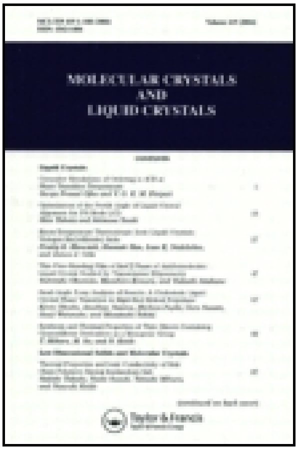

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Transient Absorption Spectroscopy of a Photochromic Dinitrobenzylpyridine

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Transient Absorption Spectroscopy of a Photochromic Dinitrobenzylpyridine

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Transient absorption of 2-(2,4-dinitrobenzyl)pyridine (α-DNBP) has been measured by a nanosecond laser photolysis to elucidate the dynamical behavior of a photoinduced intramolecular proton transfer (PIPT). On UV light photolysis, α-DNBP changes from a colorless to a dark blue form. The dark blue form consists of the OH, OH^- and NH forms whose absorption bands are located at ~400, ~490 and ~570 nm, respectively. We found an additional absorption band located at 660 nm. From the observed transient behavior of the band, we assign this band to be the lowest absorption band of the OH form. The PIPT reaction pathways and their time constants of α-DNBP also have been determined.

Keywords: photoinduced intramolecular proton transfer; α-DNBP; nanosecond laser photolysis

INTRODUCTION

A ptotochromic compound, 2-(2,4-dinitrobenzyl)pyridine (α-DNBP), shows a structure change accompanied with a photoinduced intramolecular proton transfer (PIPT). The molecular structure as well as photochemical reactions of α-DNBP are shown in Fig. 1. On irradiation of UV light, α-DNBP changes from a colorless (CH_2 form) form to a dark blue from. The dark blue form consists of three forms, an N-H quinoid tautomer (NH form), an aci-nitro isomer (OH form) and an aci-nitro anion (OH^- form) [1,2]. The absorption bands of the OH, OH^- and NH forms are located at ~400, ~490 and ~570 nm, respectively. Recently, Shinohara et al. found a new absorption band located below the lowest absorption band of the NH form (~650 nm) by use of α-DNBP dispersed in polymer films as a sample [3]. They concluded that this absorption band is the lowest absorption band of the OH form, judging from the experimental results of the thermochromic reaction of the dark blue form and from the theoretical results of the molecular orbital calculations.

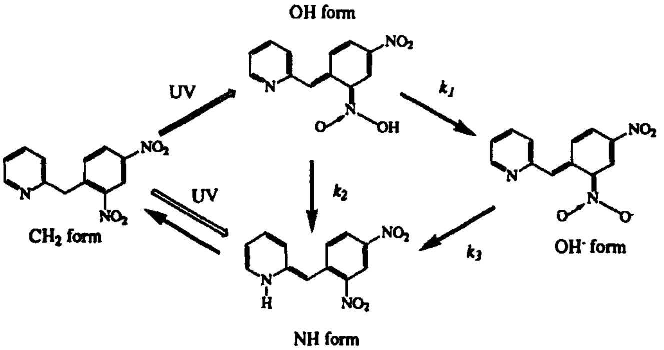

Figure 1: Molecular structure and chemical reactions of α-DNBP.

However, no absorption band has been observed above ~600 nm in the transient absorption measurement of α-DNBP solution so far [1,2]. In order to confirm whether or not the lowest absorption band of the OH form exists above ~600 nm and to elucidate the PIPT reaction of α-DNBP, we have measured the transient absorption of α-DNBP by a nanosecond laser photolysis in wide wavelength range from 380 to 700 nm.

EXPERIMENTAL

Commercial powders of α-DNBP were dissolved in ethanol with a concentration of 1×10^{-3} M without further purification. The concentration of α-DNBP was chosen relatively high to get strong absorbance at the pump wavelength (355 nm). During the measurement, the solution of α- DNBP was circulated by a peristaltic pump through a flow quartz cell with a 1 mm thickness.

The third harmonic (355 nm) of an Nd:YAG laser with a pulse duration of 3 ns was used as an excitation laser source for the transient absorption measurement. A tungsten lamp was used as a probing light source. The excitation and probe beams were impinged on the same sample position. The probe beam passed through the sample was focused on the entrance slit of a single monochromator and detected by a photomultiplier and a digital sampling oscillograph. The laser and oscillograph were synchronized by a digital pulse generator. The overall time resolution of the system was about 25 ns.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra (a) and the differential absorption spectra (b) of the dark blue form of α-DNBP dispersed in a poly(methylmethacrylate) film at various temperature. The differential absorption spectra were obtained by subtracting the absorption intensity at 100 K from those at 140, 160 and 200 K. Each absorption spectrum consists of the absorption bands due to the OH, OH^- and NH forms, which are located at 400, 490 and 570 nm, respectively. As temperature rises, the intensity of the absorption band of the NH form increases and that of the OH or OH$^-$ form decreases. We found an additional absorption band at the lower energy side of the absorption band of the NH from. As shown in Fig. 2(b), the thermal characteristics of this band is quite similar to that of the OH form located at 400 nm. This strongly suggests that the additional absorption band corresponds to the lowest absorption band of the OH form.

