Kinetic and structural studies of the photochromic process of 3*H*-naphthopyrans by UV and NMR spectroscopy

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The photomerocyanines resulting from the UV irradiation of closed colourless 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran and its 3,3-bis(4-fluorophenyl) derivative have been studied by UV–VIS and NMR spectroscopy.

Kinetic bleaching studies have been carried out on a UV–VIS spectrometer at the photostationary state in acetonitrile solution. A thermal biexponential back-isomerization is observed. These two different kinetics can be attributed to two different isomers of the photomerocyanine.

NMR spectroscopy allows us to obtain a ^{1}H, ^{13}C and ^{19}F (where present) structural identification of these two forms: complete assignment for the predominant isomer (*trans–cis*) and partial assignment for the second one (*trans–trans*). The presence of a third form (which quickly decays) is also observed. Each open form follows a mono-exponential decay, with very different bleaching rate coefficients. This is the first time that ^{19}F NMR has been used to identify the number and structure of isomers produced by irradiation, illustrating the advantages of this technique.

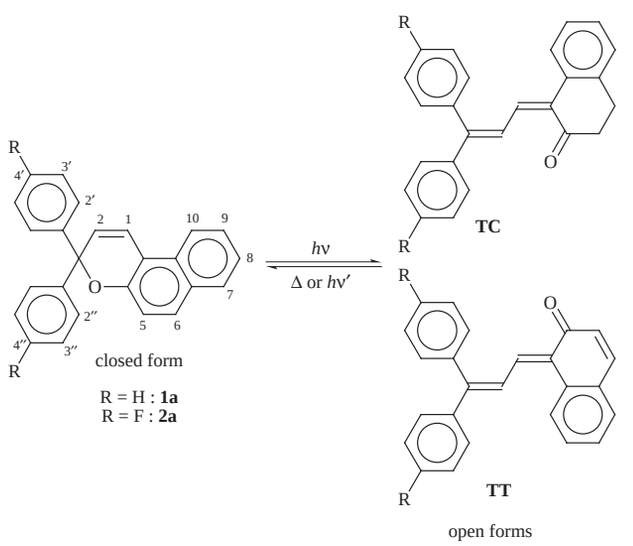
Photochromic compounds can be defined as chemical species that on irradiation convert to other species with a different absorption spectrum. They are of interest because they have a wide variety of applications. Indeed, they can be used as ophthalmic glasses, optical filters, optical switches and temporary or permanent memories.[1,2]

Although the photochromic properties of 3*H*-naphthopyrans were reported by Becker *et al.* in 1966,[3] interest in this family has mainly developed since the early 1990s.[4] 3*H*-Naphthopyrans undergo a photoinduced ring opening process to the corresponding open forms, the photomerocyanines, which are responsible for yellow to red colour formation on exposure to sunlight. When they are mixed with spirooxazines (purple to blue), a neutral colour is obtained, which is adequate for commercially acceptable lenses.[5]

Recently, we have reported the results of NMR studies on the kinetics of thermal bleaching and the structure of the photomerocyanines resulting from the irradiation of spirooxazines.[6]

In the present paper, a kinetic analysis of thermal bleaching is carried out using UV, ^{1}H and ^{19}F NMR spectroscopy. ^{1}H, ^{13}C and ^{19}F NMR studies are performed to characterise the structure of each stereoisomer resulting from the irradiation of symmetric molecules in the 3*H*-naphthopyran family: the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran **1a** and its 3,3-bis-(4-fluorophenyl) derivative **2a** were specially synthesised in order to use the fluorine atom as a NMR molecular probe. Of the nuclides belonging to main group 7 of the Periodic Table, ^{19}F is by far the most important for structural determination by NMR spectroscopy. The ^{19}F nucleus is as easy to observe as ^{1}H, since it too has a spin of $\frac{1}{2}$, a natural abundance of 100%, and an almost equally high NMR sensitivity.

The photocolouring process takes place *via* a heterolytic cleavage of the C–O bond, resulting in the formation of only two transoid isomers of the photomerocyanine, the *trans–cis* (**TC**) and the *trans–trans* (**TT**), because of the symmetry on carbon 3 (Scheme 1).



