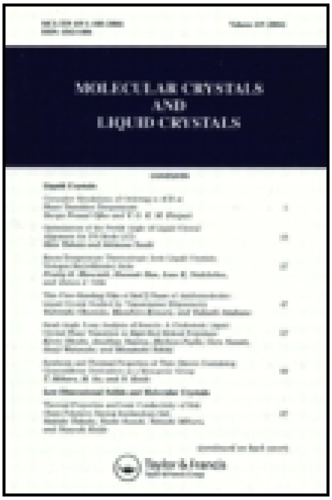

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Synthesis and Photochromic Behavior of Fluoro 2H-1-Benzopyrans Containing a Carbazole Moiety

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*The synthesis of new photochromic 2,2-di(4′-fluoro-phenyl)-2*H*-1-benzopyrans fused to an indole moiety is described. Spectrokinetic data (λ_{max} of colored form, colorability and rate constant of bleaching) obtained by UV-Visible spectroscopy and the structure of photomerocyanines elucidated by NMR spectroscopy, are reported.*

Keywords: fluoro-benzopyrans; hydroxycarbazole; NMR; photochromism; synthesis; UV-visible spectroscopy

INTRODUCTION

Among the different classes of photochromic families, benzopyrans represent an important group, which were first investigated by Becker and Michl who established their photochromic properties in a rigid matrix at 77 K [1,2]. The photochromism of benzopyrans involves a

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bond cleavage of the spiro carbon and the oxygen atom of the pyran ring under UV irradiation. This heterolytic breaking leads through a zwitterionic intermediate to a cis-cisoid isomer whose rearrangement gives rise to a set of stereoisomers of the photomerocyanine. Such structures commonly named open and colored forms, have a distinct absorption spectrum, generally in the visible range and return to the initial closed form via thermal or photochemical pathways.

Equilibrium between closed and open forms has found a large variety of applications, mainly in a use as variable-transmission materials. In the course of development of novel applications, research is turned to the design of systems that are responsive to solar irradiation at room temperature and exhibit good photochromic properties (high colorability, low response to visible light and fast thermal bleaching) associated with high fatigue resistance [3].

The photochromism at room temperature of 2*H*-1-benzopyran was observed after structural modifications, such the presence of phenyl groups at the sp^3 C-atom and the heteroaromatic annellation with five or six-membered rings [4,5,6,7,8]. The 2,2-disubstituted-2*H*-naphtho[2,3-*b*]pyran (annellation 6,7) is photochromic only at very low temperatures, even when conjugate substituants are present, which is the result of the loss of aromaticity of both rings in the naphthalene nucleus present in the open form [1,2]. As reported in a previous paper, benzopyrans containing a carbazole moiety present significantly different properties according to the position of annellation [9].

In the present paper, we report the synthesis of 2,2-diphenyl-2*H*-1-benzopyrans substituted by fluorine atoms in *para* position of both phenyl groups and annellated in position 6–7 to a carbazole moiety, and their spectrokinetic properties ($\lambda_{\max}$ of colored form, colorability and rate constant of bleaching) obtained by UV-Visible spectroscopy. In addition, 1 and 2D NMR spectroscopy has been used to characterize the structures of open forms after UV irradiation and to investigate their kinetic behavior.

EXPERIMENTAL

General Remarks

Solvents (Riedel-Haën and Merck) were used without further purification. Column chromatography was performed on silica gel Merck 60 (70–230 mesh). IR spectra were recorded on a Perkin-Elmer-FTIR-1600 spectrophotometer using KBr disks and wavenumbers are given in cm^{-1}. UV/VIS spectra were recorded on a CARY 50 Varian spectrophotometer. The mass spectra were obtained under electronic impact (EI = 70 eV) on AutoSpecE spectrometer. Melting points (°C), measured in capillary tubes on Büchi 535 apparatus, are uncorrected. All new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy.

Spectrokinetic Studies under Flash Photolysis

The flash photolysis experiments were monitored by a Warner and Swasey rapid spectrometer (acquisition time 1 ms, repetitivity 1.25 ms) [10,11]. Flashes (duration 50 µs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25°C) 100 mm cells were used. The light from the analysis lamp (50 W, quartz-iodide) was filtered using a Schott GC400 high-pass filter.

Spectrokinetic Studies under Continuous Irradiation

Irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriel Instruments). The light from the UV lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder at the right angle to the monitoring beam using an optical fiber system (77654 Oriel Instruments). A light flux of 40 W m^{-2}, measured with a Goldilux Photometer with UV-A probe was used. A thermostated (10 and 20°C) 10 mm quartz cell, containing the sample solution (3.5 ml), equipped with magnetic stirring was used. In a preliminary experiment, the visible absorption spectrum of the closed form and the $\lambda_{\max}$ of the open form were determined. In a second experiment the absorbance at photostationary equilibrium, A_{eq}, was measured at $\lambda_{\max}$ and then the decrease in the absorbance *vs*. time was monitored. The rate constants were calculated using a multi exponential model.

