

PHOTOPHYSICS, PHOTOCHEMISTRY AND KINETICS OF INDOLINOSPIROPYRAN DERIVATIVES AND AN INDOLINTHIOSPIROPYRAN

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Summary

Three indolinospiropyran derivatives and an indolinthiospiropyran were studied in solution using nanosecond and microsecond laser flash techniques. A fluorescence lifetime was also obtained for the indolinthiospiropyran. All these compounds showed photochromism under laser flash conditions. No triplet transients were observed and oxygen (*versus* nitrogen) had no effect on the spectra, the kinetics of formation (shorter than 1 ns) or the disappearance (longer than 400 μ s) of the colored photoproduct. The transients were in the transoid opened form (merocyanine) existing in several trans conformations coming exclusively from the singlet excited state on the picosecond time scale. No cisoid form was observed down to 1 ns. No evidence of aggregation of the species in hexane was observed in contrast to 6'-nitroindolinospiropyran.

1. Introduction

The spiropyrans are well known for their photochromic properties [1]. Upon irradiation, they have been shown to convert to products having spectra similar to those of merocyanine dyes [2]. Other studies by Becker and coworkers [3 - 5] proved that only the chromene moiety of the indolinospiropyrans exhibited photochromism, and they elucidated several aspects of the photophysics of these systems, including the intramolecular energy transfer between the two halves of the substituted indolinospiropyrans. Photochromism was also established for an indolinthiospiropyran [6]. 1,3,3-trimethyl-6'-nitrospiro[indoline-2,2'-[H]benzopyran] (6'-nitroBIPS) was extensively studied to investigate its property of photoinduced spontaneous aggregation [7, 8]. In the aggregation process, the existence of a triplet state of the spiropyran as one of the moieties was proven to be essential [7]. As an extension of our study [9] of 6'-nitroBIPS, we performed nanosecond and microsecond laser flash photolysis of three other

derivatives of the spiropyran as well as a thiospiropyran in order (1) to characterize the multiplicity of the excited state(s) involved and (2) to identify the possible transients of the process. A fluorescence lifetime was also obtained in one case.

2. Experimental details

The spiropyrans were synthesized and purified as described previously [4]. All the solvents were spectrograde and were used without further purification. Absorption spectra were recorded using a Hewlett-Packard 8450 A UV-visible spectrophotometer.

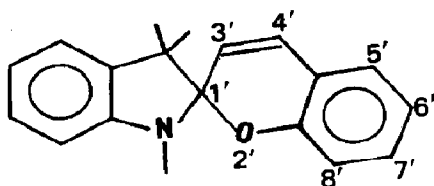
The microsecond laser flash experiments were carried out using a Q-switched Nd-YAG laser (pulse width, 11 ns). The rise time of the system is about 0.3 μ s. The third and the fourth harmonic, that is 355 nm and 266 nm, were used as the excitation source. The kinetic absorption spectrometer used to detect optical density changes ΔOD after excitation has been described previously [10]. The output of the laser was 80 mJ and the energy of the beam was controlled by the use of wiremesh screens. The commonly chosen energies were in the range 1 - 20 mJ. The typical concentration employed was about 10^{-4} M l $^{-1}$.

The solutions were examined in a rectangular quartz cell with a path length along the monitoring light of 5 mm, and they were degassed by bubbling nitrogen through them during each experiment. Also, oxygen was used to aid in the detection of triplet excited state transients.

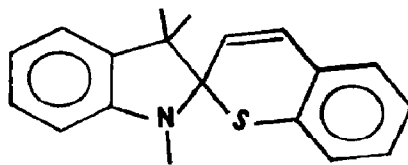
The third and fourth harmonics generated from a mode-locked Nd-YAG laser (full width at half-maximum (FWHM), 200 ps; about 24 mJ) were used for the nanosecond experiments. The kinetic absorption-emission spectrometer has been described previously [10]. The rise time of the detection system (photomultiplier tube and digitizer) was 1 ns.

3. Results

Three spiropyran derivatives (8'-methoxyBIPS (1); 6',8'-dibromoBIPS (2); β -naphthoBIPS (3)) and an indolinothiospiropyran (4)



1 - 3



4

were studied using laser flash techniques at room temperature in solution.

Previous steady state experiments were performed at low temperature (77 K) in polar and non-polar solvents and only **1** was found not to be photochromic in hydrocarbons [1, 4]. All the compounds we studied were found to be photochromic under laser flash conditions. Immediately after the pulse (about 0.3 μs) **1** ($\lambda^{\text{exc}} = 266 \text{ nm}$; 11 ns; about 1 mJ) and **2** ($\lambda^{\text{exc}} = 355 \text{ nm}$; 11 ns; about 1 mJ) showed absorption spectra typical of the transient opened form with two main absorption bands at 420 and 570 nm and 410 and 620 nm respectively. Figure 1 shows the transient absorption spectrum of **2** in hexane. The intensity of the transient absorption did not evolve up to 400 μs (the longest time measurable). The transients were not affected in any manner by the presence of oxygen. Nanosecond experiments were performed for the spiropyrans, and the rise times monitored at the absorption maxima of the transients were shorter than the time-detection limit of 1 ns. No changes in absorption characteristics were observed up to 400 μs .

