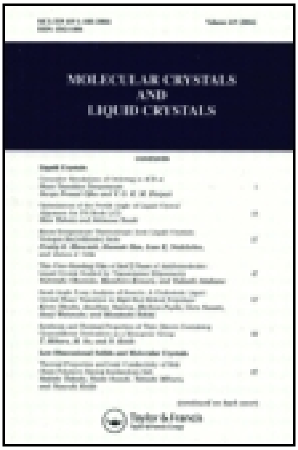

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Photochromic Reaction of Microcrystalline 6-Nitroindolinospiropyran Studied by Femtosecond Diffuse Reflectance Spectroscopy

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Transient absorption spectra of 1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (6-nitro-BIPS) microcrystalline powder were measured by femtosecond diffuse reflectance spectroscopy and compared with those in the benzene solution and in a PMMA film. A very similar photochromic reaction occurs even in the crystal, although the structure of the generated photo-colored form in crystalline phase is not as planar as that of a stable form (trans-planar merocyanine) in solution. Photocoloration and the following thermal back reaction dynamics are considered in terms of free volume of the matrix and limited motion of the molecule.

Keywords: excited state dynamics; photochromic reaction; organic crystal; spiropyran; time-resolved diffuse reflectance spectroscopy

INTRODUCTION

Spiropyrans belong to the most important class of organic photochromic compounds and their photochemical reactions have been intensively studied[1,2]. Upon UV irradiation, the bond between the spiro carbon and the

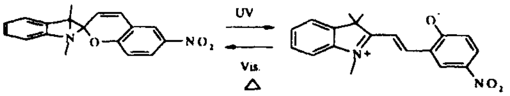

FIGURE 1 Structures of 6-nitro BIPS (left) and merocyanine form (right).

oxygen undergoes fission, followed by isomerization to stable planar merocyanine forms, as illustrated in Figure 1. The photochromic behavior has been investigated throughly in solutions and rigid matrices such as polymer films, while not in crystal. The photochromic reaction in crystalline phase should differ from that in solution, because of limited freedom in geometrical structural change, namely, hindered rotational and translational motions of molecules embedded in the crystal lattice[3]. Indeed, crystalline 6-nitro BIPS does not show photocoloration upon steady UV irradiation. In the present work, to investigate the crystalline environmental effects on the photochromic reaction in detail, we have measured transient absorption spectra of 6-nitro BIPS microcrystalline powder using femtosecond diffuse reflectance spectroscopy. It is clearly demonstrated that C_{spiro}-O bond cleavage upon light irradiation takes place even in crystalline phase. The photochemical dymanics is compared to that in benzene solution and in PMMA film.

EXPERIMENTAL

The details of femtosecond diffuse reflectance spectroscopic system have been reported elsewhere[4]. The excitation laser pulse is the second harmonic (390 nm) of an amplified femtosecond laser pulse (780 nm, 3~4 mJ / pulse, 170 fs, 10 Hz), and a femtosecond white-light as a probe pulse was generated by focusing the amplified laser pulse into water. Transient absorption is given by $\%absorption = 100 \times (1 - R / R_0)$, where R and R_0 represent the intensity of the diffuse reflected light of the probe pulse with and without excitation, respectively. The temporal resolution of transient absorption measurement by this spectroscopic system is less than a few ps[4].

6-Nitro-BIPS (Aldrich) was recrystallized from hexane and crushed to powder with a motar. The powder sample was contained in a quartz cell with 1 mm optical path length and degassed with a vacuum pump. PMMA films doped with 6-nitro BIPS were prepared by casting the benzene solution ([6-nitro BIPS] = 1.1 wt%, [PMMA] = 22 wt%) onto a glass plate. The transient absorption spectra of the solution and the PMMA film were measured by the conventional transmittance-mode spectroscopic system[5].

RESULTS AND DISCUSSION

The transient absorption spectra of 6-nitro-BIPS microcrystalline powder after excitation with a femtosecond 390 nm laser pulse (0.55 mJ/cm^2) at room temperature are shown in Figure 2. After a broad spectrum with the maximum around 530 nm, a new peak at 630 nm grows up to 6 ns. The transient absorption at 77 K, on the other hand, did not show any appreciable change at delay times from 0 to 6 ns. The spectral shape was very similar to that immediately after excitation at room temperature. Therefore, the band around 530 nm will be ascribed to the excited state of the closed form. The absorption band with its peak at 630 nm can be assigned to be a ring-opened form of 6-nitro BIPS, which is based on a spectral similarity with that of the photomerocyanine in solution.

The temporal profiles of absorption at 630 nm and 525 nm are shown in Figure 3(a). These results indicate that photo-induced C_{spiro}-O bond cleavage occurs with a rate of 2 ns even in crystalline phase at room

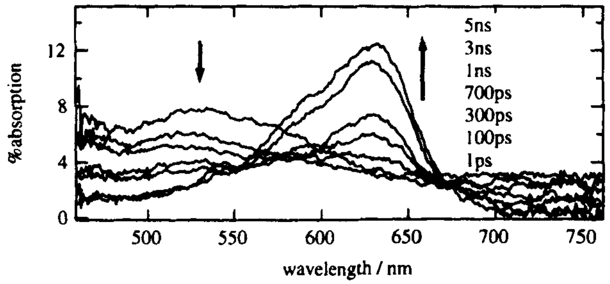

FIGURE 2 Transient absorption spectra after exciting 6-nitro BIPS microcrystalline powder with a 390 nm femtosecond laser pulse (0.55 mJ/cm^2) at room temperature.

