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Photochromism of 8-thienyl-naphthopyrans investigated by NMR spectroscopy

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In memoriam of Professor Alain Lablache-Combier.

Abstract

The photochromism of four 8-thienyl-naphthopyrans substituted either directly or via an acetylenic bridge to one or two thienyl groups, has been investigated by NMR spectroscopy. The two expected transoid photomerocyanines TC (transoid-*cis*) and TT (transoid-*trans*) have been characterised. From the numerical analysis of the kinetics recorded during photocolouration under UV irradiation and during thermal relaxation in the dark, several kinetic parameters related to the photochemical and thermal isomerization processes were determined. Their relative values are discussed and compared to two H-substituted parent compounds.

Keywords: Photochromism; Naphthopyrans; NMR spectroscopy; Kinetic analysis

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1. Introduction

Naphthopyrans have been extensively investigated because of their good photochromic properties [1–3]: high colourability, rapid thermal relaxation and good fatigue resistance offering potential applications in the optical glass industry [4] and optoelectronics [5–8]. To modulate these photochromic properties, various thiophene substituted naphthopyrans have been synthesised [9–22]. Some of them have been investigated by femtosecond and nanosecond transient absorption spectroscopy [23]. The ring opening reaction responsible for photochromism has been shown to occur in the S_1 state with a time constant of about 150 ps. Moreover, we have previously reported some NMR results about a diphenyl-naphthopyran substituted by one thienyl group in 8-position [24] and about a biphotochromic compound where two naphthopyran units are linked by an acetylene–thiophene–acetylene bridge [25]. With the exception of these NMR preliminary studies, it appears that no further NMR investigations of these thienyl naphthopyrans have been carried-out.

The purpose of this paper is to thoroughly investigate the photocolouration and thermal relaxation of a series of several 8-thiophene-linked naphthopyrans using kinetic analysis of NMR data recorded under continuous irradiation and in the dark at variable temperature. Previous studies have underlined that NMR is a powerful spectroscopy as it gives not only structural elucidation but also makes it possible to monitor the course of reactions by following the kinetics of photocolouration and thermal relaxation [26–28]. We present here the kinetic and structural results obtained by NMR spectroscopy of four diphenyl-naphthopyrans substituted at the 8-position via or not an acetylenic bridge with one or two thienyl entities (Scheme 1). For comparison, the two H-substituted molecules (CF-**1** and CF-**4**) have also been studied.

2. Experimental

2.1. Materials

The compounds had previously been synthesised by members of our team [20].

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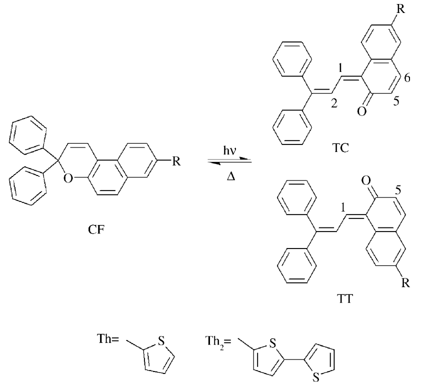


Compound	R
1	-H
2	-Th
3	-Th$_2$
4	-C≡C-H
5	-C≡C-Th
6	-C≡C-Th$_2$

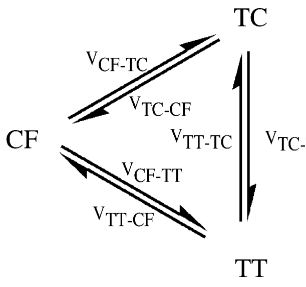
Scheme 1. Photochromic equilibrium and corresponding structures of the various isomers.

2.2. NMR investigations and experimental conditions

Thermostated samples (concentration between 6×10^{-3} and 10^{-2} M in toluene-d_8) were irradiated directly in the NMR tube (5 mm), using a 1000 W Xe–Hg HP filtered (Schott 011FG09, $259 < \lambda < 388$ nm) short-arc lamp (Oriel). After irradiation, the sample was rapidly transferred into the thermoregulated probe of a Bruker Avance-DPX NMR spectrometer (^{1}H, 300 MHz).

