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NMR proofs of the involvement of an allenyl-naphthol as a key-intermediate in the photochromic process of [3*H*]-naphthopyrans

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Abstract—The NMR characterization of an intermediate, proved to be involved in the photochromic process of fluoro-substituted-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans is reported. An *o*-allenyl-naphthol structure was deduced and a plausible reaction mechanism was proposed.

Photochromic compounds have been extensively studied, as they are potential photo-memory and photoswitching materials.[1] In photochromic families, 3*H*-naphtho[2,1-*b*]pyran are of interest because of their favorable photochromic properties associated with high fatigue resistance.[2] They yield merocyanine forms by UV light and the process is reversible by visible light or heat. While a better understanding of pyran properties has been obtained in recent years, the number and nature of the transient species[3] that are formed must be clearly established to further improve performance in commercial applications. In previous works, we reported the results obtained after UV irradiation of fluoro-substituted diphenyl-[3*H*]-naphthopyrans. On the basis of ^{1}H, ^{19}F and ^{13}C NMR spectroscopy, the structures of photomerocyanines were unambiguously identified and the kinetic and thermodynamic parameters were calculated. Whatever the initial structure of molecules, 3,3-di(4-fluorophenyl)-3*H*-naphtho[2-1,b]-pyran (**CF-1**)[4] and 3-(2-fluorophenyl)-3-phenyl-3*H*-naphtho[2-1,b]pyran (**CF-2**),[5] (Scheme 1), each possible transoid isomer was detected. In both cases of molecules cited, an intermediate structure was also detected after UV irradiation. This structure converts thermally and rapidly into transoid-cis-type (**TC**-type) photomerocyanines, proving its intervention in the photochromic process. Nevertheless, no identification of its structure was published because of a low concentration and its too rapid disappearance. Our interest has since focused on the structural identification of this intermediate form and we present here the exact NMR structure[†] of the intermediate form involved in the photochromic process of **CF-1** and **CF-2**. The molecules are fluoro-substituted to use ^{19}F as a NMR molecular probe, which makes it possible to follow the behavior of each structure.

When a low temperature (213 K) solution of naphthopyran **CF-1** (Fig. 1a) in acetone-d_6 was exposed to UV irradiation for 20 min, using a 1000 W Xe-Hg lamp, filtered by a band-pass glass filter ($259<\lambda<388$ nm), **TC**-type and **TT**-type photomerocyanines were yielded, together with the intermediate form, hereby called **Int-1** (Fig. 1b). When the UV irradiated solution was then exposed to visible light ($\lambda>400$ nm) for 10 min, a significant conversion of orange merocyanines into colorless structure **Int-1** was observed (Fig. 1c). At 213 K, **Int-1** was obtained almost exclusively and no significant thermal decay was observed. In the ^{1}H NMR spectrum recorded (Fig. 2a), a singlet signal at 9.83 ppm, exchanged when a drop of D_2O was added, is assigned to a hydroxy function. TOCSY-1D experiments underline the scalar correlations between H-10 at 8.31 ppm (Fig. 2b) and the protons H-9 (7.39 ppm), H-8 (7.32 ppm) and H-7 (7.87 ppm), and between H-6 at 7.81 ppm (Fig. 2c) and the proton H-5 at 7.30 ppm. ROESY-1D (Fig. 2d) makes it possible to measure a

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[†] Spectra were recorded on a Bruker DPX 300 spectrometer at frequencies of 300.09 MHz for ^{1}H, 282.37 MHz for ^{19}F and 75.46 MHz for ^{13}C, using standard pulse sequences.