Scheme 1 Photochromic equilibrium between closed (**a**) and open forms (**b**, **c**) of 3*H*-naphthopyrans

Results

Kinetic studies by UV and NMR spectroscopy

Kinetic studies were carried out on a UV–VIS spectrometer at the photostationary state in acetonitrile solutions. Here, the multikinetics of 3*H*-naphthopyrans are studied with a polychromatic light source in different conditions.

Up to now, flash-photolysis studies[7–11] have provided some information on kinetics, giving values for bleaching rate constants and some fluorescence lifetimes. However, this method has its drawbacks and does not simulate the real conditions

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Table 1 Spectrokinetic data at the photostationary state obtained by UV spectroscopy

		$k_\Delta/10^{-3}$ s^{-1}	
	λ_{obs}/nm	$T = 281$ K	$T = 293$ K
1b	425	28.5	112.3
1c	425	0.46	0.50
2b	424	36.1	166.7
2c	424	0.30	0.66

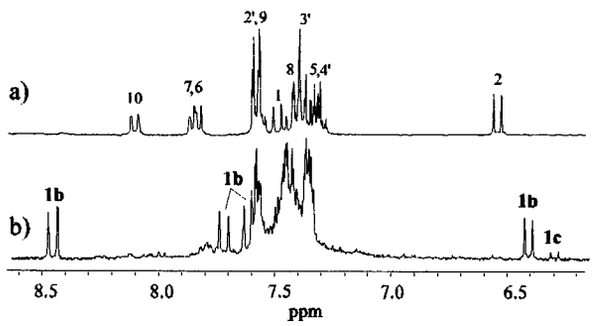


Fig. 1 ^{1}H NMR spectra of **1a** (a) before and (b) just after irradiation at 228 K

encountered when using photochromic compounds. Recently, we set up a computer-controlled photostationary states apparatus, designed to analyse bleaching processes using a continuous light source, our objective being to mimic solar irradiation. With this latter method, two rate constants of bleaching can be distinguished and measured.[12]

The multikinetics of compounds **1a** and **2a** were followed and calculated, at the open form maximum absorption wavelength, by using the eqn. (1), where $A\mathrm{o}_b = a_b + a_c + \mathrm{offset} =$

$$f(t) = a_b\exp(-k_b t) + a_c\exp(-k_c t) + \mathrm{offset} \qquad (1)$$

maximal absorbance at the photostationary state; k_b = first (fast) thermal bleaching rate constant (open form **b**); $A\mathrm{o}_c = a_c$ + offset = maximal absorbance for the second kinetic; k_c = second (slow) thermal fading rate constant (open form **c**); offset = residual absorbance.

All the photochromic parameters obtained at the photostationary state are collected in Table 1.

UV spectroscopy indicated two open forms for **1a** and **2a**, with different thermal bleaching rates. These results confirm that a thermal biexponential back-isomerization occurs from both **1a** and **2a**. Conceivably, these different kinetics could be attributed to both different isomers of the open form.

However, with this method, we cannot say which structures are responsible for which kinetics, so NMR spectroscopy was used to obtain a structural identification of these two forms.

After irradiation of the sample, ^{1}H NMR spectra of **1a** and **2a** were recorded in [$^2H_3$]acetonitrile at regular time intervals (t) and at different low temperatures (T). In these spectra, it was possible to distinguish new signals although the residues of the signals of the closed form were still present, because the conversion was not 100%. The predominant signals correspond to an open isomer (**1b** and **2b**) (Figs. 1 and 2). These decayed rapidly, although some other low intensity signals, belonging to a second isomer (**1c** and **2c**) were very persistent (%**b**:%**c** *ca.* 8, just after irradiation). In the case of **2a**, a third form (**2d**) could be seen, but its signals (weak) disappeared very quickly (Fig. 2).

The presence of fluorine atoms in compound **2a** allowed us to use it as a ^{19}F NMR molecular probe. In the spectrum obtained after irradiation (Fig. 3), we can easily distinguish six signals: one at δ −114.99 belonging to **2a**; two at δ −111.96 and −112.49, with similar high intensity; two at δ −112.10 and −112.12, with similar low intensity; one at δ −115.28, which disappears quickly.