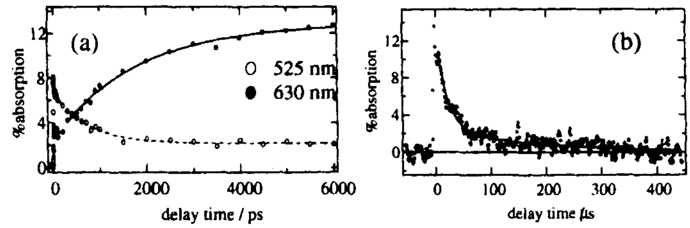

FIGURE 3 Temporal profiles of transient absorption of 6-nitro BIPS microcrystalline powder monitored at 525 nm and 630 nm in the ps to ns time region (a), and that at 633 nm in a μs time region (b).

temperature. The decay of excited state and the rise of the merocyanine are not correlated directly with each other.

The decay kinetics of the generated ring-opened form was examined by measuring the transient absorption at 633 nm in a μs time region, where He-Ne laser as a probe light and a high-speed Si pin-photodiode (THORLABS 201/579-7227) were applied. The temporal profile shown in Figure 3(b) has a main decay component with a rate of 20 μs and an additional slow one of 150 μs.

The transient absorption spectra of 6-nitro BIPS in PMMA film (5 wt%) and in benzene solution (5×10^{-2} mol/l) were also measured. The transient absorption spectra of the PMMA film are shown in Figure 4. The

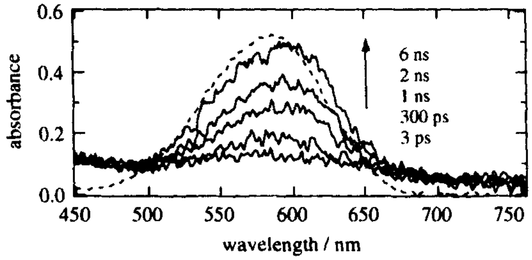

FIGURE 4 Transient absorption spectra (—) of a PMMA film doped with 6-nitro BIPS (5 wt%) after excitation with a 390 nm femtosecond laser pulse, and the absorption spectrum at a few sec. after excitation (- - -). Excitation intensity is 4 mJ/cm^2.

absorption spectra in the ps to ns time region are close to those in benzene solution, and the result on the benzene solution is in good agreement with the picosecond transient absorption experiment of 6-nitro BIPS in benzene by S. A. Krysanov *et al*[6]. Therefore, the absorption band around 590 nm in Figure 4 can be assigned to be the absorption of a merocyanine isomer. It grows with the time constant of about 2 ns, and the absorption spectrum at 5 ns is slightly red-shifted compared to the absorption spectrum of the long-lived merocyanine isomer. It is worth noting that the rise of about 2 ns is much slower than in solution, which will be due to the fact that molecules in the PMMA film have some higher energy barrier to rotate and to translate compared with those in solution.

The characteristics of the absorption spectra and the rise and decay profiles of the ring-opened isomers in crystalline phase, PMMA film, and benzene solution are summerized in Table 1. It is found that the photo-induced ring-opening reaction depends on the flexibility of the environment. The bond cleavage in the microcrystal is slower than in solution, and the thermal ring-closure is much faster than in PMMA film and also in solution. In crystalline phase, the generated ring-opened form after the C_{spiro}-O bond cleavage should keep a similar structure to that of the spiro form due to restricted conformational changes in the crystalline lattice, leading to a rapid thermal decay to the original spiro form.

This non-planar structure in crystal is consistent with its absorption peak which is red-shifted compared to the benzene solution and the PMMA film. A photocolored form of 6-nitro BIPS having the absorption peak at 630 nm was reported by T. Bercovici *et al.*[7] when a

TABLE 1 Characteristics of absorption spectra and their kinetics of ring-opened isomers in crystalline phase, PMMA film, and benzene solution.

	peak (nm)	rise time constant	decay time constant
crystal	630	2 ns	20 μs, 150 μs
PMMA	590	2 ns	several ten min. [8]
benzene	585	100 ps	30 s (toluene) [9]

rigid methylcyclohexane/decalin solution was irradiated by UV light at −160 °C. They examined temperature dependence of steady-state photomerocyanine absorption spectra in detail. The peak wavelength shifted to 560 nm by heating the sample to −140 °C, but the peak did not back to 630 nm by cooling again to −160 °C. On the other hand, a reversible thermochromic behavior was found for the sample in the temperature range from −120 °C to 0 °C. Furthermore, it is worth noting that the absorption band with the peak at 630 nm was not observed in the femtosecond transient absorption spectra of the benzene solution and the PMMA film at any delay times at room temperature. These experimental results indicate that the ring-opened form isomer with the absorption peak at 630 nm is very unstable and identified as an intermediate of the photochromic reaction only in very low-temperature matrices. This unstable conformer is now observed as a transient species in the crystalline phase at room temperature.

In conclusion, it is directly confirmed that the photochromic reaction of 6-nitro BIPS occurs even in crystalline phase. Since a very rapid thermal decay of the generated ring-opened form, the crystal does not show photocoloration with steady UV light irradiation.

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