Photo- and pH-Induced Transformations of Flavylium Cation: "Write–Lock–Read–Unlock-Erase" Cycles

Fernando Pina,*[a] Maria João Melo,[a] Mauro Maestri,*[b] Paolo Passaniti,[b]
Nadia Camaioni,[c] and Vincenzo Balzani[b]

Dedicated to Professor Fritz Vögtle on the occasion of his 60th birthday

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The structural transformations of flavylium ion in aqueous solutions caused by pH jumps and photoexcitation have been investigated. At pH < 1, the stable form is the colored cationic species ($\mathbf{A}H^+$). By increasing pH, the concentration of $\mathbf{A}H^+$ decreases and, at pH = 5, this form is no longer present. The species obtained immediately after a pH jump undergo transformation processes with pH-dependent rate constants. At pH = 5.2 and 20 °C, the final product is the uncolored *trans*-chalcone ($\mathbf{C}_t$). This form can be transformed by light excitation into the *cis*-chalcone ($\mathbf{C}_c$) isomer, which is in equilibrium with the hemiacetal form ($\mathbf{B}_2$). This mixture is relatively inert due to the existence of a kinetic barrier that slows down the back thermal isomerization of $\mathbf{C}_c$ to the stable $\mathbf{C}_t$ form. Such a back reaction to $\mathbf{C}_t$ can be totally prevented if the irradiated solution is submitted to a pH jump to pH = 1, which transforms the photoproducts into the stable $\mathbf{A}H^+$ species. In basic solution, two more species were detected, namely the anionic forms $\mathbf{C}_c^-$ and $\mathbf{C}_t^-$ of the *cis* and *trans* chalcone. $\mathbf{C}_t^-$ is a stable, not photosensitive and luminescent species, whereas $\mathbf{C}_c^-$ is not stable, being converted into $\mathbf{C}_t^-$ in the dark. The photochemical and pH-induced transformations of the flavylium cation in the pH range 0–11 can be taken as a basis to design *write–lock–read–unlock–erase* cycles for an optical molecular-level memory with multiple readout capacity.

Introduction

Anthocyanins are the largest water-soluble group of natural molecules responsible for the brilliant colours found in plants, flowers, and fruits.[1−3] Anthocyanins are attractive and highly desirable as food colourants (jams, wines, etc.),[1] and their farmaceutical properties are also beginning to be exploited (e.g., for the treatment of cardiovascular diseases).[4]

Synthetic flavylium salts, exhibiting a basic chemical structure identical to anthocyanins, are excellent model compounds for the study of the chemical behaviour of natural anthocyanins and promising candidates for the use in food-coloring industry.[2] Interesting is also the recent discovery[7−10] that flavylium ions represent examples of multistate/multifunctional compounds potentially useful for the design of molecular-level system for information processing.[11−13]

Systematic investigations[5][6] have shown that in acidic and neutral aqueous solution flavylium ions can undergo complex structural transformations as represented in Scheme 1. Such transformations, which are accompanied by changes in the absorption and emission spectra, can be induced by pH changes and/or by light excitation and can be studied by using pH jump and continuous irradiation as well as flash photolysis techniques.[14−16] Of particular interest is the reversible photoinduced isomerization of the thermally stable (in a certain pH range) *trans*-chalcone form which, in the case of the 4′-methoxyflavylium ion, is the starting point of a *write−lock−read−unlock−erase* photochromic cycle for information processing at the molecular level.[7] More recently we have shown that, in the case of 4′-hydroxyflavylium ion, the light- and pH-induced transformations can also be taken as a basis for simple logic operations and create a remarkably intricate network of chemical processes.[8]

Previous studies[7−10] have clearly shown that substituents in the 4′- or 7-positions have a strong influence in determining the thermal and photochemical reactivity of the different forms originating from synthetic flavylium ions. In order to extend the knowledge of the reversible transformation processes that take place in this family of compounds, we have performed an investigation on the behaviour of the unsubstituted flavylium cation. The thermal reactions of this compound in acidic and neutral solutions had already been investigated by McClelland and Gedge.[5] By using the pH-jump technique, these authors were able to obtain the values of the kinetic and thermodynamic constants connecting the various forms which are involved in the ob-