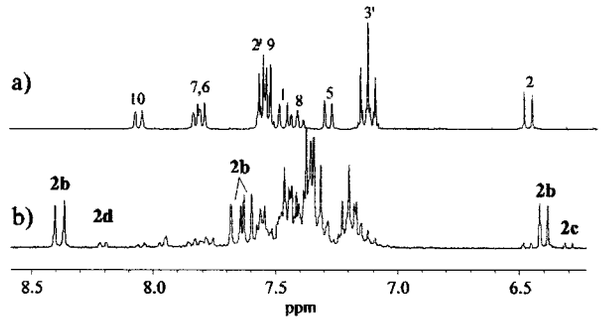


Fig. 2 ^{1}H NMR spectra of **2a** (a) before and (b) just after irradiation at 228 K

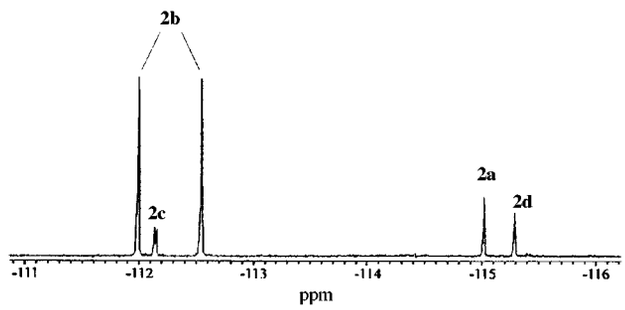


Fig. 3 ^{19}F NMR spectrum of **2a** just after irradiation at 228 K

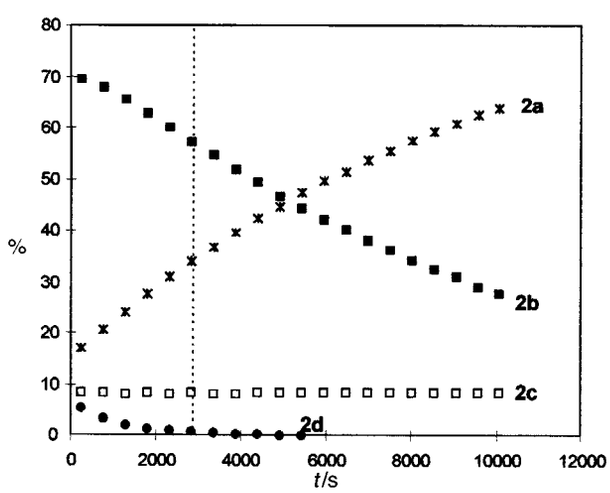


Fig. 4 Evolution of closed and open forms of **2** after irradiation at 228 K

For each ^{1}H spectrum, the signals of the predominant forms were integrated (**1b** and **2b**). Signals of forms **c** and **d** were not integrated due to their low intensity. Nevertheless, we were able to integrate all the signals for the ^{19}F spectra. That allowed us to plot a curve of the percentages as a function of time (Fig. 4).

Both ^{19}F intense signals belong to the same form, the major isomer **2b**. Its evolution curve can be divided into two parts: the first part corresponds to a sum of two exponential curves, one decreasing and one increasing. The possibility that **2b** may be formed by thermochromism is rejected due to the low temperature. In fact, this phenomenon is suppressed when isomer **2d** has fully disappeared. At this point (second part of the curve), the kinetic of decolouration for **2b** becomes mono-exponential. Kinetic parameters of bleaching (k_Δ) can be determined (Table 2). Both ^{19}F low signals correspond to another form, the minor isomer **2c**, for which the value of k_Δ determined is lower, showing its far greater stability.

Table 2 Spectrokinetic data obtained by ^{1}H and ^{19}F NMR spectroscopy

	$k_{\Delta}/10^{-4}$ s^{-1}		
	$T = 228$ K	$T = 243$ K	$T = 258$ K
1b	1.59	7.45	43.4
2b[a]	1.02	10.6	60.1
2c[a]	5.85×10^{-2}	—	—
2d[a]	9.34	—	—

[a] Data obtained by ^{19}F NMR spectroscopy.

