Photochromic Processes in Spiro(1,3,3-trimethylindolo-2,2'-naphth[1,2-b]-1,4-oxazine) studied using Two-laser Two-colour Techniques†

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The photochemistry of the photomerocyanine from the title compound shows dramatic differences between polar and non-polar media; in the latter it involves the intermediacy of a ground state species with a lifetime of *ca.* 4 µs which regenerates the merocyanine almost quantitatively.

Spiro-oxazines represent an important class of photochromic compounds. Their mode of reaction is important from a mechanistic point of view, as well as in connection with their possible technological applications. In this communication we report preliminary data on the two-laser photochemistry of spiro(1,3,3-trimethylindolo-2,2'-naphth[1,2-b]-1,4-oxazine), (**I**). The title compound was prepared following a literature procedure.[1] Our studies involve the formation of the long-lived photomerocyanine (**II**) upon UV laser excitation of (**I**) followed by visible dye laser excitation of (**II**). We demonstrate for the first time the involvement of a long-lived, UV-absorbing intermediate in the reversible photodecolouration of (**II**), a process that is characteristic of non-polar solvents.

Transient phenomena were recorded employing instrumentation decribed elsewhere.[2] A few preliminary experiments revealed that the (**I**)/(**II**) photosystem is essentially insensitive to oxygen; however, we preferred to carry out all our experiments under a nitrogen atmosphere. While the minor photoconversion observed (*vide infra*) does not appear to induce the formation of any new transients, we employed a flow system to ensure that a fresh solution was irradiated by each laser shot.

It should be noted that (**II**) represents a mixture of four isomers. While our experiments do not distinguish between different isomers, it should be kept in mind that the distribution of isomers may be solvent dependent and that those with intramolecular hydrogen bonds may be favoured in non-polar media. The quantum yield for photocolouration is largely solvent independent.[3]

Laser photolysis (308 nm, ~5 ns, ≤20 mJ/pulse) of (**I**) in various solvents leads to the transient spectrum of (**II**), illustrated in the insert in Figure 1 in the case of cyclohexane. Typical lifetimes for (**II**) exceed 500 ms.[1,3] Dye laser (590 nm, ~250 ns, <600 mJ/pulse) irradiation of (**II**) in cyclohexane

(I)   (II)
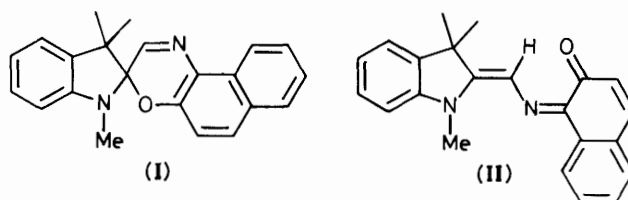
leads to bleaching within the duration of the laser pulse followed by almost complete (*ca.* 98%) recovery of the coloured form (**II**) with a lifetime around 4 µs, Figure 1a. At sufficiently high laser energies (around 300 mJ/pulse) the bleaching is essentially complete, indicating that all isomers of (**II**) absorb at 590 nm and are highly photosensitive. In the 300 nm region we observe that the dye laser induces a transient absorption which decays concurrently with the recovery of the bleaching shown in Figure 1. Clearly, the photochemistry of (**II**) is reversible and involves the intermediacy of a species (**X**) which is less absorbing than (**II**) everywhere except in the 300 nm region. No differences in the spectra of (**II**) before and after the bleaching/recovery were detected, suggesting that the initial and final isomer distributions of (**II**) are very similar.

