

## Photochemistry of 7-Hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium and Related Compounds

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2-Styryl-1-benzopyrylium derivatives exhibit deeper hues and absorption spectra that are substantially red-shifted when compared with their 2-phenyl-1-benzopyrylium analogues. They follow the same pH and light-dependent network of chemical reactions previously described for 2-phenyl-1-benzopyrylium compounds. In this work, the photochromic properties of 7-hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium chloride are reported. This compound was fully characterized by UV–vis absorption, fluorescence emission, pH jumps, and flash photolysis, and its properties were compared with the analogue 7,4'-dihydroxyflavylium (7-hydroxy-2-(4-hydroxyphenyl)-1-benzopyrylium). The *trans*-chalcones of both compounds lacking the hydroxyl in position 2 were synthesized and used as model compounds since they exhibit *cis*–*trans* isomerization but cannot be involved in the other processes resulting from the ring closure. The transient absorption of two triplets attributed to the chalcones Ct/Ct<sup>−</sup>, and a tautomer was detected by nanosecond flash photolysis, independent of the existence of the 2-hydroxyl substituent. The experimental results are compatible with the main formation of *cis*-chalcone from the singlet state. In the case of the styryl derivatives, the fraction of triplet formed from excitation of Ct is much higher, and the fraction of isomerization is much smaller. For this reason, the photochemistry of 7-hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium in water is much less efficient than that of its parent 7,4'-dihydroxyflavylium; however, in the presence of CTAB micelles, intense red colors can be obtained upon irradiation, confirming the usefulness of this family of compounds as photochromic systems.

## Introduction

Within the family of chalcones, the 2-hydroxychalcone derivatives are certainly the most challenging as far as their behavior in solution is concerned. Differently from chalcones lacking a hydroxyl group in position 2, 2-hydroxychalcones are involved in a complex network of chemical reactions that follow the photoinduced formation of the *cis*-chalcone.<sup>1–5</sup> This is due to the possibility of a ring closure on the *cis*-chalcone species to give the tautomeric hemiketal B, a process that occurs on the subsecond time scale. On the other hand, at lower pH values, B can dehydrate on a time scale of seconds to give the intensely colored flavylium cation AH<sup>+</sup>, the stable species in acidic medium; see Scheme 1.

Natural 2-hydroxychalcones can be obtained from anthocyanins,<sup>6</sup> the ubiquitous molecules responsible for most of the red and blue colors of flowers and fruits, following exactly the same network of chemical reactions as those represented in Scheme 1,<sup>7,8</sup> which can be driven by pH changes and light excitation.<sup>9</sup> Other families of derivatives from which 2-hydroxychalcones originate include deoxyanthocyanidins<sup>10</sup> and natural<sup>11</sup> and synthetic flavylium compounds,<sup>1,8,9,12b</sup> also undergo reactions reported in Scheme 1. The interest of 2-hydroxychalcones is thus related to their peculiar photochromic system exhibiting multistate, multifunctional characteristics.<sup>1–4,9,12</sup>

In this work, we report on the 7-hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium chloride (DHS) network of reactions. 7-Hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium chloride can be considered to be a derivative of 7,4'-dihydroxyflavylium (DHF) obtained by the introduction of a double bond between rings C and B; see Scheme 2.

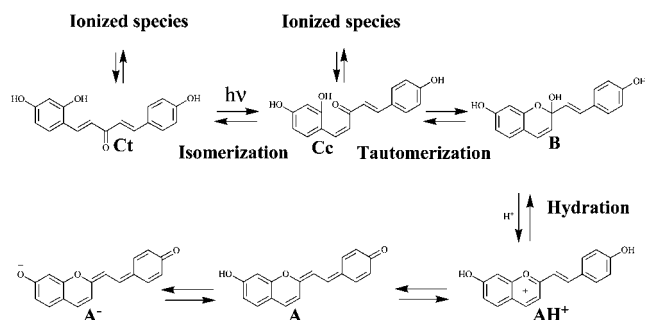
It is worth noting that, while 2-phenyl-1-benzopyrylium compounds have been extensively studied, only a few works regarding 2-styryl-1-benzopyrylium were published, despite the fact that their synthesis was reported as early as 1922.<sup>13–18</sup>

The most significant works concerning 2-styryl-1-benzopyrylium are a 1967 patent by Jurd pointing out the practical use of these molecules<sup>15</sup> and a theoretical study carried out by Amic regarding the fading of the color in these compounds at moderately acidic pH values.<sup>17</sup> As observed by the former author, the existence of a styryl group attached to the benzopyrylium at position 2 has the advantage of exhibiting deeper hues than are possible to achieve with flavylium-type structures, wherein a phenyl nucleus is attached at position 2. In addition, these compounds present good stability in acidic media, and by consequence, Jurd claimed in his patent the use of 2-styryl-1-benzopyrylium compounds as an alternative to anthocyanins in coloring acidic fruits and vegetables.

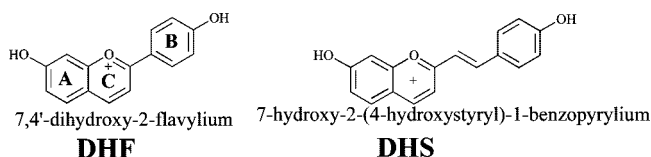
On the other hand, after the work of Dubois, Brouillard, and McClelland, the network of pH-dependent chemical species arising from the 2-phenyl-1-benzopyrylium core was firmly established.<sup>7,8</sup> On the basis of the experimental results carried out on 7-hydroxy-2-(4-methoxystyryl)-1-benzopyrylium chloride, Amic and co-workers concluded that 2-styryl-1-benzopyrylium compounds follow the same network of chemical reactions of anthocyanins and synthetic flavylium compounds (Scheme 1).<sup>17</sup> These previous observations prompted us to investigate in more detail how the introduction of the double bond affects the kinetics and the thermodynamics of the network of chemical reactions reported in Scheme 1 and particularly how the photochromic properties of the chalcones derived from 2-styryl-1-benzopyrylium systems compare with those arising from the 2-phenyl analogues. Model chalcone compounds lacking the 2-hydroxyl group had to be synthesized and studied

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## SCHEME 1



## SCHEME 2



as model compounds. The role of chemical reactions in the triplet excited state was studied by laser flash photolysis in order to investigate the photochemical pathway that leads to the photochromic effect.

## Experimental Section

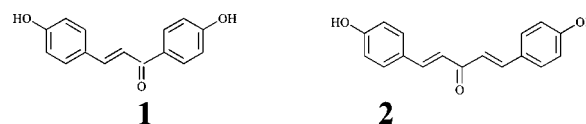
**General for Synthesis.** All reagents and solvents used were of analytical grade. The NMR spectra at 298.0 K were obtained on a Bruker AMX400 operating at 400.13 ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ ). Mass spectra were run on Applied Biosystems Voyager PRO (MALDI TOF MS). Elemental analysis was performed on a Thermofinnigan Flash EA 1112 Series instrument.

