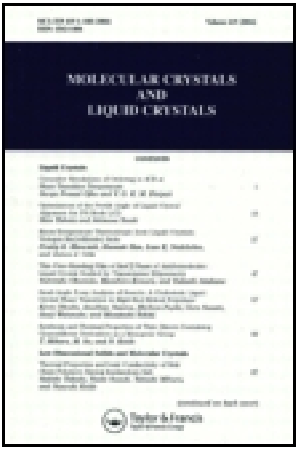

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TRIPLET REACTIVITY OF SPIRO-INDOLINO-OXAZINES STUDIED BY PHOTOSENSITISATION

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Abstract The quantum yields for the direct and triplet sensitised colour-forming reactions of five spiro-indolino-oxazines were determined in methylcyclohexane. Higher triplet than singlet reactivities were generally found.

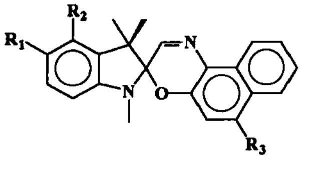
INTRODUCTION

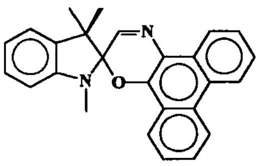
The involvement of the triplet state in the colour-forming reaction of spiranic photochromic systems has been the object of previous investigations.[1-3] For some spiropyrans a contribution of triplet mechanism was found, while for spiro-oxazines only a singlet mechanism is generally accepted. Particular interest has been devoted to photosensitisation to extend the λ-range for producing the coloured merocyanine form towards the visible. In a qualitative approach to the problem, the sensitisation efficiency was determined in terms of "colorability" under fixed conditions.[4-6] Only a few data of quantum yield for the direct and sensitised reaction can be found in the literature.[1,7,8]

In this paper we devised a method to follow spectroscopically the formation of the photomerocyanine under stationary irradiation and to determine the quantum yields of the direct and sensitised reactions from the best-fitting curves.

RESULTS AND DISCUSSION

The molecules studied (supplied by EniChem Synthesis) were four naphto-spiro-indolino-oxazines (*1, 2, 3, 4*) and one phenanthro-spiro-indolino-oxazine (*5*).





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	1	*2*	*3*	*4*
R_1	H	H	Br	CH_3
R_2	H	H	H	CH_3
R_3	H	pyperidine	H	H

Assuming that the back photochemical reaction is negligible,[8] the rate law for the formation of the photomerocyanine (PM) is given by Eq. (1):

$$d[PM]/dt = I_{SO}\Phi_d + I_S\Phi_{sens} - k_\Delta[PM] \qquad (1)$$

where Φ_d and Φ_{sens} are the photochemical quantum yields of the direct and sensitised reactions, I_{SO} and I_S are the intensities of the monochromatic radiation absorbed by the spiro-oxazine (SO) and the sensitiser (S), respectively, and k_Δ is the kinetic parameter of the thermal back reaction. Obviously, in the absence of the sensitiser, the second term on the right side is missing, while the first one is missing when the light is absorbed by the sensitiser only.

The 366 nm and 436 nm lines from a medium pressure Hg source (Osram, 500 W), selected by interference filters, were used for the irradiation of SO (or SO plus S) solutions in methylcyclohexane using a 1-cm path length cell (T = 280 K). The intensity of the irradiation light was measured by ferrioxalate actinometry. The molar extinction coefficients of PMs were determined from solutions of SO irradiated to complete conversion into the coloured form at 220 K.

The increase of the photomerocyanine absorbance (A_{PM}), followed under irradiation at the absorption maximum wavelength (550-590 nm), was fitted by a mono-exponential function, Eq. (2), as shown in Figure 1 for compound *1*.