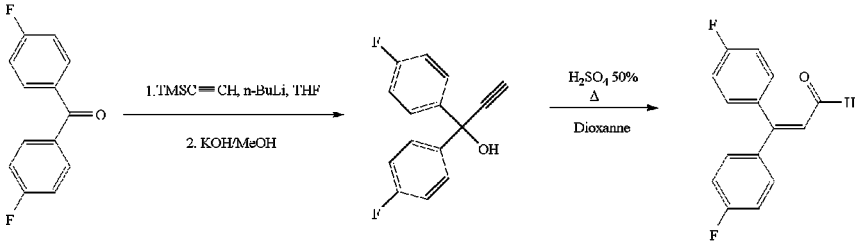
NMR Spectroscopy

1D (^{1}H, ^{1}H-1D-roesy, ^{13}C-J-mod and ^{19}F with ^{1}H decoupling) and 2D (^{1}H-^{1}H cosy-gp, ^{1}H-^{1}H roesy, ^{1}H-^{13}H HSQC-gp, ^{1}H-^{13}C HMBC-gp) NMR spectra were acquired using Bruker 300 NMR spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) and 282 MHz (^{19}F), equipped with a BBI probehead fitted with an actively shielded z-gradient coil for delivering pulsed field gradient (DPX spectrometer) or with a QNP (^{1}H, ^{13}C, ^{19}F, ^{31}P) probe head (AC spectrometer). UV irradiation of the samples in the NMR tube were performed in a home-built apparatus with a 1000 Watts Xe-Hg lamp, equipped with filter Schott 011FG09 ($259 < \lambda < 388\,\text{nm}$ with $\lambda_{\text{max}} = 330\,\text{nm}$ and $T = 79\%$). During irradiation, the sample was kept spinning for homogenization and the temperature was controlled with a variable temperature unit. After irradiation had been stopped, the tube was transferred into the NMR probe, also thermoregulated, of the spectrometer.

RESULTS AND DISCUSSION

Synthesis and NMR Characterization

The 2-hydroxy-9-methylcarbazole (**1**) was obtained from the commercial 2-hydroxycarbazole by methylation with NaH and CH_3I and demethylation with pyridinium hydrochloride in 34% overall yield. 2-bromo-7-hydroxy-9-methylcarbazole (**2**) was prepared in 66% overall yield by crossed Ullmann reaction from commercially available compounds followed by treatment with triethylphosphite at 160°C, *N*-methylation with NaH and CH_3I and demethylation [12]. Among several methods available to obtain heteroannellated 2,2-diaryl-2*H*-chromenes we have considered the most adequate method for basic phenols like hydroxycarbazoles. The choice of this method led us to prepare the α,β-unsaturated aldehyde, 3,3-di-(4′-fluorophenyl)prop-2-enal **4**, starting from the corresponding benzophenone and passing through the 1,1-di(4′-fluorophenyl)-2-propyn-1-ol **3**, (Scheme 1) [13]. The method involves the organotitanium mediated condensation of a "phenol" with an α,β-unsaturated aldehyde, leading to C-alkylation in *ortho*-position that through a subsequent electrocyclisation yields the new benzopyrans **CF-1** and **CF-2** (Scheme 2) [14]. All the known compounds (**1**, **2**, **3** and **4**) showed melting points and spectral characteristics in accordance with literature values [9,15,16].



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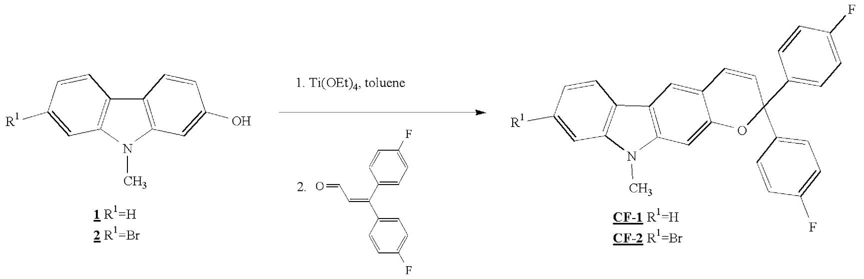
SCHEME 1 General synthesis of 3,3-di-(4′-fluorophenyl)prop-2-enal, **4**.



SCHEME 2 General synthesis of [indole]benzopyrans **CF-1** and **CF-2**.

