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Photoprocesses in 2,2-diphenyl-5,6-benzo(2*H*)chromene

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Abstract

The photocolouration of 2,2-diphenyl-5,6-benzo(2*H*)chromene (Chr), upon irradiation of the ring-closed form (Np), and the subsequent relaxation kinetics of one merocyanine isomer into Np were studied in several solvents at different temperatures. Deactivation of the excited Np form leads via the singlet manifold predominantly to the ring-opened *cis–trans* (*ct*) isomer which converts thermally into Np. The activation energy, $E_{ct\to\mathrm{Np}} \approx 77\,\mathrm{kJ\,mol^{-1}}$, and the pre-exponential factor, $A \approx 10^{12}\,\mathrm{s^{-1}}$, are essentially independent of the solvent polarity. The *trans–trans* (*tt*) isomer, which is suggested to be formed photochemically in a competing step, is thermally more stable. The triplet pathway of photocolouration can be induced by energy transfer using several sensitizers with a triplet energy of $>200\,\mathrm{kJ\,mol^{-1}}$. The thermal relaxation time after either direct or naphthalene-sensitized colouration is the same. The mechanisms of ring opening and ring closure are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chromene; Photochromism; Photocolouration; Photoisomerization; Relaxation kinetics

1. Introduction

Indoline spirobenzopyrans (BIPSs) and their 6-nitro substituted derivatives (NO_2-BIPS) exhibit photochromism between the ring-closed spiropyran form and the open photomerocyanine isomer(s) [1–8]. A triplet state with *trans* geometry and a more twisted (*cis*) isomer have been spectroscopically and kinetically observed upon excitation of either the more stable of the merocyanine forms ($\lambda_{exc} > 400$ nm) or of the ring-closed form ($\lambda_{exc} < 400$ nm) [9–15].

A related system, where photochromism also takes place and which does not contain a heterocyclic part, is based on the 3*H*-naphtho[2,1-*b*]pyran structure, often called chromene [16]. For 2,2-diphenyl-5,6-benzo(2*H*)chromene (Chr), a frequently studied chromene, and 2,2-dialkyl derivatives many details are known [16–31]. Favaro and co-workers [30] have shown recently that two photomerocyanines with *cis–trans* (*ct*) and *trans–trans* (*tt*) structure are involved in the photocolouration of Chr in methylcyclohexane (MCH). A triplet intermediate with a lifetime of 450 ns has been reported for a nitrochromene in toluene [21].

In this paper, the photochromism and the thermal relaxation after UV-excitation of the ring-closed (Np) form of Chr in solvents of low, medium and high polarity were studied at various temperatures. The relaxation time and the activation parameters for the ring closure were determined. Irradiation of the Np form is suggested to generate both the *ct* and *tt* photomerocyanines (Scheme 1). The spectroscopy and the kinetics are outlined and mechanistic implications are discussed.

2. Experimental

Chr (3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran) was synthesized according to methods described elsewhere [16]. The molar absorption coefficient of the open form in MCH at 357 nm is $1.6 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$ [30]. Acetone (Merck, Uvasol), acetonaphthone (Fluka), benzophenone, naphthalene, 9-bromophenanthrene, 9-fluorenone, biacetyl and acridine (Aldrich) were checked for purity. The solvents (Merck) were of the purest spectroscopic quality available, e.g., acetonitrile (Uvasol), dimethylformamide (DMF); MCH and ethanol were purified by distillation. The absorption spectra were recorded with a diode array spectrophotometer (Hewlett Packard, 8453). Most time-resolved experiments were performed with the 308 nm output of an excimer laser (Lambda Physics, EMG 200). In some cases the second or third harmonic from a Nd-laser (JK lasers), $\lambda_{exc} = 530$ or 354 nm, respectively, were used. The laser set-up was essentially the same as used previously [11,14]. Absorbancies of 0.5–2 (in 1 cm cuvettes) were typically used

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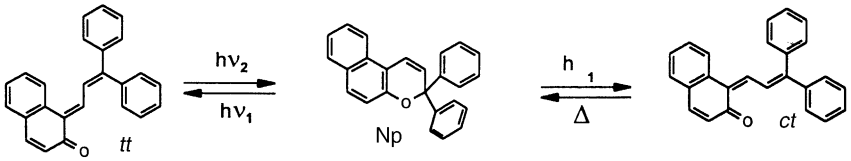


Scheme 1.