The synthesis of *p*-hydroxystyrylmethylketone and 7-hydroxy-2-(4-hydroxyphenyl)-1-benzopyrylium chloride (DHS) was published elsewhere.<sup>19</sup>

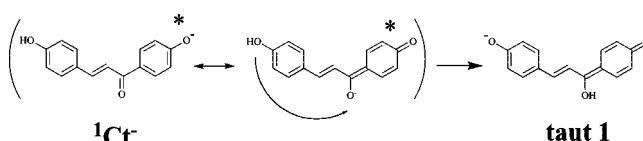
**Synthesis of (*E*)-1,3-Bis(4-hydroxyphenyl)prop-2-en-1-one (4,4'-Dihydroxychalcone).** *p*-Hydroxybenzaldehyde (2 mmol, 0.244 g) and 4'-hydroxyacetophenone (2.42 mmol, 0.33 g) were dissolved in 5 mL of diethyl ether; 2 mL of ethanol and 2 mL of sulfuric acid were then added. The solution became orange and was left under stirring for 3 h. A dark yellow solid precipitated by the addition of water, which was filtered off, and the solid was carefully washed with water and dried. Purification was made by flash chromatography in diethyl ether/hexane (1:1). A yellow solid was obtained (0.23 g, 0.96 mmol). Yield: 46.9%.  $^1\text{H}$  RMN ( $\text{CD}_3\text{OD}$ , 400.13 MHz)  $\delta$  (ppm): 7.99 (2H, d,  $^3J = 8.6$  Hz), 7.70 (1H, d,  $^3J = 15.5$  Hz), 7.60 (2H, d,  $^3J = 8.1$  Hz), 7.54 (1H, d,  $^3J = 15.2$  Hz), 6.88 (2H, d,  $^3J = 8.5$  Hz), 6.83 (2H, d,  $^3J = 8.3$  Hz).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100.62 MHz)  $\delta$  (ppm): 191.02, 163.64, 161.35, 145.71, 132.17, 131.62, 131.13, 127.83, 119.51, 116.83, 116.32. EA calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_3$ : C 74.99, H 5.03; found: C 74.67, H 5.30. MALDI-TOF/MS 241.1 (100%) [ $\text{M} + \text{H}$ ] $^+$ ; 242.1 (21.5%) [ $\text{M} + 2\text{H}$ ] $^+$ .

**Synthesis of (1*E*,4*E*)-1,5-Bis(4-hydroxyphenyl)penta-1,4-dien-3-one.** *p*-Hydroxybenzaldehyde (0.32 mmol, 0.039 g) and *p*-hydroxybenzalacetone (0.32 mmol, 0.052 g) were dissolved in 2 mL of ethanol; 1 mL of sulfuric acid was then added. The solution became dark red and was left under stirring for 5 h. A dark brown solid was precipitated by the addition of water, which was filtered off, and the solid was carefully washed with water and dried (0.072 g, 0.27 mmol). Yield: 84.2%.  $^1\text{H}$  ( $\text{CD}_3\text{OD}$ , 400.13 MHz)  $\delta$  (ppm): 7.69 (2H, d,  $^3J = 15.7$  Hz), 7.55 (4H, d,  $^3J = 6.0$  Hz), 7.04 (2H, d,  $^3J = 15.4$  Hz), 6.81 (4H, d,  $^3J = 6.3$  Hz). EA calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_3$ : C 76.68, H 5.30;

## SCHEME 3



## SCHEME 4



found: C 76.75, H 5.41. MALDI-TOF/MS: 267.1 (100%) [ $\text{M} + \text{H}$ ] $^+$ ; 268.1 (28.4%) [ $\text{M} + 2\text{H}$ ] $^+$ .

**Measurements.** Solutions were prepared using Millipore water and absolute ethanol (when needed). The pH of the solutions was adjusted by addition of HCl, NaOH, or the universal buffer of Theorell and Stenhagen<sup>20</sup> and was measured on a Radiometer Copenhagen PHM240 pH/ion meter. UV-vis absorption spectra were recorded on a Varian-Cary 100 Bio spectrophotometer or on a Shimadzu VC2501-PC.

Light excitation was carried out using a medium-pressure mercury arc lamp, and the excitation bands (436 nm) were isolated with interference filters (Oriol). The incident light intensity was measured by ferrioxalate actinometry.<sup>21</sup>

Second and subsecond flash photolysis experiments were performed as previously described.<sup>22</sup> Nanosecond laser flash photolysis experiments were run on a LKS.60 nanosecond laser photolysis spectrometer from Applied Photophysics.

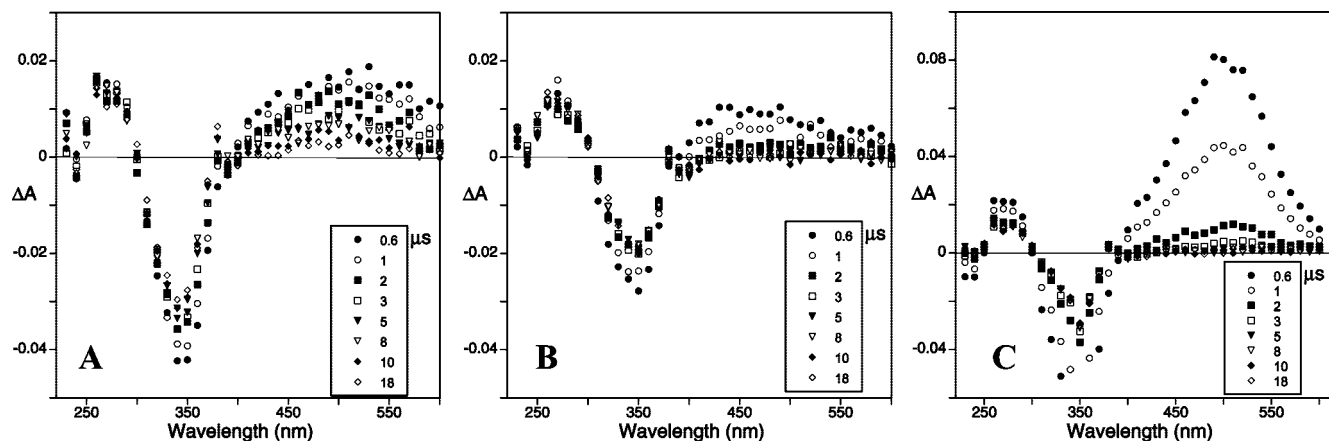
**Data Analysis.** Laser flash photolysis traces at each wavelength were analyzed with a global analysis method. Least-squares fittings of the experimental data with single or double exponential kinetics were performed using Solver from MS Excel, by adjusting globally the rate constants to all kinetic traces for each pH and the exponential factors for each kinetic trace at a specific wavelength.

## Results and Discussion

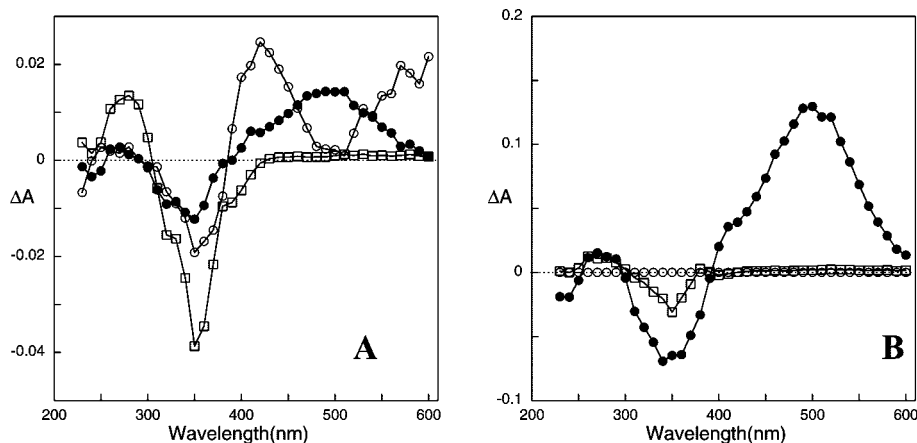
**Chalcones Lacking Hydroxyl in Position 2.** In order to clarify the photochemical studies, chalcones **1** and **2** were synthesized; see Scheme 3. The advantage of these model compounds is the possibility of working at acidic pH values without the formation of the network reported in Scheme 1. This strategy was crucial to the comprehension of the transient absorptions of the 2-hydroxychalcone systems; see below.

The UV-vis absorption titration of **1** (see Supporting Information) is compatible with the existence of two acid/base equilibria with  $\text{pK}_a$ 's of 7.9 and 9.0. Identical  $\text{pK}_a$  values were obtained by means of fluorescence emission titration, excluding the existence of ESPT (excited-state proton transfer) in the framework of the Weller theory.<sup>23</sup> However, the much lower emission intensity of the  $\text{Ct}^-$  species in comparison with Ct and  $\text{Ct}^{2-}$ , suggests the possibility of a singlet excited-state deactivation channel of this species by formation of a tautomer mediated by water, as shown in Scheme 4.

