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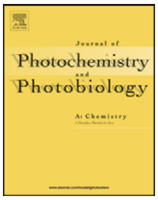

Drastic solvent effect on thermal back reaction of spiroperimidine photochromic compounds

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ABSTRACT

The photochromic behavior of two spiroperimidine compounds, 2,3-dihydro-2-spiro-7′-(8’-imino-7′,8′-dihydronaphthalen-1’-amine)perimidine, PNI and 2,3-dihydro-2-spiro-4′-[8′-aminonaphthalen-1′(4H)-one]perimidine, PNO-p has been studied by absorption and transient absorption spectroscopies. Both PNI and PNO-p exhibit extremely large solvent effect on the thermal back reaction from the colored (open) to the initial (close) state. The lifetime of the colored state ranges from 600 μs (methanol) to 22 days (acetonitrile) at room temperature. The relative energies of isomers have been estimated by the DFT calculations.

1. Introduction

Exploration of a new photochromic compound may offer a breakthrough for establishing novel photoresponsive materials. Recently, Davis and Tamaoki have reported a new class of photochromic compounds (PNI and PNO-p) [1]. Upon irradiation at 405 nm, the initial yellow solutions of PNI and PNO-p turn brown and deep blue, respectively. The photochromism of these molecules is due to a photocleavage of the C–N bond at the spiro carbon (Scheme 1). The main characteristics of these photochromic compounds are as follows: (1) they can be easily synthesized via a one-step reaction of inexpensive commercially available reagents (1,8-diaminonaphthalene and MnO_2), (2) they exhibit ‘T-type’ photochromism with good fatigue resistance, (3) their colored open states absorb almost the entire visible-light region, and (4) they possess primary amine groups enabling them to be attached to other functional groups [2].

From the viewpoint of applications, these photochromic compounds are potential candidates for photochromic lenses and light controlling materials, which turn to dark color upon irradiation of light such as sunlight, and return to original color in the dark. Advantages of PNI and PNO-p over other photochromic compounds are possibly low-cost synthesis and the neutrality of color of the open states of these compounds. Usually, synthesis of most reported photochromic compounds requires multi-step reactions using commercially available precursors [3–5], which makes their production cost-intensive. For photochromic glasses, color neutrality, which depends on the broadness of the visible-light absorption spectrum, is usually achieved by mixing compounds absorbing at various regions of the visible-light range [6,7].

Although the basic photochromic properties have been reported in the preliminary study, collection of additional data such as effects of medium (solvent or polymer) and theoretical calculations are prerequisites toward practical applications. The recent report on photochromic properties of PNI in polymer matrices shows that the rate of the thermal back reaction depends mainly on the glass transition temperature (T_g) of the polymer [8]. The purpose of this study is to investigate how solvent affects their photochromism, especially thermal back reaction, to obtain information on the mechanism of thermal back reaction, and to gain clues on how to control the photochromic reactions in view of applications. Herein we report the drastic solvent effect on the lifetime of the colored states of PNI and PNO-p. The back reaction is greatly enhanced in protic solvents. The effect is mainly attributable to the catalytic intermolecular proton shift where solvent protons are involved.

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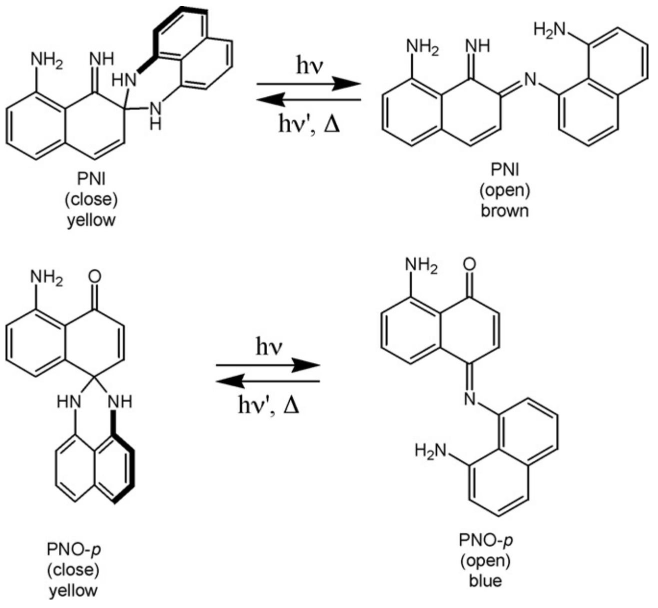


Scheme 1.

