PICOSECOND ABSORPTION SPECTROSCOPY OF THE FLUORESCENT STATE OF *trans*-THIOINDIGO

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Summary

The induced absorption spectra of *trans*-thioindigo solutions at room temperature were investigated using picosecond absorption spectroscopy in the time interval 10 ps - 5 ns. Two transient absorption bands with maxima at 610 nm ($\epsilon = 6.4 \times 10^4$ M^{-1} cm^{-1}) and 480 nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) were assigned to the $S_n \leftarrow S_1$ transitions from the lowest excited singlet state of *trans*-thioindigo.

1. Introduction

The photochemistry of the thioindigoid dyes, which are interesting from both scientific and practical viewpoints, have recently received much attention. A number of mechanisms have been proposed for the direct *trans–cis* photoisomerization of these compounds. The results of fluorescence studies [1, 2] have shown that the photoisomerization occurs in the lowest excited singlet state S_1. These results have been interpreted further in terms of the flexibility of the thioindigo central double bond in the S_1 state [3]. However, nanosecond absorption studies [4 - 8] have shown an involvement of the triplet state in the *trans–cis* photoisomerization and have revealed the *trans* configuration [6, 7] of the intermediate triplet state.

Detection of both the intermediate and the final states in one experiment is necessary for the unequivocal elucidation of the photoisomerization mechanism. Absorption pulse methods appear to be the most suitable for this purpose. The triplet–triplet $T_n \leftarrow T_1$ absorption spectra for the thioindigoid dyes are well characterized [4 - 8]. The singlet–singlet $S_n \leftarrow S_1$ absorption spectra have not been assigned in previous nanosecond experiments. In the present work picosecond absorption spectroscopy was used to identify these transitions.

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2. Experimental details

An undegassed solution of 5×10^{-4} M *trans*-thioindigo in chloroform was investigated at room temperature in a 1 mm quartz cell.

The apparatus used to measure the picosecond transient absorbance spectra was the same as that described in detail elsewhere [9]. Briefly, it includes a mode-locked neodymium–phosphate glass laser and amplifier system to produce single TEM_{00} pulses of duration 6 ps at 1055 nm. The second harmonic at 528 nm was used as an excitation pulse. For probing, the 1055 nm pulse generates a broad band continuum in D_2O. A double-beam optical system consisting of a semitransparent aluminium mirror and five miniature mirrors forms the reference (1) and monitoring (2) interrogating continuum pulses. The monitoring pulses are delayed by 10 ps, 400 ps, 1 ns, 2.5 ns and 5 ns with respect to the excitation pulse. The absorbance change ΔA in a sample was detected photographically and was calculated for each time using two alternate laser shots in the presence (p) and the absence (a) of the excitation pulse:

$$\Delta A = \gamma^{-1}\{(D_1^{p} - D_2^{p}) - (D_1^{a} - D_2^{a})\}$$

where γ and D are the contrast and the blackening of the film respectively. The angle between the polarization planes of the excitation and the probe beams was adjusted to 55° to eliminate effects due to rotational relaxation.

3. Results and discussion

Excitation of a sample using the 528 nm picosecond pulse resulted in the immediate bleaching of the ground state absorption band at 546 nm (negative ΔA) as shown in Fig. 1. At the same time two transient absorption bands were formed, one on each side of the band at 546 nm. One band was narrow with a peak at 610 nm and the other was broader with a maximum

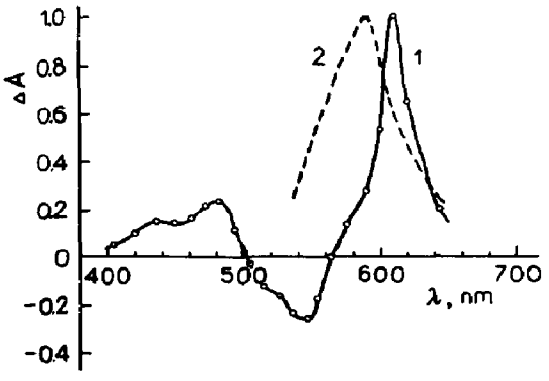

Fig. 1. Transient absorption spectrum of *trans*-thioindigo in a chloroform solution at room temperature measured 10 ps after excitation using a 528 nm picosecond pulse (○, curve 1) and the triplet–triplet absorption spectrum of *trans*-thioindigo [7] (curve 2).

at 480 nm. The triplet–triplet $T_n \leftarrow T_1$ absorption spectrum from ref. 7 is included in Fig. 1 for comparison.

Figure 2 shows the kinetic behaviour of the absorbance at various wavelengths. We were interested in four absorption regions, the transient absorptions at 610 and 440 nm and the ground state absorptions of the *cis* isomer at 480 nm and the *trans* isomer at 546 nm. The characteristic decay times were 16 ± 1 ns for the 610 nm band and 15 ± 2 ns for the 440 nm band. The recovery of the *trans* absorption band at 546 nm occurs with the same characteristic time of 15 ± 2 ns. Within the limits of error the absorbance at 480 nm does not depend on time in the interval 10 ps - 5 ns.

