Primary Processes in Photochromic Reaction of 4-Diethylamino-4'-dimethylamino-2-hydroxychalcone in Toluene

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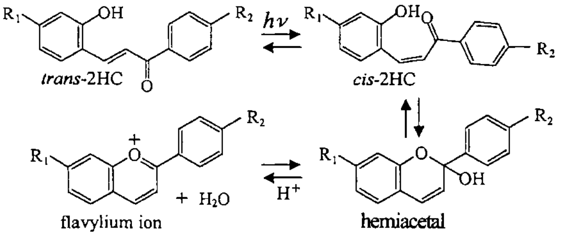
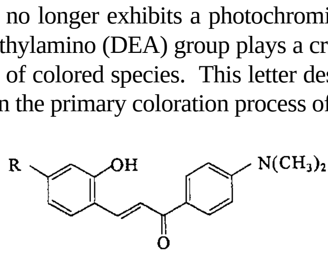
A photochromic behavior was found for *trans*-4-diethylamino-4'-dimethylamino-2-hydroxychalcone in toluene, and colored species undergoing dark reaction to regenerate *trans*-isomer may be ascribed to *cis*-isomer with the lifetime of 77 min at room temperature. It is demonstrated that a *trans*→*cis* isomerization in the lowest triplet state is significantly responsible for the primary process of the coloration.

Flavonoids are one of exclusive components in large bioorganic molecules, and are responsible for the color of flowers and fruits. Anthocyanins are known as the most important flavonoid pigments in nature, and chalcones make a class of flavonoids. It is characteristic that flavonoids can exist in both colored and colorless forms.[1] Indeed, various 2-hydroxychalcones (2HCs) in weak acid solution exhibit photochromic reactions involving flavylium cation with anthocyanin skeleton as colored species.[2–5] A clean photochromic system without pollution may be brought about by combining coloration of 2HC with discoloration of flavylium ion in the dark. However, primary photochemical process leading to the formation of colored species remains equivocal.



A photochromic behavior was found for *trans*-4-diethylamino-4'-dimethylamino-2-hydroxychalcone (**1a**) just dissolved in organic solvents such as toluene. Such a simple photochromic system is very suitable to elucidate the coloration of various 2HCs. Since 4'-dimethylamino-2-hydroxychalcone (**1b**) in toluene no longer exhibits a photochromic behavior, it is implied that diethylamino (DEA) group plays a crucial role on the destabilization of colored species. This letter describes a laser photolytic study on the primary coloration process of **1a** in toluene.



1a : R = $N(C_2H_5)_2$
1b : R = H

Figure 1 shows progressive absorption spectral changes induced by UV photolysis of **1a** and **1b** in air-saturated toluene, respectively. In a 10-Hz YAG laser pulse (355 nm) excitation of **1b**, the absorption band (λ_{max} = 370 nm) exhibits a gradual redshift with an isosbestic point at 391 nm, until it is replaced by the absorption band (λ_{max} = 382 nm).[6] The 382-nm absorption band exhibits no spectral change in the dark, but the 370-nm absorption band is generated again by the >450-nm steady-light illumination of an absorption tail. Therefore, the 382-nm absorption band may be ascribed to a photostationary state (PSS) attained. Collected PSS solution (110 mL) was distilled by the use of a vacuum line to evacuate toluene, and remained crystals were dissolved in 1-mL DMSO-d_6. Observed NMR signals (δ = 6.67 and 7.09 ppm) with J = 13 Hz may be ascribed to *cis* ethylenic protons.[7] It is thus demonstrated that *cis*-isomer of **1b** is responsible for a thermally stable colored species.