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[a] Departamento de Química,
Centro de Química Fina e Biotecnologia,
Universidade Nova de Lisboa,
P-2825 Monte de Caparica, Portugal
E-mail: fjp@dq.fct.unl.pt
[b] Dipartimento di Chimica "G. Ciamician",
Università di Bologna
Via Selmi 2, I-40126 Bologna, Italy
E-mail: mmaestri@ciam.unibo.it
[c] Istituto FRAE-CNR, via Gobetti 101, I-40129 Bologna, Italy
E-mail: camaioni@bofra3.frae.bo.cnr.it

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served transformations. In this work, we have (i) reexamined the thermal reactions of the unsubstituted flavylium cation in acidic and neutral solution, (ii) extended the study to basic solutions, and (iii) investigated the effect of continuous and pulsed photoexcitation. The results have then been elaborated on the basis of a previously reported kinetic method[14,15a] to obtain all the kinetic and thermodynamic parameters that control the complex network of observed reactions.

Results and Discussion

Equilibria in the Dark

It is well-known that in aqueous solution synthetic flavylium ions can undergo structural transformations involving several forms connected by equlibria that can be displaced by pH changes and light excitation.[1−10] As we will see below, in the case of the unsubstituted flavylium ion as many as seven species can be involved (Scheme 1). McClelland and Gedge[5] investigated the thermal reactions of the flavylium cation in acidic and neutral aqueous solutions and identified the five species connected by the following equilibria:

$$\mathbf{AH^+} \underset{}{\overset{K_h^4}{\rightleftharpoons}} \mathbf{B_4} + \mathrm{H^+} \tag{1}$$

$$\mathbf{AH^+} \overset{K_h}{\rightleftharpoons} \mathbf{B_2} + \mathrm{H^+} \tag{2}$$

$$\mathbf{B_2} \overset{K_t}{\rightleftharpoons} \mathbf{C_c} \tag{3}$$

$$\mathbf{C_c} \overset{K_i}{\rightleftharpoons} \mathbf{C_t} \tag{4}$$

Such species are the flavylium cation $\mathbf{AH^+}$, two hemiacetal forms $\mathbf{B_2}$ and $\mathbf{B_4}$ obtained by hydration of the flavylium cation in the 2 or 4 position, respectively, the *cis*-chalcone species $\mathbf{C_c}$ formed from hemiacetal $\mathbf{B_2}$ through a tautomeric process, and the *trans*-chalcone form $\mathbf{C_t}$ resulting from the isomerization of *cis*-chalcone. McClelland's results indicate that the $\mathbf{B_4}$ species is always a small fraction (ca 1%) of $\mathbf{B_2}$, so that $\mathbf{B_4}$ will be neglected in the following discussion.

As shown previously[14,15a] the molar fraction of the acidic form $\mathrm{AH^+}$ can be obtained from Equation (5):

$$\frac{[AH^+]}{C_o} = \alpha = \frac{[H^+]}{[H^+] + K'_a} \tag{5}$$

where C_o is the total concentration and K'_a is given by Equation (6):

$$K'a = K_h + K_hK_t + K_hK_tK_i \tag{6}$$

Equation (5) accounts for the complex equilibria described by Equations 2 to 4 in terms of a single acid−base equilibrium [Equation (7)] between the acidic species $\mathrm{AH^+}$ and a conjugated base **CB** having a concentration equal to the sum of the concentrations of $\mathbf{B_2}$, $\mathbf{C_c}$, and $\mathbf{C_t}$ and molar fraction given by Equation (8):[15a]

$$\mathrm{AH^+} \overset{K'_a}{\rightleftharpoons} \mathbf{CB} + \mathrm{H^+} \tag{7}$$

$$\frac{[CB]}{C_o} = \frac{[B_2] + [C_c] + [C_t]}{C_o} = \beta = \frac{K'_a}{[H^+] + K'_a} = 1 - \alpha \tag{8}$$

The individual expressions of the molar fractions of each component of **CB** can be easily calculated as shown in ref.[15a] If the pH is sufficiently high to consider all the compounds in the form of **CB** ($\beta = 1$), the relationships shown in Equation (9) apply:

$$\frac{[B_2]}{C_o} = \frac{K_h}{K'_a}; \quad \frac{[C_c]}{C_o} = \frac{K_hK_t}{K'_a}; \quad \frac{[C_t]}{C_o} = \frac{K_hK_tK_i}{K'_a} \tag{9}$$

