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NMR characterization of allenyl-naphthol in the photochromic process of 3,3-diphenyl-[3*H*]-naphtho[2-1,b]pyran

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Abstract

Allenyl-naphthol was produced after UV irradiation followed by visible light irradiation of 3,3-diphenyl-[3*H*]-naphtho[2-1,b]pyran (CH). Elucidation of its structure was obtained by 1D and 2D NMR spectroscopy. Kinetic study showed that its thermal bleaching followed a monoexponential decay, leading to an increase of concentration of TC merocyanine.

Keywords: Photochromism; Naphthopyrans; Allenyl-naphthol; NMR spectroscopy

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1. Introduction

Benzo and naphthopyran derivatives are an important class of photochromic materials [1,2]. They were originally studied for their potential in offering complementary colors (yellow to orange) to the well-known (blue) indolinospironaphthoxazines [3]. Since the pioneering work of Becker and Michl who first established these properties in a rigid matrix at 77 K [4], many studies have been carried out demonstrating photochromic behavior at room temperature. Owing to their good photochromic properties associated with high fatigue resistance [5,6], this family of compounds has been used in recent years in the manufacture of plastic photochromic lenses. The photochromic activity of these compounds is due to the reversible light-induced cleavage of the bond between the heterocyclic oxygen atom and the quaternary carbon: the closed colorless form undergoes ring-opening to reach the corresponding open forms, the photomerocyanines, which are responsible for coloration. While a better understanding of pyran properties has been obtained in recent years, the number and nature of the transient species which are formed must be clearly established in order to further improve performance in commercial applications. Typically, UV-Vis spectroscopy [7–9] has been used to study kinetics and has resulted in the determination of the intrinsic properties which are responsible for the photochromic process. Nevertheless, this method gives only absorbance values, with the disadvantage of presenting overlapping spectra. In previous works [10,11], we reported the results obtained after UV irradiation of fluoro-substituted 2,2-di(4-fluorophenyl)-[2*H*]-benzopyrans and, 3,3-di(4-fluorophenyl) and 3-(2-fluorophenyl)-3-phenyl-[3*H*]-naphthopyrans. To investigate fluorinated structures, ^{19}F NMR spectroscopy was chosen as an original method for detecting photoproducts. 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. Moreover, an unprecedented *o*-allenyl-phenol (-naphthol) structure was unambiguously identified by combining ^{1}H and ^{13}C NMR evidence [12,13].

While such a structure has never been detected before by any other method, a doubt may persist as to the influence of fluorine atom. We therefore report the results on the behavior at low temperature, to reduce the rates of bleaching of photoproducts, of 3,3-diphenyl-[3*H*]-naphtho[2-1,b]pyran (CH) after UV and visible irradiation (Scheme 1).

2. Experimental

2.1. Materials

3,3-Diphenyl-[3*H*]-naphtho[2-1,b]pyran was synthesized according to standard procedures [14]. NMR experiments were carried out in acetone-d_6. The concentration of solutions was 10^{-2} M.

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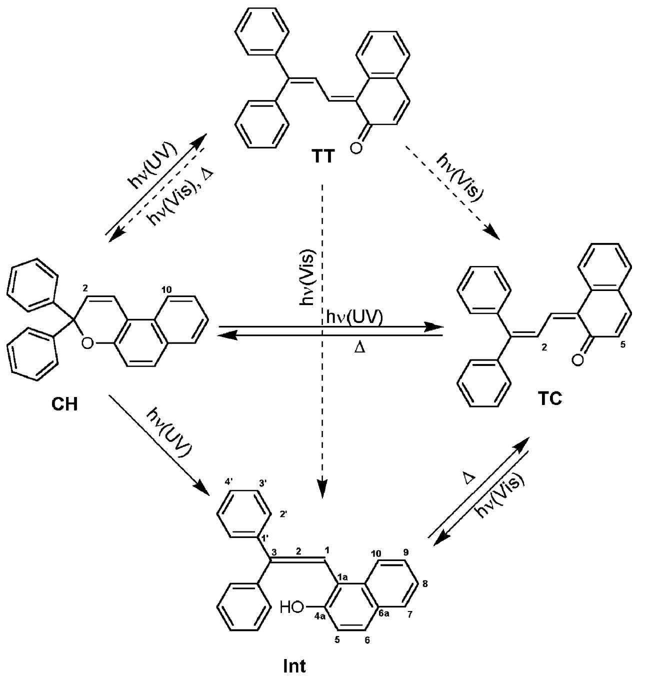

Scheme 1.