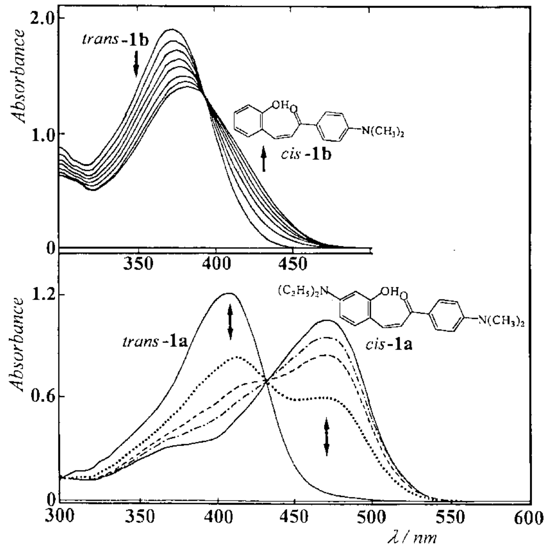


Figure 1. Absorption spectral changes caused by 10-Hz YAG laser pulse (355 nm) excitation of **1a** (0.038 mM) and **1b** (0.14 mM) in air-saturated toluene at 298 K. Spectra of photolysed solutions were recorded after each 200 laser shots.

As is distinct from no *cis*→*trans* reaction of **1b** in the dark, the absorption band (λ_{max} = 472 nm) increases in intensity at the expense of that (λ_{max} = 408 nm) of **1a**, and vice versa in the dark. Namely, almost reversible spectral changes take place with an isosbestic point at 432 nm. From single exponential fitting against both the recovery of the 408-nm absorption and the decay of the 472-nm absorption, lifetime of colored species was determined to be 77 min at 298 K. It is reasonable to assume a *trans*→*cis* photoisomerization of **1a** in analogy of **1b**. Namely, *cis*-isomer of **1a** may be the colored species with the absorption band (λ_{max} = 472 nm). From the Arrhenius plots of dark reaction rates of *cis*-**1a**, apparent activation energy was estimated to be 64 kJ mol^{-1}. This value is much less than ca. 200 kJ mol^{-1} (barrier height for *cis*→*trans* isomerization of stilbene in the ground state).[8] Such a low barrier height implies a destabilization of *cis*-**1a** as well as a stabilization of transition state. Both the introduction of DEA group and the steric repulsion of bulky substituents on ethylenic molecular frame may be responsible for the destabilization. It is probable that the stabilization due to the intramolecular (–OH···O=C<) H-bonding interaction is far less than the destabilization.

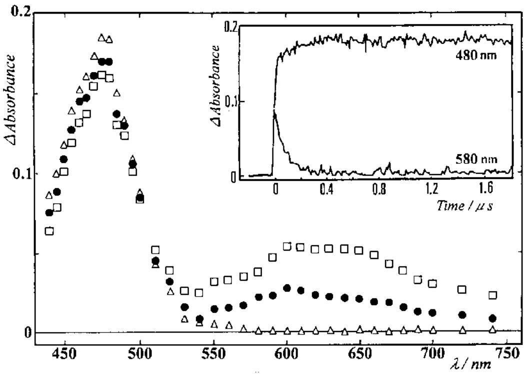


Figure 2. Time-resolved absorption spectra depicted after smoothing transient absorption signals, which was obtained in a 355-nm YAG laser pulse excitation of **1a** (0.047 mM) in air-saturated toluene. Times after laser pulse excitation are 55 ns (□), 165 ns (●), and 600 ns (△). Fresh sample solution was used for each laser shot.

In order to elucidate the primary process to generate *cis*-**1a**, transient absorption spectra were measured by a nanosecond UV laser pulse excitation of *trans*-**1a**. Figure 2 shows the time-resolved absorption spectra of *trans*-**1a** in aerated toluene at room temperature. Transient absorption band (λ_{max} = 475 nm) is generated immediately and slowly after laser pulse excitation. The band is similar to the absorption spectrum of *cis*-**1a**. Rise-time of growing transient absorption was determined to be 94 ns in air-saturated solution, while those were determined to be 27 and 520 ns in O_2- and N_2-saturated solutions, respectively. They are in agreement with the lifetimes of the long wavelength band (λ_{max} = 610 nm). The oxygen-quenching rate constant was estimated to be 3.6×10^9 $M^{-1}s^{-1}$, which is reasonable for the rate constant of triplet quenching by molecular oxygen. These facts strongly suggest that *cis*-**1a** in the ground state (S_0) is generated from a triplet species.