2. Experimental

2.1. Materials and methods

PNI and PNO-p were synthesized basically according to the previous report [1]. However, the isolation yields of both compounds were improved up to 15% and 18% for PNI and PNO-*p*, respectively. Spectroscopic grade solvents were used for spectroscopic measurements.

UV–vis absorption spectra were measured by JASCO V-570 spectrophotometer. Transient absorption spectra were measured with 308 nm pulses (XeCl, ~20 mJ/pulse, 10 ns fwhm) from an excimer laser (Lambda Physik LPX-100). A xenon lamp (Wacom, KXL-151, 150 W) was used as a monitoring light source. The detailed set-up was described previously [9–11]. Sample solutions were deaerated by Ar gas purge. Irradiation was carried out by high-pressure mercury lamp through appropriate filters (405 nm, ~1 mW/cm^2) or by LED (λ_{max} = 410 nm, 18 nm fwhm, ~7 mW/cm^2).

Theoretical calculations were performed by the GAUSSIAN 03W program package [12] on a DELL Workstation PWS650 (Xeon CPU 3.20 GHz × 2, 2.0 GB RAM). The B3LYP method was employed with a 6-31G(d,p) basis set. For each optimized geometry, frequency analyses were carried out and we found no imaginary frequency. Zero-point energy corrections were also calculated using computed harmonic frequencies.

3. Results and discussion

3.1. Absorption spectra

Absorption spectra of PNI and PNO-p are shown in Figs. 1 and 2, respectively. Absorption maxima (λ_{max}) of close and open (colored) states are listed in Table 1. As for the close forms of PNI and PNO-p, there are small solvent dependences in λ_{max} and spectra shape, regardless of the polar or protic nature of the solvents.

In toluene, as already reported in the previous report, both PNI and PNO-p exhibit color change from yellow to deep brown (PNI) and deep blue (PNO-p) upon irradiation with 405 nm light [1]. The photochromic reaction of PNI was also observed upon irradiation with 405 nm in DMSO, acetonitrile, ethanol, 1- and 2-propanol, and *t*-butyl alcohol (*t*-BuOH) by steady state UV–vis spectrophotometer.

Table 1
Solvent dependence of absorption maxima of close and open forms, thermal recovery rates of close forms and photostationary state (pss) composition of PNI and PNO-p.

	PNI				PNO-p			
Solvent	λ_{max} (nm) close	λ_{max} (nm) open	k sec^{-1} (τ) open-close	% Open form at pss	λ_{max} (nm) close	λ_{max} (nm) open	k sec^{-1} (τ) open-close	% Open form at pss
Toluene	410	490 590 (sh)	6.3×10^{-5} (4.4 h)[d]	66	398	520, 595	1.6×10^{-4} (1.7 h)[d]	75
DMSO	413	505	1.6×10^{-6} (10 d)[d]	45	406	541	3.6×10^{-7} (32 d)	81
Acetonitrile	403	489	5.2×10^{-7} (22 d)[b]	26	397	525 (sh)	3.9×10^{-7} (29 d)[c]	22
MeOH	403	500[a]	1.7×10^{3} (600 μs)[a]		404	–	–	
EtOH	406	515(sh)	1.9×10^{-3} (8.7 min)	7	406	–		
1-Propanol	407	507	2.2×10^{-4} (75 min)	45	408	550 (sh)	3.1×10^{-4} (55 min)	30
2-Propanol	407	507	1.8×10^{-5} (15 h)	51	408	546 (br)	2.1×10^{-5} (13 h)	93
t-BuOH	408	506	6.2×10^{-5} (4.5 h)	82	410	542	2.9×10^{-5} (9.6 h)	99

[a] Determined by transient absorption spectroscopy.
[b] At 313 K.
[c] At 323 K.
[d] At 303 K.