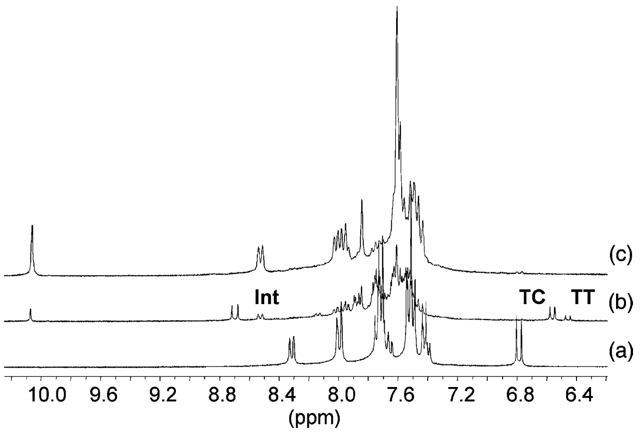

Fig. 1. ^{1}H NMR spectra at 213 K of a 10^{-2} M solution of CH in acetone-d$_6$: (a) before, (b) after 20 min of UV irradiation, (c) +10 min of visible irradiation.

2.2. NMR spectroscopy

1D and 2D (^{1}H–^{1}H COSY-gp, ^{1}H–^{1}H ROESY, ^{1}H–^{13}C HSQC-gp and ^{1}H–^{13}C HMBC-gp) NMR spectra were