Equations (1) to (7) concern the thermodynamic equilibrium. For several flavylium compounds the rates of the thermal *cis-trans* isomerization reactions [Equation (4)] are much slower than the rates of the reactions involved in the other equilibria. In such a case, a pseudo-equilibrium can be attained and Equations (10) to (13) can be used to evaluate the pseudoequilibrium constant, indicated by $K^\wedge_a$, and the molar fractions:

$$\frac{[AH^+]}{C_o} = \alpha = \frac{[H^+]}{[H^+] + K^\wedge_a} \tag{10}$$

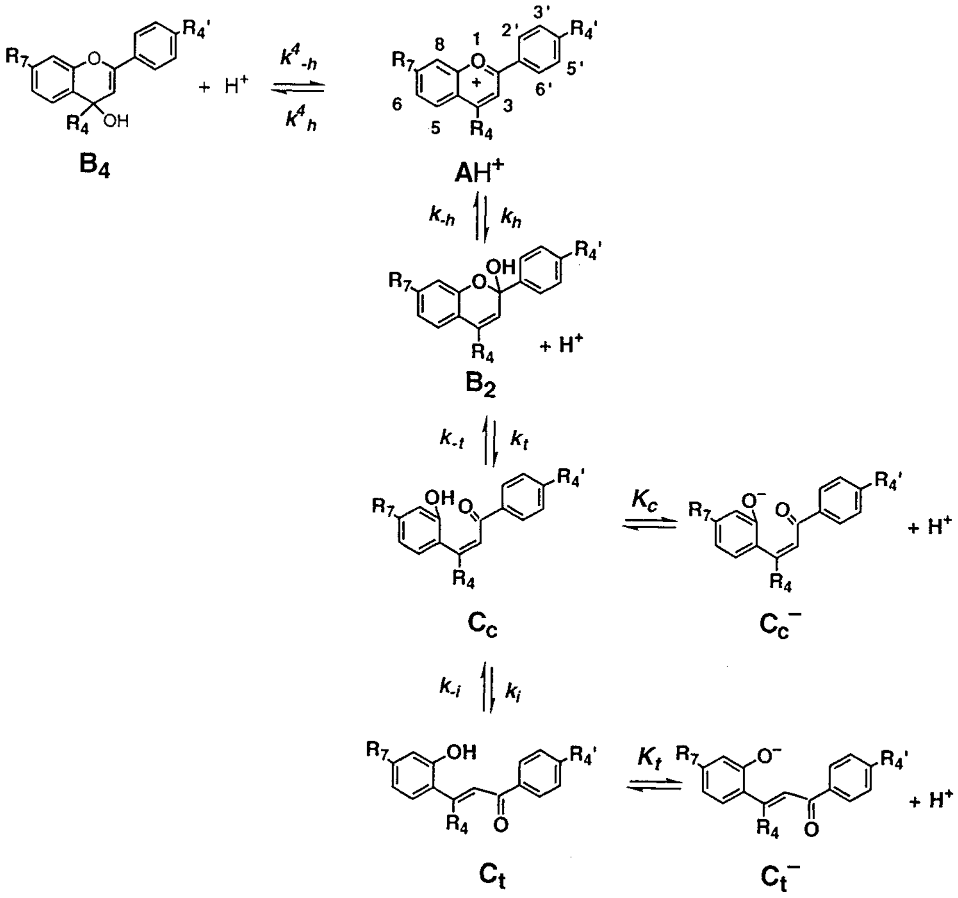
$$K^\wedge a = K_h + K_hK_t \tag{11}$$

$$\frac{[CB]}{C_o} = \frac{[B_2] + [C_c]}{C_o} = \beta = \frac{K^\wedge_a}{[H^+] + K^\wedge_a} = 1 - \alpha \tag{12}$$

$$\frac{[B_2]}{C_o} = \frac{K_h}{K^\wedge_a}; \quad \frac{[C_c]}{C_o} = \frac{K_hK_t}{K^\wedge_a} \tag{13}$$

We have reexamined the thermal behaviour of the unsubstituted flavylium cation extending our study to basic solutions and we have found spectral evidence for the existence of two more species, namely the anionic forms $\mathbf{C_c}^-$ and $\mathbf{C_t}^-$ of the *cis* and *trans* chalcone.