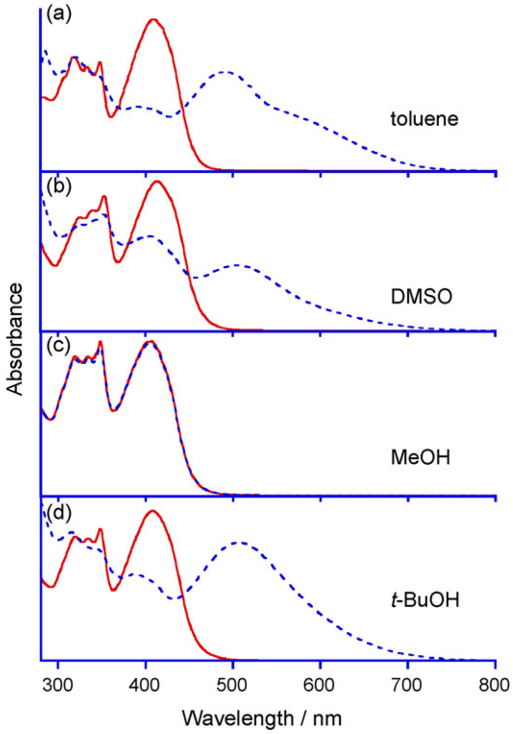


Fig. 1. Absorption spectra of PNI in various solvents, before (solid lines) and after (dashed lines) light irradiation.

In toluene, the open form of PNI has a peak at 490 nm and a shoulder around 590 nm. On the other hand, the shoulder disappears and only a single peak was observed around 500 nm in polar solvents such as DMSO, 1- and 2-propanol, and *t*-BuOH. In polymer matrices, this shoulder is also prominent in hydrophobic polymers such as polystyrene, polycarbonate and 1,2-polybutadiene. However, it was not observed in hydrophilic polymers such as polyvinyl alcohol, poly(2-hydroxyethyl methacrylate) and polyvinyl pyrrolidone [8]. Thus, this absorption seems to be dependent on the polarity of the medium.

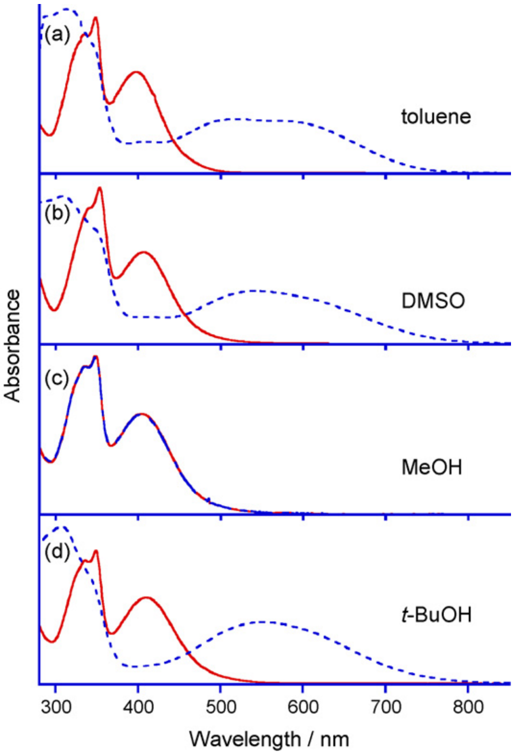


Fig. 2. Absorption spectra of PNO-p in various solvents, before (solid lines) and after (dashed lines) light irradiation.

The open form of PNO-p exhibits similar solvent effect. In toluene, two peaks were observed at 520 and 595 nm, of which the latter becomes a shoulder peak in DMSO and *t*-BuOH. No change in steady state absorption spectra upon irradiation was observed for PNI in MeOH and PNO-p in MeOH and EtOH.

