that they could be applied to reversible image recording materials. Interestingly these naphthalenoanthracenophanes were confirmed to be non-fluorescent and, to show no oxygen concentration dependence in the reaction quantum yield.

The polymer film dispersing la or lb lost its fluorescence when exposed to light.

By use of a pulse laser, for example, fluorescent spot was thermally obtained on this non-fluorescent film. This method is so sensitive that the spots could be easily detected even when the conversion is low on exposure to weak ultraviolet light.

Furthermore, la and lb were found to be stable to prolonged heating compared with [3.3]paracyclo(9,10)anthracenophane derivative⁴⁾ and triple-layered anthracenophane,¹⁵⁾ which gave isomers due to the thermal Diels-Alder reaction.

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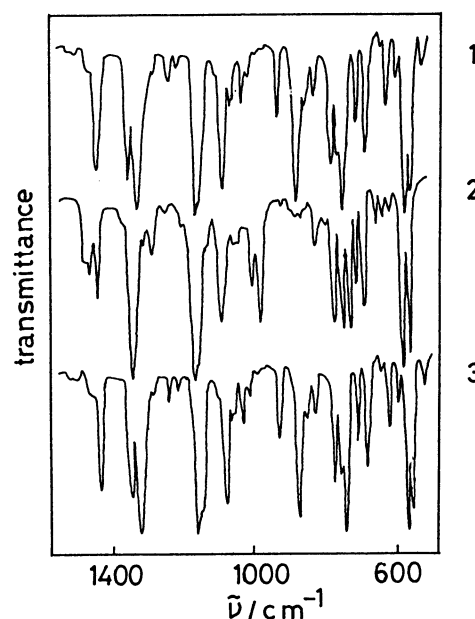


Fig. 5. IR spectral changes of la in a KBr pellet by irradiation at 420 nm, followed by heating at 150 °C.

1: Original compound,
2: irradiated compound,
3: after irr.-heating procedure was repeated 4 times.

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- 9) Diazaparacyclophane and diaza(9,10)anthracenophane were also synthesized according to the same method in 41% and 3% yields, respectively. Details will be reported later.
- 10) Diazaparacycloanthracenophane with N-H bond was easily prepared in good yield from the cyclophane with trifluoroacetyl groups. The chemical modification and photochromism are now under investigation.
- 11) The reaction was carried out by use of the modified synthetic method of non-layered diazapyridinophanes(M.Iwata and H.Kuzuhara, Chem. Lett., 1981, 1749).
- 12) There were few differences between 1a and 1b in their electronic spectra, NMR spectra, and their photochromic behaviors.
- 13) The photo-products of 1a and 1b were found to be the intramolecular-cyclization products 3a and 3b, respectively, on the basis of the NMR spectrum of 3a shown in Fig. 3. 3a (colorless crystals) reverted to 1a during the determination of melting point and the measurement of mass spectrum.
- 14) Chloroform had been previously evaporated in vacuo when the photo-products in chloroform were heated.
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