2.3. Data analysis

The calculated evolution in concentrations was obtained by numerical integration of the set of differential equations written from a three-species system (Scheme 2), using homemade curve fitting software [29].



Scheme 2. Possible isomerization paths between the three photoisomers.

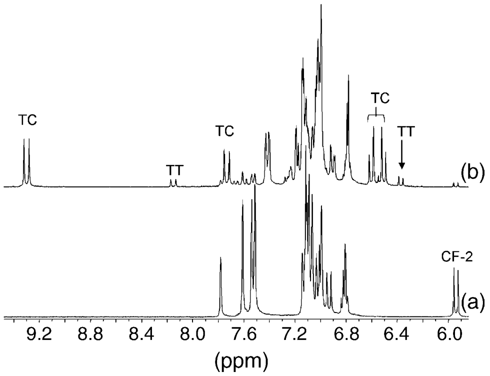


Fig. 1. ^{1}H NMR spectra of CF-**2**: (a) before and (b) after 20 min of UV irradiation at 228 K.

The rate equations have been assumed to be first-order-like [30] with $v_{ij} = h_{ij}[X_i]$, where $h_{ij} = \Phi_{ij}\varepsilon_i l I_0 F + k_{ij}$.

We found that the fitting procedure was very selective among the various possible processes taken under consideration. For instance, the simulated kinetic curves were significantly distant from their corresponding experimental data if some important pathway was omitted or if the presence of a forbidden process was artificially imposed.

3. Results

3.1. Structural identification of photoproducts

^{1}H NMR spectra in Fig. 1 show that after UV irradiation, there is a decrease in the initial closed form CF and the simultaneous appearance of the two photomerocyanines, TC (transoid-*cis*) and TT (transoid-*trans*).

The system of two doublets at 6.50 and 6.60 ppm with a vicinal coupling constant of 9.55 Hz was assigned to protons H$_5$ and H$_6$ while the doublet at 9.31 ppm ($^3J = 11.55$ Hz) characterised protons H$_1$ or H$_2$. These protons belong to one between the two possible open forms, TC-**2** or TT-**2**. 2D NMR COSY and ROESY experiments were performed and it made it possible to identify the major photoproduct as the transoid-*cis* isomer (TC-**2**) of photomerocyanine and the second as its transoid-*trans* (TT-**2**) isomer [31]. The same procedure was applied to all of the investigated structures and the set of chemical shifts is reported in Table 1.

Table 1
^{1}H NMR characteristic chemical shifts of TC and TT photomerocyanines

	Chemical shift/ppm					
	1	**2**	**3**	**4**	**5**	**6**
H$_1$ (TC)	7.75	7.74	7.75	7.61	7.64	7.65
H$_2$ (TC)	9.26	9.31	9.32	9.22	9.25	9.25
H$_5$ (TC)	6.50	6.50	6.53	6.41	6.45	6.46
H$_6$ (TC)	6.68	6.60	6.69	6.47	6.57	6.58
H$_1$ (TT)	8.13	8.16	8.17	8.08	8.07	8.11
H$_5$ (TT)	6.35	6.39	6.40	6.26	6.31	6.32

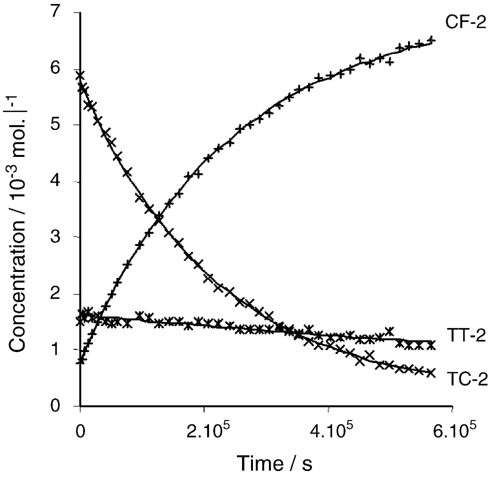


Fig. 2. Thermal relaxation of compound CF-**2** at 233 K (starting time $t = 0$ corresponds to the end of UV irradiation of the thermostated sample).