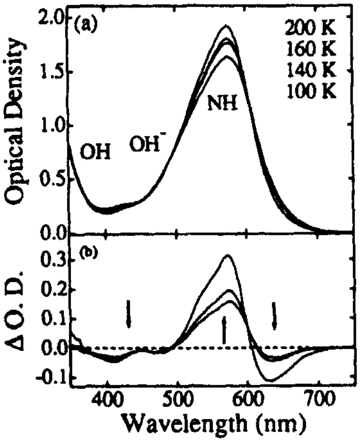

Figure 2: Absorption spectra (a) and absorption change (b) of the dark blue form of α-DNBP dispersed in a poly(methylmethacrylate) film at various temperature.

The time evolution of the transient absorption at given probe wavelengths is shown in Fig. 3. The probing wavelengths of the spectra a), b) and c) are 400, 490 and 570 nm, which almost equal to the absorption peaks of the OH, OH$^-$ and NH forms, respectively. The probing wavelength of the spectrum d) is 660 nm, which corresponds to the absorption peak of the additional absorption band.

The spectrum a) rises rapidly in time less than the time resolution of the instrumental response (25 ns), and then decreases

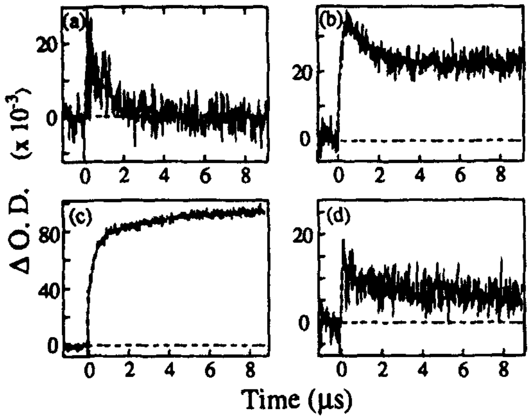

Figure 3: Transient absorption spectra of α-DNBP at given wavelengths of 400 (a), 490 (b), 570 (c) and 660 nm(d).

exponentially with a time constant of 1.4 μs. The spectrum b) has two rising components; one increases like the spectrum a) and the other does with a time constant of 0.9 μs. Then the spectrum decays within a few μs and becomes a plateau. The absorption band of the NH form overlaps with that of the OH form in the spectral region of 490 nm and the long-lived component, which gives the plateau is due to the NH form. In the spectrum c), three rising components were observed with time constants of ≤25 ns, 1.0 μs and 3.8 μs. In the spectrum d), the fast rise within the time resolution of the instrumental response and the fast decay with a time constant of 1.4 μs were observed. Temporal behavior of the spectrum d) is quite similar to that of the spectrum a), strongly indicating that the spectrum d) is due to the OH form. From this, we conclude that the lowest absorption band of the OH form is located at ~660 nm as pointed out by Shinohara et al. [3].

The broken curve in each spectrum in Fig. 3 is the best-fit obtained by assuming the reaction pathways as shown in Fig. 1. From the fit, the time constants of $1/k_1$, $1/k_2$ and $1/k_3$ were determined to be 0.9, 3.8 and 1.0 μs, respectively. The values of $1/k_1$ and $1/k_3$ are much faster than those obtained by Kimura et al. [2]. The difference between their results and ours probably come from use of the different kind of the solvent.

CONCLUSION

We have measured the transient absorption of α- DNBP by the nanosecond laser photolysis, in order to elucidate the dynamical behavior of the PIPT reaction. On UV light photolysis, α-DNBP changes from the colorless to the dark blue form. The dark blue form consists of the OH, OH^- and NH forms, whose absorption bands are located at ~400, ~490 and ~570 nm, respectively. We found the additional absorption band located at 660 nm in the transient absorption measurement for the first time. From the transient behavior of the band, this band is considered to be the lowest absorption band of the OH form. The PIPT reaction pathways and their time constants of α-DNBP also have been determined.

Acknowledgments

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References

[1] E. Klemm et al., *Chem. Phys. Lett.*, **55**, 113 (1978).
[2] H. Kimura et al., *J. Mol. Struct.*, **293**, 1 (1993).
[3] S. Shinohara et al., *J. Phys. Soc. Jpn.*, **68**, 1725 (1999).