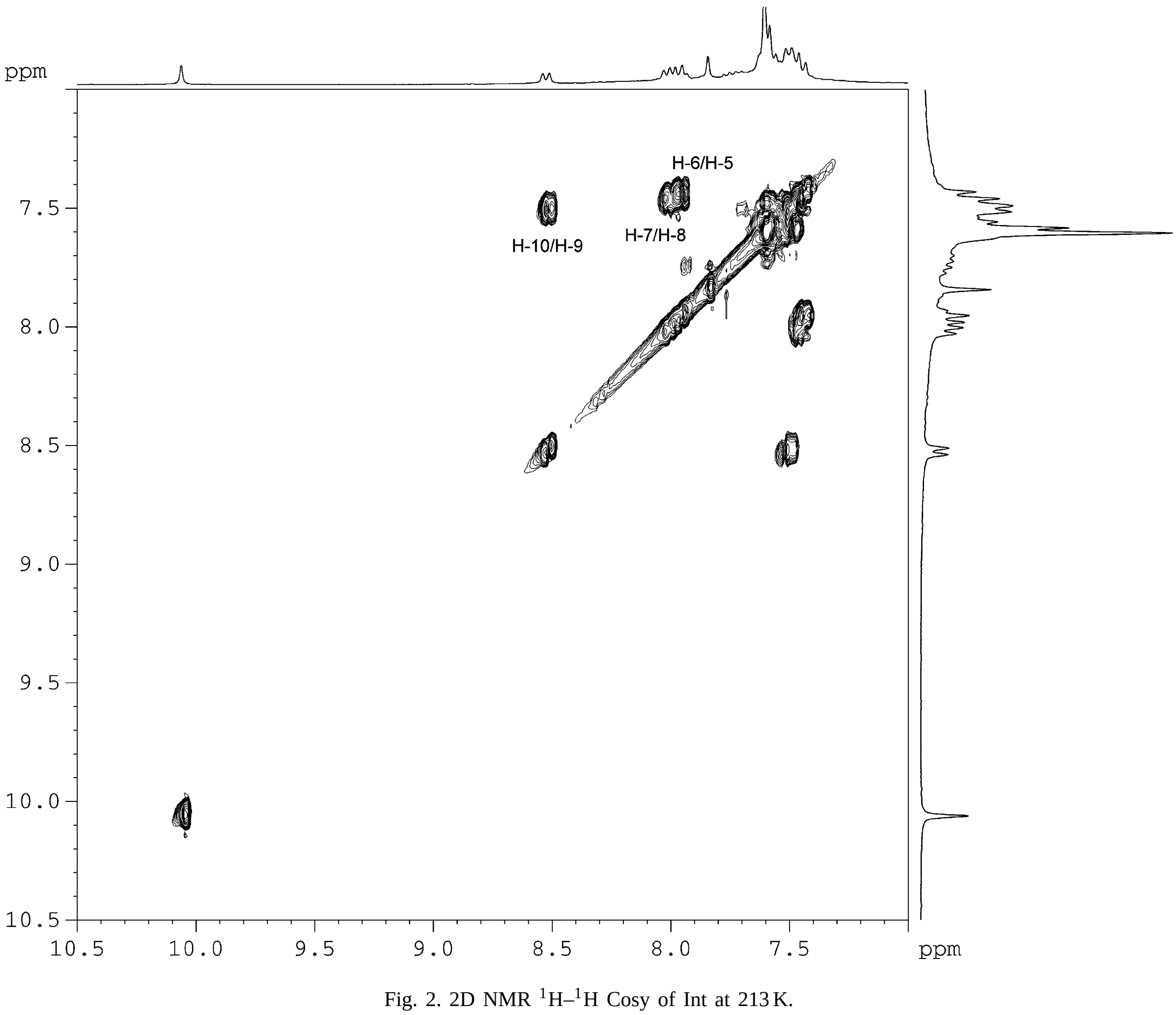

Fig. 2. 2D NMR ^{1}H–^{1}H Cosy of Int at 213 K.

acquired using a Bruker DPX 300 NMR spectrometer operating at 300.09 MHz (^{1}H) and 75.02 MHz (^{13}C) equipped with a BBI probehead fitted with an actively shielded *z*-gradient coil for delivering pulsed field gradients.

2.3. UV and visible irradiation

UV and visible irradiation of the samples in the NMR tube, were performed in a home-built apparatus. The emission spectrum of a 1000 W Xe–Hg high-pressure filtered short-arc lamp (Oriel), was focused on the end of a silica light-pipe (length 6 cm, diameter 8 mm), leading the light to the spinning sample tube, inserted in a quartz dewar. The temperature of the sample was controlled with a variable temperature unit (B-VT1000-Bruker, 123–423 K, *T* range). The filters used are the Schott 011FG09: 259 nm $< \lambda <$ 388 nm with $\lambda_{max} =$ 330 nm and $T =$ 79%, and the Oriel 3–74: $\lambda >$ 400 nm for UV and visible irradiation, respectively.

3. Results

When a low temperature (213 K) solution of CH (Fig. 1a) was exposed to UV irradiation for 20 min, TC and TT photomerocyanines were yielded [10] together with a supplementary form, hereby called Int (Fig. 1b). When the UV irradiated solution was then exposed to visible light ($\lambda >$ 400 nm) for 10 min, a significant conversion from orange merocyanines into a colorless structure Int was observed (Fig. 1c). In theses conditions, Int was obtained almost exclusively and no significant thermal decay was observed ($k_{\Delta}^{213} = 0.8 \times 10^{-5}\,s^{-1}$).

In the ^{1}H NMR spectrum (Fig. 1c), a singlet signal at 10.06 ppm, suppressed when a drop of D_2O was added, is assigned to a hydroxy function. Four protons, the multiplicities of which are doublet (at 8.52, 8.02 and 7.97 ppm) and singlet (at 7.84 ppm, characteristic of H-1), are easily distinguished outside the overlapping signals between 7.4 and 7.7 ppm.