for $\lambda_{exc} = 308$ nm, corresponding to Chr concentrations of 0.03–0.1 mM. The Chr concentration under sensitized conditions was ≤ 1 mM, i.e. the decay of the triplet state of the donor was at least three times faster than without acceptor. Using a high enough sensitizer concentration, the amount of direct excitation of the Np form was 10% or less, as measured by absorption. For continuous irradiation, the 366 nm line of a 200 W Xe–Hg lamp combined with an interference filter were used. As reference for Φ in other solvents ($\lambda_{irr} = 366$ nm) the quantum yield of colouration in MCH of 0.9 [30] was used. The kinetic measurements at higher and lower temperatures were carried out with the photolysis set-up and the diode array, respectively. In appropriate cases the same $\tau_{t\text{-Np}}$ values were obtained with both methods.

3. Results

3.1. Photocolouration

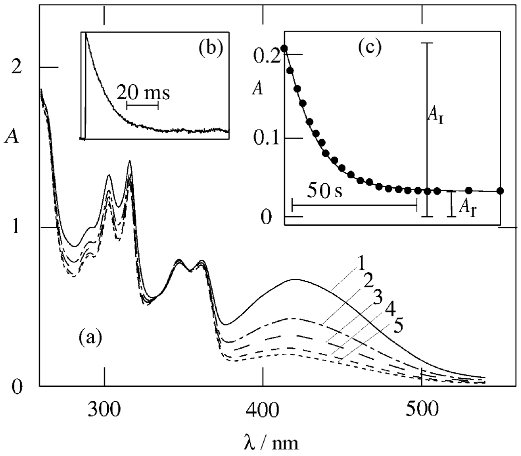


Fig. 1. (a) Absorption spectra of Chr in MCH at 25 °C after photolysis with 20 pulses at 308 nm (1) and during decolouration ((2)–(5)); relaxation kinetics at 430 nm (b) in DMF at 120 °C and (c) in MCH at 25 °C.

The absorption spectrum of the ring-closed Np form of Chr has two bands centred at 220 and ca. 300 nm and a longer wavelength maximum (λ_{Np}) at 340–355 nm. Continuous irradiation at 366 nm or pulsed excitation at 308 or 354 nm of Chr in several solvents at ambient temperature yields a new broad band with maximum (λ_{vis}) at 420–440 nm (Table 1) and isobestic points due to subsequent spectral changes in the UV. Examples of the photoinduced absorption spectra are shown in MCH (Fig. 1a), toluene (Fig. 2a), acetonitrile (Fig. 3a) and ethanol (Fig. 4a) at 25 °C. The quantum yields upon continuous irradiation at 366 nm or pulsed excitation at 308 nm are $\Phi = 0.7$–0.9. The isobestic points in the UV range remain on further irradiation which indicates that secondary photoreactions are absent. The changes are due to photoconversion into merocyanines, the major form is denoted as *ct*:

$$\mathrm{Np} \xrightarrow{h\nu} {}^{1}\mathrm{Np}^{*} \tag{1}$$

$$^{1}\mathrm{Np}^{*} \rightarrow ct \tag{2}$$

Table 1
Absorption maxima of the Np and *ct*/*tt* merocyanine forms and quantum yield of colouration[a]

Solvent	λ_{Np} (nm)	λ_{vis}[b] (nm)	Φ	ΔA[c]
MCH	304, 315, 348, 360	410/418	0.9	1.0
Toluene	305, 318, 346, 360	420/428	0.8	0.85
DMF	304, 315, 348, 360	463/468	0.7	0.75
Acetonitrile	303, 310, 342, 356	415/422	0.8	0.8
Ethanol	304, 318, 344, 356	425/430	0.8	0.7

[a] At 25 °C using $\lambda_{irr} = 366$ nm.

[b] The first and second value refers to the initial and respective final maximum.

[c] Relative values at λ_{vis} and 1 μs after the 308 nm pulse.