Figure 2 shows the transient absorption spectra of **3** obtained by microsecond laser flash photolysis in hexane and in ethanol. In the hexane solution, immediately after the pulse (about 0.3 μs), we observed a transient

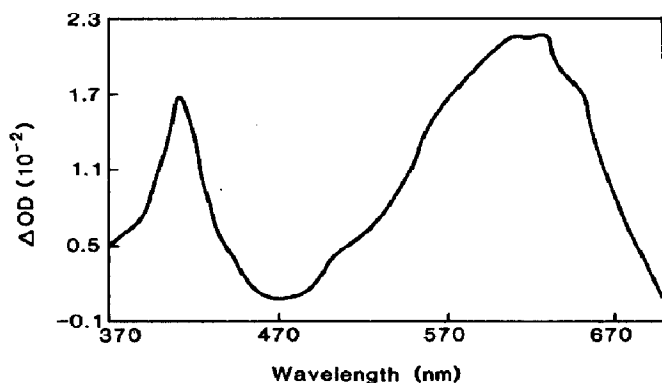


Fig. 1. Transient absorption spectrum (ΔOD spectrum) of **2** in hexane recorded 1 μs after a 355 nm laser flash.

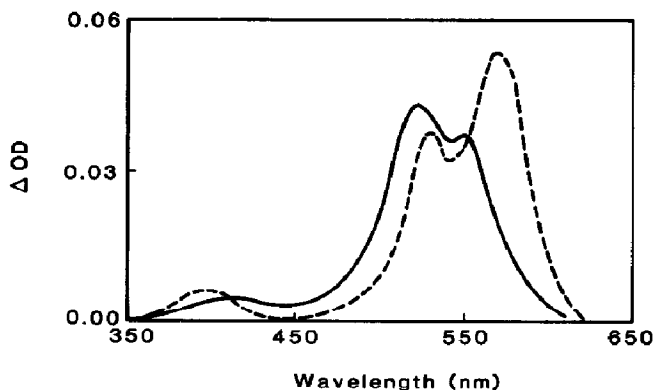


Fig. 2. Transient absorption spectra of **3** in hexane (—) and in ethanol (---) recorded 1 μs after a 355 nm laser flash.

with two absorption maxima, at 520 nm (the most intense) and at 550 nm. A weak absorption band was also observed near 400 nm. In the ethanol solution, immediately after the pulse, we observed two absorption maxima, at 530 nm and 570 nm (the most intense). In both solvents the absorption characteristics of the transients did not change up to 400 μ s. The nano-second experiment gave a detection-limited rise time (1 ns) in both solvents at the absorption maximum. No other transient was observed on the time scale 1 - 800 ns. Oxygen had no effect on the spectra, the rate of formation or the disappearance of the transients. Heiligman-Rim *et al.* have previously observed such a solvent dependence of the photochromism of 3 after steady state irradiation and they showed that the transoid merocyanine form existed in different trans stereoconformers [11]. The relative stability of these stereoisomers was dependent upon the polarity of the solvent.

4 was seen to possess photochromism in the steady state experiment in 3-methylpentane (3MP) at 77 K [6]. Immediately after irradiation at 355 nm (11 ns pulse; about 1 mJ) of a hexane solution of 4, we observed an intense sharp band with its maximum at 440 nm and a broad band from 470 nm to wavelengths longer than our detection limit of 800 nm (see Fig. 3). These transitions are similar to the transition observed in the steady state experiment in 3MP at 77 K. At low laser power (about 1 mJ), the region 470 - 650 nm was seen to be an isosbestic region in which no decay or rise was observed. We monitored the kinetics at 440 nm and at a series of wavelengths in the region 650 - 750 nm. For all the wavelengths monitored, we found a bi-exponential decay with values of 20 μ s and 400 μ s for the decay times. On increasing the laser power (up to 10 mJ), we were able to see the same behavior (bi-exponential decay) at different wavelengths in the wider range 470 - 650 nm. The presence of oxygen did not affect the spectrum, the kinetics of formation or the disappearance of the colored photoproduct.

We monitored the rise time at 440 nm and at 700 nm after irradiation at 355 nm (200 ps pulse) and found it to be shorter than our time detection limit (1 ns).

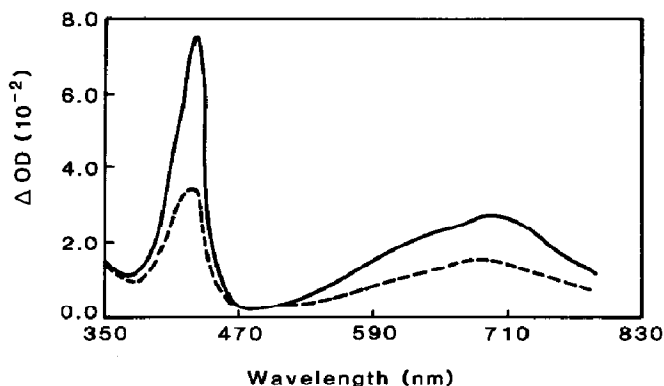


Fig. 3. Transient absorption spectra (Δ OD spectrum) of 4 in hexane recorded (—) 2 μ s or (---) 74 μ s after a 355 nm laser flash.