Irradiation of compound **1** was carried out at pH = 1.2 and 6.1 at the excitation wavelength of 365 nm, and the qualitative behavior is similar at both pH values; see Figure 1SC, Supporting Information. During the first seconds of the reaction, the trans species is consumed, and a steady state is reached, most probably by formation of the *cis*-chalcone due to a photoisomerization reaction. However, for longer irradiations times, subsequent spectral variations take place, leading to



**Figure 1.** Transient absorption spectra of compound **1** in a mixture of water (90%) and ethanol (10%). Time indicates the delay after the laser pulse. (A) pH = 6.1; solution saturated with argon. (B) pH = 6.1; air-equilibrated solution. (C) pH = 1.2; air-equilibrated solution.



**Figure 2.** Pre-exponential factors calculated from global analysis of the decays obtained for compound **1** in a mixture of water (90%) and ethanol (10%) at 6.1 (A) and 1.2 (B) in air-equilibrated solutions (○,  $a_{1\lambda}$ ; ●,  $a_{2\lambda}$ ; □,  $a_{3\lambda}$ ).

different species. We did not investigate in detail the second photoproduct, which could be due to a photoinduced oxidation process.

In Figure 1, the results from the nanosecond flash photolysis of the nonionized compound **1** are presented. Immediately after the flash, a bleaching of the Ct species can be observed together with the formation of an absorption band extended into the visible. This absorption cannot be attributed to the *cis*-chalcone (Cc) because this species does not absorb at these wavelengths, as shown from the irradiation experiments (Supporting Information). An alternative would be the formation of ionized chalcones, Ct<sup>-</sup> or Ct<sup>2-</sup>, by successive deprotonation of the singlet excited state. ESPT was excluded above on the basis of the coincidence of the fluorescence emission titration curves with those obtained from the absorption spectra (see Supporting Information). Moreover, such ionized species do not have absorption features at wavelengths above 480 nm (Ct<sup>2-</sup> peaks at 435 nm and Ct<sup>-</sup> peaks at around 400 nm, while the transient absorption spectra peaks at around 500 nm). On this basis, the most reliable alternative is the attribution of the transient absorption to the triplet state, in agreement with the transient absorptions reported by Norikane<sup>24</sup> and Givens and Wirz<sup>25</sup> for analogous *p*-hydroxyacetophenones. The decay constants of the transient absorptions are affected by molecular oxygen, as expected for a triplet state, but the effect is not the same through all of the wavelengths because the shapes of the curves in Figure 1A and B, respectively, in the absence and presence of oxygen are not identical, as would be expected for a quenching occurring in a single species.

The existence of two different transient absorptions is clearly confirmed from the data at acidic pH values, one experiment that is only possible in chalcones lacking the hydroxyl in position 2. At pH = 1.2, the transient absorption is more intense, and the shape of the curve is compatible with the formation of a single absorption band and single exponential kinetics; Figure 1C (see also Figure 2).

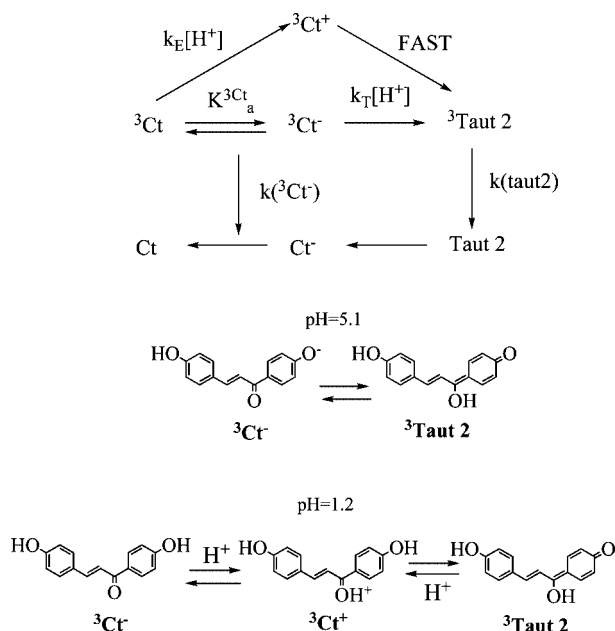
A global analysis of the decays was carried out according to the following expression (see Supporting Information for a comparison between single and double exponential kinetics)

$$\Delta A_{\lambda} = a_{1\lambda}e^{-t/\tau_1} + a_{2\lambda}e^{-t/\tau_2} + a_{3\lambda} \quad (1)$$

where  $\Delta A_{\lambda}$  refers to the measured change in absorbance at wavelength  $\lambda$ ,  $\tau_1$  and  $\tau_2$  are the lifetimes of the two detected processes,  $a_{1\lambda}$  and  $a_{2\lambda}$  are the respective amplitudes, and  $a_{3\lambda}$  is the residual amplitude after the two processes had finished. At pH = 6.1 (air-equilibrated), the experimental data could be fitted with  $\tau_1 = 1.5 \mu\text{s}$  (black circles) and  $\tau_2 = 0.38 \mu\text{s}$  (open circles) with components represented in Figure 2A; the same experiment carried out in argon saturated solutions leads to similar spectral variations with lifetimes of  $\tau_1 = 6 \mu\text{s}$  and  $\tau_2 = 0.35 \mu\text{s}$ . At pH = 1.2, only one process is observed with a lifetime of  $0.74 \mu\text{s}$ ; see Figure 2B.

An explanation for this behavior can be found in Scheme 5, in partial agreement with previous results reported by Wirz for a related compound (*p*-hydroxyacetophenone)<sup>25</sup> and by Phillips.<sup>26</sup> Excited-state proton transfer would occur at pH = 6.1,

## SCHEME 5



leading to the formation of ionized species  $^3\text{Ct}^-$  in equilibrium with  $^3\text{Ct}$ . As pointed out by Wirz, such process would be fast since the deprotonation rate constant should be greater than  $3 \times 10^7 \text{ s}^{-1}$  and, therefore, undetectable in our laser flash photolysis experimental setup due to fluorescence interferences. The corresponding transient absorption (open circles) has a valley at around 500 nm, with a shape roughly symmetric to the absorption of transient 1 (black circles). This suggests a sequential process where  $^3\text{Ct}^-$  evolves to a tautomeric species ( $^3\text{Taut2}$ ) responsible for the absorption of transient 1. On the other hand, transient 1 is the only transient absorption at pH = 1.2. In this case, the tautomer would be directly formed from  $^3\text{Ct}$  by acidic catalysis.

Taking the kinetic model of Scheme 5, it is possible to obtain the following expressions for the amplitudes of eq 1 (see Supporting Information)

$$a_{1\lambda} = [^3\text{Ct}]_0 (\chi_{3\text{Ct}} \Delta \varepsilon_{3\text{Ct}\lambda} + \chi_{3\text{Ct}^-} \Delta \varepsilon_{3\text{Ct}^-\lambda} - \Delta \varepsilon_{3\text{Taut2}\lambda} \alpha) \quad (2)$$

$$a_{2\lambda} = [^3\text{Ct}]_0 \Delta \varepsilon_{3\text{Taut2}\lambda} \alpha \quad (3)$$

$$a_{1\lambda} + a_{2\lambda} = [^3\text{Ct}]_0 (\chi_{3\text{Ct}} \Delta \varepsilon_{3\text{Ct}\lambda} + \chi_{3\text{Ct}^-} \Delta \varepsilon_{3\text{Ct}^-\lambda}) \quad (4)$$

in which  $[^3\text{Ct}]_0$  is the amount of triplet Ct species formed from intersystem crossing of the singlet excited state, and

$$\alpha = \frac{k_T[\text{H}^+] \chi_{3\text{Ct}^-} + k_E[\text{H}^+] \chi_{3\text{Ct}}}{k_E[\text{H}^+] \chi_{3\text{Ct}} + (k(^3\text{Ct}^-) + k_T[\text{H}^+]) \chi_{3\text{Ct}^-} - k(^3\text{Taut2})} \frac{[\text{H}^+]^2 + \frac{k_T}{k_E} K_a^3\text{Ct} [\text{H}^+]}{[\text{H}^+]^2 + \left( \frac{k_T}{k_E} K_a^3\text{Ct} - \frac{k(^3\text{Taut2})}{k_E} \right) ([\text{H}^+] + K_a^3\text{Ct} \frac{(k(^3\text{Ct}^-) - k(^3\text{Taut2}))}{k_E})} \quad (5)$$

$$\chi_{3\text{Ct}} = \frac{[^3\text{Ct}]}{[^3\text{Ct}] + [^3\text{Ct}^-]} = \frac{[\text{H}^+]}{[\text{H}^+] + K_a^3\text{Ct}} \quad (6)$$

$$\chi_{3\text{Ct}^-} = 1 - \chi_{3\text{Ct}} = \frac{K_a^3\text{Ct}}{[\text{H}^+] + K_a^3\text{Ct}} \quad (7)$$