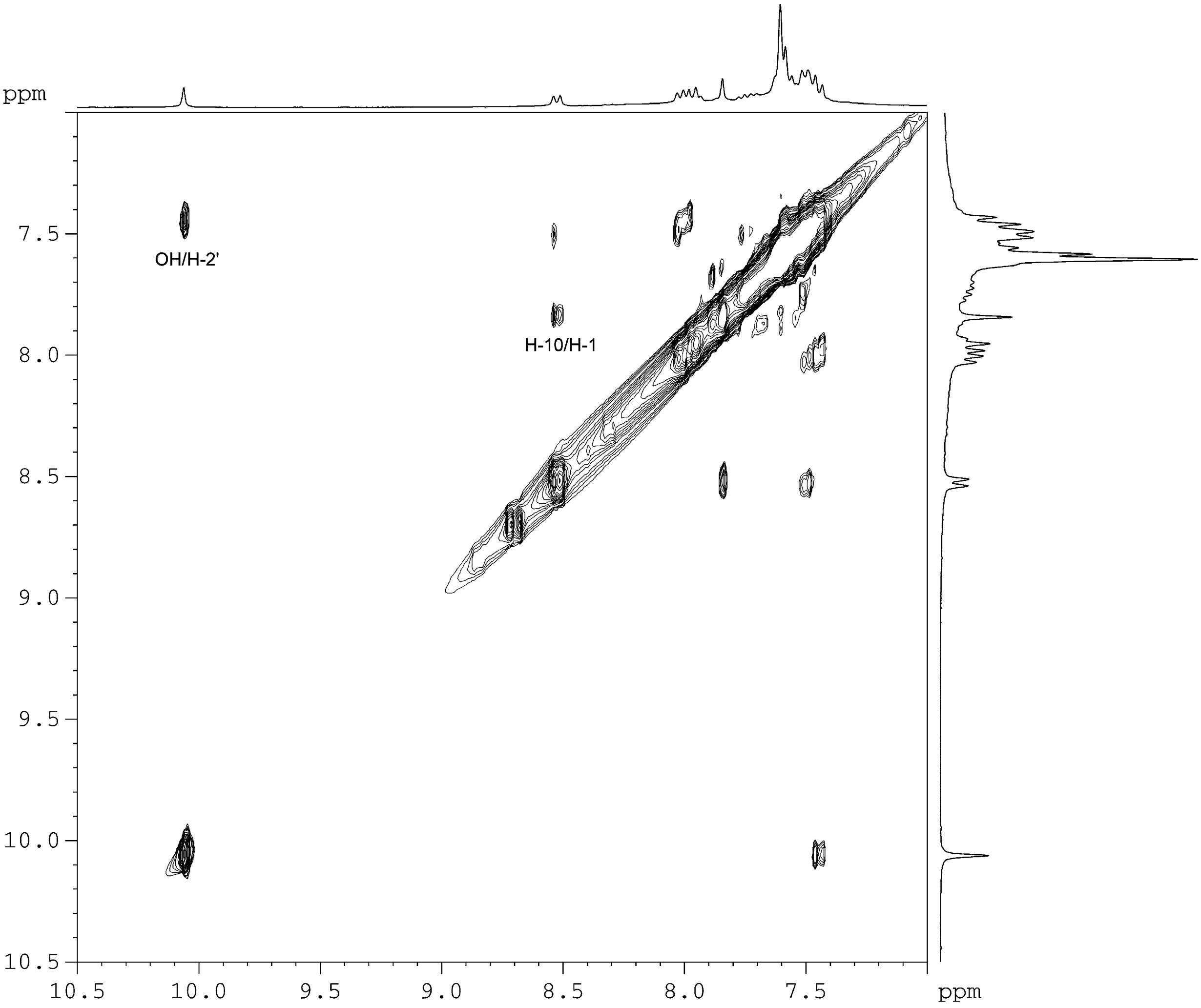

Fig. 3. 2D NMR ^{1}H–^{1}H Roesy of Int at 213 K.