Dye laser excitation of (**II**) in polar solvents (acetonitrile, methanol, ethanol) leads only to permanent bleaching (see Figure 1b); *i.e.* no 'recovery' phase takes place in time scales longer than the dye laser pulse duration. The observable bleaching must be due largely to recovery of (**I**), since the samples are quite resistant to prolonged irradiation (*vide infra*). Addition of moderate concentrations of methanol to a cyclohexane solution of (**I**) led to a shortening of the recovery lifetime (*e.g.* 1.7 µs for 0.4 M MeOH) and a significant increase in the unrecoverable fraction of the absorption due to (**II**). Our tentative interpretation of these results is that in polar solvents the photochemistry of (**II**) probably involves a competition of processes that regenerate (**I**) with the forma-
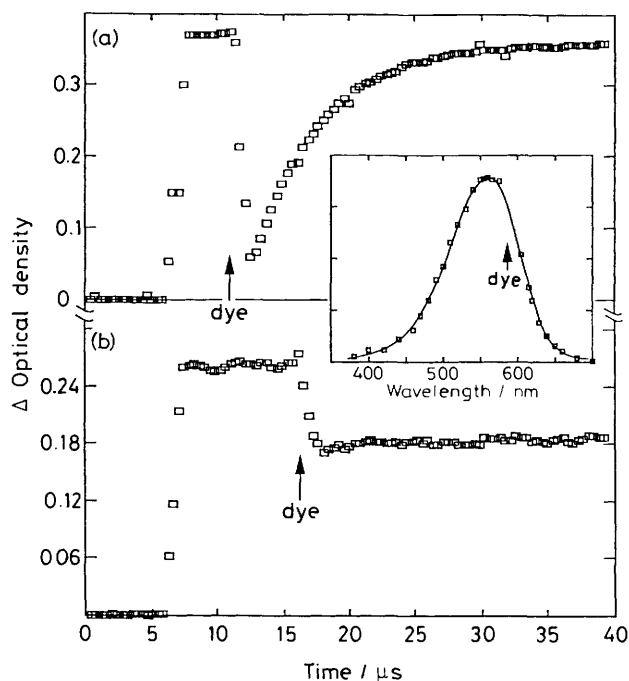
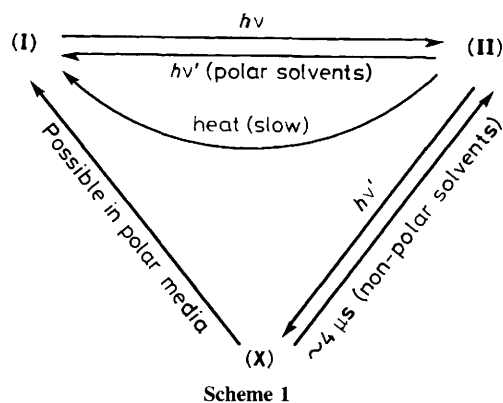**Figure 1.** Two-laser experiments showing the photoexcitation of **(I)** by a 308 nm pulse, followed by a 590 nm dye laser pulse for 7×10^{-5} M solutions of **(I)** in (a) cyclohexane and (b) acetonitrile; traces recorded at 540 nm. Insert: transient absorption spectrum for **(II)** in cyclohexane, recorded in the time range between the two laser pulses (9—10 μs in the figure). Owing to the intense dye laser pulse, it is not possible to record data between 575 and 605 nm.

Scheme 1

tion of **(X)**, which is now less important but recovers in <250 ns.

The data presented above is consistent with the basic mechanism of Scheme 1. Clearly some of these processes will be more complex than suggested by the single arrows used in the scheme. Thus there are significant differences between the photoprocesses observed in polar and non-polar solvents.

The samples of **(I)** can endure extensive irradiation, although it is clear that some minor decomposition takes place. While we have not carried out detailed quantum yield studies, comparison with the behaviour of other systems examined in our laboratories makes us confident that the loss of **(I)** occurs with $\Phi_{-I} < 0.05$. The characterization of low quantum yield products from the photolysis of submillimolar solutions is difficult, but we are trying to address this problem. Preliminary data show spectral changes in the 260—350 nm region, and the formation of one and two new products in the one- and two-laser irradiations, respectively. Overall deterioration is higher in two-laser compared with one-laser irradiations and also more pronounced in non-polar compared to polar solvents.

Finally, we hope that the characterization of the low quantum yield products will eventually help us assign the structure of **(X)**. Clearly **(X)** must be substantially less conjugated than **(II)** and perhaps comparable to **(I)**. Further, **(X)** must be able to revert to **(II)** and probably to **(I)**. Compound **(X)** cannot be an excited state or biradical, since it is insensitive to oxygen. It cannot be a geometric isomer of **(II)** since its spectrum is too different from the visible band of **(II)**. Twisted, unrelaxed conformers of **(II)** are also unlikely, since this relaxation takes place in the picosecond time scale;[4,5] finally, charge separated intermediates (*e.g.* zwitterions) are unlikely, given the ready formation and long lifetime of **(X)** in cyclohexane. While we are unable to propose a definite structure for **(X)**, the most likely explanation is that it must be a ground state, neutral isomer of **(II)**.

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