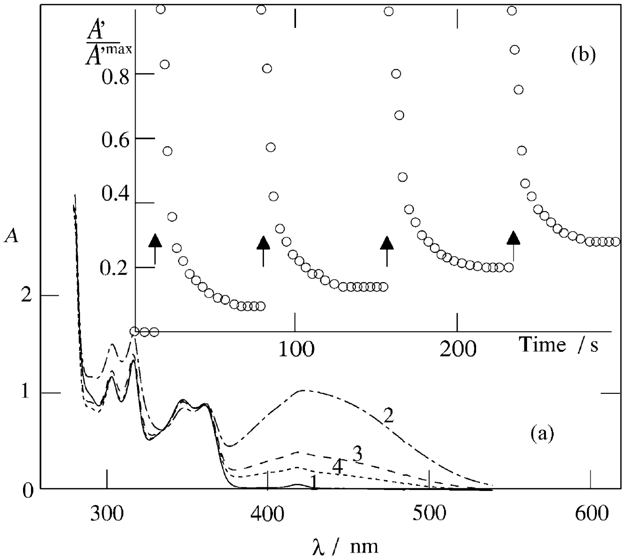


Fig. 2. Absorption of Chr in toluene at 25 °C (a) spectra prior to (1) and after photolysis with 20, 3 and 1 pulses ((2)–(4), respectively) at 308 nm and (b) repeated measurement of the relative absorbance at 430 nm after pulsing (10 times, 0.5 Hz).

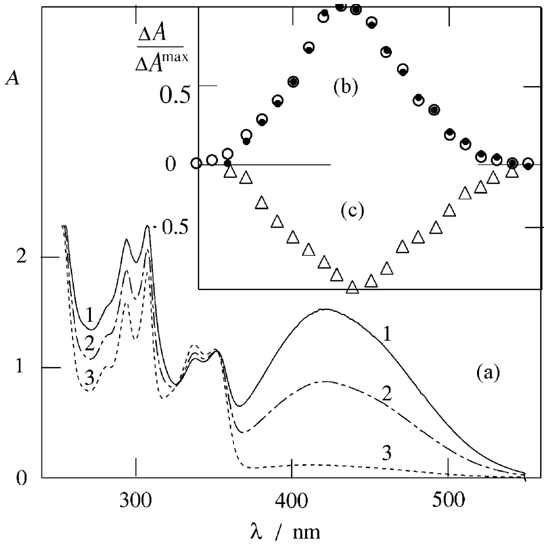


Fig. 3. (a) Absorption spectra of Chr in acetonitrile at 25 °C after 308 nm photolysis (1) and during decolouration ((2) and (3)); transient absorption spectra (b) at 100 ns (○) and 100 ms (●) after the 308 nm pulse and (c) bleaching spectrum at 100 ns (△) after the 530 nm pulse.

Similar spectra with maximum at λ_{vis} were observed throughout. Pulsed excitation of Chr at 308 nm reveals an absorption increase within 20 ns to yield a long-lived intermediate; eventually the major part of the latter reverts back (Figs. 1b and c, 2b and 4b and c). A triplet state as precursor of the photocolouration at room temperature is unlikely since no changes could be detected between 20 ns and 1 s and the presence or absence of oxygen has no effect. Concerning the emission properties of Chr, no fluorescence could be monitored either in fluid or glassy media and no phosphorescence was detected even at −196 °C.

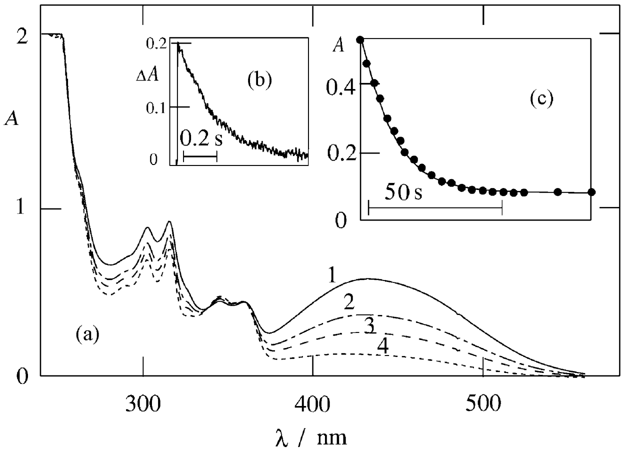


Fig. 4. (a) Absorption spectra of Chr in ethanol at 25 °C after 308 nm photolysis (1) and during decolouration ((2)–(4)); relaxation kinetics at 440 nm at (b) 70 °C and (c) 25 °C.