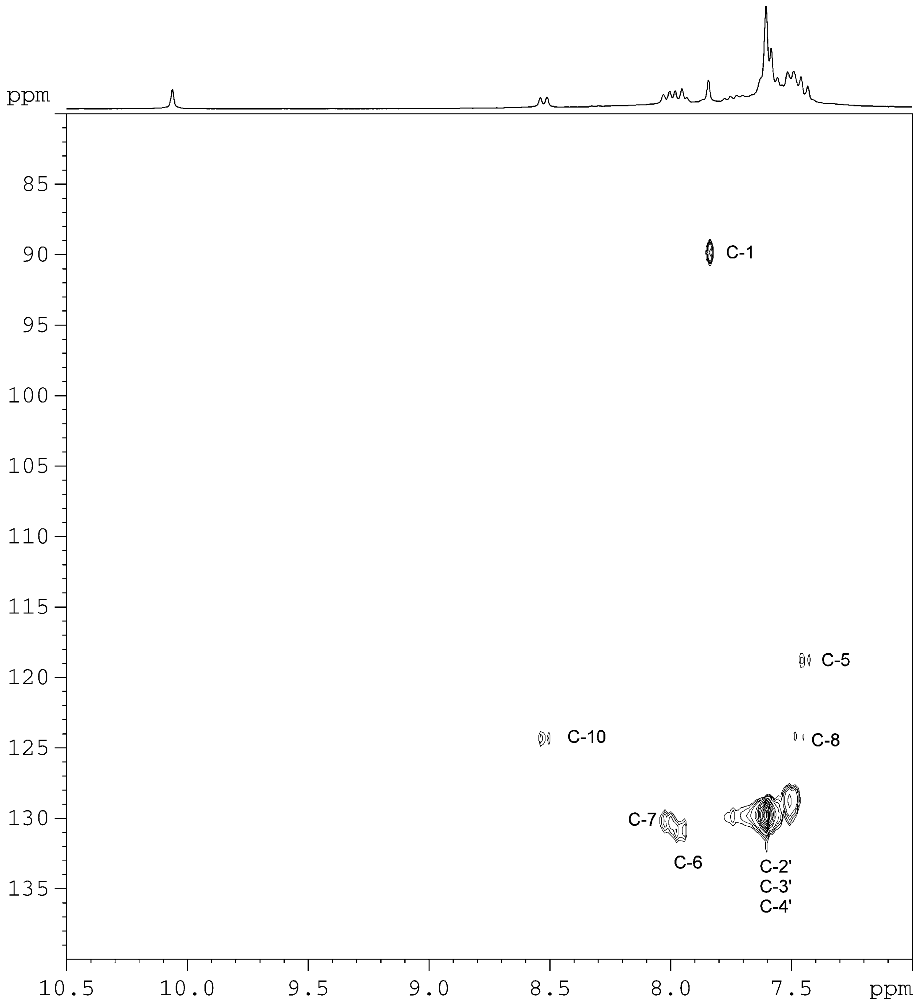

Fig. 4. 2D NMR ^1H–^{13}C HSQC of Int at 213 K.

^1H–^1H Cosy experiment underlines the scalar correlations between the signals at 8.52 and 7.51 ppm, between those at 8.02 and 7.46 ppm, and between those at 7.97 and 7.44 ppm (Fig. 2).

^1H–^1H Roesy makes it possible to measure a dipolar effect between the proton H-1 at 7.84 ppm and the proton deduced to be H-10 at 8.52 ppm (Fig. 3).

By recording 2D NMR HSQC (direct ^1H–^{13}C correlations, Fig. 4) and HMBC (long-range ^1H–^{13}C correlations, Fig. 5), the carbon-skeleton was deduced. In particular, the three characteristic resonances at 89.9, 210.7 and 110.5 for C-1, C-2 and C-3, respectively, proved the presence of an allene function.

^1H and ^{13}C NMR data is assembled in Table 1.

At the end of the 2D NMR experiments (at 213 K), a small part of Int has disappeared. To a better understanding of its fate, a kinetic study of thermal bleaching was carried out at a higher temperature (228 K) to obtain a significant evolution of its concentration.

