

Reversible Trans-Cis Photoisomerization of *N,N'*-di(*p*-dimethylaniline)benzald-1,4-diimine

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We confirmed that the **1** compound, *N,N'*-di(*p*-dimethylaniline)benzald-1,4-diimine, with two imine bond showed a reversible trans-cis photoisomerization which was recovered to the original state in 8 minutes through the spectroscopic studies.

key words: Photoisomerization, aromatic imine molecules, absorption, emission

More recently, the photofunctional fluorescent compounds have already been utilized in various fields and the increasing demand for those having superior and multi-functionality is attracting further research interest [1,2]. In addition, photoisomerism of the fluorescent compounds have been contributed in the extension of the photofunctionality [3]. We have been simply and systematically synthesized the aromatic imine conjugated systems showing the multi-function such as the fluorescence tuning as well as the high fluorescence property by the connection of imine bond through one-pot condensation reaction [4]. These aromatic imine conjugated systems have been applied in the studies on the switching and recognizing ability of macrocycle as guest molecules [5]. We found for the first time that the reversible trans-cis photoisomerization of *N,N'*-di(*p*-dimethylaniline)benzald-1,4-diimine (**1**) having two imine bond was appeared by photoirradiation (Fig. 1). This **1** compound was synthesized by the previous method [5-b]. In fact, trans-cis photoisomerization has been almost reported in the azo derivatives with nitrogen-nitrogen double bond and the derivatives with carbon-carbon double bond such as stilbene [3,6]. Therefore, we report here

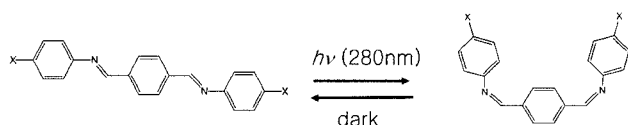


Figure 1. Trans \leftrightarrow cis photoisomerization of **1** compound (X = dimethylamine).

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the spectroscopic results on the trans-cis photoisomerization of **1** compound.

UV-Vis absorption spectra were measured by using a Hitachi U-3300 spectrophotometer. The fluorescence spectra were obtained on a SLM8100 spectrofluorometer (AMINCO, USA) with a Xe-arc lamp light source using 4 nm or 8 nm band pass excitation and emission monochromators.

As reported previously, the absorption peaks of **1** compound showed at 280 nm and 436 nm, respectively, having the long absorption tailing until 550 nm in chloroform. As shown in Fig. 2, the absorption change was appeared when the photoirradiation (use of 280 nm UV filter and 450 W Xenon lamp) was tried in the chloroform solution of **1** compound (1.00×10^{-5} mol dm⁻³). Herein, the emission quartz cell (1 cm \times 1 cm) was used as the sample vessel and the homogeneous solution was kept by stirring for the photoisomerization. In addition, in order to eliminate the thermal effect of isomerization, the cooling system was equipped in front of the Xenon lamp.

Before photo-irradiation, as a trans-isomer, the absorption peaks were appeared at 280 nm and 436 nm, respectively, but a trans-isomer was changed into a cis-isomer by the photo-

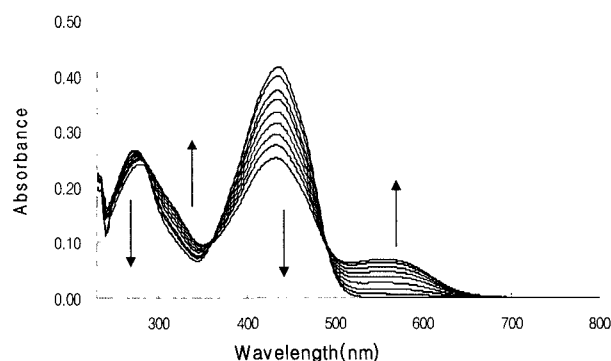


Figure 2. Electronic absorption spectra on the trans \rightarrow cis photoisomerization of **1** compound in chloroform; the interval time of photoirradiation was 50 sec.

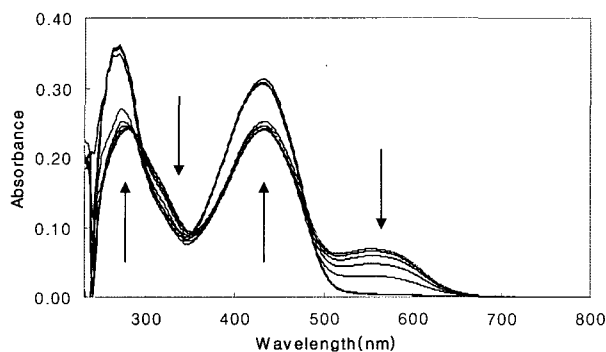


Figure 3. Electronic absorption spectra on the cis→trans photoisomerization of **1** compound in chloroform; the interval time of absorption measurement was 65 sec.

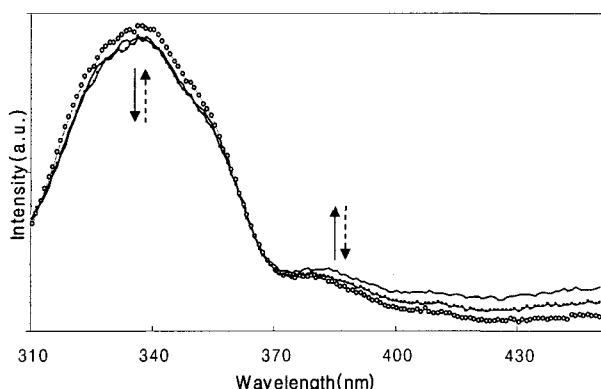


Figure 4. Emission spectra on the trans ↔ cis photoisomerization of **1** compound at $\lambda_{\text{ex}} = 287$ nm in chloroform; the circle mark of spectra indicates the spectrum of initial state (non-irradiation) and the interval time of spectra was 2.5 min.

irradiation [7]. In other words, the absorption peaks of 280 nm and 436 nm were decreased while the new absorption peak was appeared at 550 nm with the isosbestic points of 290 nm, 360 nm and 490 nm by the cumulative times of photo-irradiation. Trans-cis photoisomerization was saturated in 8 minutes and the interval time of photo-irradiation was 50 sec. Meanwhile, as shown in Fig. 3, when the irradiated sample was standed out in the dark room at 25°C, cis-trans isomerization was appeared, and it was recovered to the original state in 8 minutes and the interval time of absorption measurement was 65 sec.

As shown in Fig. 4, the fluorescence spectrum of **1** compound (1.00×10^{-5} mol dm⁻³) was measured in chloroform at 25°C.

The fluorescence peaks were appeared at 340 nm and 380 nm, respectively, by the excitation wavelength 287 nm. Trans-cis photoisomerization was also appeared with the isosbestic point of 365 nm although its change was not remarked. Its photoisomerization was also saturated in 8

minutes and the interval time of spectra was 2.5 min. From the above results, we found the interesting reversible trans↔cis photoisomerization in the aromatic imine molecule having the terminal group of the electron-donating dimethylamine and the longer aromatic structure. As the more advanced study, we have an experiment on the molecular recognition of the imine derivatives in the macrocycle host by the photoisomerization.

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- In the case of the aromatic imine conjugated systems having the terminal groups such as methyl, methoxy, and halogen etc, the spectroscopic behavior of their photoisomerization was not clear.