3.2. Relaxation kinetics

It has been reported that the relaxation kinetics of the *ct* merocyanine in MCH is described by a first-order decay law at elevated temperatures, whereas below 25 °C a second longer lived component due to the *tt* merocyanine becomes apparent [30]:

$$ct\xrightarrow{\Delta}\mathrm{Np} \qquad (3)$$

First-order decay of the absorbance at 400–480 nm after pre-irradiation of Np at 308 or 366 nm was also found in the present work for Chr in several solvents at elevated temperatures. The rate constant (inverse relaxation time: $1/\tau_{ct\text{-Np}}$) was obtained from the ratio $(A_{\mathrm{I}}-A)/(A_{\mathrm{I}}-A_{\mathrm{r}})$ vs. irradiation time, where A_{I} is the photoinduced absorption increase and A_{r} the remaining absorption (Figs. 1b and 5, inset). The relaxation time in solvents of low as well as high polarity at 25 °C is of the order of 10 s. The log of the rate constant depends linearly on $1/T$ throughout. From these Arrhenius plots (Fig. 5), the activation energy ($E_{ct\to\mathrm{Np}}$) was determined. The values for $E_{ct\to\mathrm{Np}}=76$–$79\,\mathrm{kJ\,mol^{-1}}$ and the pre-exponential factor $A=(1$–$4)\times10^{12}\,\mathrm{s^{-1}}$ are essentially independent of the solvent polarity (Table 2).

In order to measure the relative amount of remaining absorbance ($A_{\mathrm{r}}/A_{\mathrm{I}}$), Chr in toluene (Fig. 2b) or in MCH was pulsed (10 times, 0.5 Hz) at 308 nm; after a relaxation period of 50–100 s this procedure was repeated several times. The

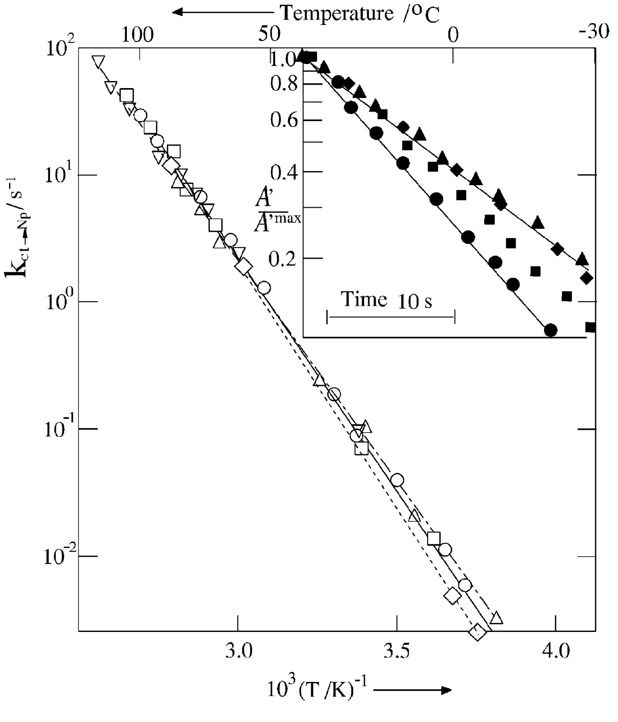


Fig. 5. Arrhenius plots of the relaxation kinetics (at 410–450 nm) after excitation (308 nm) of Chr in MCH (circles), toluene (squares), acetonitrile (△,▲), DHF (▽) and ethanol (diamonds); inset: semi-logarithmic plots of the normalized absorption vs. time at 25 °C.

Table 2
Factor A, activation energy and relaxation time for thermal decolouration[a]

Solvent	A (10^{12} s^{-1})	$E_{ct\rightarrow \mathrm{Np}}$ (kJ mol^{-1})	$1/\tau_{ct\text{-Np}}$[b] (s^{-1})
MCH	1.1	76	0.10
Toluene	2.4	77	0.08
DMF	2.0	77	0.08
Acetonitrile	4.0	77	0.15
Ethanol[c]	3	79	0.06

[a] Using $\lambda_{exc} = 308$ nm.
[b] Measured at 25 °C using $\lambda_{obs} = 400$–500 nm.
[c] Same values for naphthalene-sensitized excitation, argon-saturated.

A_r/A_I ratio increases significantly when the concentration corresponds to $A_{308} = 2$–3, whereas for $A_{308} = 0.3$–0.5, it remains almost constant, as was also found upon 366 nm irradiation (not shown). This indicates that the stable photoisomer is enriched, when the light is mainly absorbed by the Np form, but a photostationary composition is established, when the stable photoisomer is also excited. When the coloured solution was kept for 1–2 days in the dark, it became colourless, but we were unable to measure the slow relaxation kinetics. The rate constants of the slow relaxation kinetics of Chr in MCH or in toluene are much smaller than 10^{-4} s^{-1} at room temperature and smaller than 10^{-3} s^{-1} at 90 °C.