We also found a very weak fluorescence emission in 3MP at 77 K with an emission maximum at 370 nm. The fluorescence lifetime of **4** in 3MP at 77 K was determined using the fourth harmonic (266 nm; 200 ps FWHM) of an Nd-YAG laser and was monitored at 370 nm. The fluorescence emission trace was deconvoluted to extract the emission of **4** from the emissions of the quartz sample tube and Dewar which were seen when separately irradiated at 266 nm. The fluorescence lifetime was found to be 8 ns.

4. Discussion

All the studied spiropyran derivatives have features in common. The C—O bond breakage giving the transoid merocyanine form occurs on the picosecond time scale. The absence of triplet transients and the lack of influence of oxygen on the photochemistry leads us to believe that the transients come exclusively from the singlet excited state. We note that even in the case of the heavy-atom-substituted indolinospiropyran **2**, no triplet transients were observed. At least in two cases, **3** and **4**, it could be determined that the transoid merocyanine form exists in several trans stereoisomers in solution. However, whereas, in the case of **3**, the stereoisomers are seen to be stable in the time domain investigated (up to 400 μ s), they thermally close back on the microsecond time scale in the case of **4**. Moreover, we also studied a thiopyran derivative and found its opened colored form to thermally close back to the original compound in 240 μ s whereas the pyran derivative showed no decay for the opened form up to 400 μ s [12]. In the case of **3** and **4**, the subnanosecond rise time of the conformers implies that the conformational changes take place in the excited state.

For all the spiropyrans studied, no evidence of photoinduced spontaneous aggregation was found since no new absorption band was observed near 630 nm, the absorption maximum of the aggregates in the case of the 6'-nitroBIPS [7, 8]. This result confirms that the existence of a triplet excited state of the spiropyran is essential for the aggregation process to occur.

In the case of 6'-nitroBIPS, it has been proposed [2, 13] that there is an initial formation of a cisoid ring-opened photoproduct which undergoes isomerization to the transoid opened form (merocyanine form). We have found previously [9] that the transoid form comes from the cisoid form in 10 ns in hexane but in less than 1 ns in acetonitrile. Recently, this cisoid opened form was isolated in the case of a 6'-nitrospiropyran derivative in which the trans isomer was not formed because of steric hindrance [14]. In the case of the spiropyrans studied here, no evidence of the existence of the cisoid form was found down to 1 ns. We also note that minimum neglect of differential overlap calculations on 6-nitrochromene did not reveal any stable open isomer of cisoid geometry [15]. We therefore believe that in the case of the spiropyran derivatives studied in this work the cisoid opened

form undergoes isomerization to the transoid form on the picosecond time scale. From this and previous work [9] it has been found that only in the case of the nitro-substituted indolinospiropyran in a hydrocarbon solvent does the cisoid form exist for longer than 1 ns. We therefore believe that for all non-nitro-substituted indolinospiropyrans the cisoid opened form undergoes isomerization to the transoid form on the picosecond time scale.

Acknowledgments

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References

- 1 R. C. Bertelson, in G. H. Brown (ed.), *Photochromism*, Wiley-Interscience, New York, 1971, p. 45.
- 2 T. Bercovici, R. Heiligman-Rim and E. Fisher, *Mol. Photochem.*, **1** (1969) 23.
- 3 J. Kolc and R. S. Becker, *J. Phys. Chem.*, **71** (1967) 4045.
- 4 N. W. Tyer and R. S. Becker, *J. Am. Chem. Soc.*, **92** (1970) 1289.
- 5 N. W. Tyer and R. S. Becker, *J. Am. Chem. Soc.*, **92** (1970) 1295.
- 6 J. Kolc and R. S. Becker, *J. Phys. Chem.*, **72** (1968) 997.
- 7 V. Kongrauz, J. Kiwi and M. Grätzel, *J. Photochem.*, **13** (1980) 89.
- 8 V. Kongrauz, *Isr. J. Chem.*, **18** (1979) 304.
- 9 C. Lenoble and R. S. Becker, *J. Phys. Chem.*, **90** (1986) 62.
- 10 R. S. Becker and K. Fredmann, *J. Am. Chem. Soc.*, **107** (1985) 1477.
- 11 R. Heiligman-Rim, Y. Hirshberg and E. Fisher, *J. Phys. Chem.*, **66** (1962) 2465.
- 12 C. Lenoble and R. S. Becker, *J. Photochem.*, **33** (1986) 187.
- 13 Y. Kalisky, T. E. Orlowski and D. J. Williams, *J. Phys. Chem.*, **87** (1983) 5333.
- 14 A. Kellmann, S. Lindquist, S. Monti, F. Tfibel and R. Guglielmetti, *J. Photochem.*, **28** (1985) 547.
- 15 F. Zerbetto, S. Monti and G. Orlandi, *J. Chem. Soc., Faraday Trans. II*, **80** (1984) 1513.