$$\mathrm{TT} \xrightarrow{k_{\mathrm{TT}\to\mathrm{TC}}} \mathrm{TC} \xrightarrow{k_{\mathrm{TC}\to\mathrm{CF}}} \mathrm{CF}$$

Scheme 3. Successive irreversible paths during thermal relaxation.

3.2. Kinetic studies

3.2.1. Thermal relaxation after UV irradiation

The kinetics of thermal relaxation after UV irradiation were monitored by recording ^{1}H NMR spectra at regular time intervals at different temperatures between 218 and 248 K. The purpose of UV irradiation was to shift the system from its equilibrium position which corresponds to 100% pure closed form CF. By measuring several specific NMR signals, the peak-intensities of the initial closed form and of the two photoproducts, TC and TT, can be integrated and the time-evolution of their respective concentrations can be plotted during thermal relaxation in the dark (Fig. 2).

Among the six reversible processes (shown in Scheme 2), only two successive irreversible paths (Scheme 3 with $h_{ij} = k_{ij}$) were found to be sufficient to obtain a good fit between the experimental data points and the calculated kinetic curves.

By plotting $\ln(k_{\mathrm{TC}\to\mathrm{CF}}/T)$ and $\ln(k_{\mathrm{TT}\to\mathrm{TC}}/T)$ versus $1/T$, we obtained straight lines, thus verifying Eyring's equation:

$$\ln\left(k_{i\to j}/T\right) = -\Delta H^{\#}/RT + \Delta S^{\#}/R + \ln(k_{\mathrm{B}}/h)$$

with k_{B}: Boltzmann's constant = 1.38×10^{-23} J K^{-1}, h: Planck's constant = 6.626×10^{-34} J s and $R = 8.314$ J mol^{-1} K^{-1}).

From the slope and the intercept, the values of the enthalpy of activation $\Delta H^{\#}$ and of the entropy of activation $\Delta S^{\#}$ were calculated. Results are grouped in Table 2.

The values of the determined rate constants concord with the well-known thermal instability of the TC isomer, while TT photomerocyanines exhibit very slow (compounds **2**–**4**), or not significant relaxation in our temperature range [26,31]. The TT → TC relaxation in compounds **1**, **5** and **6** is so slow that within the kinetic relaxation time, no clear-cut evolution could be detected; hence the corresponding rate constant has been neglected and taken equal to 0. This behaviour can easily be understood as the TC isomer is the only structure that can be directly converted to CF by single bond rotation while the TT conversion to CF needs a double bond isomerization to TC followed by a single bond rotation to CF [32].

The determined values of the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ are in accordance with those generally reported ($50 < \Delta H^{\#} < 100$ kJ mol^{-1} and $-100 < \Delta S^{\#} < -10$ J mol^{-1} K^{-1}) [1,2,32,33]. Moreover, plotting $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Fig. 3) [34] clearly shows the different kinetic behaviour of the two relaxation processes: TT → TC on the "slow" side and