3.3. Sensitized colouration

In order to test for the triplet pathway, the method of sensitized colouration was applied using several high-energy donors (D) and $\lambda_{exc} = 308$ nm. Decay of the triplet state of the donor (^{3}D*), e.g. naphthalene in argon-saturated ethanol, observed at 415 nm, is faster in the presence of Chr. The amount of direct excitation of the Np form was 10% or less, as measured by absorption of the photomerocyanine at longer wavelengths, when triplet quenching by oxygen blocks the triplet pathway. The spectrum after energy transfer is the same as upon direct excitation (Fig. 6a). The ΔA_{440} value, which at the end of the pulse is <20% of the maximum value, increases with the same kinetics as the decay of ^{3}D*, the rate constant is $k_4 \approx 8 \times 10^9$ M^{-1} s^{-1}. Further examples with benzophenone and acetone in argon-saturated acetonitrile are shown in Fig. 6b and c, respectively. These findings demonstrate that another pathway of photocolouration via triplet states exists:

$$^3\mathrm{D}^* + \mathrm{Np} \rightarrow \mathrm{D} + {}^3\mathrm{Np}^* \quad (4)$$

$$^3\mathrm{Np}^* \rightarrow ct \quad (5)$$

Here, among the possible triplet states of the ring-closed form (^{3}Np*) and the open photomerocyanine isomer(s), at least the former has to be involved, reaction (5), after energy transfer reaction (4). The rate constants for energy transfer k_4 are listed in Table 3.

No phosphorescence was monitored for Chr either in the Np form or in the merocyanine form. Apparently, the lifetime of the ^{3}Np* state is shorter than 1 μs, which is not accessible with our method due to a too high Chr concentration. This estimate is consistent with a triplet lifetime of 450 ns for a nitrochromene [21]. In order to estimate the triplet state energy (E_T) of the Np form, several sensitizers were used. From the plot of log k_4 vs. E_T (not shown) of the energy donors, a value of ca. (200 ± 20) kJ mol^{-1} was obtained for the ^{3}Np* level. This is only slightly lower than the value of 230 kJ mol^{-1} for 2,2-dimethyl-6-methoxy-7,8-benzo(2*H*)chromene [31]. The fast relaxation time of the absorbance at 420–440 nm, after pre-irradiation of the Chr/naphthalene system, was found to be very similar to that in the non-sensitized experiment, i.e. the activation energies for thermal relaxation under direct and sensitized colouration are the same (Table 2).

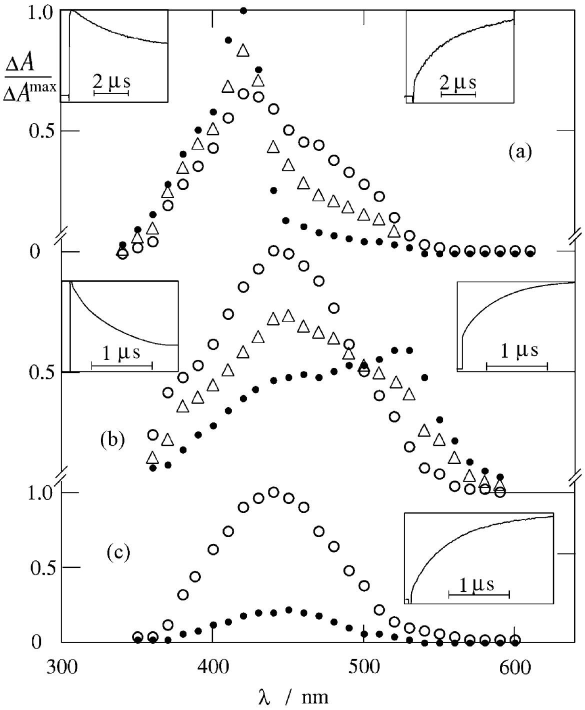


Fig. 6. Transient absorption spectra of Chr at 25 °C upon sensitized excitation (argon-saturated) using (a) naphthalene in ethanol, (b) benzophenone and (c) acetone in acetonitrile monitored at <100 ns (●), 1 μs (△) and 10 μs (○) after the 308 nm pulse; inset: triplet decay at (a) 414 nm and (b) 520 nm (left) and colouration at 440 nm ((a)–(c), right).