The amount of  $^3\text{Taut2}$  formed is therefore given by the ratio  $\alpha$ . Such a ratio would be pH-dependent, increasing with  $[\text{H}^+]$  for high pH but reaching unity for low pH. At very low pH, a sequential step is not required since the reaction proceeds directly from  $^3\text{Ct}$  to  $^3\text{Taut2}$ . It is worth taking into account that this scheme ignores  $^3\text{Ct}^{2-}$ , which might be a too strong assumption for higher pH. The formation of such species could also give rise to Taut1 via a protonation reaction. However, no strong evidence for the presence of these compounds is available with the current experimental data.

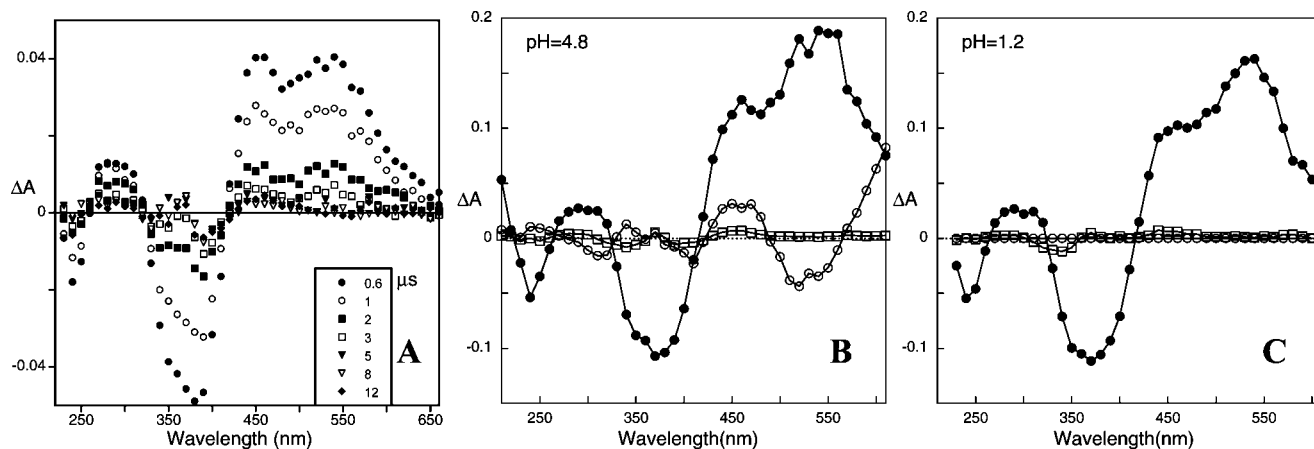
In the case of compound **2**, both absorption and emission are significantly red-shifted in comparison with compound **1**, but in general, the trend is similar; see Supporting Information. The pH-dependent absorption and fluorescence emission spectra can be accounted for by considering two acid–base equilibria with  $\text{p}K_a$ 's of 8.3 and 8.8. As in the previous compound **1**, the contribution of the  $\text{Ct}^-$  form to the emission is smaller than that in the other forms. It is worth noting that in compound **2**, the acidic constants are much closer than those in compound **1**, a behavior explained by the symmetry observed in the former, where the two hydroxyls are identical and more distant from each other.

The transient absorption of compound **2** in Figure 3 is also similar to the one reported for compound **1** in Figure 2, with  $\tau_1 = 1.0 \mu\text{s}$  and  $\tau_2 = 0.37 \mu\text{s}$  at pH = 4.8 and  $\tau_1 = 1.0 \mu\text{s}$  at pH = 1.2. One difference is, however, the lack of significant remaining absorption after the triplet decays (compare Figure 1B with Figure 3A), suggesting that only a small amount of a cis species is formed upon light absorption, rendering the quantum yield of the photochemical reaction very low. This is probably the reason why there is no experimental evidence for the formation of a cis–cis species since this last species would be a consequence of the isomerization of trans–cis, which is lacking. On the other hand, the ratio between the absorption maximum of the triplet divided by the maximum of the bleaching of Ct taken immediately after the flash is 0.6 for compound **1** and 1.6 for compound **2**. In other words, the fraction of triplet formation in compound **2** is much higher, but at the same time, the recovery of Ct is also much higher, and by, consequence the conversion of Ct to Cc is very small. This result is compatible with an isomerization taking place in the singlet excited state; in the case of compound **2**, the triplet is privileged with a consequent loss in isomerization efficiency. The Taut2 formation yield appears to be rather independent of the pH, being the same at pH = 4.8 and 1.2. If the  $\alpha$  parameter is given by eq 5, then such a result means that acidic catalysis for the formation of Taut2 may be dominating.

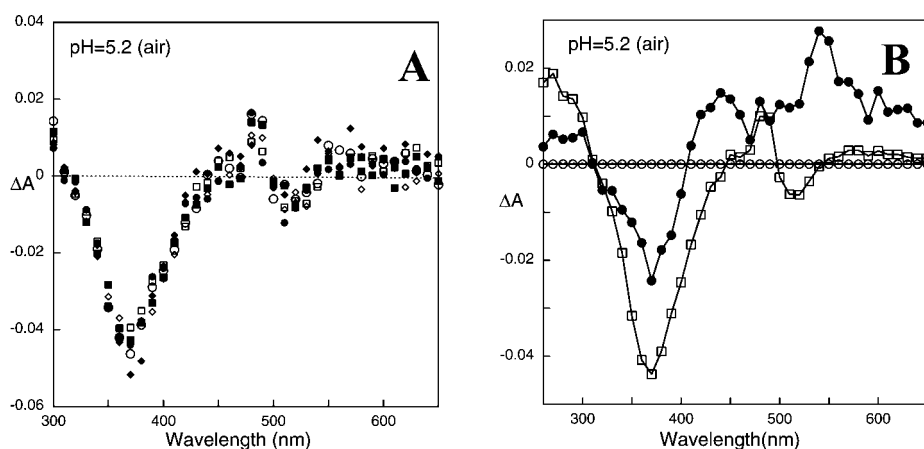
In conclusion, compounds **1** and **2** behave similarly as far as absorption and emission are concerned, but photoinduced formation of Cc is much more efficient in the former.

**7,4'-Dihydroxyflavylium.** 7,4'-Dihydroxyflavylium was studied with great detail in previous work.<sup>1,21,27</sup> Here, we present the transient absorption spectra of the corresponding neutral chalcone, 2,4,4'-trihydroxychalcone, not yet reported at this time scale; Figure 4.