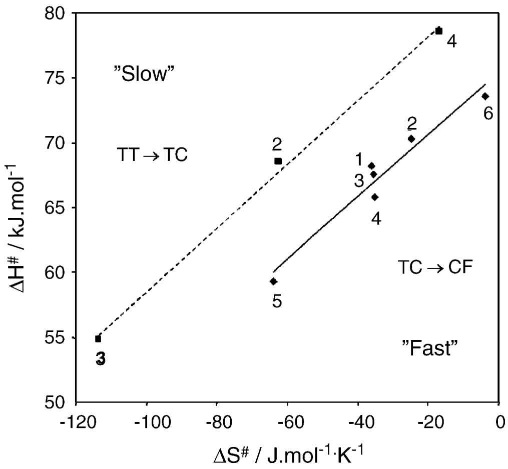


Fig. 3. $\Delta H^{\#}$ vs. $\Delta S^{\#}$ plots of the various relaxation processes. Isokinetic relationships are visualized by the straight lines (dotted line TT → TC: 3 determinations; continuous line TC → CF: 6 determinations).

Table 2
Thermal rate constants (k_{Δ}) and activation parameters $\Delta H^{\#}$ (kJ mol^{-1}) and $\Delta S^{\#}$ (J mol^{-1} K^{-1}) of the relaxation processes (all the values which appeared as non-significant during the fitting procedure have been omitted)

	218	228	233	238	243	248	$\Delta H^{\#}$	$\Delta S^{\#}$
TC→CF-**1**	–	1.54×10^{-5}	3.15×10^{-5}	–	1.59×10^{-4}	2.86×10^{-4}	68.2	−36.0
TC→CF-**2**	–	1.70×10^{-5}	4.65×10^{-5}	9.72×10^{-5}	1.96×10^{-4}	3.85×10^{-4}	70.3	−24.8
TC→CF-**3**	–	2.29×10^{-5}	4.79×10^{-5}	1.07×10^{-4}	2.13×10^{-4}	4.37×10^{-4}	67.5	−35.5
TC→CF-**4**	1.11×10^{-5}	6.04×10^{-5}	1.26×10^{-4}	2.54×10^{-4}	5.30×10^{-4}	–	65.8	−35.1
TC→CF-**5**	1.18×10^{-5}	5.90×10^{-5}	1.32×10^{-4}	–	3.69×10^{-4}	–	59.3	−63.9
TC→CF-**6**	6.80×10^{-6}	4.02×10^{-5}	–	2.36×10^{-4}	4.73×10^{-4}	–	73.6	−3.8
TT→TC-**2**	–	–	–	2.54×10^{-6}	5.19×10^{-6}	1.07×10^{-5}	68.5	−62.3
TT→TC-**3**	–	1.58×10^{-6}	2.95×10^{-6}	5.50×10^{-6}	9.90×10^{-6}	1.76×10^{-5}	54.8	−113.5
TT→TC-**4**	–	6.67×10^{-7}	–	3.17×10^{-6}	9.76×10^{-6}	–	78.5	−16.9

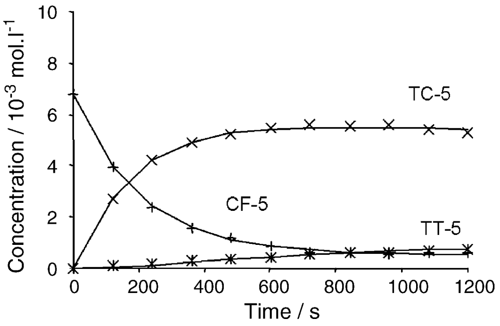


Fig. 4. Photocolouration process of CF-**5** at 218 K under UV irradiation (symbols are experimental concentrations; solid lines are best fits from our model).

TC → CF on the "fast" side. Within the TT → TC process no clear-cut substituent effect is visible (due to the lack of data) although an interesting feature appears on the TC → CF process. It must be pointed out that compounds **4–6** (i.e. with an acetylenic bridge) lie on the "fast" side of the straight line, while non-acetylenic compounds (**1–3**) lie on the "slow" side. This separation corresponds to faster TC → CF relaxation rate constant for acetylenic compounds.