Table 3
Rate constants for triplet energy transfer[a]

Donor	E_T (kJ mol^{-1})	k_4 (10^9 M^{-1} s^{-1})
Acetone	334	9
Benzophenone	287	7
Naphthalene	254	8
Acetonaphthone	248	5
9-Bromophenanthrene	238	8
Fluorenone	223	4
Biacetyl	197	2
Acridine	184	<1

[a] In argon-saturated acetonitrile at 25 °C using $\lambda_{exc} = 308$ nm.

4. Discussion

4.1. Deactivation of the excited ring-closed form

Based on the photostationary and spectrokinetic methods Ottavi et al. [30] recently proposed that the ring closure of Chr contains two components, a major shorter and a minor longer lived one. These components are attributed to the *ct* and *tt* photomerocyanines, respectively. The *ct* and *tt* isomers are photochemically convertible and exhibit the same absorption spectrum with $\lambda_{\max} = 422$ nm in MCH. The quantum yields of the Np → *ct*, *ct* → *tt* and *tt* → *ct* processes are $\Phi = 0.9$, 0.3 and 0.2, respectively, and the activation energy relating to the major barrier is $E_{ct\to\mathrm{Np}} = 60\,\mathrm{kJ\,mol^{-1}}$ [30]. Larger $E_{ct\to\mathrm{Np}}$ values are presented in this work (Table 2).

To account for the observation that at room temperature in the 10^3 s time domain only the major component in the 400–500 nm range is thermally reversible, but part of this absorption remains constant (Fig. 2b), we suggest that the *tt* isomer is thermally relatively stable, at least in the temperature range examined, and the observed relaxation should be attributed to reaction (3). Concerning the formation of the *tt* isomer two possibilities are considered:

(a) Deactivation of the $^1\mathrm{Np}^*$ state leads to both the *ct* and *tt* isomers (Scheme 2):

$$^1\mathrm{Np}^* \rightarrow tt \tag{2'}$$

(b) The *tt* isomer is formed from the *ct* isomer (rather than from the ring-closed form itself) in a secondary excitation step [30]:

$$ct \xrightarrow{h\nu} {}^1ct^* \tag{6}$$

$$^1ct^* \rightarrow tt \tag{7}$$

Possibility (b) can be excluded due to the lack of intensity dependence of the amount of remaining absorbance in the 400–500 nm range. A further argument in favour of possibility (a) is that the remaining absorption A_r is easily detectable at low conversion in all solvents examined. Moreover, the $A_\mathrm{r}/A_\mathrm{I}$ ratio increases upon repeated flashing of the Np form (Fig. 2b), i.e. the amount of the stable photoisomer is enriched. For case (a), it follows that the difference in absorption spectra of irradiated vs. non-irradiated Chr should be the sum of the *ct* and *tt* isomers when recorded prior to relaxation and due to the *tt* isomer when recorded after relaxation.

4.2. Deactivation of the excited photomerocyanines

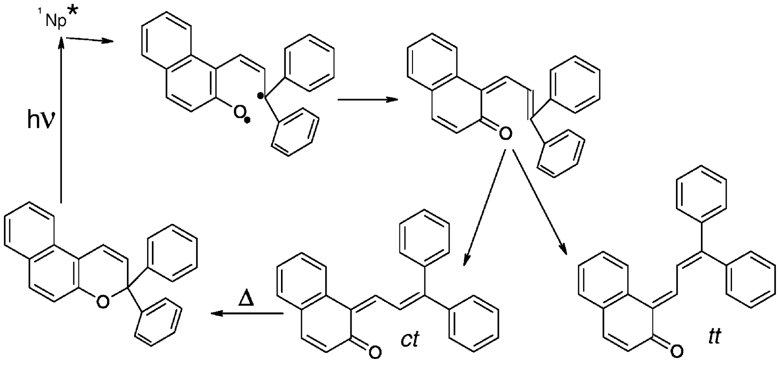
An open question was the fate of the excited *tt* state. The proposed conversion [30] into the *ct* form may be replaced by two additional deactivation routes into the *ct* merocyanine and the Np form (9):