Benzopyran **CF-1**. White solid. Yield 30%. Mp 234.2–234.5. IR: 2956, 2927, 1629, 1600, 1504, 1230, 833, 746. UV/Vis (closed form): 285 (48560), 302 (27120), 341 (7840), 358 (12660). ^{1}H NMR (300 MHz, toluene-d_8): δ 2.9 (s, 3H, **CH3**), 5.75 (d, $^3J_{3\text{-}4} = 9.8$ Hz, 1H, **H-3**), 6.60 (d, 1H, **H-4**), 6.70 (s, 1H, **H-11**), 6.84 (dd, $^3J_{3'\text{-}2'} = 9.0$ Hz, $^3J_{3'\text{-F}} = 8.6$ Hz, 4H, **H-3′** = **H-3″**), 6.94 (dd, $^3J_{9\text{-}8} = 8.0$ Hz, $^4J_{9\text{-}7} = 0.9$ Hz, 1H, **H-9**), 7.21 (ddd, $^3J_{7\text{-}8} = 8.3$ Hz, $^3J_{7\text{-}6} = 7.7$ Hz, 1H, **H-7**), 7.31 (ddd, $^4J_{8\text{-}6} = 1.3$ Hz, 1H, **H-8**), 7.38 (dd, $^4J_{2'\text{-F}} = 5.3$ Hz, 4H, **H-2′** = **H-2″**), 7.50 (s, 1H, **H-5**), 7.90 (dd, 1H, **H-6**). ^{13}C NMR (75 MHz, toluene-d_8): δ 28.0 (**CH$_3$**), 82.3 (Cq, **C-2**), 96.8 (CH, **C-11**), 108.8 (CH, **C-9**), 114.6 (Cq, **C-4a**), 115.3 (CH, d, $^2J_{3'\text{-F}} = 21.7$ Hz, **C3′** = **C3″**), 118.9 (CH, **C-5**), 119.7 (CH, **C-7**), 120.0 (CH, **C-6**), 123.4 (Cq, **C-6a**), 124.8 (Cq, **C-5a**), 125.1 (CH, **C-8**), 125.6 (CH, **C-4**), 126.4 (CH, **C-3**), 129.6 (CH, d, $^3J_{2'\text{-F}} = 8.3$ Hz, **C2′** = **C2″**), 141.0 (Cq, **C-1′** = **C-1″**), 141.3 (Cq, **C-9a**), 142.2 (Cq, **C-10a**), 152.0 (Cq, **C-1a**), 162.5 (Cq, d, $^1J_{4'\text{-F}} = 258$ Hz, **C-4′** = **C-4″**). ^{19}F NMR (282 MHz, toluene-d_8): δ-113.92 ppm. MS: m/z (%): 423 (M$^+$, 100), 328 (54), 313 (6), 211 (8), 201 (5). Exact mass for $C_{28}H_{19}F_2NO$: 423.1435. Found: 423.1454.

Benzopyran **CF-2**. White solid. Yield 30%. Mp 259.7-260. IR: 2958, 2927, 2857, 1727, 1629, 1596, 1506, 1232, 838, 809. UV/Vis (closed form): 303 (27760), 310 (26400), 343 (8690), 360 (12220). ^{1}H NMR (300 MHz, toluene-d_8): δ 2.7 (s, 3H, **CH3**), 5.71 (d, $^3J_{3\text{-}4} = 9.7$ Hz, 1H, **H-3**), 6.53 (d, 1H, **H-4**), 6.57 (s, 1H, **H-11**), 6.79 (dd, $^3J_{3'\text{-}2'} = 8.9$ Hz, $^3J_{3'\text{-F}} = 8.7$ Hz, 4H, **H-3′** = **H-3″**), 7.12 (d, $^4J_{9\text{-}7} = 1.8$ Hz, 1H, **H-9**), 7.26 (dd, $^3J_{7\text{-}6} = 8.1$ Hz, 1H, **H-7**), 7.31 (dd, $^4J_{2'\text{-F}} = 5.4$ Hz, 4H, **H-2′** = **H-2″**), 7.32 (s, 1H, **H-5**), 7.48 (d, 1H, **H-6**). ^{13}C NMR (75 MHz, toluene-d_8): δ 27.9 (**CH$_3$**), 82.3 (Cq, **C-2**), 96.7 (CH, **C-11**), 111.7 (CH, **C-9**), 115.0 (CH, d, $^2J_{3'\text{-F}} = 21.7$ Hz, **C3′** = **C3″**), 115.1 (Cq, **C-4a**), 117.1 (Cq, **C-5a**), 118.4 (CH, **C-5**), 120.5 (CH, **C-6**), 122.1 (Cq, **C-6a**), 122.4 (CH, **C-7**), 124.9 (CH, **C-4**), 125.1 (Cq, **C-8**), 126.5 (CH, **C-3**), 129.2 (CH, d, $^3J_{2'\text{-F}} = 8.3$ Hz, **C2′** = **C2″**), 141.1 (Cq, **C-1′** = **C-1″**), 142.0 (Cq, **C-9a**), 142.6 (Cq, **C-10a**), 152.0 (Cq, **C-1a**), 162.2 (Cq, d, $^1J_{4'\text{-}F} = 258$ Hz, **C-4′ = C-4″**). ^{19}F NMR (282 MHz, toluene-d$_8$): δ-113.71 ppm. MS: m/z (%) 503 (100, 81Br), 501 (98, 79Br), 422 (9), 406 (75), 393 (6), 327 (7), 250 (5), 201 (9), 163 (5), 75 (6). Exact mass for $C_{28}H_{18}BrF_2NO$: 501.0540. Found: 501.0550.