We now consider the identity of the states exhibiting the transient absorption. The absorption band at 610 nm has not previously been observed by nanosecond spectroscopy. It cannot be assigned to the triplet–triplet absorption for two reasons: firstly, the peak at 610 nm differs from that of the triplet–triplet absorption band at 580 - 595 nm [4 - 8], and secondly the rise time of the $T_n \leftarrow T_1$ absorption should be equal to the fluorescence lifetime of *trans*-thioindigo which is 14 ± 0.2 ns in chloroform solution measured using the nanosecond pulse fluorometer. The transient band at 610 nm can be assigned only to the $S_n \leftarrow S_1$ absorption from the lowest excited singlet state S_1. Indeed, the rise time of this band is shorter than 10 ps and its decay time is close to the fluorescence lifetime and to the recovery time of the ground state absorption. The small difference between the decay time and the fluorescence lifetime is probably due to the build-up of the triplet–triplet absorption band which overlaps strongly with the 610 nm band (Fig. 1). The straight line obtained for the transient decay in the ΔA–t plot is due to the shortness of the time interval (5 ns or less) compared with the fluorescence lifetime of *trans*-thioindigo (14 ns).

Kinetic features similar to those of an $S_n \leftarrow S_1$ transition were observed for the absorbance at 440 nm belonging to the short wavelength transient band. This transient band for *trans*-thioindigo was found earlier [5] using

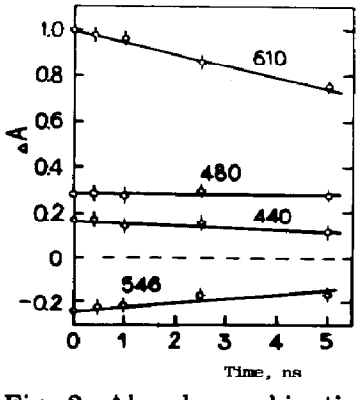

Fig. 2. Absorbance kinetics at 610, 546, 480 and 440 nm of *trans*-thioindigo in a chloroform solution at room temperature after excitation using a 528 nm picosecond pulse. The point at zero abscissa refers to the 10 ps delay time.

nanosecond flash photolysis. An $S_n \leftarrow S_1$ absorption in the same spectral region at about 460 nm with a lifetime of 50 ps was observed [10] for indigo which has an electronic structure similar to that of thioindigo.

The extinction coefficients ϵ of the $S_n \leftarrow S_1$ absorption bands can be determined from the condition that the population of the S_1 state is equal to the population transferred from the S_0 state: $\Delta c_{610} = \Delta c_{546}$. Application of this condition gives

$$\epsilon_{610} = \frac{\Delta A_{610}}{|\Delta A_{546}|} \epsilon_{546} = (6.4 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\epsilon_{480} = (1.3 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$$

These values for ϵ represent the upper limits because the overlap of the $S_n \leftarrow S_1$ and $S_1 \leftarrow S_0$ absorptions is neglected in the calculations.

The intense $S_n \leftarrow S_1$ band at 610 nm was not observed earlier using a nanosecond laser because the 600 nm spectral region contains a strong *trans* isomer fluorescence peak which cannot be avoided completely in the nanosecond arrangement. This is because the detecting light beam is not a laser beam but is obtained from a xenon lamp and has to be focused by a lens located between the cell and the monochromator which also focuses the fluorescent light [11]. The observation of the thioindigo transients shows the advantage of picosecond flash photolysis in solving problems which generally occur in nanosecond flash photolysis.

Thioindigo was found to be an inappropriate compound for the elucidation of the photoisomerization mechanism in this class of dye. The absorption spectrum of the *cis* isomer $S_0(cis)$, which peaks at 480 nm, overlaps strongly with that of the two species $S_0(trans)$ and $S_1(trans)$. The time independence, or more correctly the very slow decay, of the absorbance at 480 nm is thus the result of two processes: the recovery of the $S_0(trans)$ state population tends to increase ΔA_{480} and the decay of the $S_1(trans)$ state results in a decrease in ΔA_{480}. Unfortunately the long lifetime of the $S_1(trans)$ state does not allow the contributions of the $S_1(trans)$ and the $T_1(trans)$ states to the *cis* absorbance to be distinguished within the 10 ps - 5 ns time interval.

All these spectral and temporal difficulties can be avoided in the *peri*-naphtho-thioindigoid dyes. The ground state absorption spectra of the *trans* (590 nm) and *cis* (450 nm) isomers are very well separated. It is therefore possible to convert the *trans* isomer into the *cis* isomer and to study the photoisomerization in both directions. Moreover, the *trans* isomer has a short fluorescence lifetime (about 0.5 ns) such that the role of the singlet and triplet states in the photoisomerization can be elucidated. The results of a picosecond laser study of the *peri*-naphtho-thioindigoid dye show [12] that *trans* $\rightleftharpoons$ *cis* photoisomerization occurs via the corresponding *trans* and *cis* triplets.

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