From Fig. 3, it appears that the enthalpy–entropy compensation temperature lies around 250 K for both processes. At temperature below than T_{iso}, a substituent induced variation in $\Delta H^{\#}$ is greater than the corresponding variation in $T\Delta S^{\#}$ so that the variation of the free enthalpy of activation ($\Delta G^{\#}$) is enthalpy controlled.

3.2.2. *Photocolouration under UV irradiation*

The kinetics of photocolouration under UV irradiation were investigated at 218 K for all of the compounds. This temperature was selected so that the possible parasitic effects of thermal relaxation would be negligible. After each irradiation period of 120 s, NMR spectra were recorded at 218 K (Fig. 4). Irradiation was stopped when the photosteady-state was attained.

From the kinetic modelling of the concentration versus time curves recorded under continuous irradiation using the three-species system (Scheme 2), it has been possible to obtain excellent fits by considering the presence of two coupled photo-equilibria between CF and TC and between TC and TT.

This result shows that both photobleaching and photoisomerization occur in TC and that there is no direct photochemical path between TT and CF. The set of the four apparent rate constants (h_{ij}) is reported in Table 3.

Compared with non-substituted compounds **1** and **4**, the time to reach 50% photoconversion appears longer (720 s) for the acetylenic dithienyl compound **6** but from two to five times shorter for the other compounds. This specific behaviour of compound **6** is also seen when examining the isomeric distribution CF:TC:TT at the photosteady-state or even after a long irradiation period. Values ranging around 4–9:75–82:10–17 are encountered for compounds **1–5** while compound **6** appears less photoconvertible reaching only: 25:59:16. Concerning the CF/TC ($h_{\text{CF}\to\text{TC}}$ and $h_{\text{TC}\to\text{CF}}$) photocolouration–photobleaching equilibrium (Fig. 5a), it appears that for **2–5**, the apparent rate of photocolouration $h_{\text{CF}\to\text{TC}}$ is about 10 times higher than the apparent rate of photobleaching $h_{\text{TC}\to\text{CF}}$. Nevertheless, this ratio is lower than that in non-substituted compound **1** (≈23). Here also compound **6** behaves differently in exhibiting the lowest ratio. This data also shows the influence of the thienyl groups on the photobleaching whatever the nature of junction (compounds **5** and **6** > compound **4**, and compounds **2** and **3** > compound **1**). Such a result is consistent with previous reports showing for instance that substitution in 8-position diminishes colourability by increasing the photobleaching reverse process [22].

Fig. 5b illustrates the behaviour of various compounds versus the *cis–trans* photoisomerization between TC and TT. While compounds **1–5** seem to behave similarly (all in the dashed square), once again a specific behaviour is observed for **6**. Such high photoisomerization rates are related to lower colourability leading to no more than # 75% conversion at the photosteady-state. Another feature of compound **6** is the high value of the $\Phi_{\text{TC}\to\text{TT}}/\Phi_{\text{TC}\to\text{CF}}$ ratio corresponding to TC's greater trend to be converted into TT than into **6**. This peculiar photochemical behaviour could be related to its photoluminescence properties which would explain its lower photocolouration, already reported by Coen et al. [35] and concord with the fact that the