3.2. *Transient absorption spectra*

Transient absorption spectra observed for PNI in MeOH and in toluene are shown in Figs. 3 and 4, respectively. In MeOH, the transient species with the absorption maxima around 500 nm was observed. Along with the absorption, a bleaching due to the decrease of the ground state was observed around 410 nm. As can be seen in Fig. 3(b), the time constant of the recovery of the bleaching at 405 nm corresponds to that of the decay of absorption at 500 nm. The bleaching curve was fitted with a single exponential function ($k = 1.7 \times 10^3\ \mathrm{s}^{-1}$). The shape and the λ_{max} are similar to those observed by the steady state absorption spectra in other alcoholic solvents such as *t*-BuOH (Fig. 1(d)). Thus, the transient species is assigned to the open form.

The shape of the transient absorption spectra of PNI in toluene (Fig. 4(a)) was similar to that of the absorption spectra (Fig. 1a), although a shift of the spectra was observed. The ground state bleach was centered around 410 nm. The absorption band around 490 nm decayed faster than that around 590 nm. As depicted in Fig. 4b, the time profiles of the ground state bleach at 390 nm and the transient absorption at 450 nm were similar to each other and they exhibited biexponential decays with a long-lived component, which did not decay in this time scale. The rate constants of the short-lived ($k = 5 \times 10^4\ \mathrm{s}^{-1}$) and long-lived ($k = 8 \times 10^3\ \mathrm{s}^{-1}$) components observed at both 390 and 450 nm were identical.

The fact that the transient absorption band around 490 nm and 590 nm have different decay profiles indicates that these bands are attributable to independent species. These two species are ground state because they have relatively long lifetime (>20 μs) and both absorption bands were not quenched by the addition of oxygen into the solution. The transient species with λ_{max} of around 490 nm is assigned to the open form, due to the similarity of the absorption spectra in other solvents. Since there are no other photochemical side products, a plausible candidate for another species with λ_{max} of around 590 nm may be the open-iso form (Scheme 2), whose imine moiety is inverted relative to the open form.

3.3. *Isomers of open forms*

The open form can exist as two isomers having *syn*- and *anti*-configurations at the C=N double bond, as shown in Scheme 2. The open-iso form might exist in the solution because the isomerization of the C=N bond proceeds photochemically and thermally [13,14]. Existence of similar species, which is in equilibrium with the open form, has been proposed in the case of photochromic spiroperimidines, which are derivatives of PNI [2]. Steady state and transient absorption spectra of PNI in toluene (Figs.1a and 4) indicate that there are at least two species which exhibit absorption around 490 and 590 nm. As suggested in the previous section, the transient species with λ_{max} of around 490 nm in Fig. 4a is assigned to the open form, due to the similarity of the absorption spectra in other solvents. The time profile of the decay of the open form seems to contain two components (short-lived and long-lived) as shown in Fig. 4b. The long-lived component is the back isomerization process for the recovery of the initial close form as revealed

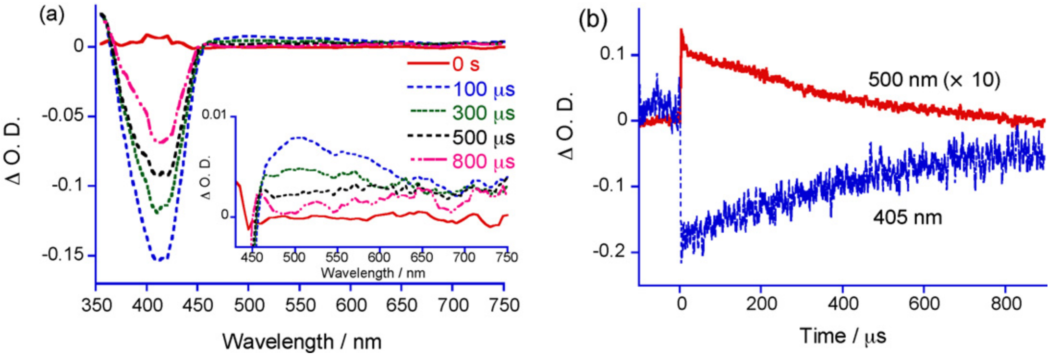


Fig. 3. Transient absorption spectra of PNI in MeOH (a) and time profiles monitored at 405 nm and 500 nm (b). Inset shows the enlarged spectra between 480 nm and 750 nm.