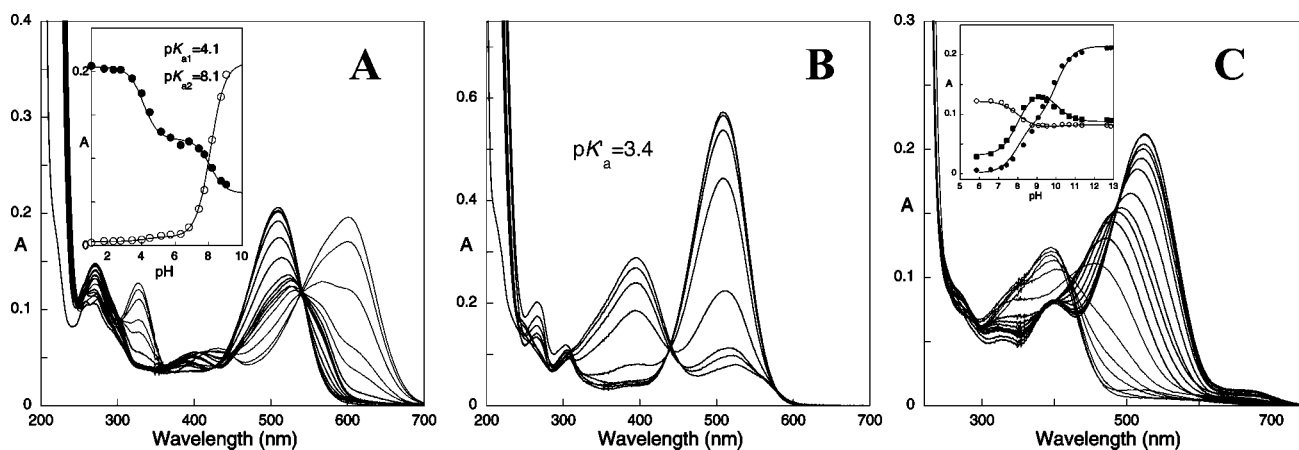




**Figure 3.** Transient absorption of compound **2** in a mixture of water (90%) and ethanol (10%) at pH = 4.8 in an air-equilibrated solution (A). Pre-exponential factors obtained from global analysis of the decays at pH = 4.8 (B) and 1.2 (C) in air-equilibrated solutions ( $\circ$ ,  $a_{1\lambda}$ ;  $\bullet$ ,  $a_{2\lambda}$ ;  $\square$ ,  $a_{3\lambda}$ ).



**Figure 4.** Transient absorption of the chalcone of 7,4'-dihydroxyflavylium at pH = 5.2 in a mixture of water (90%) and ethanol (10%) in an air-equilibrated solution (A). Pre-exponential factors obtained from global analysis of the decays (B) ( $\circ$ ,  $a_{1\lambda}$ ;  $\bullet$ ,  $a_{2\lambda}$ ;  $\square$ ,  $a_{3\lambda}$ ).

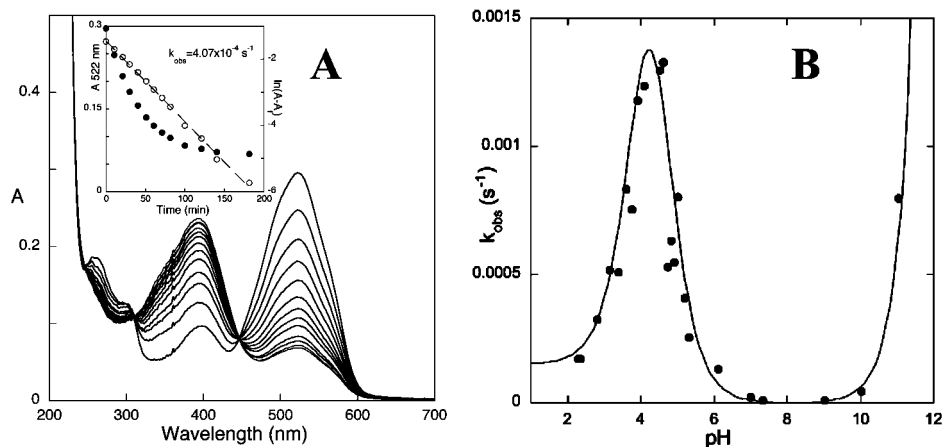


**Figure 5.** UV-vis spectral variations occurring upon a pH jump from a stock solution of DHS  $1.6 \times 10^{-5}$  M at pH = 1.0 to basic pH values; spectra recorded immediately after the pH jump (<1 min after adding base) (A) and upon thermodynamic equilibrium being reached ( $\sim 24$  h) (B). (C) Spectral variations upon pH jumps of a solution at pH = 12 ( $\text{Ct}^{2-}$ ) to less basic pH values, leading to the protonation of the *trans*-chalcones; fittings at ( $\bullet$ ) 525, ( $\circ$ ) 400, and ( $\blacksquare$ ) 445 nm, with  $pK_a$ 's of 8.0 and 10.0.

Differently from compounds **1** and **2**, the data could be fitted by a monoexponential with  $\tau = 0.42 \mu\text{s}$ . It is worth noting that in 7,4'-dihydroxyflavylium, the intensity of the transient absorptions from the triplets is relatively small. Moreover, there is a significant bleaching at around 365 nm after the triplets decay indicating that Ct is efficiently converted into Cc, in accordance with the high quantum yield of isomerization presented by this compound.<sup>27</sup>

**7-Hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium chloride (DHS).** Figure 5 illustrates the UV-vis spectral variations occurring upon pH jumps from a stock solution of DHS at pH = 1.0. The results are similar to those observed for DHF. At acidic pH values, the dominant form is the flavylium cation exhibiting a maximum at 510 nm ( $\epsilon = 32\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ).

When a pH jump from thermal equilibrated solutions of the  $\text{AH}^+$  species is carried out to moderately acidic and basic



**Figure 6.** (A) Spectral and temporal (inset) evolution upon a pH jump from a thermal equilibrated solution of DHS at pH = 1 to 5.2 (B) The  $k_{\text{obs}}$  as a function of pH; fitting was performed using eq 8, and for basic pH values, a linear dependence of  $[\text{OH}^-]$  was obtained; kinetic constants are listed in Table 2.

**TABLE 1: Thermodynamic Constants Obtained in Aqueous Solutions at 298 K for DHF and DHS<sup>a</sup>**

compound	$\text{p}K_{\text{a}}'$	$\text{p}K_{\text{a1}}$	$\text{p}K_{\text{a2}}$	$\text{p}K_{\text{Ct1}}$	$\text{p}K_{\text{Ct2}}$	$K_{\text{h}}K_{\text{t}}K_{\text{i}}$ ( $\text{M}^{-1}$ )
DHS	3.4	4.1	8.1	8.0	10.0	$3.2 \times 10^{-4}$
DHF	3.1	4.0	8.0	8.0	10.4	$6.9 \times 10^{-4}$

<sup>a</sup>  $\text{p}K_{\text{Ct1}}$  and  $\text{p}K_{\text{Ct2}}$  were obtained in 90% water and 10% ethanol. Estimated error 10%.

pH values, the spectra obtained immediately after the pH jump are those of the quinoidal base A or ionized quinoidal base  $\text{A}^-$ , depending on final pH, with absorption maxima occurring, respectively, at 515 and 605 nm and  $\text{p}K_{\text{a}}$ 's of 4.1 and 8.1. Thermal equilibrated solutions present pH-dependent absorption spectra qualitatively similar to those of DHF, Figure 5B. At acidic pH values, the  $\text{AH}^+$  species is the dominant form, and at moderately acidic pH values, a mixture of Ct and A prevails. The observed  $\text{p}K_{\text{a}}'$  is 3.4.

When pH jumps are carried out to the basic medium, formation of ionized *trans*-chalcones occurs, the respective rate depending on pH; see below. These solutions can further be reacidified in order to obtain the  $\text{p}K_{\text{a}}$  of the *trans*-chalcones, Figure 5C. The equilibrium in basic medium is achieved between  $\text{Ct}^{2-}$  and  $\text{Ct}^-$ , but at neutral to moderately acidic medium, Ct (major species) and A (minor species) are present; see Figure 5B. In order to avoid the interference of the species A on the determination of the  $\text{p}K_{\text{a}}$  of the Ct/ $\text{Ct}^-$  equilibrium, the spectra at moderately acidic pH values were obtained immediately after the pH jump from stock solution at pH = 12, Figure 5C.

Information about the kinetic behavior of the system can be obtained through a series of pH jumps from thermal equilibrated solutions at pH = 1 to higher pH values, an example being shown in the inset of Figure 6A for pH = 5.2. The process follows a first-order kinetics and clearly shows the immediate formation of the quinoidal base A that is transformed into Ct. The equilibrium is reached with a remaining percentage of A of ~20 %.