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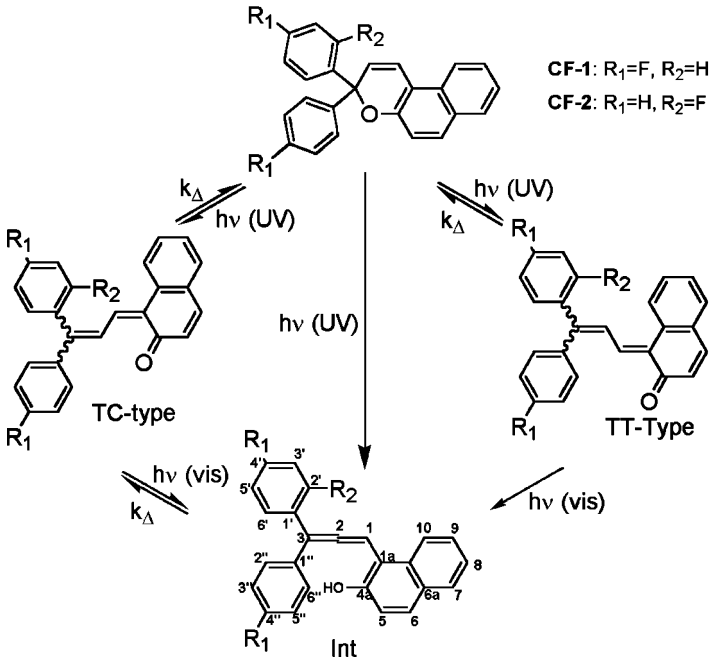

Scheme 1.

dipolar effect between H-10 and the singlet signal at 7.68 ppm directly attributed to the proton H-1. By recording 2D NMR HSQC-gs (direct ^{1}H–^{13}C correlations) and HMBC-gs (long-range ^{1}H–^{13}C correlations), the carbon-skeleton was deduced. In particular, an allene function was unambiguously proved with ^{13}C NMR resonances at 90.5, 211.2 and 108.8 ppm for C-1, C-2 and C-3, respectively (Fig. 3).

The same procedure was applied to naphthopyran **CF-2** and it produced the intermediate **Int-2** (Fig. 4). As previously, characteristic ^{1}H singlet signals at 9.90 and 7.70 ppm were attributed to the hydroxy function in the 4a-position and to the H-1 of the allenic system, respectively. The allenic system was once again deduced from 2D NMR experiments. The HSQC-gs yields a cross signal for the H-1 proton, connected over one bond with the carbon C-1 at 90.7 ppm, whereas the HMBC-gs performs long-range correlations for H-1 connected by two-bonds with C-2 at 210.9 ppm and by three-bonds with C-3 at 105.4 ppm.

Consequently, an *o*-allenyl-naphthol structure was unambiguously identified by combining ^{1}H and ^{13}C NMR evidence (Table 1). Allenyl-naphthol has already been cited as an intermediate product in the synthesis of naphthopyran derivatives.[6] Moreover, Gericke et al.[7] reported that the drastic action of a strong base on benzopyran derivative generates a transient allenyl phenol. Nevertheless, it has never been mentioned that such a structure could have a role in the photochromic process. Based on previous kinetic and structural studies,[4,5,8] which pointed out the leading role of this labile intermediate, we can propose that the allenyl-naphthol generates via a 1,5-hydrogen shift the **TC**-type photomerocyanine, which undergoes a thermal ring-closure to regenerate the initial 3*H*-naphthopyran. In conclusion, the present result paves the way for new approaches to a better understanding for mechanistic aspects of naphthopyran photochromism.

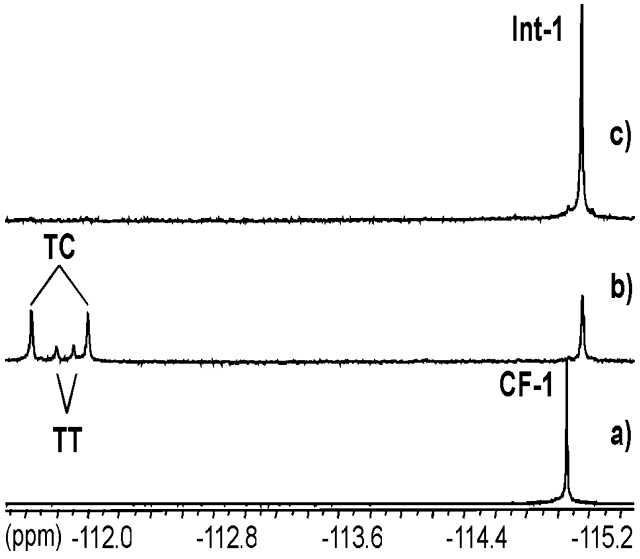

Figure 1. ^{19}F NMR spectra at 213 K of a 10^{-2} M solution of **CF-1** in acetone-d_6. (a) Before, (b) after 20 min of UV irradiation, (c) +10 min of visible irradiation.