Table 3 ^{1}H, ^{13}C and ^{19}F chemical shifts and multiplicity of **1a** and **2a** in CD_3CN

	δ_H		δ_C		δ_F
Position	**1a**	**2a**	**1a**	**2a**	**2a**
1	7.47 (d)	7.48 (d)	119.6	120.1	
2	6.56 (d)	6.46 (d)	128.3	127.9	
5	7.31 (d)	7.28 (d)	118.0	118.1	
6	7.81 (d)	7.81 (d)	129.8	130.3	
7	7.83 (dd)	7.84 (dd)	128.3	128.3	
8	7.42 (ddd)	7.43 (ddd)	123.8	124.1	
9	7.56 (ddd)	7.57 (ddd)	126.8	127.0	
10	8.08 (dd)	8.09 (dd)	121.2	121.3	
2′ = 2″	7.58 (dd)	7.54 (dd)	126.4	128.5	
3′ = 3″	7.40 (dd)	7.13 (dd)	128.0	114.9	
4′ = 4″	7.31 (dd)	—	127.4	162.0	−114.98

Comparison between rate constants deduced by NMR and UV spectroscopies is difficult because of the difference in experimental temperature. Kinetic studies by NMR at temperatures higher than 273 K were not possible due to the shorter half-life of photomerocyanines. Nevertheless, both spectroscopies have shown the presence of two isomers, one with a fast bleaching (**1b** and **2b**) and another with a slow one (**1c** and **2c**). Moreover, NMR spectroscopy has allowed a third form, **2d**, to be distinguished, which seems to convert to isomer **2b**. This form could not be observed by UV because experimental temperatures were too high. By NMR, only one signal for the two fluorine atoms is observed, so there is still equivalence of the phenyl groups. It seems its structure is near to that of the closed form. Moreover, this form decays very quickly, and leads to an increase of concentration of the isomer **2b**. At present, this form could not be identified due to its very brief half-life ($\tau_{\frac{1}{2}}$ *ca.* 13 min) and its low concentration.

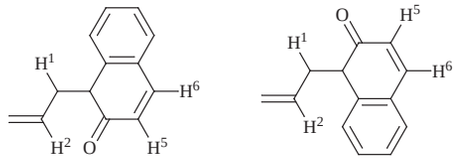
Regarding the structures of **2b** and **2c**, the fluorine atoms and the phenyl groups are now differentiated, as opposed in the closed form **2a**, where they are equivalent. This can be explained by the hybridation of carbon C-3. In the closed form, it is sp^3 hybridised, but in photomerocyanine, a sp^2 hybridation results in a nonequivalence of the phenyl groups. Consequently, these two forms correspond to transoid isomers of photomerocyanine, and NMR studies can be undertaken in order to obtain a structural identification.

NMR studies

Firstly, a complete ^{1}H, ^{13}C and ^{19}F (where present) NMR study of the closed forms **1a** and **2a** in CD_3CN was carried out in one and two dimensions. Results are reported in Table 3.

As the half-life of the predominant open isomer was longest at 228 K, the NMR experiments were run at this temperature. Fig. 1 shows the ^{1}H NMR spectrum of the open forms of **1a**.

Among the predominant signals (**1b**), four doublets at 6.41, 7.59, 7.75 and 8.43 ppm were separated from the overlapping signals between 7.3 and 7.6 ppm. From the values of their coupling constants, the signals at 6.41 and 7.59 ppm were assigned to H-5 and H-6, (H-5 is assigned at 6.41 ppm by reference to spirooxazines[6]) and those at 7.75 and 8.43 ppm to H-1 and H-2 (the signal at 8.43 ppm is assigned to H-2 because the low electron density of C=O bond causes resonance to occur at relatively low field).



TC **TT**

Fig. 5 Representation of five bonds between H-1 and H-5 in **TC** and **TT** structures

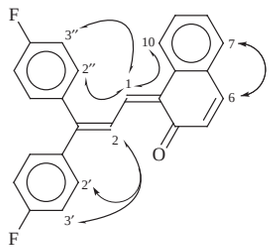


Fig. 6 Dipolar correlations in the **TC** form of **2**

The magnitude of the coupling constant between H-1 and H-2 is equal to 11.6 Hz. Due to the partial character of the double bond and considering the Karplus equations, this ^{3}J value is typical of a transoid coupling (dihedral angle *ca.* 180°).

