

Photoinduced Intramolecular Proton Transfer in 2- and 4-(2,4-dinitrobenzyl)pyridine

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Abstract

Photoinduced absorption changes and thermal bleaching of the absorption were measured at different temperatures in 2- and 4-(2,4-dinitrobenzyl)pyridine (α - and γ -DNBP) dispersed in polymer films in order to elucidate the mechanism of the photoinduced intramolecular proton transfer (PIPT) in DNBP. Three photoinduced absorption bands which correspond to the NH, anion and OH forms emerge in the visible light region after UV light irradiation. The efficiency of the PIPT to the NH form in γ -DNBP is much lower than that in α -DNBP. The thermal conversion from the OH to the anion/NH forms in γ -DNBP is faster, while the conversion from the NH to the stable form is slower than that in α -DNBP. Based on molecular orbital calculations and the potential energy diagram of the PIPT reaction by taking into account the different distances of the reaction pathway between α - and γ -DNBP, the observed differences of the PIPT reaction between α - and γ -DNBP are discussed.

keywords: photoinduced intramolecular proton transfer; dinitrobenzyl-pyridine; photochromic compounds

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1. Introduction

Organic photochromic compounds have attracted much interest because of their potentially superior properties for applications such as rewritable photomemory and optical storage [1]. Because a photoinduced intramolecular proton transfer (PIPT) does not require large molecular rearrangement, the reaction time of PIPT is expected to be very fast and the reaction can take place for many cycles even in solid state [2,3]. As a result of this property, photochromic compounds accompanied by PIPT might be promising candidates for fast photomemory and molecular protonic devices.

2-(2,4-dinitrobenzyl)pyridine (α -DNBP) and its geometrical isomer, 4-(2,4-dinitrobenzyl)pyridine (γ -DNBP) are such compounds that show a structural change accompanied by PIPT as shown in Fig. 1. On irradiation with UV light, DNBP changes from colorless (CH_2 form) to dark blue. The dark blue form consists of three photoproducts, an N-H quinoid tautomer (NH form), an aci-nitro acid isomer (OH form) and an aci-nitro anion (anion form) [4-8]. Both the NH and OH forms are created directly from the CH_2 form upon UV irradiation and the OH form thermally relaxes to the NH form partially via the anion form, followed by relaxation to the CH_2 form. On the other hand, in solid state, α -DNBP effectively shows PIPT, while γ -DNBP does not [9,10]. The discrepancy of the PIPT reaction between α - and γ -DNBP might come from the different distance of the PIPT pathway and the difference in steric hindrance between DNBP molecules. In order to elucidate the PIPT reaction of DNBP, photoinduced absorption changes and thermal bleaching of the absorption have been measured at different temperatures in α - and γ -DNBP dispersed in polymer films.

2. Experimental

Commercial powders of α - and γ -DNBP were purified from acetone solution, and then dispersed in poly(methylmethacrylate) (PMMA) films with a concentration of 0.1 M (1M=1mol/dm³) [11]. The typical thickness of the films was 100 μ m. The samples were kept at low temperature in a temperature-controlled cryostat. The UV light irradiation of the samples was performed with the 365 nm line from a high pressure mercury lamp. The photoinduced absorption change and thermal bleaching of the absorption were measured by a single grating monochromator with a CCD detector cooled by liquid nitrogen.

3. Results and discussion

Figure 2 shows the absorption spectra of α - and γ -DNBP dispersed in PMMA films measured after UV light irradiation at various temperatures. The absorption intensity in the visible light region increases with the UV irradiation time. Each absorption spectrum is decomposed into three absorption bands with a Gaussian shape, which correspond to the NH, anion and OH forms as shown in broken lines [6-8]. The absorption intensity of the NH form in γ -DNBP is about one order of magnitude smaller than that in α -DNBP, while that of the OH form is almost of the same order of magnitude in both α - and γ -DNBP. This result shows that the efficiency of the PIPT reaction leading to the NH form in γ -DNBP is much lower than that in α -DNBP.

