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Cis/Trans Isomerization of Perinaphthothioindigo Dye Adsorbed on Silica Gel

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Synopsis. The photoinduced and thermal cis/trans isomerization of the title compound adsorbed on silica gel has been studied by the immersion method. The cis/trans photoisomerization of the adsorbed state can be reversibly induced by irradiation. Thermal isomerization of the cis-to trans-isomer proceeds very fast on the surface. The results are compared with those obtained in solution.

Although the reversible cis/trans isomerization of olefins is a well-known phenomenon, it is limited for the studies in liquid phase as well as in polymer matrix. More recently, interest has increased in the photochemical reactions of organic molecules which are imposed by adsorption on the surface such as silica gel or alumina.[1—3] Organic molecules often change their spectroscopic and photochemical properties when adsorbed and immobilized on surfaces of solids. Breuer and Jacob studied the photoisomerization of thioindigo adsorbed on alumina by photoacoustic spectroscopy and showed that while the trans-to-cis isomerization can be induced by irradiation, the cis-isomer cannot be back converted.[2] The reverse change for thioindigo adsorbed on silica gel was reported by Mostoslavskii and Nazariko; while the cis-isomer can isomerize to the trans-isomer on irradiation, the photoconversion of the trans- to cis-isomer does not occur.[3]

We describe here the photochemical study and thermal kinetics of the perinaphthothioindigo dye (PNTI) adsorbed on silica gel by the immersion method. There is a growing interest in the field of application of writing and erasing of information with visible light.[4] This application requires that the photochromic process is reversible on the solid surface.

Experimental

General Methods. UV spectra were obtained by using a Hitachi UV-340 spectrometer and an Ohtsuka Denshi MCPD (multichannel photodiode array detector) spectrometer. The solvents used in measuring spectra were spectroanalytically pure cyclohexane, benzene, and chloroform. Nitrobenzene was distilled twice under reduced pressure before use. PNTI (bis[perinaphtothiopyran-(2)]-indigo, HRMS Calcd for $C_{24}H_{12}O_2S_2$: M, 808.4043, Found: *m/z* 808.4029.) was prepared by intramolecular Friedel-Crafts acylation of α-naphthalenethioacetic acid, followed by oxidative dimerization.[5] Silica gel for thin-layer chromatography (Silica gel 70 Plate-Wako/glass plate) was employed and activated by heating in an oven at 120 °C for at least 3 hours. In some cases, silica gel was treated in the oven of 650—700 °C in order to decrease the silanol group on silica gel, although the reduced amount of the group was not determined. Silica gel/glass plate(s) prepared by adsorbing PNTI in a $CHCl_3$ solution onto nonhydrated silica gel and suspending the glass plate(s) in cyclohexane, was utilized for optical studies. Light scattering in this heterogenious system was minimized by the refractive indices of the solvent and silica gel. The large-pore silica gel employed is characterized by its supplier as having a surface of 450 $m^2\,g^{-1}$, and a surface density of 5 equivalents of SiOH group/nm^2. PNTI was adsorbed in the concentration of $1—10\times10^{-6}$ $mol\,g^{-1}$ of silica gel.

Determination of Quantum Yield Ratios of Cis/Trans Photoisomerization of PNTI in Solvents. The apparatus used consisted of an optical bench with light source (150 W tungusten–helogen lamp), filters (KL-54 and Toshiba L-42 filters, and a cold filter CF-A) and sample holders to permit simultaneous irradiation of two samples. The samples were in 1-cm quartz cell and the $\phi_{t\to c}/\phi_{c\to t}$ ratios were determined from cis:trans ratios of photostationary state on irradiation of 540 nm by using the following equation, $[cis]/[trans]=(\phi_{t\to c}/\phi_{c\to t})(\varepsilon_t/\varepsilon_c)$.

Determination of Quantum Yields of Cis/Trans Photoisomerization of PNTI in Solvents and on Silica Gel. The apparatus used was the same as that for the quantum yield ratios determination, with exception of the filter system, where KL-63, Toshiba L-42, CF-A, and a reduced filter ND-40 for the trans-to-cis isomerization and KL-51, L-42, CF-A, and ND-40 for the cis-to-trans isomerization were used. The silica gel/glass plate(s) was perpendicularly placed in 1-cm quartz cell. The qauntum yields of the cis/trans photoconversion were measured relative to the Reinecke's salt (aqueous $KCr(NH_3)_2(NCS)_4$) actinometer.[6] As the photoisomerization of PNTI adsorbed on silica gel accompanied a relatively fast thermal cis-to-trans isomerization, corrections of the thermal reaction during irradiation were made. The results are shown in Table 1.