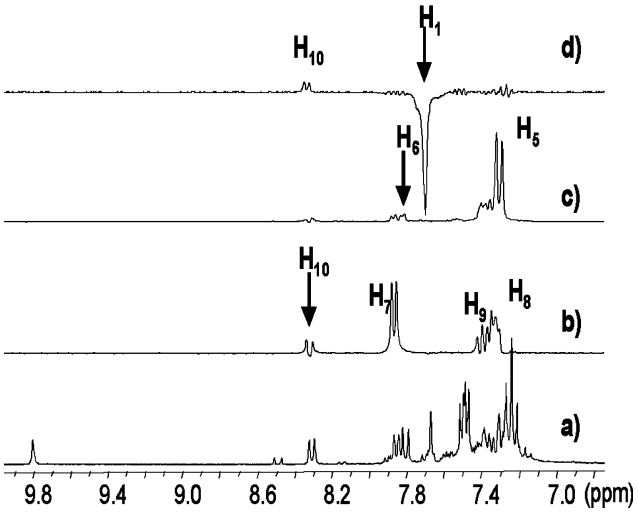

Figure 2. (a) ^{1}H NMR spectrum, (b) ^{1}H Tocsy with irradiation of H-10, (c) ^{1}H Tocsy with irradiation of H-6, (d) ^{1}H Roesy with irradiation of H-1, at 213 K of a 10^{-2} M solution of **Int-1** in acetone-d_6.

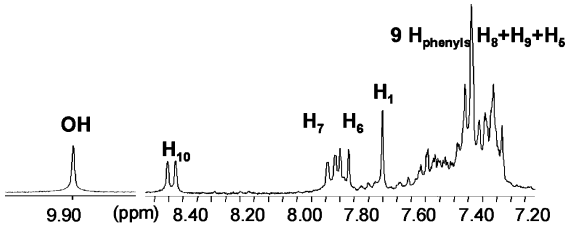

Figure 4. ^{1}H NMR spectrum at 213 K of a 10^{-2} M solution of **Int-2** in acetone-d_6.