Acid Solutions: In strongly acid solution (e.g., pH = 0), the flavylium cation $\mathrm{AH^+}$ is the thermodynamically stable form of the system. Its absorption spectrum (Figure 1**a**, spectrum I) shows an intense band with $\lambda_{\max} = 394$ nm ($\varepsilon = 34000\ \mathrm{M^{-1}\ cm^{-1}}$). On increasing the pH of the solution by a pH jump to pH = 5.2, the band at 394 nm disappears within the mixing time and the spectrum II of Figure 1**a** is obtained. In agreement with McClelland and Gedge,[5] we associate this spectral changes with the transformation of $\mathrm{AH^+}$ into $\mathbf{C_c}$ and $\mathbf{B_2}$ (Scheme 1). Figure 2 shows the spectral variations obtained after 5 minutes upon a series of pH jumps from 1.0 to different final pH values. These spectra are due to the presence of the three species $\mathrm{AH^+}$, $\mathbf{B_2}$, and $\mathbf{C_c}$, whose relative amounts depend on the final pH of the solution. The inset of Figure 2 shows the molar frac-



Scheme 1. Structural transformations taking place in flavylium compounds. The compound investigated in this paper is the unsubstituted member of the family ($R_7 = R_4 = R_{4'} = H$)

tion of AH^+ as a function of the final pH, calculated from the absorbance changes at 394 nm. A best fitting procedure on this plot gives a pK_a value of 3.0 for the dissociation equilibrium of AH^+ to give the B_2 and C_c species. On a much longer time scale (half life 16 hours), a stable product is formed the spectrum of which (curve III in Figure 1a) shows absorption maxima at 302 and 354 nm. This second, slower equilibration process is assigned to the conversion of AH^+ into the thermodynamically stable product C_t through the C_c/B_2 mixture (Scheme 1). Figure 3 reports the spectral variations observed as function of time upon a pH jump to pH = 2.6 and shows that the observed conversion follows first order kinetics. A similar behaviour is observed at any other pH value in the acid region. The values of the rate constants are 4.2×10^{-6} s^{-1} at pH = 2.6, 9.8×10^{-6} s^{-1} at pH = 3.7, and 1.5×10^{-5} s^{-1} at pH = 5.0, showing that the rate of formation of C_t is pH dependent. The molar fraction of C_t present at the final equilibrium at the various pH values and Equation (8) allow us to calculate the equilibrium constant between AH^+ and C_t (pK'_a = 1.64). The reaction leading to C_t is also temperature dependent and exhibits an activation energy of 89 kJmol^{-1} at pH = 5.2.

Using the kinetic treatment illustrated above, the data obtained by McClelland and Gedge,[5] and the results of our investigation we have obtained the plots of Figure 4 which shows the molar fraction distributions of the various species present at 20°C in aqueous solution in the pH range 0−7. The thermodynamically stable species are AH^+ at pH < 1 and C_t at pH > 3, while B_2 and C_c are present as transi-

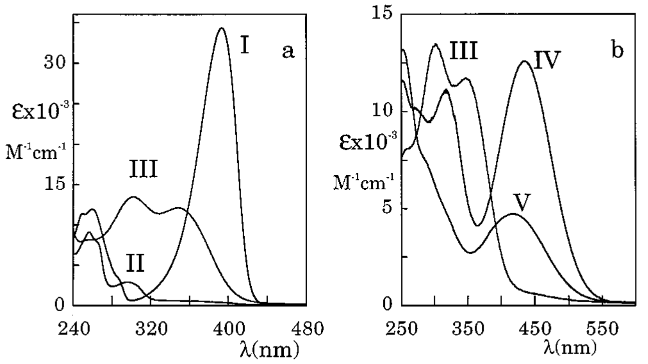


Figure 1. Absorption spectra of the flavylium ion under different experimental conditions. (a) Acidic or neutral solutions: I, pH = 0, where only the thermodynamically stable species AH^+ is present; II, pseudoequilibrium after a pH jump to pH = 5.2, where the C_c and B_2 species are present; III, spectrum of the thermodynamically stable product C_t formed upon equilibration after a pH jump to pH = 5.2. (b) basic solutions: III, see above; IV, spectrum obtained after a pH jump from 5.2 to 11.0, assigned to the form C_t^-; V, spectrum obtained immediately after a pH jump from 1.0 to 11.0, assigned to the form C_c^-.