Studies by UV-Visible Spectroscopy

The new fluorobenzopyrans **CF-1** and **CF-2** exhibit photochromic behavior at room temperature in toluene solutions. The relevant parameters (activation wavelengths of closed forms, maxima wavelengths of the colored forms, colorability and thermal bleaching rate) were evaluated under flash photolysis and continuous irradiation. Both methods are extensively used although the information obtained by the two methods can be very distinct since the time scales of observation and the light flux applied are completely different. The data are summarized in Table 1 together with the corresponding [indole]benzopyrans without fluorine atoms (**Ref 1**–2,10-dihydro-10-methyl-2,2-diphenylpyrano[2,3-*b*]carbazole and **Ref 2**–8-bromo-2,10-dihydro-10-methyl-2,2-diphenylpyrano[2,3-*b*]carbazole), and the reference compounds **Ref 3**–3,3-di(4′-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran, **Ref 4**–3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.

Continuous Irradiation

From a general point of view, all the closed forms have absorption bands in the near UV. For benzopyrans **CF-1** and **CF-2** when compared with **Ref 1** and **Ref 2** the introduction of the fluorine atom

TABLE 1 Maximal Wavelengths of the Colored Forms (λ_1, λ_2), Colorability (A_0, A_{eq}), Fading Rates (k_1 and k_2) of the Described 2*H*-1-benzopyrans and Five Reference Compounds in Toluene Solutions under Flash Photolysis (2.5×10^{-5} M–**Ref 1** to **Ref 4** and 8.33×10^{-6} M – **CF-1** and **CF-2**, at 25°C) and Continuous Irradiation (1×10^{-4} M at 20°C)

	Flash photolysis				Continuous irradiation				
Compound	A_0	λ_1 (nm)	k_1 (s^{-1})	k_2 (s^{-1})	A_{eq}	λ_1 (nm)	λ_2 (nm)	k_1 (s^{-1})	k_2 (s^{-1})
CF-1	2.8	461	0.32 (68)	0.03 (32)	0.48	451	699	0.03 (100)	–
CF-2	3.5	461	0.44 (81)	0.03 (19)	0.32	450	688	0.05 (100)	–
Ref 1 [9]	2.5	444	0.19 (48)	0.02 (52)	0.72	444	–	0.02 (100)	–
Ref 2 [9]	5.5	454	0.20 (81)	0.02 (19)	0.51	454	–	0.03 (96)	0.001 (4)
Ref 3 [17]	–	–	–	–	0.20	430	–	0.08	0.0002
Ref 4 [18]	0.84	432	0.09	–	0.21	432		0.06 (80)	0.0003 (20)

led to a bathochromic shift and an extension of the visible range on the spectra of open forms. The observed thermal fading rates for **CF-1** and **CF-2** fit well with a monoexponential model and are faster than the ones observed for the corresponding benzopyrans **Ref 1** and **Ref 2**. This indicates that the open forms of compounds with fluorine atoms on the *para* position of the phenyl substituants are less thermally stable than the reference compounds. As expected lower values of colorability were also observed.

Flash Photolysis

Some determinations were also performed by the flash photolysis technique and in that case the bleaching kinetics fit well with a biexponential model. This indicates that there is a significant difference in the relative quantities of photoisomers in the mixture obtained after irradiation in both methods. For compound **CF-1**, the amplitude of the first kinetic was improved (48 to 68%) and for both new compounds the first kinetic phase was faster when compared with reference compounds without fluorine atoms. For compound **CF-1**, **CF-2**, **Ref 1** and **Ref 2** the second kinetic phase observed by this method can be correlated with the one obtained by continuous irradiation indicating a similar nature of the photoisomers in the mixture responsible for them.

As a group, the 2*H*-1-benzopyrans are less photochromic and less responsive to solar irradiation than the corresponding naphthopyrans due to their UV absorption at lower wavelengths. However compounds **CF-1** and **CF-2** exhibit a stronger photocolouration efficiency (2.8 and 3.5 at 8.33×10^{-6} M) than the corresponding benzopyrans **Ref 1** and **Ref 2** (2.5 and 5.5 at 2.5×10^{-5} M) and even stronger than the reference naphthopyran (**Ref 4**). It is noteworthy that this faster bleaching kinetic is not accompanied by a loss in the colorability, such a result can be interesting for some applications.