A fresh solution of CH was exposed to UV irradiation, then to visible light. The irradiation in the visible region

Table 1
^1H and ^{13}C NMR data of Int in acetone-d_6 (multiplicity—s: singlet; d: doublet)

Position	δ (^1H) (ppm)	J (^1H–^1H) (Hz)	δ (^{13}C) (ppm)
1	7.84 (s)		89.9
2	–		210.7
3	–		110.5
5	7.44		118.8
6	7.97 (d)	^3J (H-5–H-6) = 8.8	130.9
7	8.02 (d)	^3J (H-7–H-8) = 7.7	130.2
8	7.46		124.2
9	7.51		128.7
10	8.52 (d)	^3J (H-9–H-10) = 8.3	124.4
2′,3′,4′	7.5–7.7		129–131
OH	10.06 (s)		–
1a	–		111.6
4a	–		154.2
6a	–		129.8
10a	–		133.4
1′	–		137.5

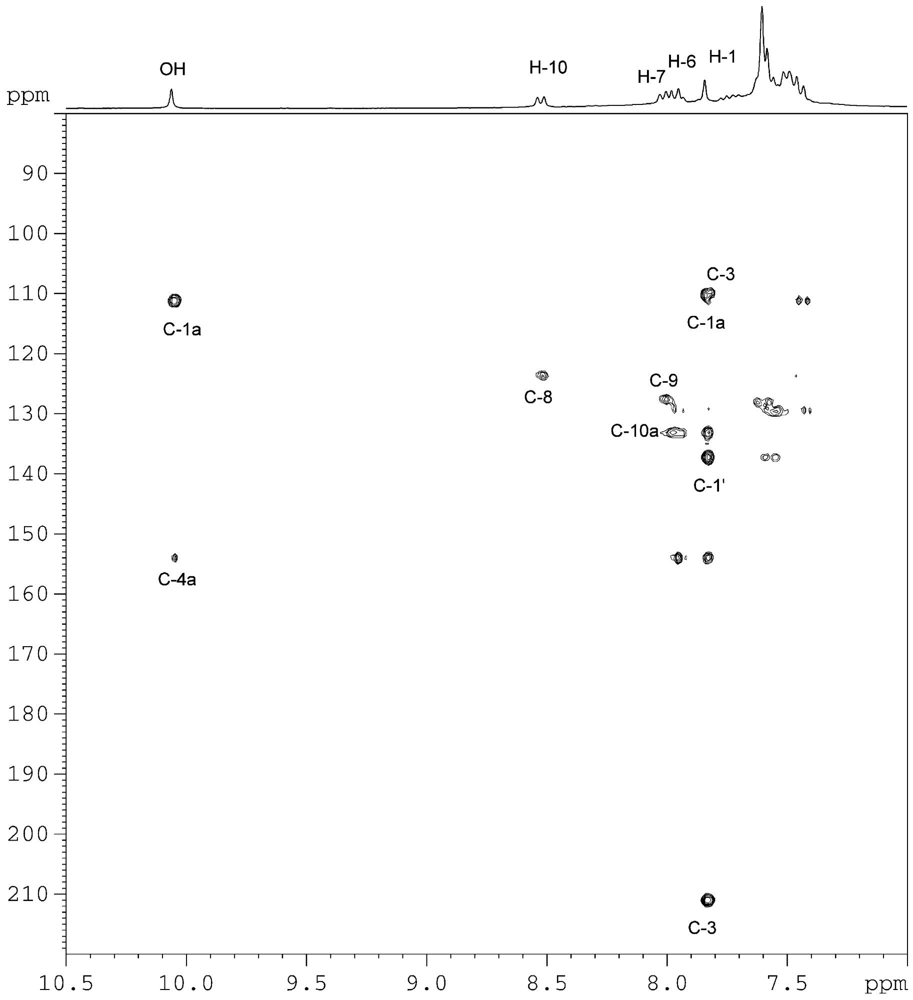

Fig. 5. 2D NMR ^{1}H–^{13}C HMBC of Int at 213 K.

was applied for 5 min implying partial photobleaching of TC isomer and complete one of TT isomer.

After the irradiation was stopped, ^{1}H NMR spectra were recorded at regular time intervals, maintaining the spectrometer temperature the same for 15 h. The integration of signals (Fig. 6) at 8.52 (H-10) and 9.81 (OH) for Int, 8.73 (H-2) and 6.55 (H-5) for TC and 8.29 (H-10) and 6.74 (H-2) for CH on each spectrum made it possible to plot curves of concentration versus time (Fig. 7) for these three photoproducts.