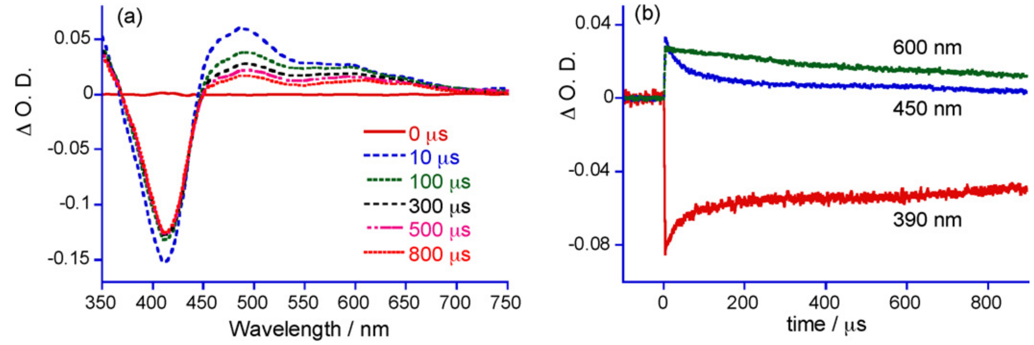
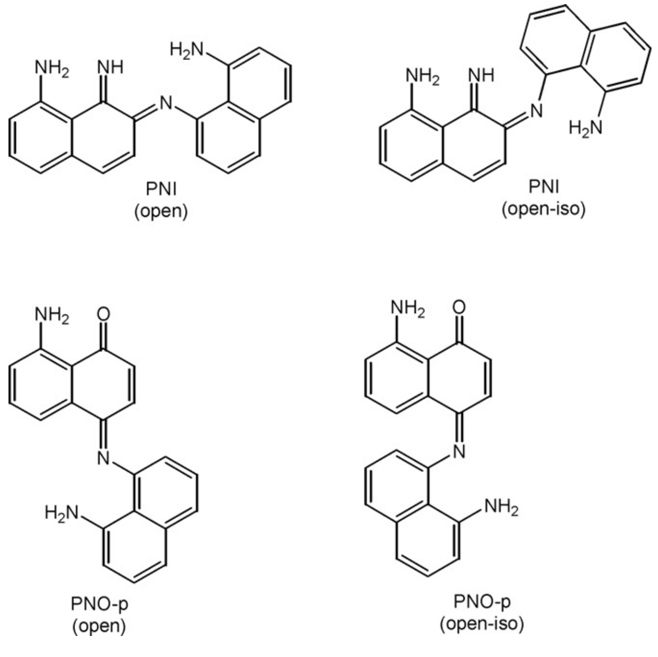


Fig. 4. Transient absorption spectra of PNI in toluene (a) and time profiles monitored at 390 nm, 450 nm and 600 nm (b).

by the steady state absorption spectroscopy. On the other hand, as for the short-lived component, along with the decay of the 450 nm (Fig. 4b), only small amount of the close form (390 nm) is recovered. During this period of time, the shape of the transient absorption is shifted (Fig. 4a). These results indicate that the short-lived process involves the conversion to another species such as the isomerization to the open-iso form. Thus, we assume that the short-lived process ($k = 5 \times 10^4\ \mathrm{s}^{-1}$) observed by the transient absorption in toluene (Fig. 4) is attributed to the thermal isomerization from open to open-iso forms. In other words, an equilibrium between two isomers is established during this period. Previous reports on related compounds also suggest the formation of open-iso form. [2,3]



Scheme 2.