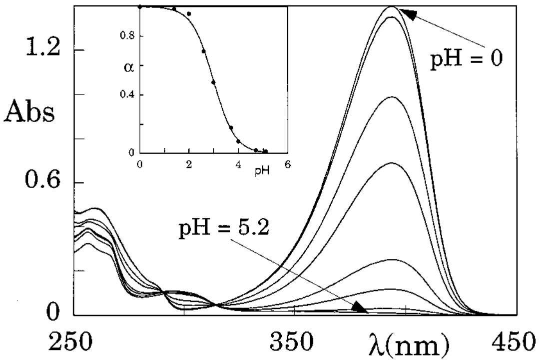


Figure 2. Absorption spectra of aqueous solutions of the flavylium cation (3.9×10^{-5} M) as a function of pH, few minutes after the pH jumps. The inset shows the molar fraction of **AH**$^+$ as a function of the final pH, calculated from the absorbance changes at 394 nm

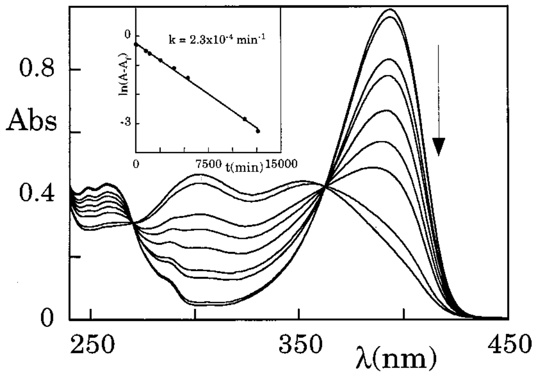


Figure 3. Spectral variations observed in the dark for an aqueous solution of the flavylium cation (2.5×10^{-5} M) upon a pH jump from pH = 1.0 to pH = 2.6 as a function of time. The inset shows that the change in absorbance at 394 nm, i.e. the conversion of the **AH**$^+$, **C**$_c$, and **B**$_2$ mixture to **C**$_t$, follows a first order kinetics.

ent species between pH 2 and 7. The behaviour of the system in the pH range 0–7 can be clearly understood on the basis of the energy-level diagram shown in Figure 5.

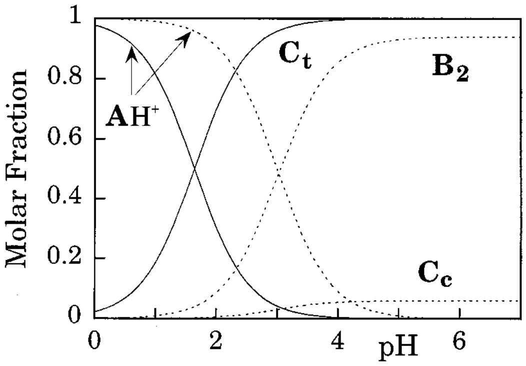


Figure 4. Molar fraction distributions of the species involved in the transformation of the flavylium cation in acidic or neutral region. Solid lines refer to the species involved in the thermodynamic equilibrium. Dashed lines refer to the pseudoequilibrium obtained by pH jump from strongly acidic conditions to higher pH values or by exciting **C**$_t$ by flash light.

Basic Solutions: As reported above, at pH = 5.2 the thermodynamically stable species is the **C**$_t$ form the spectrum of which is again reported in Figure 1**b**, curve III. A pH jump from pH = 5.2 to pH = 11.0 of a solution of **C**$_t$ causes dramatic spectral variations ending with the spectrum IV of Figure 1**b**. We associate these spectral changes with the deprotonation of **C**$_t$ to give **C**$_t^-$ (Scheme 1). Figure 6 shows the spectral variations obtained upon a series of pH jumps from 5.2. to different final pH values. The inset of Figure 6 shows the molar fraction of **C**$_t$ as a function of pH. A best fitting procedure on this plot gives a pK_a of 8.5 for the deprotonation equilibrium of **C**$_t$.