Photocoloration of CF-1 Monitored by NMR Spectroscopy

A sample of **CF-1** has been irradiated at 203 K with UV light at cumulative periods. Between each UV irradiation, ^{19}F and ^{1}H NMR spectra have been acquired to monitor the photocoloration process. Figure 1 illustrates the course of reaction. After 30 seconds of irradiation, two ^{19}F signals with equal intensities have been detected at –109.7 and –110.80 ppm and increased with the time of irradiation, while the signal of **CF-1** decreased. After about 2 minutes, two other new signals appeared at –109.7 and –109.96. In the ^{1}H NMR spectra recorded, the same phenomenon is observed with the

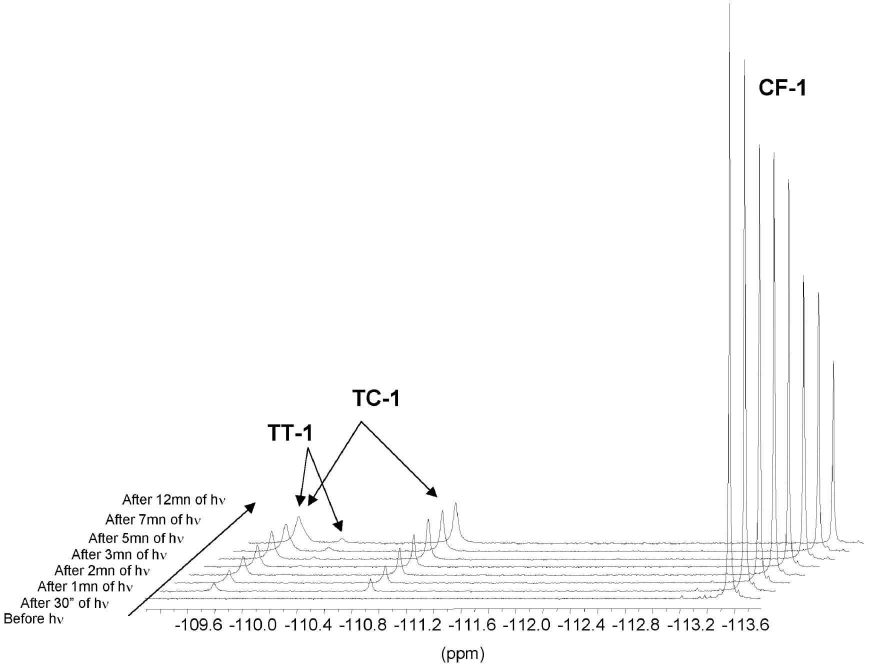


FIGURE 1 ^{19}F NMR spectra recorded during UV irradiation at 203 K.

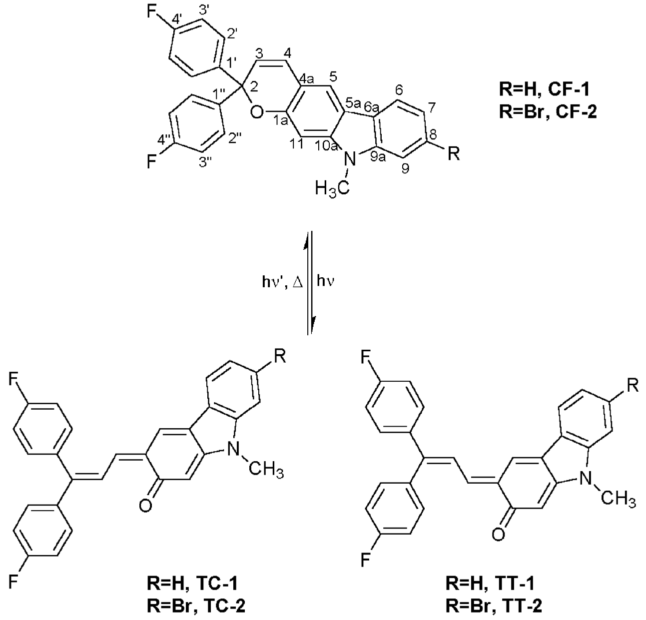
rapid formation of two doublet and two singlet signals at 6.00, 6.03, 6.34 and 9.60 ppm, with a concentration increase. A new doublet then appeared at 8.40 ppm after 2–3 minutes of irradiation. After irradiation had been stopped, all the new resonances followed a thermal decay and the initial NMR peaks were retrieved thus, indicating that they correspond to open photomerocyanines.

