

# Picosecond Laser Study of Thioindigoid Dyes Photoisomerization

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The transient species in the *trans*  $\rightleftharpoons$  *cis* photoisomerization of the perinaphto-thioindigoid dye were identified by picosecond laser spectroscopy in the time domain 10 ps–5 ns. An excitation of the *trans* isomer with a 6 ps, 528 nm pulse to the singlet state  $S_1$  (the peak of  $S_n \leftarrow S_1$  absorption at 700 nm) results in the intersystem crossing  $S_1 \rightsquigarrow T_1$  (the peak of  $T_n \leftarrow T_1$  absorption at 730 nm) with the quantum yield of 0.7 and rate constant  $(1.4 \pm 0.3) \cdot 10^9 \text{ s}^{-1}$ . An excitation of the *cis* isomer results also in the intersystem crossing (the peak of  $T_n \leftarrow T_1$  absorption at 670 nm) with the rate constant  $(3.7 \pm 1.2) \cdot 10^{10} \text{ s}^{-1}$ . The triplet mechanism of the photoisomerization in the both directions is proposed.

## 1. INTRODUCTION

Thioindigoid dyes having a large difference in the *trans* and *cis* isomer absorption spectra are one of the most appropriate compounds for the reversible *trans*  $\rightleftharpoons$  *cis* photoisomerization study. The common point of view on the mechanism of thioindigoid dyes photoisomerization is absent at present. An involvement of the *trans* isomer triplet state in the *trans*  $\rightarrow$  *cis* photoisomerization was established<sup>1–4</sup> by nanosecond absorption spectroscopy. The results of the fluorescence studies,<sup>5,6</sup> were interpreted on the other hand in terms of photoisomerization in the singlet state of the *trans* isomer. The reverse *cis*  $\rightarrow$  *trans* photoisomerization is the least studied and is the most interesting. According to the mechanism proposed in Refs. [7 and 8], the *cis*  $\rightarrow$  *trans* photoisomerization occurs as a result of the transition from the lowest excited singlet state  $S_1$  of the *cis* isomer into

the state  $S_1$  of the *trans* isomer. The *trans* singlet state  $S_1$  can be depopulated to the ground  $S_0$  state due to internal or intersystem crossing.

It is necessary to detect both the singlet and triplet states in the single experiment for the elucidation of the photoisomerization mechanism. The picosecond absorption spectroscopy was applied in the present work for this purpose.

## 2. EXPERIMENTAL

The formula of the perinaphtho-thioindigoid dye (PNT) under study is shown in Figure 1. Measurements on PNT in chloroform were carried out with undegassed solutions at 291 K. The PNT *cis* isomers were prepared by illumination of *trans* solution with the 577/579 nm lines of a 1000 W mercury lamp selected by glass filters. Since the absorption spectra of the isomers of the PNT are well separated (Figure 1) it makes possible to convert the *trans* isomer completely into the *cis* isomer. The concentrations of the solutions were adjusted to give a ground-state optical density of 0.5 at the wavelength 528 nm in a 1 mm sample cell.

The apparatus used to measure transient absorbance spectra was the same as that described in detail elsewhere.<sup>9</sup> Briefly, it includes a mode-locked Nd:phosphate glass laser on the basis of an unstable resonator configuration and amplifier system to produce single TEM<sub>00</sub>

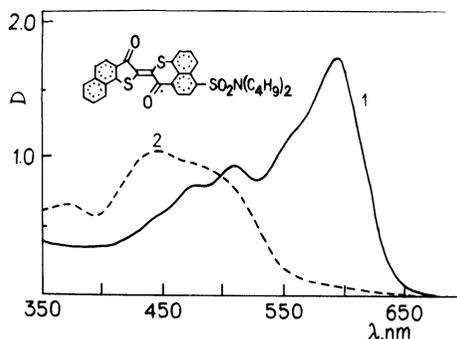


FIGURE 1 Ground-state absorption spectra of the pure *trans* (curve 1) and *cis* (curve 2) isomers of PNT dye in chloroform at room temperature.

