NMR studies of the structure of the photoinduced forms of photochromic spironaphthoxazines

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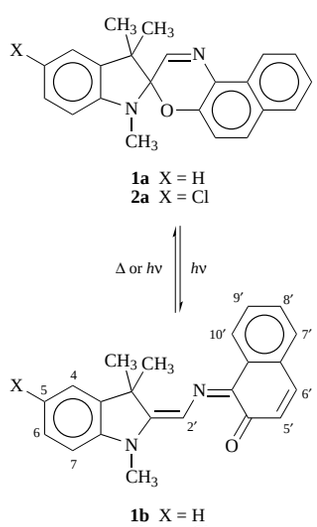
Irradiation at 355 nm with a pulsed laser of the colourless 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]-naphth[2,1-*b*][1,4]oxazine] results in formation of photomerocyanines (coloured forms of photochromic compounds); this and its chloro derivative were studied by NMR spectroscopy. This has allowed us to confirm the structure of the stereoisomers. The colourless and coloured forms exist in thermal equilibrium. Integration of certain photomerocyanine signals allowed us to calculate the thermal kinetics of bleaching k, the half-life τ and the activation enthalpy $\Delta H^{\ddagger}$ at different low temperatures and from these temperature dependence studies of the thermal decay rate, the thermal energy barrier for the decay of the coloured metastable state to the colourless form was determined.

Introduction

Organic photochromic materials have recently been the subject of intensive investigations because of the wide variety of their potential applications which include ophthalmic and sunglasses lenses, optical recording and solar energy storage.[1] Spironaphthoxazines are a class of photochromic compounds closely related to spiropyrans in which the carbon atom in the methine bridge is replaced by a nitrogen atom. These have progressively replaced spiropyrans due mainly to their ability to impart intense photocolouration in appropriate application media, their good photofatigue resistance and the relative ease with which materials can be synthesised. Spironaphthoxazines give colourless or weakly coloured solutions, which become intensely blue when exposed to UV light. When the light source is removed, the solution once again becomes colourless. Absorption of UV light by spironaphthoxazines causes cleavage of the relatively weak spiro carbon–oxygen bond by forming a coloured photomerocyanine structure (Scheme 1). The photomerocyanine reverts to the spironaphthoxazine form through a thermally or a photochemically induced ring-closure reaction.



1a X = H
2a X = Cl

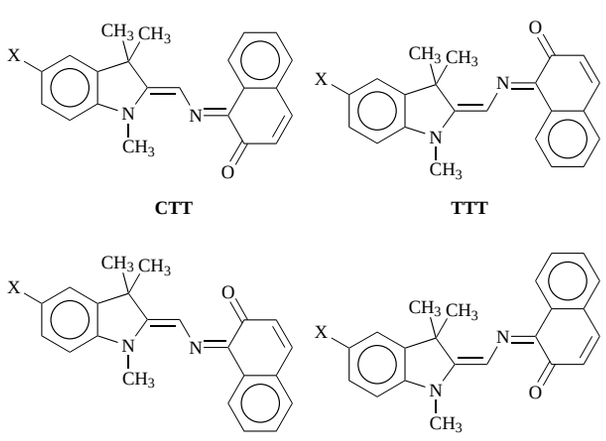
1b X = H
2b X = Cl

Scheme 1 Photochromic equilibrium between closed (**1a** and **2a**) and open (**1b** and **2b**) forms

Knowledge of the structure of the photoinduced form is required for us to be able to establish the mechanism of the photochemical transformation of spironaphthoxazine. The structure and kinetic parameters of photomerocyanines were determined by spectroscopic methods such as UV absorption,[2] flash photolysis[3] and EPR.[4] Some ^{1}H NMR studies have already been published[5–7] but only the assignment of the methyl groups, two aromatic protons (H-5′ and H-10′) and the olefinic proton H-2′ have been described.

In this paper, the results are presented of a complete ^{1}H and ^{13}C (except quaternary carbons) NMR study of two spironaphthoxazine compounds **1** and **2** obtained by working at low temperature and using a technical setup allowing for laser irradiation directly into the NMR probe. These conditions made it possible to convert spironaphthoxazines into photomerocyanines in good yields and their half-lives were sufficiently long to obtain one- and two-dimensional ^{1}H and ^{13}C spectra.