Table 3
Results from kinetic analysis of photocolouration process at 218 K

	1	**2**	**3**	**4**	**5**	**6**
$t_{[\text{CF}]0/2}$ (s)	150	320	320	240	240	720
$[\text{CF}]_{\text{exp}}$ (%)	4	12	12	10	10	35
$[\text{CF}]_{\text{PSS}}$ (%)	4	9	8	8	8	25
$[\text{TC}]_{\text{exp}}$ (%)	79	77	72	80	78	52
$[\text{TC}]_{\text{PSS}}$ (%)	79	80	75	82	78	59
$[\text{TT}]_{\text{exp}}$ (%)	17	11	16	10	12	13
$[\text{TT}]_{\text{PSS}}$ (%)	17	11	17	10	14	16
$h_{\text{CF}\to\text{TC}}$	4.4×10^{-3}	2.3×10^{-3}	2.7×10^{-3}	3.1×10^{-3}	4.6×10^{-3}	1.2×10^{-3}
$h_{\text{TC}\to\text{CF}}$	1.9×10^{-4}	2.5×10^{-4}	3.0×10^{-4}	3.0×10^{-4}	4.6×10^{-4}	5.2×10^{-4}
$h_{\text{TC}\to\text{TT}}$	6.8×10^{-4}	6.4×10^{-4}	8.5×10^{-4}	4.3×10^{-4}	2.7×10^{-4}	51×10^{-4}
$h_{\text{TT}\to\text{TC}}$	3.2×0^{-3}	4.7×10^{-3}	3.8×10^{-3}	3.4×10^{-3}	1.5×10^{-3}	18×10^{-3}
$\Phi_{\text{TC}\to\text{TT}}/\Phi_{\text{TC}\to\text{CF}}$	3.6	2.5	2.9	1.4	0.6	9.9

$t_{[\text{CF}]0/2}$: time of irradiation to convert 50% of the initial closed form. $[\text{CF}]_{\text{exp}}$, $[\text{TC}]_{\text{exp}}$, $[\text{TT}]_{\text{exp}}$: ratio of concentrations obtained after 20 min of UV irradiation. $[\text{CF}]_{\text{PSS}}$, $[\text{TC}]_{\text{PSS}}$, $[\text{TT}]_{\text{PSS}}$: ratio of concentrations expected at the PSS (see Appendix A). h_{ij}: apparent rate constant of process $i \to j$. $\Phi_{\text{TC}\to\text{TT}}/\Phi_{\text{TC}\to\text{CF}} = h_{\text{TC}\to\text{TT}}/h_{\text{TC}\to\text{CF}}$.

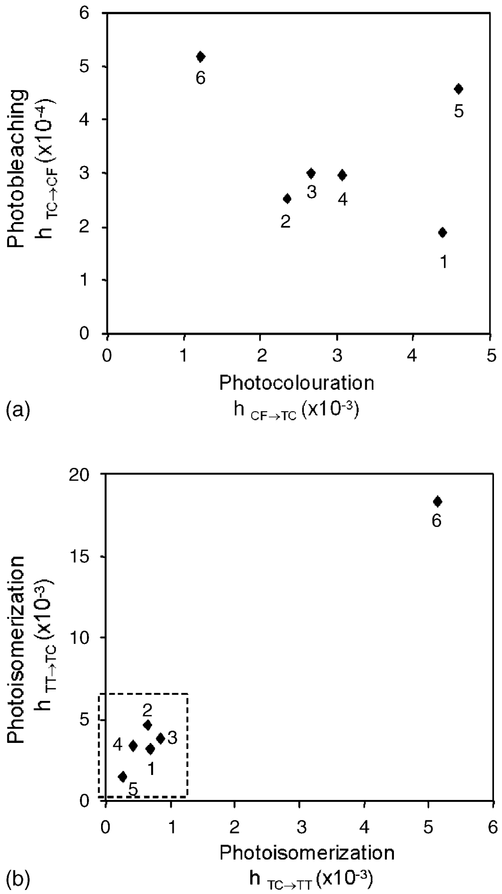


Fig. 5. Comparison of the apparent photochemical rate constants: (a) photobleaching TC → CF and photocolouration CF → TC; (b) photoisomerizations TT → TC and TC → TT.

quantum yield of fluorescence emission increases with the number of thienyl groups [25,36,37].

4. Conclusions

NMR spectroscopy made it possible to characterise the structures of both transoid photomerocyanines after UV irradiation of six naphthopyrans. The kinetic analysis of photocolouration and thermal relaxation processes made it possible to propose plausible mechanisms on the basis of time-evolution of the concentrations. UV irradiation of CF produces TC photomerocyanines which are photochemically isomerized into TT. Both processes are photoreversible. There is no direct thermal or photochemical pathway between TT and CF. The thermal pathway is very simple as it corresponds to the successive, irreversible mechanism: TT → TC → CF.