picosecond pulses at 1055 nm. The second harmonic 528 nm with an energy of 0.5–1 mJ was used as an excitation pulse. For probing, the 1055 nm pulse generates in D<sub>2</sub>O a broad-band continuum. The double-beam optical configuration consisting of five miniature mirrors forms a number of the interrogating continuum pulses delayed by 10 ps, 400 ps, 1 ns, 2.5 ns and 5 ns relative to the excitation pulse. The absorbance changes  $\Delta A$  in a sample are detected photographically and calculated for each delay time using two alternate laser shots with and without the excitation pulse.<sup>10</sup> The angle between the polarization planes of excitation and probe beams was adjusted 55° to eliminate effects due to rotational relaxation.<sup>11</sup>

The *trans*-PNT fluorescence lifetime was measured by the single photon counting with the subsequent deconvolution.

### 3. RESULTS AND DISCUSSION

On flashing a solution of *trans*-PNT in chloroform was the transient absorption band with the peak at 700 nm detected (Figure 2, curve 1). The transient is formed within the duration of the excitation pulse and its spectrum depends on the time. The displacement of the central maximum to 730 nm along with the formation of the shoulder at 660 nm and the new maximum at 820 nm are seen in the absorbance

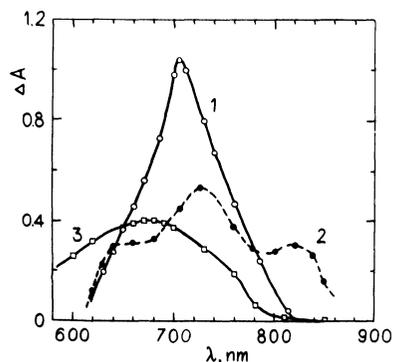


FIGURE 2 Transient absorbance spectra of *trans*-PNT measured at 10 ps (1) and 5 ns delays (2) and of *cis*-PNT measured at 400 ps (3) delay after excitation with a 528 nm picosecond pulse.

spectrum at the time moment 5 ns (Figure 2, curve 2). The kinetics of these spectral changes is shown in Figure 3, where the points with the zero absciss correspond to the 10 ps delay. Excitation of a sample with the 528 nm pulse results in the immediate bleaching (negative  $\Delta A$ ) of the ground-state absorption band at 590 nm. The transient absorption band 700 nm is formed simultaneously with the diminution of the 590 nm band. The optical density of the 700 nm band decays with the characteristic time of about 400 ps up to the some intermediate value corresponding to the long-lived induced absorption with the peak 730 nm. The decay of the 700 nm band is accompanied in the same time interval by the partial recovery of the ground-state absorption band 590 nm.  $\Delta A$  at the wavelength of the *cis* isomer absorption has the negative sign and does not depend on time in the time interval 1–5 ns (Figure 3). These results define more exactly our previous data.<sup>12</sup>

As for the *cis* PNT, excitation by the picosecond pulse results in the formation of the broad induced absorption band (Figure 2, curve 3) with the maximum at about 670 nm. The absorption band shape does not depend on time in the time interval 10 ps–5 ns. The absorption peak of the *trans* isomer at 590 nm was not detected in this time interval. It is worthwhile mentioning that this *trans* ground-state absorption absence when exciting the *cis* isomer can not be connected with the small yield of the *trans* isomer due to the small excitation pulse energy, for example. Indeed, we observed visually

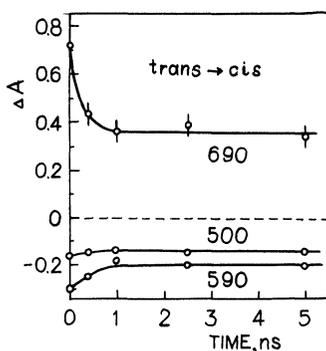


FIGURE 3 Absorbance kinetics at 690, 500 and 590 nm of *trans*-PNT in chloroform at room temperature. Excitation with a 528 nm picosecond pulse.

after the flash in the yellow solution of the *cis* isomer the presence of the strong violet spot of the *trans* isomer solution. The kinetic behavior of the transient from the *cis* isomer is shown in Figure 4. The buildup of transient absorption for *cis*-PNT following excitation at 528 nm was measured to be slower than that observed for *trans*-PNT. The detailed study of the initial kinetic curve was carried out in Ref. 12 by means of the echelon and the risetime was shown to be  $35 \pm 15$  ps. This feature of the slow going into the plateau is observed for all wavelengths (Figure 4) that proves the belonging of the induced absorption to the single transient species.