The COSY-DQF, the *J*-resolved and the COSY-DQ2D spectra make it possible to separate the three aromatic families: (H-7, H-8, H-9, H-10), (H-2′, H-3′, H-4′), (H-2″, H-3″, H-4″). These families are difficult to tell apart because of their very close chemical shifts. Nevertheless, on the *J*-resolved map, two doublets and two doublets of doublets for family (H-7, H-8, H-9, H-10) can be distinguished.

Moreover, the exact multiplicities of H-1 and H-5 can be determined. These doublet of doublet signals are coupled together with a small constant of 1.6 Hz. This long-range coupling (^{5}J) can exist when the five bonds adopt a W arrangement. The more likely conformation for this particular system is the **TC** structure (Fig. 5), which can be attributed to the major isomer **1b**.

The ^{1}H spectrum of **2a** (Fig. 2) after irradiation presents the same groups of signals, four separate doublets and overlapping signals. 2D Experiments give information on the H-7, H-8, H-9 and H-10 family. But, as for **1b**, it is not possible to separate H-7 from H-10 and H-8 from H-9, although the overlapping signals are less intense due to the presence of fluorine atoms, which allows for a simplification in the coupling system of their *ortho* and *meta* protons. We carried out an ^{1}H–^{19}F correlation on the sample just after irradiation. This 2D experiment shows the correlation between each fluorine and each proton in the different phenyl groups of both stereoisomers. The results obtained are confirmed by running different experiments on carbons in one (POWGATE and DEPT 90) and two dimensions (^{1}H–^{13}C correlation). Each carbon in the fluorophenyl groups appears as a doublet (coupling $^{2}J_{C-F}$ and $^{3}J_{C-F}$).

By measuring these coupling constants, the two doublets at 115.2 and 115.4 ppm ($J = 21.8$ Hz) are assigned to the carbons in the *ortho* position (C-3′ and C-3″) and the two doublets at 130.8 and 133.1 ppm ($J = 8.4$ Hz) are assigned to the carbons in the *meta* position (C-2′ and C-2″).

Knowing the chemical shifts of H-2′, H-3′, H-2″ and H-3″, the ^{1}H–^{13}C correlation has made it possible to identify each carbon.

Finally, we ran a ROESY, a 2D experiment pointing out dipolar correlations. The results confirmed the chemical shifts of H-6 and H-1 and assigned H-7, H-8, H-9 and H-10 unambiguously. Thus, **2b** corresponds to the **TC** geometrical structure. The different correlations are shown in Fig. 6.

Table 4 ^{1}H, ^{13}C and ^{19}F Chemical shifts of **1b**, **2b** and **2c** in CD_3CN

	δ_H			δ_C		δ_F	
Position	**1b**	**2b**	**2c**	**1b**	**2b**	**2b**	**2c**
1	7.75	7.68	7.99	139.9	139.9		
2	8.43	8.40	7.50	125.6	125.8		
5	6.41	6.41	6.32	128.0	127.9		
6	7.59	7.64	7.64	142.5	142.6		
7	7.49	7.49		129.5	129.4		
8	7.37	7.38		128.3	127.6		
9	7.32	7.37		129.0	129.3		
10	7.59	7.59		122.9	123.0		
2′	7.35	7.44	7.47	131.0	130.8		
2″	7.40	7.38	7.35	128.7	133.1		
3′	7.57	7.20	7.19	128.3	115.4		
3″	7.48	7.32	7.32	128.6	115.2		
4′	7.59	—	—	129.1	—	−111.96	−112.10
4″	7.49	—	—	129.4	—	−112.49	−112.12

Table 5 Coupling constants of **1b** and **2b** in CD_3CN

	$J_{H,H}$/Hz					$J_{H,F}$/Hz				$J_{C,F}$/Hz			
	$^3J_{1,2}$	$^5J_{1,5}$	$^3J_{5,6}$	$^3J_{2',3'}$	$^3J_{2'',3''}$	$^4J_{2',F}$	$^3J_{3',F}$	$^4J_{2'',F}$	$^3J_{3'',F}$	$^3J_{2',F}$	$^2J_{3',F}$	$^3J_{2'',F}$	$^2J_{3'',F}$
1b	11.6	1.6	9.3	*a*	*a*	—	—	—	—	—	—	—	—
2b	11.7	1.6	9.8	9.6	9.6	5.9	8.8	5.8	8.7	8.4	21.8	8.4	21.8

[a] Some values were not measured accurately due to overlapping.