In the transient absorption measurements of 2-(3,3-dimethyl-1-butenyl)anthracene in benzene at 296 K, Karatsu et al.[9] reported that an initial absorption spectrum (λ_{max} = 440 nm) was replaced by similar absorption spectrum (λ_{max} = 445 nm) with the time constant of 480 ns, and proposed a relatively slow *cis*→*trans* isomerization along a triplet energy surface. In this study, on the other hand, no evidence implying two kinds of triplet species was obtained both in spectra and kinetics of transient absorption at room temperature. Consequently, a rapid *trans*→*cis* isomerization in the triplet manifold is demonstrated. The most probable candidate for the triplet species may be *cis*-**1a** in the lowest triplet state (T_1). In order to clarify this argument, transient absorption measurements in visible region were carried out at low temperatures. Figure 3 shows the 620-nm transient absorption signals of *trans*-**1a** in degassed toluene solution at 191, 211, and 238 K. Exponential decays of 2.6 μs (238 K), 5.9 μs (211 K), and 17 μs (191 K) were observed. Remarkable is that a short-lived component is detected at 191 K in addition to the long-lived component. This short-lived species with the lifetime of ca.100 ns exhibits a relatively intense transient absorption spectrum (λ_{max} = 580 and 670 nm). Since **1a** possesses bulky substituents on ethylenic frame, the *trans*→*cis* isomerization of **1a** is strongly affected by solvent viscosity. Freezing point of toluene is 180 K. It is thus reasonable that the isomerization of **1a** in the triplet manifold extensively slows down at 191 K to be detectable by a nanosecond laser-flash photolysis. Assuming that a perpendicular triplet is too short-lived to be detected, it is reasonable that the respective short- and long-lived species are ascribed to *trans*- and *cis*-triplets.

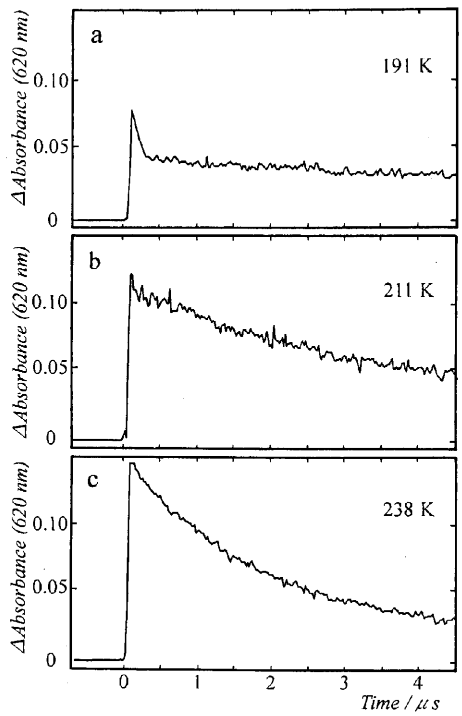


Figure 3. The 620-nm transient absorption signals obtained in a YAG laser pulse excitation of **1a** (0.057 mM) in degassed toluene at 191 (a), 211 (b), and 238 K (c).

From the aforementioned tentative assignments, observed transient species immediately after laser pulse excitation at room and low temperatures are *cis*-triplet and *trans*-triplet of **1a**. A significant instantaneous absorption band (λ_{max} = 475 nm) at room temperature is very similar to the absorption spectrum of *cis*-**1a** (S_0). In contrast to this, no appreciable one was observed at 191 K. The fact implies that the *trans*→*cis* isomerization in the singlet manifold is not essential for **1a**. Consequently, the significant 475-nm absorption band at room temperature may be mainly ascribed to *cis*-triplet rather than cis-**1a** (S_0). It is concluded that the *trans*→*cis* isomerization in the triplet manifold is significant for **1a**.

References and Notes

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6 The isosbestic point at 391 nm is lost by further laser pulse excitation, probably due to photochemical reaction of colored species not to regeneration of *trans*-**1b**.

7 NMR signals (δ = 7.89 and 8.02 ppm) with *J* = 16 Hz may be ascribed to *trans* ethylenic protons. More than 60% *trans*→*cis* conversion yield was estimated.

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