Kinetics for Thermal Cis-to-Trans Isomerization of PNTI. The cis isomer of PNTI in solvents and on silica gel was prepared from the corresponding trans isomer by irradiation of filtered light (λ>620 nm). The thermal isomerization of the cis-isomer was followed spectrometrically by monitoring the increase in absorption of the trans isomer. Plots of $-\ln(A_\infty-A_t)/(A_\infty-A_0)$ vs. time were almost linear. The rate constants, *k*, were obtained from the straight portion whose correlation factors were more than 0.99. The results are shown in Table 2.

Results and Discussion

Solution of PNTI dissolved in organic solvent was violet blue. The color of PNTI adsorbed on silica gel was similar to that in solution. Table 1 shows that the color derives from an intense band ($\varepsilon_{\lambda_{max}}=20740\ M^{-1}\,cm^{-1}$ in benzene; 1 M=1 mol dm^{-3}) with λ_{max} 615—635 nm. A π–π^* assignment for the band is reasonable in view of its intensity and the red shift with increasing solvent polarity. The absorption in longer wavelength was observed on silica gel as well as in nitrobenzene.[7] Exposure of *trans*-PNTI solution to visible light of >600 nm revealed a pink-red color, which was

Table 1. Spectral Shifts of PNTI and Quantum Yields for Trans/Cis Photoisomerization

	$\lambda_{\max}$/nm trans (log ε)	$\lambda_{\max}$/nm cis (log ε)	Isosbestic point/nm	$\phi_{t\to c}$ (630 nm)	$\phi_{c\to t}$ (510 nm)	$\phi_{t\to c}/\phi_{c\to t}$[a] (540 nm)
Cyclohexane	615 (—)	491 (—)	524	—	—	—
Benzene	621 (4.32)	502 (4.19)	536	0.023	0.058	0.20
Chloroform	624 (4.34)	510 (4.16)	545	0.005	0.035	0.17
Nitrobenzene	631 (4.32)	514 (4.17)	547	0.020	0.017	0.91
Silica gel	635 (4.32)	534 (—)	571	0.0020	0.0023	—
Silica gel[b]	644—661 (—)	540 (—)	575	0.0011	0.0046	—

a) Ratios were determined from photostationary states. b) Silica gel was dried at 700 °C.

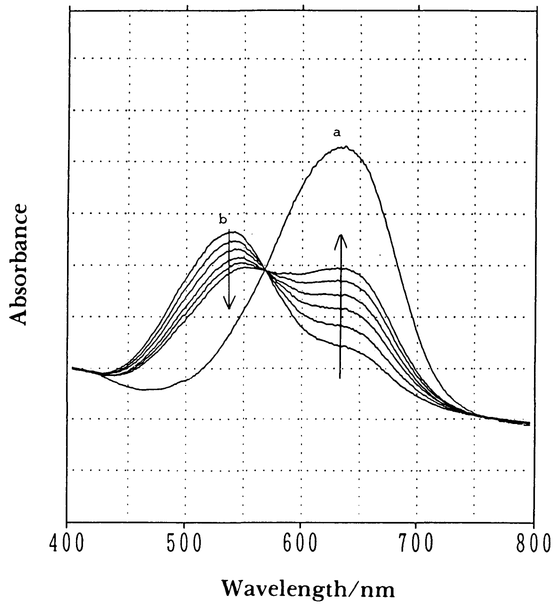

Fig. 1. Absorption spectra of PNTI adsorbed on silica gel/cyclohexane; (a) *trans*-PNTI, (b) *cis*-PNTI. The thermal cis-to-trans isomerization is shown by the arrow.

assigned to *cis*-PNTI. The electronic spectral changes resulted in about 120 nm blue shift, affording the cis-isomer of the intense visible transition ($\varepsilon_{\lambda_{\max}}$=8370) with an isosbestic point at 536 nm in benzene. The extent of red shift of the cis-isomer by increasing solvent polarity was higher in compared to that of the trans-isomer. The reverse cis-to-trans photoisomerization was possible with visible light of 510 nm. Such photochromic phenomena were also observed on silica gel dipped in cyclohexane solvent. When immersed in cyclohexane, essentially all of PNTI was adsorbed on silica gel, as evidenced by the absence of PNTI absorption band of the supernatant liquid or the filtered solution. Figure 1 depicts such changes in the cis/trans isomerization on silica gel. If the sample of spectrum (a) was irradiated with light of >600 nm, spectrum (b) was obtained. Similarly, irradiation of the sample (b) with light of 510 nm easily converted into curve (a) with an isosbestic point at 571 nm.