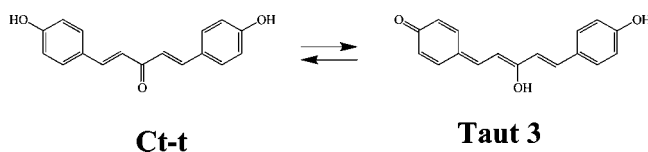
Representation of the rate constants calculated as in Figure 6A at different pH values is shown in Figure 6B, where the fitting was made with eq 8 in the acidic region<sup>28</sup> (constants are defined in Scheme 1) and a direct  $[\text{OH}^-]$  dependence was assumed in the basic region,  $k_{\text{OH}} = 0.6 \text{ s}^{-1}$ . The bell-shaped curve in the acidic region and the exponential increase

**TABLE 2: Kinetic Constants Obtained in Aqueous Solutions at 298 K for DHF and DHS<sup>a</sup>**

compound	$K_{\text{h}}K_{\text{t}}k_{\text{i}}$ ( $\text{M}^{-1} \text{ s}^{-1}$ )	$K_{\text{t}}k_{\text{i}}/k_{-\text{h}}$ ( $\text{s}^{-1}$ )	$k_{-\text{i}}$ ( $\text{s}^{-1}$ )
DHS	$2.9 \times 10^{-7}$	$5.5 \times 10^{-5}$	$1.5 \times 10^{-4}$
DHF	$3.8 \times 10^{-7}$	$2.1 \times 10^{-5}$	$1.8 \times 10^{-4}$

<sup>a</sup> Estimated error 10%.

#### SCHEME 6



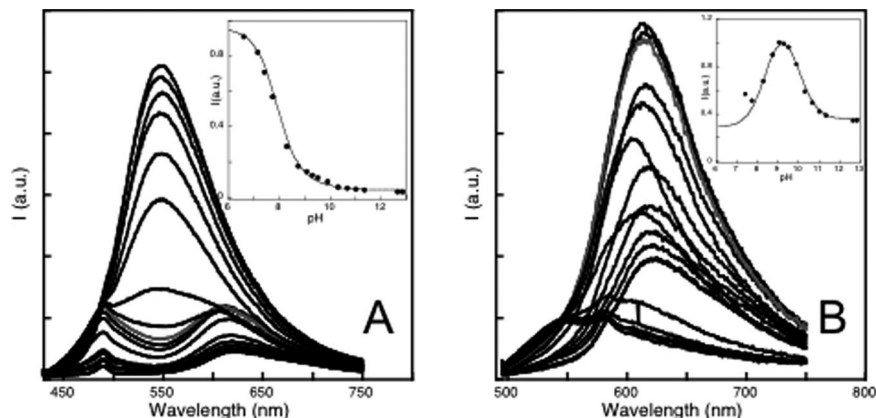
at higher pH values is very similar to the one obtained for the DHF analogue, Tables 1 and Table 2.

$$k_{\text{obs}} = \frac{\frac{[\text{H}^+]}{[\text{H}^+] + K_{\text{a}}} k_{\text{i}} K_{\text{T}} K_{\text{h}} + k_{-\text{i}} [\text{H}^+]}{[\text{H}^+] + \frac{k_{\text{i}} K_{\text{T}}}{k_{-\text{h}}}} \quad (8)$$

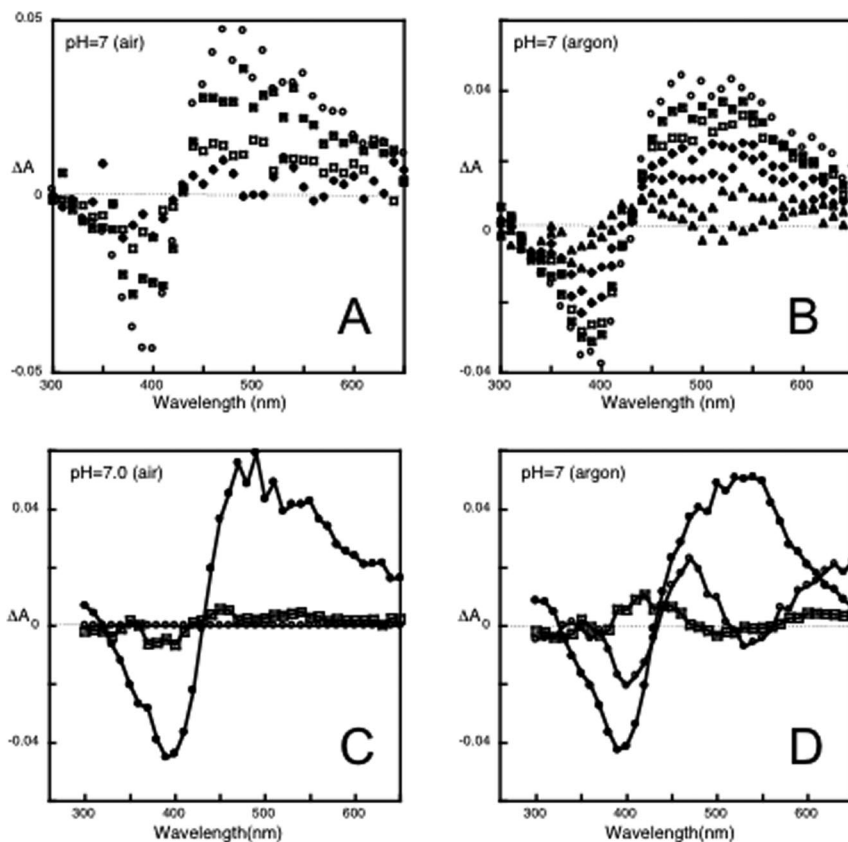
**Fluorescence Emission and Transient Absorptions.** The fluorescence emission spectra of the *trans*-chalcones of DHS follow the same pattern of the parents lacking the hydroxyl in position 2, Figure 7. The titration curves can be fitted by the same set of  $\text{p}K_{\text{a}}$ 's of the absorption, excluding once more the existence of ESPT from the singlet excited state.

Transient absorption spectra are represented in Figure 8 and present the same general trend of the chalcones lacking the 2-hydroxyl substituent, and by consequence, they are assigned to  $^3\text{Ct}^3\text{Ct}^-$  and to the t-t absorption of a tautomer (see Scheme 6).

One important point is the great recovery of the absorption at around 390 nm, as observed for compound 2 but not for compound 1, showing only a small amount of Cc produced upon the flash. The global analysis of the transient absorptions obtained in the absence of oxygen reveals the presence of the two triplets with lifetimes of 3.3 (●) and 0.5  $\mu\text{s}$  (○), while in the presence of oxygen, the data can be fitted with a monoexponential lifetime of 1.0  $\mu\text{s}$ .



**Figure 7.** Fluorescence emission titration of the *trans*-chalcones of DHS in water (90%) and ethanol (10%). (A)  $\lambda_{\text{exc}} = 420$  nm; inset: fitting of the emission at  $\lambda_{\text{em}} = 550$  nm was achieved with  $\text{p}K_a$ 's of 8.0 and 10.0. (B)  $\lambda_{\text{exc}} = 485$  nm; inset: fitting of the emission at  $\lambda_{\text{em}} = 620$  nm was achieved for  $\text{p}K_a$ 's of 8.4 and 10.0.