Due to symmetry of phenyl groups, only two transoid isomers of the photomerocyanine are expected, the TC (Transoid-Cis) and the TT (Transoid-Trans) (Scheme 3).

As two pairs of fluorine resonances are detected, they are straightforwardly assigned to both transoid photomerocyanines. In these open structures, phenyl groups are no longer equivalent due to the hybridization sp^2 of carbon C-2. To assign the exact isomery of each photoproduct, 2D NMR experiments have been performed.

Structural Identification of Open Photomerocyanines

^{1}H-^{1}H Cosy experiment of **CF-1** after irradiation (Fig. 2) underlines scalar correlations between the doublet signal at 9.6 ppm and a doublet in the overlapping part at 6.90 ppm (^{3}J = 12.1 Hz), and between



SCHEME 3 Photochromic equilibrium.

two signals at 6.00 and 6.89 ppm. ^1H-^1H Roesy experiment (Fig. 3) makes it possible to differentiate the two singlet resonances at 6.03 and 6.34 ppm. Indeed, only the first present a dipolar effect with the *N*-methyl group, thus being assigned to proton H-11. The other, deducing to correspond to proton H-5, shows effectively spatial proximity with proton at 6.90 ppm, (H-4) and proton at 7.2 ppm (H-6). The previous cited doublet at 9.6 ppm is assigned to proton H-3, deshielded due to the effect of C=O, and a dipolar effect is measured with a doublet-doublet signal at 7.0 ppm, belonging to proton H-2″. All these confirmations are in agreement with a Transoid-Cis structure (TC). The second detected photoproduct, which has less intense resonances, is deduced to be the Transoid-Trans isomer (TT). A scalar correlation is observed between two doublet signals ($^3J = 11.8$ Hz) at 8.4 and 7.1 ppm. Such multiplicity and coupling constant value allow for associating them to the protons H-4 and H-3, respectively.

Photomerocyanine **TC-1.** ^1H NMR (300 MHz, toluene-d_8): δ 2.05 (3H, **CH3**), 6.0 (1H, **H-9**), 6.03 (1H, **H-11**), 6.34 (1H, **H-5**), 6.64 (2H, **H-3′**), 6.65 (2H, **H-2′**), 6.78 (2H, **H-3″**), 6.89 (1H, **H-8**), 6.90 (1H, **H-4**), 7.00 (2H, **H-2″**), 7.06 (1H, **H-7**), 7.2 (1H, **H-6**), 9.6 (1H, $^3J_{3\text{-}4} =$ 12.1 Hz, **H-3**). ^{13}C NMR (75 MHz, toluene-d_8): δ 27.0 (**CH_3**), 99.0