To assess the relative stability of isomers (close, open and open-iso), we carried out theoretical calculations at B3LYP/6-31G(d,p) level. The calculated relative energies are listed in Table 2. For both PNI and PNO-p, open-iso forms have higher energies than other isomers, indicating that open forms are most abundant at the colored state in both PNI and PNO-p. The energy difference between close and open forms is very low. Contrary to our expectation, the open form of PNI is more stable than close form by 0.262 kcal mol^{-1} with the zero point energy (ZPE) correction. In our calculations, however, stabilization by solvent molecules was not included. Minkin has reported that the relative stability of isomers may be altered by solvent in spiroperimidine photochromic compounds [3]. Our experimental results show that the most stable isomer is the close form both in PNI and PNO-p. Thus, the close form might be relatively more stabilized by solvent molecules.

3.4. Thermal back reaction

The lifetimes (τ), defined by $1/k$, of the photoactivated colored (open) states of PNI and PNO-p in toluene are 4.4 and 1.7 h at 303 K, respectively [1]. On the other hand, in polar aprotic solvents such as DMSO and acetonitrile, their lifetimes were relatively long (up to a month) at ambient temperature for both PNI and PNO-p (Table 1). To our surprise, in polar protic solvents, their lifetimes strongly depend on the solvent. We observed a tendency that as the size of the alkyl group of the alcohol increases, the lifetime of the open form increases. For example, upon light irradiation of a methanol solution of PNI, the absorption spectrum remained unchanged as observed (Fig. 1c) by a steady state conventional spectrometer. However, a transient species with a lifetime of 600 μs was observed by transient absorption spectroscopy (Fig. 3). This transient species exhibited an absorption maximum (λ_{max}) at 500 nm with the shape

Table 2
Relative energies (kcal mol^{-1}) of isomers of PNI and PNO-p calculated at B3LYP/6-31G(d,p) level.

	PNI			PNO-p		
	Close	Open	Open-iso	Close	Open	Open-iso
Energy	0.0	0.886	7.411	0.0	1.660	6.741
Energy[a]	0.0	−0.262	6.060	0.0	0.332	5.669

[a] With zero point energy (ZPE) correction.

of the spectrum resembling that of the open form in toluene. Again, the transient species is assigned to the open state. In ethanol, the photoactivated colored state with a lifetime of 9 min was observed by steady state spectrometer although the isomer ratio of the colored state was as low as 7%. In *t*-BuOH, the lifetime was 4.5 h. The ratio of the longest (22 days, acetonitrile) and the shortest (600 μs, methanol) lifetimes is 3.3×10^9.

Similar trend was observed in the case of PNO-p. However, the open form was not observed by the transient absorption spectroscopy in methanol, presumably due to the fast back reaction and/or low quantum yield of the photocoloration reaction. Existence of another intermediate state (X) structurally different from close and open states may be the reason for the absence of a transient absorption. A discussion on such a species is provided in the next section.

It is known that photochromic spiropyrans and spirooxazines exhibit solvent effect on the thermal back reaction from colored merocyanine (open form) to colorless spiro form [15–17]. The effect is basically ascribed to the polarity of the solvent. Generally, the thermal back reactions are accelerated by less than 100 times by changing solvent. In contrast, the solvent effect on the lifetimes of open forms of PNI and PNO-p reported here is extremely larger than that reported for spiropyrans and spirooxazines.