We were also able to confirm the geometric isomeric form of photomerocyanine.[7] Indeed, it can exist as eight stereoisomers with regard to the C–N bond: of these, four are *cisoid* isomers and are unlikely because of steric restrictions,[8] and four are *transoid* isomers (CTT, TTT, CTC and TTC).



CTT **TTT**

CTC **TTC**

transoid Steroisomers of photomerocyanines (**1b** and **2b**)

Table 1 Thermodynamic functions of photomerocyanines in CD_3CN

	k/mol^{-1} dm^3 s^{-1}		$\Delta H^{\ddagger}$/kJ mol^{-1}		$\tau_{1/2}$/min	
T/K	**1b**	**2b**	**1b**	**2b**	**1b**	**2b**
228	4.46×10^{-4}	1.06×10^{-3}	60.92	52.04	27	11
236	1.02×10^{-3}	2.48×10^{-3}	60.85	51.98	11	5
243	3.31×10^{-3}	6.18×10^{-3}	60.79	51.91	3	2
251	1.02×10^{-2}	—	60.72	—	1	—

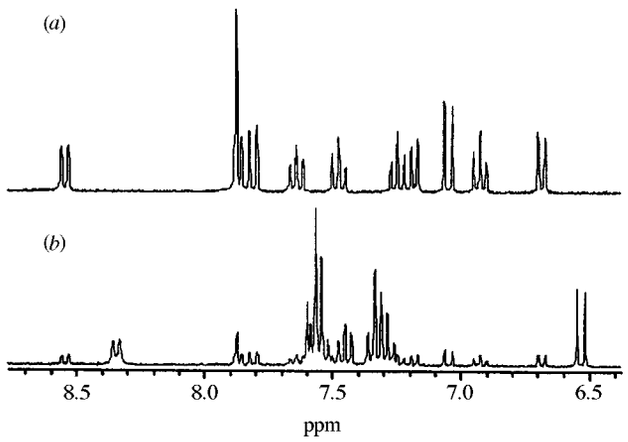


Fig. 1 ^{1}H NMR spectra of **1** before (*a*) and during irradiation (*b*)

Using the same technical device, we studied the thermal bleaching of photomerocyanine and determined various thermodynamic and kinetic parameters.

Results and discussion

Photomerocyanines have a lifetime of *ca.* 1 ms at room temperature although the acquisition time for NMR experiments is *ca.* 1 s. We therefore carried out kinetic studies at different temperatures to determine the longest lifetime.

^{1}H NMR spectra of photomerocyanines were recorded after irradiating the sample with 10 000 laser pulses, at regular intervals (t) and at different temperatures (T). The conversion between closed and open forms is not 100%. In the spectra, therefore, we were able to observe weak signals corresponding to closed form **a** and intense signals (which disappear after a certain time) corresponding to the open form **b**. The integration of some signals (N–CH_3, H-5′ and H-10′ of closed **a** and open **b** forms) in each spectrum made it possible to plot curves: ln (% **b**) = f(t). This thermal decay follows first-order kinetics and the slopes of the straight lines give the value of the kinetic constant of bleaching k, eqn. (1). The half-life $\tau_{1/2}$ can also be calculated for each temperature.

$$\ln(\%\ \mathbf{b}) = -kt + A \qquad (1)$$

From k and according to the Arrhenius equation, the activation energy for the transition, E_a, is calculated to be 62.8 and 53.9 kJ mol^{-1} (5250 and 4506 cm^{-1}) for **1b** and **2b**, respectively, eqn. (2).

$$\log k = -\frac{E_a}{2.3\,RT} + \log B \qquad (2)$$

The activation enthalpy $\Delta H^{\ddagger}$ was also determined, eqn. (3).

$$\Delta H^{\ddagger} = E_a - RT \qquad (3)$$

All these results are reported in Table 1. They agree with Chu's results,[2] which supports the validity of our experimental procedure.

As the half-life of photomerocyanines was longest at 228 K in CD_3CN, the NMR experiments were run at this low temperature. The aromatic ^{1}H NMR spectra of **1** before and during irradiation are presented in Fig. 1.