Figure 3 shows the thermal bleaching of the absorption spectra in the dark blue form at various temperatures. The dark blue form is thermally stable for long time at low temperature, and becomes unstable at high temperature. To clarify the thermal conversion among the photoproducts, we estimated each absorption intensity of the NH, anion and OH forms at a given time. The temporal behavior of the thermal bleaching in

photochromic compounds dispersed in polymer films is given by $\ln(I_t/I_0) = -\alpha(t/t_0)^{0.5}$, where t and I_t are the time and the absorption intensity at t , respectively [12]. Figure 4 shows $\ln(I_t/I_0)$ versus $(t/t_0)^{0.5}$ of the NH, anion and OH forms at various temperatures. Here, t_0 is set to be 1 min. At low temperature, the absorption intensity of the OH form decreases, while that of the anion and NH forms first increases and then slowly decreases with time, indicating that thermal conversion from the OH to the anion/NH forms takes place. The conversion from the OH to the anion/NH forms in γ -DNBP is faster than that in α -DNBP. With increasing temperature the absorption intensity of the NH form decreases faster with time, indicating that the NH form thermally returns back to the CH₂ form. The conversion from the NH to CH₂ form in γ -DNBP is slower than that in α -DNBP.

To explain the above differences of the PIPT reaction between α - and γ -DNBP, we calculated the formation energy of the CH₂, NH and OH forms by molecular orbital calculations with the MOPAC program package, while that of the anion form could not be obtained within our simple model. The formation energies of the CH₂, NH and OH forms in α -DNBP (γ -DNBP) are estimated to be 38.0 (39.2), 50.3 (52.5) and 67.1 (66.4) kcal/mol, respectively. The CH₂ form is most stable both in α - and γ -DNBP. The formation energy of each form is almost the same in both α - and γ -DNBP. We therefore tentatively assume that the potential surface of each form in α -DNBP is the same as that in γ -DNBP even in the excited state of the CH₂ form.

Figure 5 shows schematic potential energy diagrams of the PIPT reaction against the CH₂-NH and OH-NH reaction coordinates. The difference of the potential energy diagrams between α - and γ -DNBP is mainly in the distance of the reaction pathways. The optical excitation to the excited state of the CH₂ form (upward arrows) induces a

conversion to the NH/OH forms. Because the distance of the reaction pathway from the CH₂ to the NH form in γ -DNBP is much longer than that in α -DNBP, a large activation energy E_{γ}^* is required for the conversion resulting in a less efficient conversion to the NH form in γ -DNBP especially at low temperature. On the contrary, the photoconversion efficiency from the CH₂ to the OH form is expected to be the same for α - and γ -DNBP, because the molecular structure of the methylene/nitro groups is the same which may lead to the almost same distance of the reaction pathway. Similarly, the thermal conversion from the NH to the CH₂ form in γ -DNBP is expected to be smaller than that in α -DNBP because of the thermal activation energy E_{γ} being larger than E_{α} (see Fig. 5). The experimental results are well explained by the above consideration.

Based on the OH-NH reaction coordinates shown in Fig. 5, we expect that the thermal conversion from the OH to the NH form in γ -DNBP is slower than that in α -DNBP while the observed conversion in γ -DNBP is faster than that in α -DNBP. This indicates that the conversion to the NH form via the anion form contributes significantly to the formation of the NH form, which takes place through thermal conversion of the anion form to the NH form as shown in Fig. 1. For further understanding the whole PIPT reactions in DNBP including the above thermal conversion, a more elaborate calculation is needed which can evaluate the formation of the anion form.

In γ -DNBP single crystals, even at room temperature, we did not observe the clear absorption bands due to the NH and OH forms after UV-light irradiation of a few hours. Not only large distances of the PIPT reaction pathways but also steric hindrance between DNBP molecules prevents the PIPT reaction of γ -DNBP in the solid state.

In conclusion, we measured the photoinduced absorption change and thermal bleaching of the absorption at different temperatures in α - and γ -DNBP dispersed in

polymer films in order to elucidate the mechanism of the PIPT reaction in DNBP. Based on molecular orbital calculations and the potential energy diagram of the PIPT reaction, the discrepancy of the PIPT reactions between α - and γ -DNBP can be understood.