Each of the trans- and the cis-isomer in solution or on silica gel was effectively converted into the another isomer on irradiation with 630 nm and 510 nm light, respectively. Exposure to 540 nm light (i.e., near isosbestic point) brought about the photostationary state containing the mixture of two isomers. Quantum yields ($\phi_{t\to c}$ and $\phi_{c\to t}$) and their ratios ($\phi_{t\to c}/\phi_{c\to t}$) of the isomerization were determined on the direct irradiation of 630 nm, 510 nm, and 540 nm, respectively. Quantum yields in solution and on silica gel were rather small. The ratios of quantum yields, $\phi_{t\to c}/\phi_{c\to t}$, in benzene and nitrobenzene were estimated to be 0.2 and 0.9, respectively, suggesting that the ratio depends upon the polarity of solvent used. Such a polar contribution should be reflected in surface photochemistry of dyes. The ratio on silica gel seems to have the similar propensity to that in nitrobenzene because of high polarity of silica gel. However, the present experiment shows that quantum efficiencies of PNTI on silica gel are less than those in solvents. This lowering of quantum efficiencies might imply the presence of some constraints upon the molecule motions of PNTI adsorbed on silica gel or the formation of a hydrogen-bonding between the carbonyl oxygen of PNTI and a silanol group at the excited state.

The thermodynamically less stable cis-isomer is thermally or catalytically converted to the trans-isomer. This thermal cis-to-trans isomerization of PNTI in the dark proceeded at lower rates ($t_{1/2}$=ca. 30 h at 30 °C) in three solvents examined, whereas the thermal isomerization on silica gel occurred quite rapidly ($t_{1/2}$=ca. 0.3 h at 18.5 °C). The surface of silica gel is characterized by the presence of silanol groups, siloxane bridges, and accompanying water molecules, and often bears an acidic property. Present marked increase in the isomerization rate may be due to the acidic ability of silica gel used[8] and this catalytic isomerization will be explained by a protonation of α,β-unsaturated carbonyl groups.[9] Since silanol groups change into siloxane groups on heating at high temperature, the thermal isomerization of PNTI adsorbed on heat-treated silica gel was expected to retard relative to that on untreated one. The thermal isomerization on silica gel was reduced with the decrease in the silanol groups, though the variable amount was not so large as shown in Table 2. Thus, silanol groups on silica gel may not only exert as active sites of adsorption but also promote the thermal cis-to-trans isomerization

Since the dehydration of the silanol groups leads to the raise of the hydrophobic property and/or to the reduction in acidity, the spectroscopic and photochemical properties of PNTI adsorbed are changeable.

Table 2. Rate Constants of Thermal Cis-to-Trans Isomerization of PNTI

	(°C)	$k\times10^4/\mathrm{s}^{-1}$	$t_{1/2}/\mathrm{h}$
Benzene	30	0.0614	31.3
Chloroform	30	0.0629	30.6
Nitrobenzene	30	0.0666	28.9
Silica gel	18.5	6.09	0.31
Silica gel[a)]	18.5	2.7—4.8	0.71—0.40

a) Silica gel was dried at 700 °C.

In fact, the cis/trans photoisomerization and the thermal cis-to-trans isomerization of PNTI on silica gel were influenced, as stated above. However, the $\lambda_{\max}$ value for the trans-isomer on the absorbent reached to around 660 nm, depending upon the heat-treated conditions of silica gel, as the surface became more hydrophobic. This may be explained by an assumption that the thermal treatment of silica gel may result in the change of the adsorption mode, from the unimolecular to the multimolecular adsorption or the solid-like state,[10)] which leads to the additional red shift in the absorption spectra of PNTI on silica gel.

Our results on PNTI are somewhat different from those on thioindigo adsorbed on silica gel obtained by other authors.[3)] No trans-to-cis photoisomerization of thioindigo adsorbed is observed. This may result in the effective cancellation of the trans-to-cis photoisomerization by the thermal back-reaction during irradiation.

In conclusion, reversible cis/trans photoisomerization of PNTI on silica gel surface is possible, even though with poor quantum efficiencies. The dark reversion rate is makedly accelerated by silica gel, the effect being changed by variable amounts of silanol groups.

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