Studies on the chemical shifts of protons in the closed forms have already been published.[9] For **1b**, we observed the

Table 2 ^{1}H and ^{13}C chemical shifts of photomerocyanines in CD_3CN

	δ_H (multiplicity)		δ_C	
Position	**1b**	**2b**	**1b**	**2b**
$C(CH_3)_2$	1.89 (s)	1.86 (s)	26.8	27.3
N-CH_3	3.63 (s)	3.59 (s)	30.3	27.0
4	7.57 (dd)	7.61 (d)	121.7	122.9
5	7.28(ddd)	— —	123.8	—
6	7.45(ddd)	7.45 (dd)	127.7	128.1
7	7.32 (dd)	7.23 (d)	109.9	111.5
2′	10.09 (s)	10.19 (s)	120.2	120.3
5′	6.53 (d)	6.52 (d)	128.5	129.1
6′	7.58 (d)	7.59 (d)	138.0	139.1
7′	7.55 (dd)	7.55 (dd)	127.9	128.6
8′	7.34 (ddd)	7.36 (ddd)	124.6	125.7
9′	7.54 (ddd)	7.55 (ddd)	127.9	128.6
10′	8.36 (dd)	8.32 (dd)	122.6	123.5

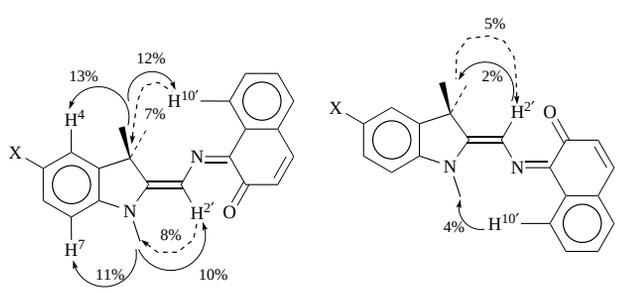
protons already assigned,[5–7] $C(CH_3)_2$, N–CH_3, H-2′, H-5′ and H-10′. Difficulties arose for the assignment of overlapping signals between δ 7.2 and 7.6, which contain four protons of spironaphthoxazine and eight of photomerocyanine.

During light irradiation we carried out a COSY–DQF experiment (in the aromatic part of the NMR spectrum) instead of COSY 45, as the latter made it impossible to distinguish between the cross peaks near the diagonal of the 2D map. It was then possible to correlate H-5′ with H-6′ and H-10′ with H9′ respectively. The range of the chemical shifts of H-7′ and H-8′ was also obtained from this experiment, but no information about the indoline unit could be gained. To get accurate values for the chemical shifts and to measure the coupling constants, a J-resolved experiment was used. We attributed H-7 as being downfield from H-4 due to the effect of the nitrogen atom.[5] Correlations give H-6 and H-5. Results are reported in Tables 2 and 3 for the two photomerocyanines **1b** and **2b**.

For the study of carbon resonances we ran a DEPT 135 spectrum and ^{1}H–^{13}C correlation. From these experiments and the proton assignments, we obtained the chemical shifts for every proton-bearing carbon atom (Table 2).

Photomerocyanines can exist in the form of four *transoid* stereoisomers (CTT, TTT, CTC and TTC). Nakamura *et al.*[7] reported that the main geometric form is TTC. That conclusion was reached after ^{1}H NOE measurements and using *ab initio* calculations.

We carried out ^{1}H NOE studies at 228 K by irradiating the protons of N–CH_3, which produced positive NOEs on the H-7 aromatic proton and on the H-2′ olefinic proton [Fig. 2(*a*)], and by irradiating H-2′ which produced positive NOE on N–CH_3 [Fig. 2(*b*)]. The intensities of the NOE effects are reported in Scheme 2. These observations enabled us to confirm that the



Scheme 2 NOE effects in TTC and CTC forms of **1b** and **2b**

main geometric structure of the coloured open form is TTC. We also obtained an NOE for the $C(CH_3)_2$ group when irradiating H-2′.

To check this last observation, we irradiated the $C(CH_3)_2$ group [Fig. 2(*c*)] which produced positive NOEs on H-4, H-10′ and H-2′, and from the irradiation of the aromatic proton

Table 3 Coupling constants ($J_{H,H}$/Hz) of photomerocyanines in CD_3CN

	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{5',6'}$	$J_{7',8'}$	$J_{7',9'}$	$J_{8',9'}$	$J_{8',10'}$	$J_{9',10'}$
1b	7.8	1.5	7.1	1.1	8.1	9.6	7.6	2.4	6.9	1.3	8.6
2b	—	2.1	—	—	8.5	10.0	8.0	*a*	6.9	1.1	9.5

[a] The value has not been measured accurately due to overlap.