$$A_{PM} = A^{\infty}_{PM}(1 - e^{-kt}) \qquad (2)$$

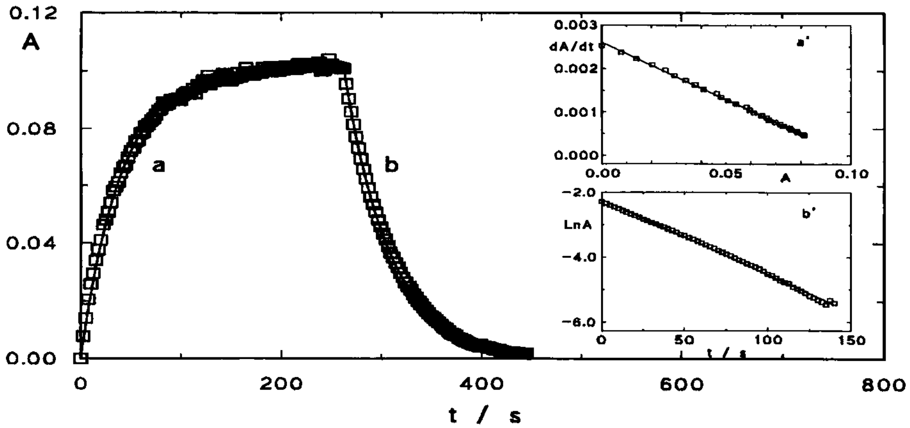

FIGURE 1 Formation (a) and bleaching (b) of *1*. Inserts: plots for the quantum yield (a') and k_Δ (b') determinations.

The quantum yields from the direct photolysis were determined from dA_{PM}/dt *vs.* A_{PM} plots (Figure 1, insert a'), using the following relationship:

$$\Phi_d = \frac{(dA_{PM}/dt)_{t\to 0}}{\varepsilon_{PM}\, I^\circ \{1 - \exp(-2.3A_{SO})\}} \tag{3}$$

The sensitised quantum yields were calculated in a similar fashion, from the equation:

$$\Phi_{sens} = \frac{(dA_{PM}/dt)_{t\to 0} - I^\circ \{1 - \exp(-2.3A_{SO})\}\Phi_d}{\varepsilon_{PM}\, I^\circ \{1 - \exp(-2.3A_S)\}} \tag{4}$$

where A_{SO} and A_S are the absorbances of SO and S at the irradiation wavelength, ε_{PM} is the molar extinction coefficient of PM and I° is the intensity of the exciting light. Corrections were also introduced, when necesssary, for inner filter effects.

The results obtained for the direct reaction and the reaction sensitised by fluorenone (E_T = 222 kJ mol^{-1} , τ_T = 3.2 μs) and camphorquinone (E_T= 213 kJ mol^{-1}, τ_T= 19 μs) are shown in Table 1 along with the bleaching constants determined in the absence of sensitiser, as described previously.[9]

TABLE 1 - Bleaching rate parameters and formation quantum yields of some merocyanines in methylcyclohexane at 280 K.

	k_Δ/s^{-1}	Φ_d	camphorquinone Φ_{sens}	fluorenone Φ_{sens}
1	0.03	0.51	~1	~1
2	0.006	0.91	0.54	0.7
3	0.02	0.43	0.46	0.8
4	0.008	0.26	0.56	~1
5	0.007	0.44	0.41	0.75

The Φ_{sens} values, generally larger than Φ_d, show that efficient triplet-triplet energy transfer occurs from S to SO. For *1*, *2* and *5*, the agreement with previous qualitative measurements[6] is very good. The rate parameters for the energy transfer, determined by Stern-Volmer equations, from both phosphorescence quenching and sensitisation measurements, indicated that the process occurs at a diffusion-controlled rate. Control experiments in solutions containing ferrocene (E_T = 163 $kJmol^{-1}$), an efficient triplet quencher, indicated the absence of a triplet contribution to the direct reaction.

The best fitting parameter, k, which accounts for the rates of the formation and bleaching processes of PM, increases with increasing SO concentration, as expected owing to the increase in the absorbed light. In the fluorenone sensitised reactions (λ_{exc}= 366 nm, absorbed by both SO and S), this parameter, which is larger than for the unsensitised reaction, accounts for both the singlet and triplet reactivities. In the camphorquinone sensitised reactions (λ_{exc}= 436 nm, absorbed only by S), k is even larger and strongly dependent on the SO structure (much larger for ***2***, ***3*** and ***5***). Having both sensitisers similar donor power and intersystem crossing yields, the marked differencies observed are attributed to specific interactions of triplet S with PM, favoured also by the longer lifetime of camphorquinone.

We also experimented benzophenone, biacetyl and dicyclopentadienyliron as sensitisers. However, the first two gave appreciable degradation, while the third one did not sensitise, probably due to its low triplet energy (E_T = 180 kJ mol^{-1}).

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