The nature of the linkage (direct or through an acetylenic bridge) affects photochromic behaviour. Indeed, the presence of an acetylenic junction leads to an increase in the photochemical and thermal bleaching of TC. The different photochemical behaviour of the compound **6**, substituted by a bithiophenic group via an acetylenic bond has been pointed-out: its rate of photocolouration is the lowest, while all other photochemical paths are accelerated.

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Appendix A

(1) Kinetic equations describing thermal relaxation according to Scheme 3:

$$[\mathrm{TT}]_t = [\mathrm{TT}]_0 \exp(-k_{\mathrm{TT}\to\mathrm{TC}}t)$$

$$\begin{aligned}[\mathrm{TC}]_t = {} & k_{\mathrm{TT}\to\mathrm{TC}}/(k_{\mathrm{TC}\to\mathrm{CF}} - k_{\mathrm{TT}\to\mathrm{TC}})[\mathrm{TT}]_0 \\ & \times (\exp(-k_{\mathrm{TT}\to\mathrm{TC}}t) - \exp(-k_{\mathrm{TC}\to\mathrm{CF}}t)) \\ & + [\mathrm{TC}]_0(\exp(-k_{\mathrm{TC}\to\mathrm{CF}}t))\end{aligned}$$

$$[\mathrm{CF}]_t = [\mathrm{CF}]_\infty - [\mathrm{TT}]_t - [\mathrm{TC}]_t$$

where $[\mathrm{TT}]_0$ and $[\mathrm{TC}]_0$ are the concentrations at time $t = 0$ at the end of the irradiation period, $[\mathrm{TT}]_t$, $[\mathrm{TC}]_t$ and $[\mathrm{CF}]_t$, the concentrations at time t, $[\mathrm{CF}]_\infty$, the initial concentration of solution and $k_{\mathrm{TT}\to\mathrm{TC}}$ and $k_{\mathrm{TC}\to\mathrm{CF}}$, the rate constants for the bleaching.

Note that these formulae do not hold for more complicated schemes, particularly if some processes are reversible.

(2) Photosteady-state concentrations:

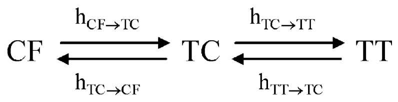
$[X]_{\mathrm{PSS}}$ values correspond to the concentrations at photostationary state. They can be calculated from the apparent photochemical rate constants $h_{i\to j}$, using the following formulae deduced from Scheme 4:

$$\%\mathrm{CF}_{\mathrm{PSS}} = 100 \times h_{\mathrm{TC}\to\mathrm{CF}} \times h_{\mathrm{TT}\to\mathrm{TC}}/D$$

$$\%\mathrm{TC}_{\mathrm{PSS}} = 100 \times h_{\mathrm{CF}\to\mathrm{TC}} \times h_{\mathrm{TT}\to\mathrm{TC}}/D$$

$$\%\mathrm{TT}_{\mathrm{PSS}} = 100 \times h_{\mathrm{CF}\to\mathrm{TC}} \times h_{\mathrm{TC}\to\mathrm{TT}}/D$$

with $D = (h_{\mathrm{TC}\to\mathrm{CF}} \times h_{\mathrm{TT}\to\mathrm{TC}}) + (h_{\mathrm{CF}\to\mathrm{TC}} \times h_{\mathrm{TT}\to\mathrm{TC}}) + (h_{\mathrm{CF}\to\mathrm{TC}} \times h_{\mathrm{TC}\to\mathrm{TT}})$.



Scheme 4. Successive reversible photoisomerization paths under UV irradiation. At 218 K, $k_{ij} = 0$, hence $h_{ij} = \Phi_{ij}\varepsilon_i l I_0 F$ (see Ref. [30]).

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