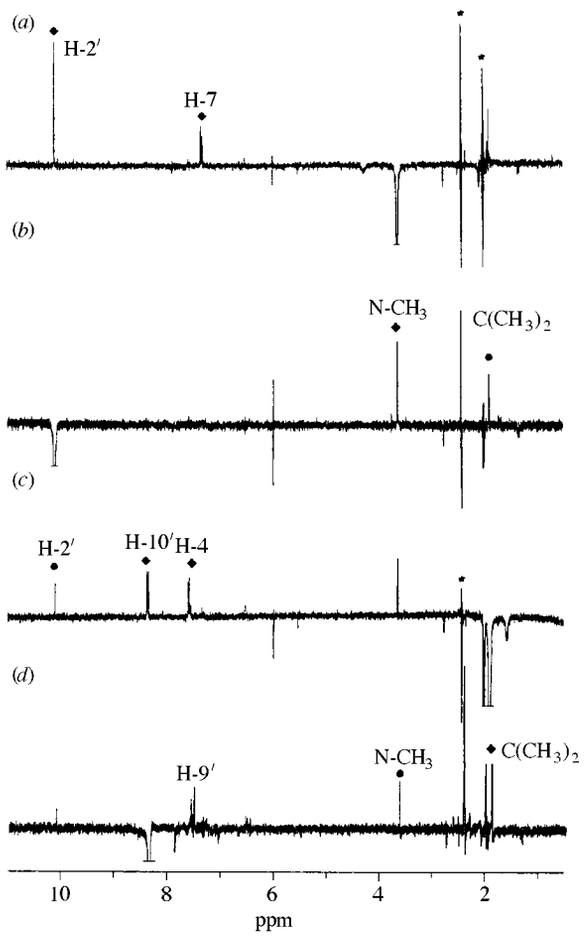


Fig. 2 ^{1}H NMR NOE difference spectra of the coloured open form **1b** obtained by irradiating (*a*) N–CH_3, (*b*) H-2′, (*c*) $(CH_3)_2$, and (*d*) H-10′. ★: Artefacts due to the solvent and water; ◆: effects on TTC form; ●: effects on CTC form.

H-10′ [Fig. 2(*d*)], we obtained an enhancement of $C(CH_3)_2$ and of N–CH_3.

All these results indicate the possible presence of a second geometric stereoisomer, CTC, as has previously been suggested.[7,10–13] This CTC isomer is the only possible structure that can account for the NOE measured. CTT and TTT stereoisomers can be ruled out because saturation of H-2′ does not produce any NOE on H-10′. However, as the extents of enhancement for equivalent spatial separations are lower, the amount of CTC is smaller than that of TTC.

Experimental

The photochromic molecules studied are Aldrich products (**1a**: 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]-naphth-[2,1-*b*][1,4]oxazine] and **2a**: the 5-chloro derivative). They were used without further purification to prepare 10^{-2} M [$^2H_3$]acetonitrile solutions.

The experimental setup for irradiating the NMR sample during data acquisition consists of a Bruker AC 300P NMR spectrometer with an Aspect 3000 computer driving a Nd/YAG pulsed laser (Quantel, YG 581-10). The third harmonic (355 nm, 100 mJ/pulse, 9–10 ns pulse width) was guided by a dichroic mirror to the bottom of a tube which passed through a specially modified 5 mm ^{1}H–^{13}C Dual NMR probe. At the upper end of this tube, a Suprasil prism fixed inside the probe head deflected the light horizontally through the receiver coils into the sample. An energy of *ca.* 50 mJ per flash was absorbed by the sample as determined actinometrically with Aberchrom 540.[14]

The spectrometer was equipped with a Eurotherm B-VT 2000 variable temperature unit. The calibration curve was established using the standard NMR procedure with a solution of 4% CH_3OH in CD_3OD. Temperature precision was within ±1 °C; the accuracy in temperature control was of the order of ±0.2 °C.

1D and 2D NMR acquisitions during light irradiation, at low temperature (228 K) were performed as follows.

First, a pseudo-continuous laser beam with a fixed number of laser shots (repetition rate: 10 Hz) made it possible to convert spironaphthoxazine into the coloured open form (*ca.* 90%). Secondly, the use of an automated microprogram modified to incorporate laser flashes in an NMR pulse sequence helped to maintain the photomerocyanine concentration at a sufficiently high level during data acquisition.

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