From the NMR results of **2b** and theoretical calculations for estimation of ^{13}C chemical shifts in substituted benzenes, using $\delta_C = 128.5 + z_F$, where z_F is the substituent constant, an assignment of ^{13}C NMR spectra of **1b** can be made. Using this information and the ^{1}H–^{13}C correlation, all the ^{1}H chemical shifts can be deduced.

The signals of the second stereoisomers (**1c** and **2c**) are lower but very stable. Some of them can be identified, in particular for **2c**, on the fluorophenyl groups, from the ^{1}H–^{19}F correlation. Moreover, the doublet at 6.32 ppm is assigned to H-5 by comparison with the **TC** form, a proton with the same environment. The COSY–DQF makes correlation with H-6 at 7.64 ppm possible. Two other doublets corresponding to H-1 and H-2 can be distinguished at 7.99 and 7.50 ppm. For **1c**, only H-5 and H-6 can be assigned at 6.32 and 7.64 ppm respectively. The ^{13}C NMR does not provide any information because of the low sensitivity in ^{13}C and the low concentration of this form.

All the results for isomers **b** and **c** from **1a** and **2a** are reported in Tables 4 and 5.

In conclusion, it is clear that the photomerocyanines from **1a** and **2a** exist as two stereoisomers because a biexponential bleaching kinetic has been shown by UV spectroscopy. The predominant form is a *trans–cis* isomer, as proved by NMR spectroscopy. The second form is thus *trans–trans*.

Consequently, these two spectroscopies are complementary: UV has high sensitivity and allows time-resolution, and NMR allows structural identification and the possibility of following the evolution of each form separately.

The presence of fluorine atoms, not only brings about some simplifications in the ^{1}H NMR spectrum of the phenyl groups (A_2B_2X system), but it also allows another approach to determine the exact number of open forms after irradiation.

Experimental

Materials

3*H*-Naphthopyrans were synthesised according to standard procedures.[13] Solvents were carefully dried and distilled prior to use.

UV–VIS detection

Maximum absorption wavelengths of photomerocyanines were obtained in acetonitrile with a DAD Beckman DU 7500 system.

Photostationary states experiments

The photochromic compounds (10^{-4} M) were dissolved in acetonitrile. Irradiation was derived from an Oriel 150 W high-pressure xenon lamp equipped with diaphragm and aqueous solution, which removed most of the infrared radiation. Polychromatic light intensity was determined by an Oriel quantum photoradiometer. The quartz analysis cell was enclosed in a thermostated copper block placed inside the sample chamber of a Beckman DU 7500 diode array spectrophotometer. The cell had an optical path length of 1 cm. The aerated solutions were stirred continuously using a mechanical stirrer. This apparatus is described in ref. 12. Spectra of photostationary mixtures were measured and the decay of the open form was followed at the maximum absorption wavelength, at two temperatures, 281 and 293 K.

NMR Spectroscopy

The experimental set-up for irradiating the NMR samples (10^{-2} M) during data acquisition consists of a Bruker AC 300P NMR spectrometer, equipped with a Dual probe, specially modified to allow for *in situ* irradiation of the sample. The computer of the spectrometer drives a Nd/YAG pulsed laser (QUANTEL, YG 581-10). 1D and 2D NMR acquisitions were performed as described in ref. 6.

For the ^{19}F NMR studies, the QNP probe used did not allow for *in situ* irradiating. We therefore irradiated the compound **2a** with a Xe-Hg high pressure lamp (1000 W) equipped with a pass band glass filter (Oriel 011FG09) at the appropriate temperature. After irradiation, the tube was quickly transferred into the QNP probe of the AC 300P NMR spectrometer.

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