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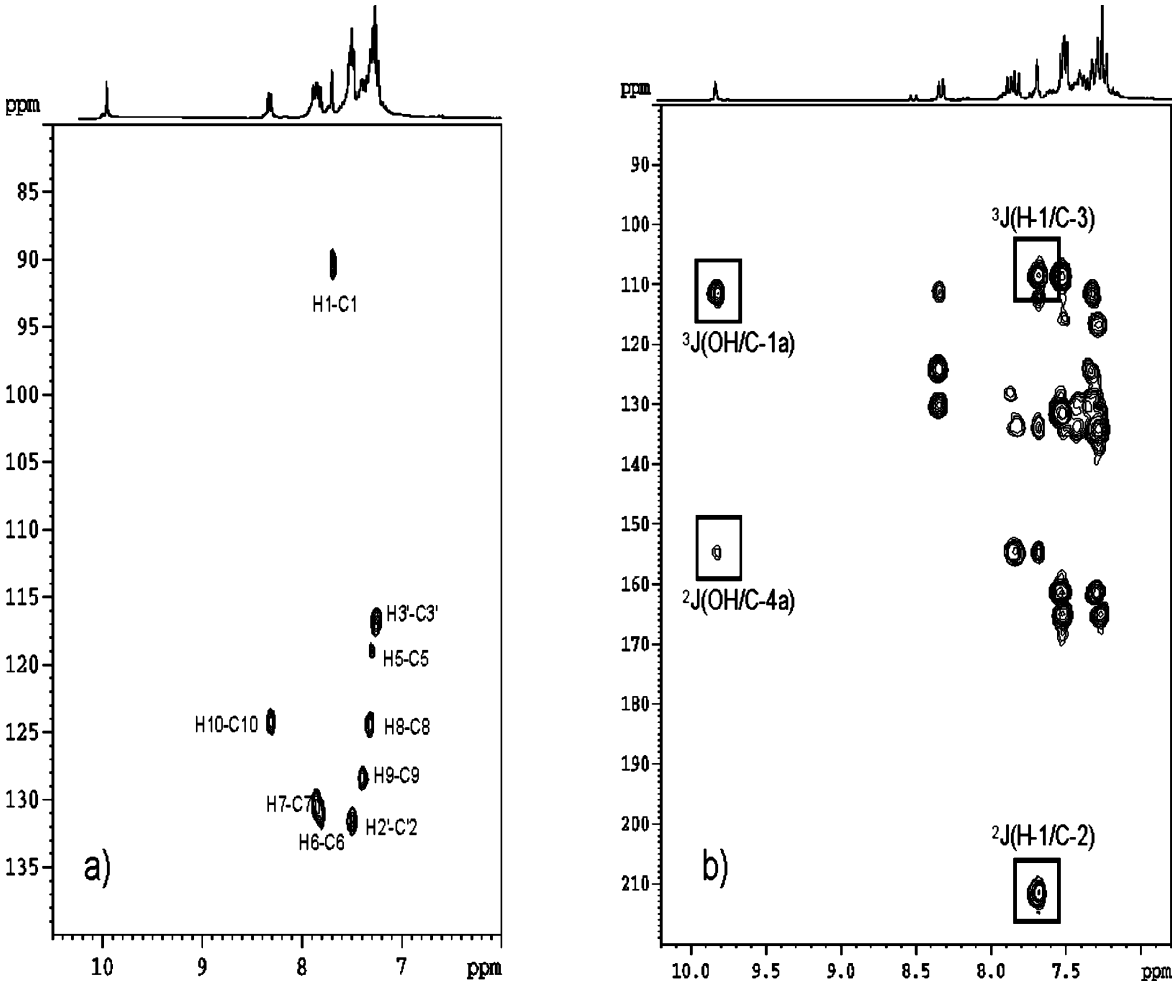

Figure 3. 2D NMR (a) HSQC-gs and (b) HMBC-gs of **Int-1** at 213 K.

Table 1. ^{1}H, ^{13}C, ^{19}F NMR data of **Int-1** and **Int-2** in acetone-d_6

Int-1			**Int-2**		
	^{1}H/ppm (J/Hz)	^{13}C/ppm		^{1}H/ppm (J/Hz)	^{13}C/ppm
1a	–	111.7	1a	–	111.6
1	7.68	90.5	1	7.70	90.7
2	–	211.2	2	–	210.9
3	–	108.8	3	–	105.4
4a	–	154.7	4a	–	154.7
5	7.30 ($^{3}J_{56}=8.9$)	118.9	5	7.30 ($^{3}J_{56}=8.9$)	119.0
6a	–	130.3	6a	–	130.5
6	7.81	131.1	6	7.84	131.4
7	7.87 ($^{3}J_{78}=7.5$)	130.5	7	7.88 ($^{3}J_{78}=8.1$)	130.8
8	7.32	124.4	8	7.34	124.7
9	7.39 ($^{3}J_{910}=8.4$)	128.4	9	7.40 ($^{3}J_{910}=8.5$)	128.5
10	8.31	124.3	10	8.44	124.6
10a	–	133.6	10a	–	133.8
1′,1″	–	134.0	Phenyls	7.30–7.60	125–135
2′,2″	7.49 ($^{3}J_{3'2'}=9.1$)	131.3	OH	9.90	–
3′,3″	7.25	116.8			
OH	9.83	–			
4′,4″ = ^{19}F	−115.2 ($^{3}J_{3'F}=8.5$, $^{4}J_{2'F}=5.4$)	162.6	2′ = ^{19}F	−112.2	162.0

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