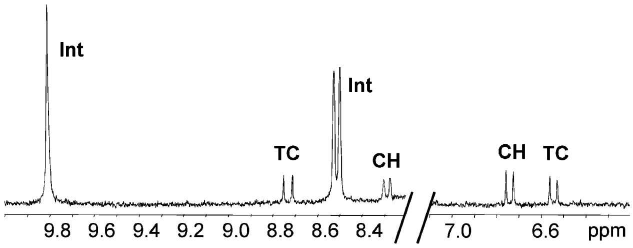

Fig. 6. Parts of ^{1}H NMR spectrum at 228 K with characteristic signals used for measuring integration.

Time-evolution of concentrations indicates a consecutive mechanism from Int via TC to CH. The kinetic equations were deduced from this mechanism, the bleaching of Int follows a monoexponential function (rate constant Int → TC, $k_1^{228} = 12.8 \times 10^{-5}\,\mathrm{s}^{-1}$) whereas the time-dependent profile of TC is bi-exponential curve (rate constant TC → CH, $k_2^{228} = 3.4 \times 10^{-5}\,\mathrm{s}^{-1}$):

$$[\mathrm{Int}]_t = [\mathrm{Int}]_0 \exp(-k_1 t)$$

$$[\mathrm{TC}]_t = \frac{k_1}{k_2 - k_1}[\mathrm{Int}]_0(\exp(-k_1 t) - \exp(-k_2 t)) + [\mathrm{TC}]_0 \exp(-k_2 t)$$

$$[\mathrm{CH}]_t = [\mathrm{CH}]_\infty - [\mathrm{Int}]_t - [\mathrm{TC}]_t$$

where $[\mathrm{Int}]_0$ and $[\mathrm{TC}]_0$ are the concentrations at $t = 0$, $[\mathrm{Int}]_t$, $[\mathrm{CH}]_t$ and $[\mathrm{TC}]_t$, the concentrations at the instant t, $[\mathrm{CH}]_\infty$, the initial concentration of solution (10^{-2} M), and k_1 and k_2, the rate parameters for the bleaching.

The set of photochemical and thermal processes are summarized in Scheme 1.

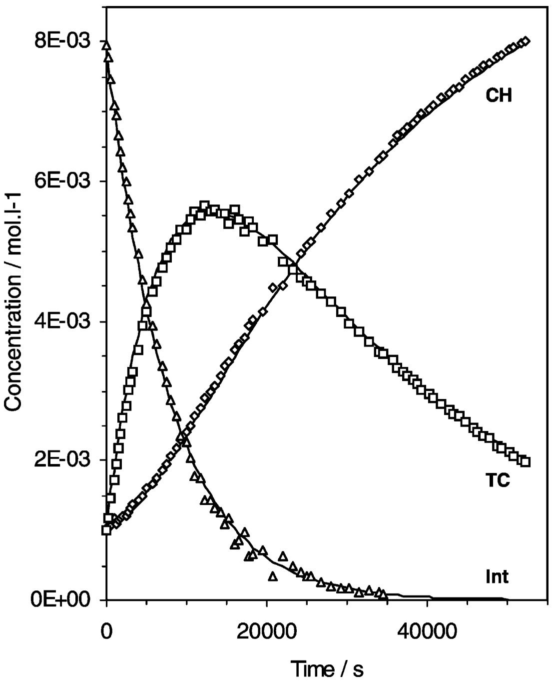

Fig. 7. Time-evolution of concentrations after irradiation at 228 K of CH (experimental points and calculated curves).

4. Conclusion

Allenyl-naphthol was produced and based on the kinetic result, it then clearly appears that it is not a degradation structure due to its disappearance going toward the photomerocyanine TC. Consequently, the formation of this photoproduct is a phenomena beyond the presence of fluorine atom in the photochromic behavior of naphthopyran family. Thus, it appears that such a structure must be included in further approaches to a better understanding of the mechanistic aspects of naphthopyran photochromism.

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