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Figure captions

Figure 1

Molecular structures and chemical reactions in α - and γ -DNBP.

Figure 2

Absorption spectra of the dark blue form in α - and γ -DNBP dispersed in PMMA films measured after UV light irradiation at various temperatures.

Figure 3

Thermal bleaching of the photoinduced absorption spectra in α - and γ -DNBP at various temperatures.

Figure 4

Temporal behavior of the thermal bleaching on the NH, anion and OH forms in α - and γ -DNBP.

Figure 5

Schematic potential energy diagrams of the PIPT reaction against the CH_2 -NH and OH-NH reaction coordinates in α - and γ -DNBP.

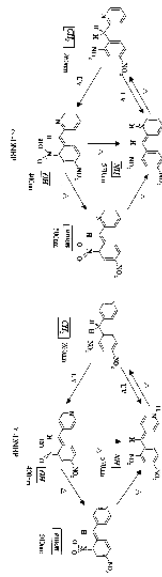


Fig. 1 *J. Takeda et al.*

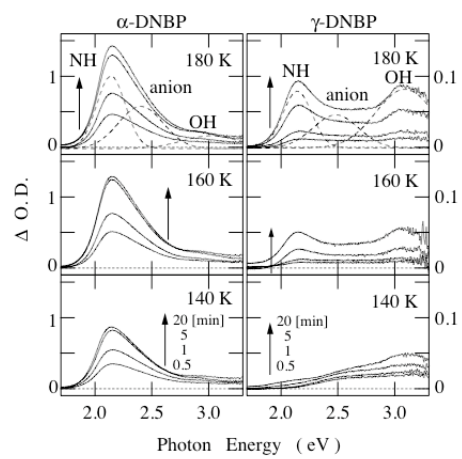


Fig. 2 J. Takeda et al.

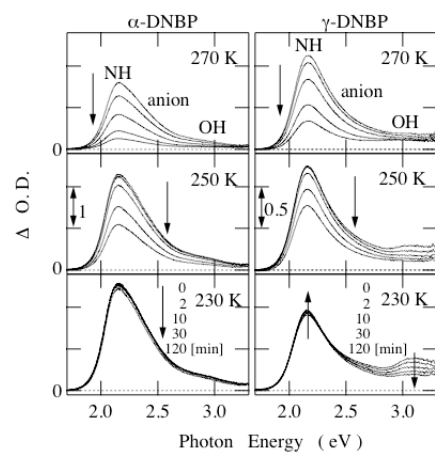


Fig. 3 *J. Takeda et al.*

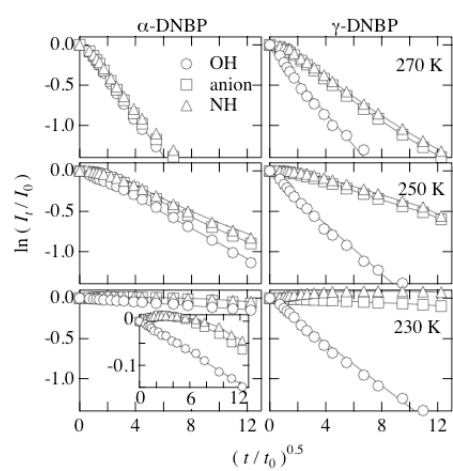


Fig. 4 *J. Takeda et al.*

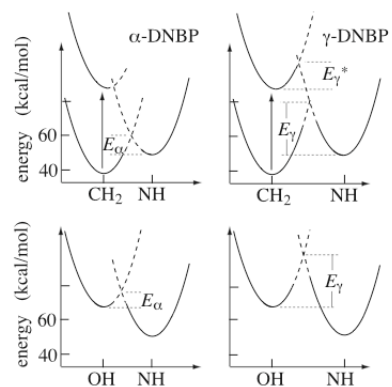


Fig. 5 *J. Takeda et al.*