$$tt \xrightarrow{h\nu} {}^1tt^* \tag{8}$$

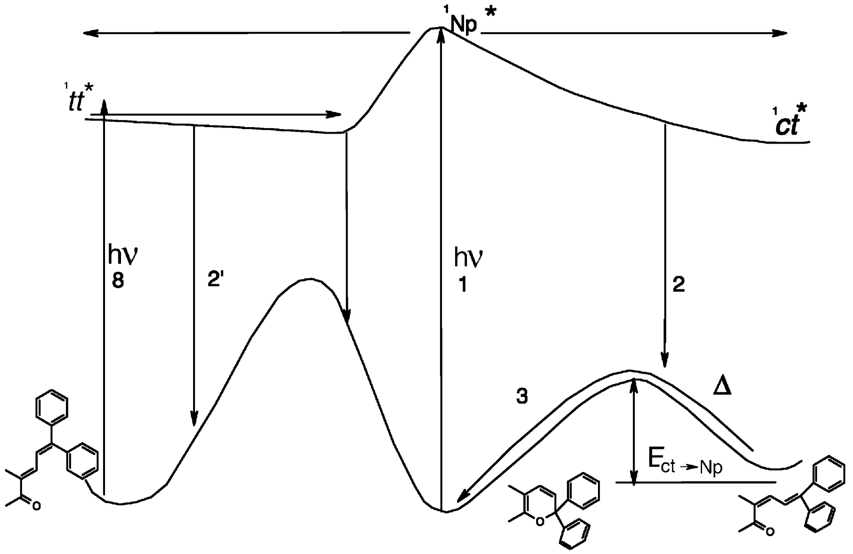
$$^1tt^* \rightarrow tt + ct + \mathrm{Np} \tag{9}$$

The existence of a photochemical pathway back to the Np form is based on the bleaching at 400–500 nm upon excitation of the photomerocyanines with $\lambda_\mathrm{exc} > 400$ nm (Fig. 3c). This process is faster than 20 ns and no triplet is involved. Therefore, irradiation at >400 nm leads to the Np form, taking into account that the *ct* isomer converts back via reaction (3).

The kinetics of photocolouration, due to the absence of any fluorescence, must be very fast, which is consistent with the high quantum yield of colouration. A strong decline of the potential energy surface of the S_1 state is expected on going from the Np form to the *tt* isomer (Scheme 3) since otherwise the quantum yield of decolouration $\Phi_{-\mathrm{col}}$ should be zero. To account for the results that $\Phi_{-\mathrm{col}}$ is substantial but well below unity [30], there should also be a $S_1 \rightarrow S_0$ deactivation pathway left from the maximum of the $E_{ct\to\mathrm{Np}}$ barrier. For 2,4-diphenyl-2*H*-benzopyran, a related photochromic material, the photoinduced ring opening into the vibrationally excited open forms in the ground state occurs in 2 ps; with respect to Chr, the relaxation time (0.05 ms) and the activation energy ($34\,\mathrm{kJ\,mol^{-1}}$) are much shorter and smaller, respectively [32].



Scheme 2.



Scheme 3.

4.3. Mechanistic remarks

The potential energy surface of the ground state along the reaction coordinate should have at least one major and one minor barrier (Scheme 3). Only the latter is observable under our conditions. The results that both the pre-exponential factor of the relaxation time and $E_{ct \rightarrow \mathrm{Np}}$ are independent of the polarity (Table 2) are in favour of a quinoid rather than an ionic merocyanine intermediate.

Formation of a weakly absorbing transient in glassy media (not shown), which is tentatively assigned to a triplet state, indicates that intersystem crossing in the Np form competes to a minor extent with ring opening. Owing to the too short triplet lifetime a phosphorescence signal could not be monitored under our conditions. The lack of triplet formation demonstrates that intersystem crossing in the closed geometry does not take place at room temperature and that the ring opening occurs in the S_1 state. To account for the oxidation products of Chr in toluene, mainly benzophenone and β-phenylcinnamaldehyde, one mechanism involving triplet oxygen and another mechanism involving singlet oxygen have been considered [25].

5. Conclusions

UV-excitation of the ring-closed form of Chr yields the *ct* and the *tt* isomers as major and minor ring-opened products, respectively. The observed thermal relaxation is ascribed to the former photomerocyanine. The quantum yields of colouration, the relaxation time and the related activation energy and the pre-exponential factor are essentially independent of the solvent polarity. In addition to this singlet pathway of photocolouration, a triplet pathway can be induced by triplet energy transfer.

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