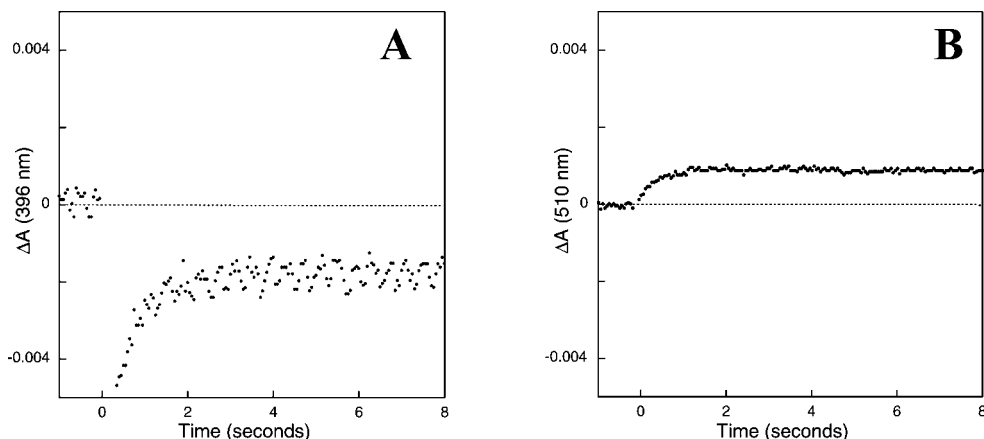


**Figure 8.** Transient absorption spectra of DHS in water (90%) and ethanol (10%) at pH = 7 obtained by nanosecond flash photolysis in air-equilibrated solution (A) and upon bubbling argon for 20 min (B); (C) pre-exponential factors obtained from global analysis of the decays in (A); (D) global analysis of the decays in (B) (○,  $a_{1\lambda}$ ; ●,  $a_{2\lambda}$ ; □,  $a_{3\lambda}$ ).

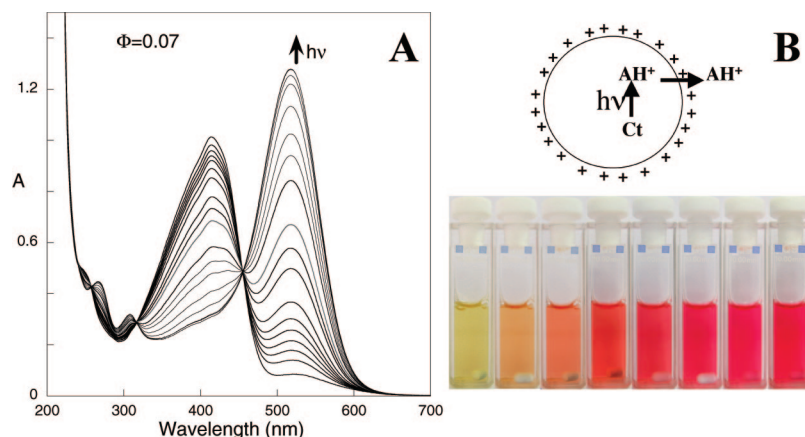
In order to get more insight on the photochemical behavior, flash photolysis experiments on the time scale of seconds were carried out. The results are presented in Figure 9 and confirm the small absorbance variations that take place during the photochemical process. The formation of the *cis*-chalcone from the *trans*-chalcone is much less efficient than that in the case of the DHF analogue, and by consequence, the amplitudes of the signals are very low. However, the trend of the changes is similar. As can be seen in Figure 9, a bleaching of the absorption of the Ct species (396 nm) occurs immediately after the flash, and a partial recovery of Ct occurs according to a monoexponential process with lifetime of  $2.1 \text{ s}^{-1}$  (Figure 9A). When the absorption is followed, at 510 nm (Figure 9B), formation of A/AH<sup>+</sup> is observed with an identical rate constant. This process

is pH-dependent, and at higher pH values, a complete recovery of the Ct species occurs, and no A is formed.

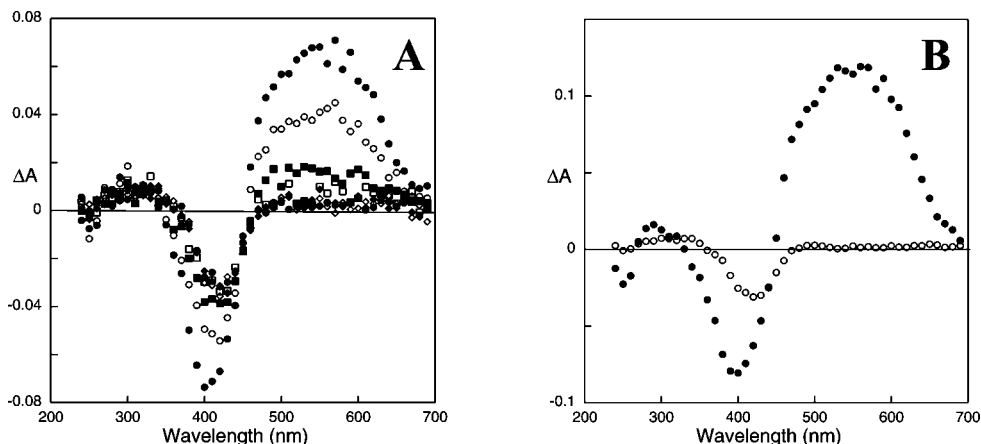
The results of the flash photolysis experiments on the second time scale can be summarized as follows. The first process immediately after the flash (not available on this time scale) is attributed to the formation of Cc at the expenses of Ct. Like in the case of the parent DHF, Cc (and B) is not thermodynamically stable, and the second process with a lifetime of  $2.1 \text{ s}^{-1}$  results from two competitive processes taking place in parallel, one backward corresponding to the recovery of Ct and the other forward leading to the colored species A (or AH<sup>+</sup> depending on pH). A third process (not shown) is due to the recovery of the Ct species from AH<sup>+</sup>/A and occurs like the kinetics obtained from the pH jump experiments reported in Figure 6B.



**Figure 9.** Transient absorption of DHS equilibrated solution at pH = 4.9 followed at 396 (A) and 510 nm (B). The fitting was achieved with  $\tau = 2.1 \text{ s}^{-1}$ .



**Figure 10.** (A) Spectral changes occurring upon irradiation of DHS ( $4.95 \times 10^{-5} \text{ M}$ ) in the presence of CTAB micelles (0.2 M) at pH = 1.44 for the following irradiation times: 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 5, 7, 9, 11, 15, 20, 30, and 40 min ( $I_0 = 2.8 \times 10^{-7} \text{ Einstein min}^{-1}$  at  $\lambda_{\text{irr}} = 436 \text{ nm}$ ). (B) Color of the solutions at 0, 1, 3, 7, 11, 20, 30 and 40 min.



**Figure 11.** (A) Transient absorption spectra obtained by nanosecond flash photolysis in 0.2 M CTAB at pH 1.44. (B) Pre-exponential factors obtained from global analysis of the decays;  $\tau = 0.9 \mu\text{s}$  (●,  $a_{2\lambda}$ ; ○,  $a_{3\lambda}$ ).

**Photochemistry.** One important difference between DHS and the DHF analogue is its much less efficient photochemistry in water. This behavior was already explained on the basis of the transient absorptions experiments shown above.

The lack of efficient photochemistry in water can be overcome by the introduction of CTAB micelles, Figure 10. Similarly to the behavior of the flavylum analogues, the Ct species is stabilized in the presence of CTAB micelles, and by consequence, it is possible to have a solution of Ct at pH = 1.4 without  $\text{AH}^+$ .<sup>28,29</sup> Irradiation of DHS in the presence of CTAB

micelles ([CTAB] = 0.2 M) gives rise to the formation of an intense red color, as shown in Figure 10. The process occurs with a quantum yield of  $\Phi = 0.07$  at  $\lambda_{\text{irr}} = 436 \text{ nm}$ , and the system reverts back to the initial state with a rate constant of  $7.9 \times 10^{-4} \text{ s}^{-1}$  at pH = 1.44 and 295 K.