Let us consider the identity of the states which exhibit the transient absorption from the *trans*- and *cis*-PNT. Three states can be formed under excitation of the *trans* isomer: the lowest excited singlet  $S_1$  (*trans*) and triplet  $T_1$  (*trans*) and the ground state  $S_0$  (*cis*). It is clear that the  $S_0$  (*cis*) state can not be responsible for the 700 nm band since the *cis* absorption maximum is at 450 nm (Figure 1). The triplet state  $T_1$  (*trans*) can not be also responsible for the 700 nm band since its risetime would be equal in this case to the fluorescence lifetime of the *trans* isomer  $0,5 \pm 0,2$  ns. The only lowest excited singlet state  $S_1$  of the *trans* isomer and not the two-step photodecomposition product can be responsible for the intense transient band 700 nm. This assignment is supported by three facts. Firstly, its buildup is shorter than 10 ps; secondly, the decay time of the 700 nm band coincides with the fluorescence lifetime of the *trans*-PNT and thirdly,

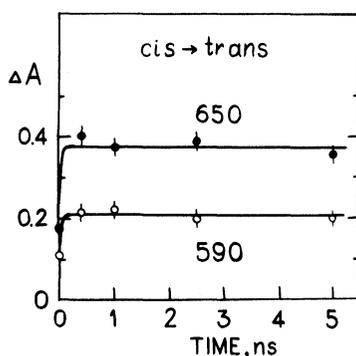


FIGURE 4 Absorbance kinetics at 650 and 590 nm of *cis*-PNT in chloroform at room temperature. Excitation with a 528 nm picosecond pulse.

decay of the 700 nm band is accompanied by the recovery of the *trans* ground-state absorption. The observed intense band of the singlet-singlet absorption  $S_n \leftarrow S_1$ , in PNT at 700 nm locates also to the long-wavelength side of the  $S_1 \leftarrow S_0$  transition as in the case of thioindigo.<sup>13</sup> Such location is probably the common property of the thioindigoid dyes. If the 700 nm band is assigned to the  $S_n \leftarrow S_1$  absorption, it is quite naturally to assign the 730 nm band to the triplet-triplet absorption  $T_n \leftarrow T_1$  of the *trans*-PNT. This assignment explains then the coincidence of the 730 nm band rise time with the 700 nm decay time and the long lifetime of the 730 nm band.

The only one transient with the 670 nm absorption band must be assigned in the case of the *cis*-PNT. According to model proposed in Ref. 8, *cis-trans* photoisomerization occurs via the triplet state of the *trans* form. It is necessary therefore to check in our experiment the possible population of four states:  $S_1$  (*cis*),  $S_1$  (*trans*),  $T_1$  (*trans*) and  $T_1$  (*cis*). The 670 nm band can not be assigned to states  $S_1$  (*trans*) and  $T_1$  (*trans*) since the absorption spectra from these states (curves 1 and 2, Figure 2) differ from that of the 670 nm transient. The  $S_1$  (*cis*) state can not be responsible for the 670 nm band because of the slow buildup of the 670 nm band. We ascribe the 670 nm transient to the triplet-triplet absorption  $T_n \leftarrow T_1$  of the *cis*-PNT. The intersystem crossing is responsible then for the slow buildup of about  $35 \pm 15$  ps that corresponds to the rate constant  $(3.7 \pm 1.2) \cdot 10^{10} \text{ s}^{-1}$ . These results indicate that excitation of the *cis* isomer results in the preferential population of the *cis* triplet state.