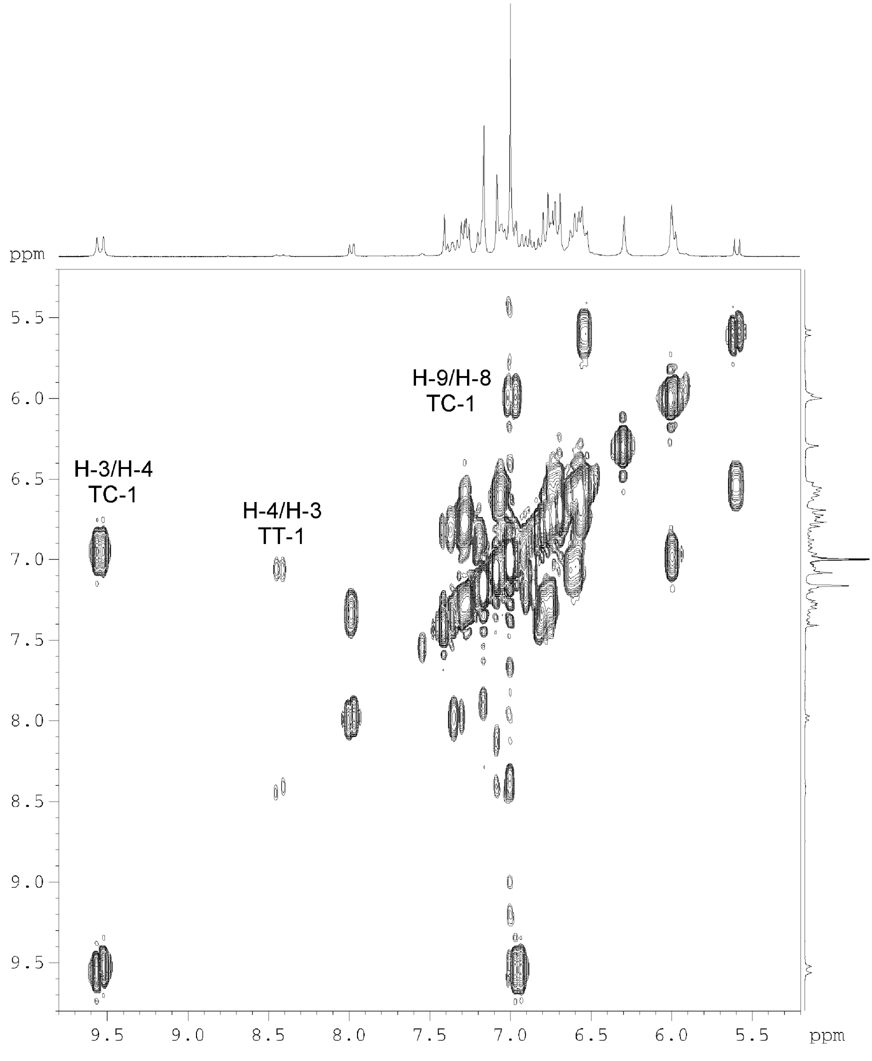


FIGURE 2 2D-Cosy of **CF-1** after UV irradiation.

(CH, **C-11**), 108.5 (CH, **C-6**), 115.8–115.9 (CH, **C-3′**, **C-3′**), 121.0 (CH, **C-8**), 121.9 (CH, **C-9**), 124.5 (Cq, **C-6a**), 126.0 (CH, **C-7**), 127.5 (Cq, **C-4a**), 128.0 (CH, **C-5**), 128.5 (CH, **C-3**), 131.8 (CH, **C-2″**), 132.0 (Cq, **C-5a**), 133.7 (CH, **C2′**), 135.0 (Cq, **C-2**), 138.1–132.2 (Cq, **C-1′-C-1″**), 146.8 (Cq, **C-9a**), 149.5 (CH, **C-4**), 154.5 (Cq, **C-10a**), 162.0 (Cq, **C-4′-C-4″**), 184.5 (Cq, **C1-a**).

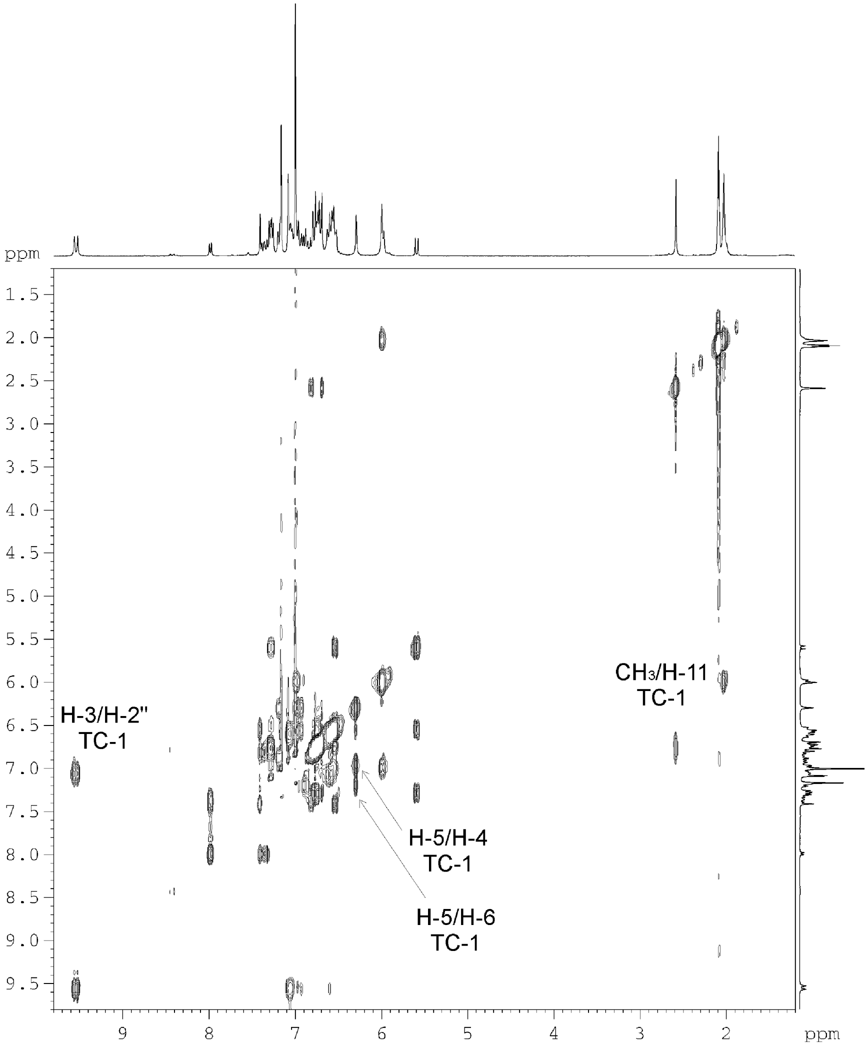


FIGURE 3 2D-Roesy of **CF-1** after UV irradiation.