Transient absorption spectra on the time scale of seconds of DHS in the presence of CTAB micelles was performed, and the results present the same pattern as that in water, but the intensity of the signals is higher; see Supporting Information. More information was obtained by the transient absorption on



the time scale of microseconds. It is clear that the triplet state followed at 470 nm decays while the Ct is recovered at 396 nm with a lifetime  $\sim 1 \mu\text{s}$ , Figure 11. However, no complete recovery of Ct was observed, and after the triplet decay, the net result is the formation of Cc at the expense of Ct, in agreement with the observation of photochromism in the presence of CTAB micelles. One possible reason for the lack of significant photochemistry in water compared with CTAB micelles could be the deactivation by internal conversion of the singlet state due to the formation of hydrogen bonding in water. In CTAB, the extent of the hydrogen bonding is reduced, and not only can more isomerization (from the singlet) take place but also more formation of the triplet state occurs.<sup>30</sup>

In addition, and according to the results reported for other 2-phenyl-1-benzopyryliums,<sup>28,29</sup> it is expected that once  $\text{AH}^+$  is formed, it is rapidly ejected to the bulk solution, favoring the forward reaction in competition with the back reaction on the time scale of seconds; see Figure 9 for comparison.

## Conclusions

New photochromic systems base on 2-styryl-1-benzopyrylium derivatives can be obtained in the presence of CTAB micelles. These systems have the advantage of exhibiting deeper hues when compared with 2-phenyl-1-benzopyrylium analogous. Through this work, evidence for a singlet state isomerization process was given by studying chalcones lacking a hydroxyl group in position 2 in water/ethanol mixed solvent, where no trans-cis isomerization is found in the triplet state due to a tautomerization reaction. Despite the poor photochemistry in water, beautiful photochromic systems based on styryl derivatives were obtained in the presence of CTAB micelles. By analogy with 2-phenyl-1-benzopyrylium, it is expected that other micelles or gels would be also good matrices to achieve photochromic systems involving 2-styryl-1-benzopyrylium derivatives.

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**Supporting Information Available:** Additional experimental results and derivation of eqs 2–7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Pina, F.; Maestri, M.; Balzani, V. *Handbook of Photochemistry and Photobiology, Vol. 3: Supramolecular Photochemistry*; Nalwa, H. S., Ed.; American Scientific Publishers: Valencia, CA, 2003, pp 411–450.
- (2) Roque, A.; Lodeiro, C.; Pina, F.; Maestri, M.; Dumas, S.; Passaniti, P.; Balzani, V. *J. Am. Chem. Soc.* **2003**, *125*, 987–994.
- (3) Matsushima, R.; Fujimoto, S.; Tokumura, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 827–832.
- (4) Giestas, L.; Folgosa, F.; Lima, J. C.; Parola, A. J.; Pina, F. *Eur. J. Org. Chem.* **2005**, *418*, 7–4200.
- (5) Roque, A.; Lima, J. C.; Parola, A. J.; Pina, F. *Photochem. Photobiol. Sci.* **2007**, *6*, 381–385.
- (6) (a) Brouillard, R. In *The Flavonoids, Advances in Research*; Harborne, J. B., Ed.; Chapman and Hall: London, 1988; pp 525–538. (b) Brouillard, R. In *Anthocyanins as Food Colors*; Markakis, P., Ed.; Academic Press: New York, 1982; Chapter 1, pp 1–40.
- (7) (a) Brouillard, R.; Dubois, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 1359–1364. (b) Brouillard, R.; Delaporte, J. *J. Am. Chem. Soc.* **1997**, *99*, 8461–8468.
- (8) (a) McClelland, R. A.; Gedge, S. *J. Am. Chem. Soc.* **1980**, *102*, 5838–5848. (b) McClelland, R. A.; McGall, G. H. *J. Org. Chem.* **1982**, *47*, 3730–3736.
- (9) Pina, F.; Maestri, M.; Balzani, V. *Chem. Commun.* **1999**, 107–114.
- (10) (a) Willstätter, R.; Everest, A. E. *Justus Liebigs Ann. Chem.* **1913**, *401*, 189–232. (b) Kong, J.-M.; Chia, L.-S.; Goh, N.-K.; Chia, T.-F.; Brouillard, R. *Phytochemistry* **2003**, *64*, 923–933.
- (11) (a) Chapman, E.; Perkin, A. G.; Robinson, R. *J. Chem. Soc.* **1927**, 3015–3041. (b) Pratt, D.; Robinson, R.; Robertson, A. *J. Chem. Soc.* **1927**, 1975–1983. (c) Melo, M. J.; Sousa, M.; Parola, A. J.; Melo, J. S.; Catarino, F.; Marçalo, J.; Pina, F. *Chem.—Eur. J.* **2007**, *13*, 1417–1422.
- (12) (a) Pina, F. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2109–2116. (b) Maestri, M.; Pina, F.; Balzani, V. In *Molecular Switches*; Feringa, L. B., Eds.; Wiley-VCH: Weinheim, Germany, 2001, pp 309–334. (c) Pina, F.; Melo, M. J.; Parola, A. J.; Maestri, M.; Balzani, V. *Chem.—Eur. J.* **1998**, *4*, 2001–2007. (d) Pina, F.; Lima, J. C.; Parola, A. J.; Afonso, C. A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1525–1527. (e) Pina, F.; Lima, J. C.; Parola, A. J.; Afonso, C. A. M. *Angew. Chem., Int. Ed.* **2004**, *116*, 1551–1553.
- (13) Buck, J. S.; Heilbron, I. H. *J. Chem. Soc.* **1922**, 1198–1212.
- (14) Jurd, L. *Food Technol.* **1964**, 157–159.
- (15) Jurd, L. *U.S. Patent* 3 301 683, 1967.
- (16) Sweeney, J. G.; Iacobucci, G. A. *J. Agric. Food Chem.* **1983**, *31*, 531–533.
- (17) Amic, D.; Trinajstić, N.; Davidović-Amic, D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1933–1938.
- (18) Buck, J. S.; Heilbron, I. M. *J. Chem. Soc. Trans.* **1922**, *121*, 1095–1101.
- (19) Gomes, R.; Diniz, A. M.; Jesus, A.; Parola, A. J.; Pina, F. *Dyes Pigm.* **2009**, *81*, 69–79.
- (20) Küster, F. W.; Thiel, A. *Tabelle per le Analisi Chimiche e Chimico-Fisiche* 12th ed.; Hoepli: Milano, 1982, pp 157–160. This universal buffer is prepared in the following way: 2.3 cm<sup>3</sup> of 85% (w/w) phosphoric acid, 7.00 g of monohydrated citric acid, and 3.54 g of boric acid are dissolved in water; 343 mL of 1 M NaOH is then added, and the solution is diluted to 1 dm<sup>3</sup> with water.
- (21) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.
- (22) Maestri, M.; Ballardini, R.; Pina, F.; Melo, M. J. *J. Chem. Educ.* **1997**, *74*, 1314–1316.
- (23) (a) Weller, A. H. *Z. Elektrochem.* **1952**, *56*, 662–668. (b) Weller, A. H. *Prog. React. Kinet.* **1961**, *1*, 187–214. (c) Beens, H.; Grellmann, K. H.; Gurr, M.; Weller, A. H. *Discuss. Faraday Soc.* **1965**, *93*, 183–193.
- (24) Norikane, Y.; Itoh, H.; Arai, T. *J. Phys. Chem A* **2002**, *106*, 2766–2776.
- (25) Conrad, P. G.; Givens, R. S.; Hellrung, B.; Rajesh, C. S.; Ramseier, M.; Wirz, J. *J. Am. Chem. Soc.* **2000**, *122*, 9346–9347.
- (26) Zuo, P.; Ma, C.; Kwok, W. M.; Chan, W. S.; Phillips, D. L. *J. Org. Chem.* **2005**, *70*, 8661–8675.
- (27) Figueiredo, P.; Lima, J. C.; Santos, H.; Wigand, M. C.; Brouillard, R.; Maçanita, A. L.; Pina, F. *J. Am. Chem. Soc.* **1994**, *116*, 1249–1254.
- (28) Gomes, R.; Parola, A. J.; Laia, C. A. T.; Pina, F. *Photochem. Photobiol. Sci.* **2007**, *6*, 1003–1009.
- (29) Gomes, R.; Parola, A. J.; Laia, C. A. T.; Pina, F. *J. Phys. Chem. B* **2007**, *111*, 12059–12065.
- (30) Doroshenko, A. O.; Pirvarenko, V. G. *J. Photochem. Photobiol. A* **2003**, *156*, 55–64.

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