An analogous value of the intersystem crossing rate constant for the *trans* isomer can be obtained from the data presented in Figure 3. Moreover, the fraction  $\alpha$  of the *trans* isomer converted into the *cis* isomer from the  $S_1$  (*trans*) state can be evaluated from the Figure 3. The fact is that the stationary residual bleaching  $\Delta A_{590}^{st}$  of the *trans* ground-state absorption at 590 nm is due to incomplete repopulation of the  $S_0$  state from the  $S_1$  state because of the photoisomerization (fraction  $\alpha$ ) and intersystem crossing (fraction  $1 - \alpha$ ). Two species give a contribution to the stationary optical density  $\Delta A_{500}^{st}$  at 500 nm, the bleached *trans* absorption and the formed *cis* absorption:

$$\Delta A_{500}^{st} = (\alpha \varepsilon_{500}^c / \varepsilon_{590}^t - \varepsilon_{500}^t / \varepsilon_{590}^t) |\Delta A_{590}^{st}| = 0.5(\alpha - 1) |\Delta A_{590}^{st}|$$

where  $\varepsilon$  = extinction coefficient, superscripts *t*, *c* refer to the *trans* and *cis* isomers, subscripts – to the wavelength. The  $\varepsilon$ -ratios are

readily obtained from the Figure 1.  $A_{500}^{st} = -0.10$  at  $\alpha = 0$ ,  $\Delta A_{500}^{st} = 0$  at  $\alpha = 1$ , according to the above relation. The experiment gives  $\Delta A_{500}^{st} = -0.14 \pm 0.03$  (Figure 3), that corresponds closely to the case  $\alpha = 0$ . The intersystem crossing is thus responsible for the residual bleaching  $\Delta A_{590}^{st}$ . Its quantum yield  $\varphi_{isc}$  is equal to the ratio of the stationary and the initial ( $t = 10$  ps) optical densities at 590 nm. From the Figure 3 we obtain  $\varphi_{isc} = 0.70 \pm 0.15$ . By means of the evident relationship  $\varphi_{isc} = \tau_f \cdot K_{isc}$  we obtain  $K_{isc} = (1.4 \pm 0.3) \cdot 10^{9-1}$  s taking into account the *trans* fluorescence lifetime  $\tau_f = 0.5$  ns.

The question that arises is the reason for the large difference between the *trans* and *cis* intersystem crossing rates. The mechanism we propose is shown in Figure 5. Our conclusion about the triplet mechanism of the *trans*  $\rightarrow$  *cis* photoisomerization is in agreement with that of the previous nanosecond experiments.<sup>1-4,7,8</sup> There is a large potential barrier in the *trans*  $S_1$  state that prevents the rotation in the singlet state. The *cis* isomer has on the contrary no such barrier in its  $S_1$  state, and the fast rotation in the  $S_1$  state is the primary process upon excitation of the *cis* isomer. Such rotation results in the decrease of the  $S_1 - T_1$  energy gap and in the increase of the spin-orbit coupling. Both possible phenomena increase drastically the intersystem crossing rate already on the initial stage of the rotation.<sup>14-16</sup> This picture of the preferential *cis* intersystem crossing differs somewhat from that of the model of Memming *et al.*<sup>7,8</sup> where the possibility of the large rotation angles in the  $S_1$  (*cis*) state is assumed.

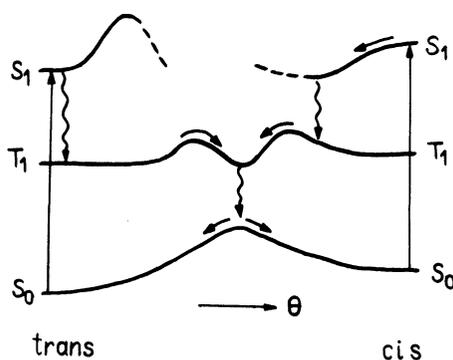


FIGURE 5 The proposed scheme of *trans*  $\rightleftharpoons$  *cis* photoisomerization of thioindigoid dyes.

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