Photomerocyanine **TC-2**. ^1H NMR (300 MHz, toluene-d_8): δ 1.8 (3H, **CH3**), 5.86 (1H, **H-11**), 6.16 (1H, **H-5**), 6.33 (1H, **H-9**), 6.61 (2H, **H-2′**), 6.62 (2H, **H-3′**), 6.67 (1H, **H-6**), 6.76 (2H, **H-3″**), 6.92 (1H, **H-7**), 6.95 (1H, **H-4**), 7.06 (2H, **H-2″**), 9.48 (1H, $^3J_{3\text{-}4} = 12.1$ Hz, **H-3**). ^{13}C NMR (75 MHz, toluene-d_8): δ 26.5 (**CH_3**), 99.0 (CH, **C-11**), 112.0 (CH, **C-9**), 115.5 (CH, **C-3′, C-3″**), 122.0 (CH, **C-6**), 123.5 (CH, **C-7**), 128.0 (CH,

C-5), 128.5 (CH, **C-3**), 131.5 (CH, **C-2″**), 133.5 (CH, **C2′**), 150.0 (CH, **C-4**), 162.0 (Cq, **C-4′-C-4″**), 184.2 (Cq, **C1-a**).

Photomerocyanine **TT-2**. ^{1}H NMR (300 MHz, toluene-d$_8$): δ 1.78 (3H, **CH3**), 5.77 (1H, **H-11**), 6.29 (1H, **H-9**), 6.77 (1H, **H-6**), 6.79 (2H, **H-2″**), 6.81 (2 + 1H, **H-2′** + **H-7**), 7.08 (1H, **H-3**), 7.39 (1H, **H-5**), 8.40 (1H, $^3J_{4\text{-}3} = 12.6$ Hz, **H-4**). ^{13}C NMR (75 MHz, toluene-d$_8$): δ 26.5 (**CH$_3$**), 99.0 (CH, **C-11**), 112.0 (CH, **C-9**), 118.8 (CH, **C-5**), 122.0 (CH, **C-6**), 123.5 (CH, **C-7**), 129.7 (CH, **C-3**), 131.5 (CH, **C-2″**), 133.5 (CH, **C2′**), 144.0 (CH, **C-4**).

Thermal Evolution of Open Photomerocyanines

^{1}H and ^{19}F NMR spectra of **CF-1** were recorded at regular time-intervals after UV irradiation at low temperature (218, 223 and 228 K). By integrating characteristic resonances in **CF-1**, **TC-1** and **TT-1**, the time-evolution curves have been plotted. The **TC-1** isomer follows monoexponential decay to return to the initial closed form (Fig. 4), while **TT-1**, which is in a very low concentration, presents no significant variation during the experiment. From Arrhenius equation, activation energy of the thermal ring-closure of **TC-1** into **CF-1**

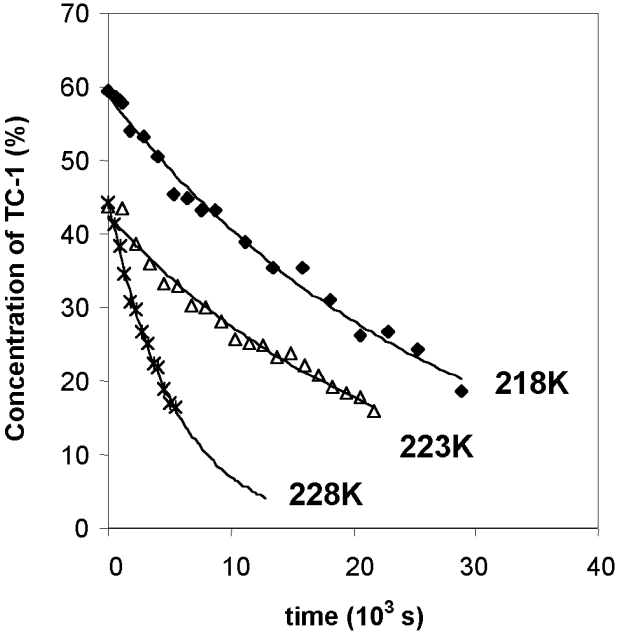


FIGURE 4 Thermal evolution of **TC-1**.

has been deduced to be equal to 65 kJ.mol^{-1}. This value is in complete agreement with those generally reported.

CONCLUSION

UV-Visible spectroscopy and NMR measurements have pointed out the formation of the two transoid isomers of photomerocyanines, TC and TT. The spectrokinetic parameters and the structural assignment have been obtained, indicating that these two spectroscopies are complementary: UV owing to its high sensitivity and time-resolution, and NMR owing to its structural identification, and the possibility of following the evolution of each form separately.

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