3.5. Effect of alcohol

The enhancement of the reaction rate of thermal back reaction of PNI and PNO-p in protic solvents seems to be attributable to the involvement of protons of the solvent molecules. In other words, proton of the –OH group may be playing an important role in catalyzing the thermal back reaction. When the open form isomerizes to the close form, one of the hydrogen atoms of $–NH_2$ group at the naphthalene ring has to be shifted to the imine nitrogen atom. In aprotic solvents, the shift takes place intramolecularly. In protic solvents, on the other hand, the –OH groups of solvent molecules can intermolecularly interact with the $–NH_2$ and imine nitrogen, and thus the shift of the proton is assisted by solvent molecules. Let us consider that the solvent molecules are interacting with the amine and/or imine groups of the photochromic molecule. There is a steric effect for the solvent molecules to form a hydrogen bond to the imine group, because there are bulky aromatic rings near imine group and solvent molecules with larger alkyl groups may hardly be able to interact with the imine moiety. On the other hand, the amine is relatively free to form a hydrogen bond, with less steric effect. Thus, we assume that the hydrogen bond between solvent molecule and imine moiety may be playing an important role in rate determining step of the thermal back reaction. The accessibility of the –OH groups of solvent molecules is decreased when the alkyl group of alcohol is bulky such as *t*-BuOH, which leads to a longer lifetime of the colored state. This effect can be ascribed to a catalytic effect and is understood to proceed via a lower activation barrier. In toluene, the open form disappears with an activation energy of 18.0 kcal mol^{-1}. In 2-propanol, however, the activation energy is only 2.1 kcal mol^{-1}.

Similar effect was expected when doped polymers, where polymers possessing –OH groups may facilitate the thermal back reaction. However, the lifetimes of open form in various polymer matrices do not follow this trend. Instead, these depend strongly on the T_g of the polymer. [8]

By careful analysis of transient absorption spectra, the reaction mechanism seems to be rather complicated. In methanol, a ground state bleach of PNI was observed around 410 nm and concomitant with a very weak transient absorption around 500 nm (Fig. 3(a)). If the decrease of close form leads to the open form quantitatively, the ratio between the bleach and the transient absorption should be close to 1: 1, because the molar extinction coefficients of close and open forms are 18700 M^{-1} cm^{-1} (410 nm) and 18400 M^{-1} cm^{-1} (490 nm), respectively [1]. Also, the spectral overlapping of these compounds is negligible at 500 nm as can be seen in Fig. 1. The large bleaching around 400 nm in the transient absorption (Figs. 3 and 4) indicates that considerable amount of close form is converted to other species. However, the transient absorption band ~500 nm due to the formation of open form (Fig. 3) is very weak. From these observations, it seems that the consumption of the close form and the formation of the open form is not one-to-one relation. Therefore, we assume that a certain amount of consumed closed form may be converted to another intermediate such as X. This species X is at equilibrium with the open form because the decay rate of the open form coincides with the recovery rate of the close form (Fig. 3(b)). The species X is not attributable to a precursor for a side reaction because no byproduct was observed after the transient absorption experiments. The intermediate X may have less conjugation because no transient absorption was observed in the wavelength region we carried out the measurement (350–750 nm). Although the structure of species X is not clear at this moment, it may be a non-coplanar structure, where a C–N bond is cleaved but the two aromatic rings are still perpendicular to each other. Similar structure is also suggested in photochromic spiropyrans [18]. The energy of species X should be comparable to that of open form because X is in equilibrium with the open form in solution. However, at this moment, the structure of the species has not been determined. Currently, theoretical calculations of the structure of species X as well as potential energy surface are being studied and will be reported elsewhere.

4. Conclusion

Controlling the photochromic reaction is one of the main goals for photochemists in basic studies as well as in applications. Photochromic properties of PNI and PNO-p have been investigated and it has been revealed that the thermal back reaction, from open to close form, of these compounds exhibit remarkable solvent dependence. The lifetime of the open form varies from 600 μs (methanol) to 22 days (acetonitrile). In other words, we can tune the lifetime by simply choosing the solvent. Protons of the hydroxyl group of alcohol solvents play a catalytic role on the thermal back reaction. The observations of this work indicate that the lifetime of the open form can be controlled even in the polymer by rational design of the environment of the photochromic compound. As for light controlling materials, such as photochromic lenses and glasses, optimization of and ability to control thermal back reaction rate can bring significant advancement in their applications. Together with the study in polymer matrices [8], the photochromic properties of these compounds shed light on the development of novel photoresponsive materials.

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