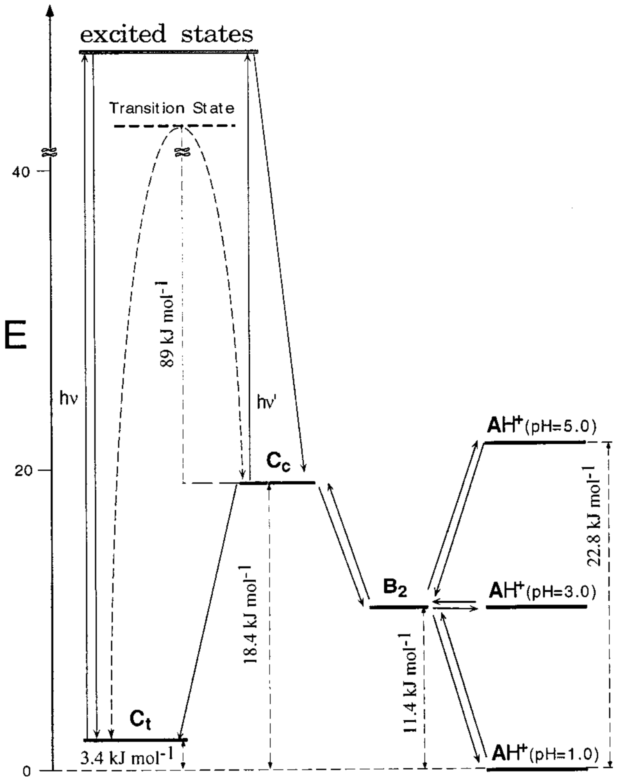


Figure 5. Energy-level diagram for the species involved in the transformation of the flavylium cation in acidic solutions

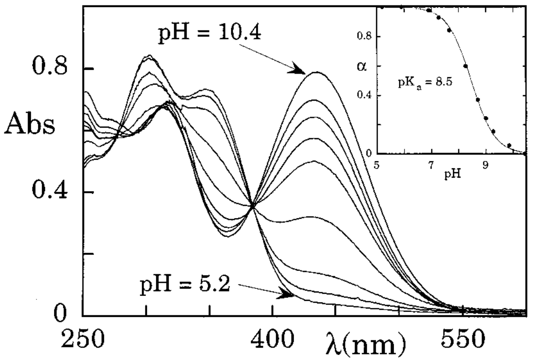


Figure 6. Absorption spectra of dark equilibrated aqueous solutions of **C**$_t$ (6.0×10^{-5} M) as a function of pH. The inset shows the molar fraction of the **C**$_t$ species as a function of pH, calculated from the absorbance changes at 432 nm, and the equilibrium constant for the deprotonation of **C**$_t$

A jump from pH = 1.0 to pH = 11.0 of a solution of **AH**$^+$ causes spectral changes during the mixing time yielding the spectrum V of Figure 1**b**. Subsequently, in the minutes time domain, the system undergoes the spectral varations reported in Figure 7. The final spectrum is identical to the spectrum of $\mathbf{C_t}^-$ obtained by a pH jump to 11.0 of a $\mathbf{C_t}$ solution. A possible explanation for this behaviour is the following: the pH jump to 11.0 causes a fast transformation of $\mathbf{AH}^+$ to $\mathbf{C_c}^-$, that subsequently undergoes a slower conversion process to $\mathbf{C_t}^-$. A similar behaviour was previously observed for the 4′-hydroxyflavylium ion in basic solution. Attempts were made to measure the pK_a for the dissociation equilibrium of $\mathbf{C_c}$ to give $\mathbf{C_c}^-$, but no clear result was obtained, probably because of the concomitant occurrence of the processes indicated in equations 14−16 that prevents a clear assignment of the spectral variations. However, an approximate value for such an equilibrium constant was estimated to be about 8.

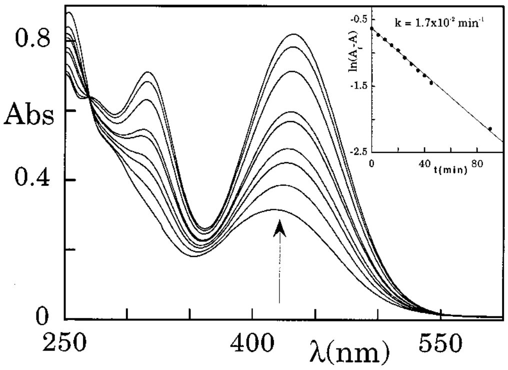


Figure 7. Spectral variations observed after a pH jump from 1.0 to 11.0 for an aqueous solution of the flavylium cation (6.0×10^{-5} M) as a function of time. The inset shows that the change in absorbance at 440 nm follows a first order kinetics

$$\mathbf{C_c} \xrightleftharpoons{Ka} \mathbf{C_c}^- \quad (14)$$

$$\mathbf{C_c} \xrightleftharpoons{K_i} \mathbf{C_t} \quad (15)$$

$$\mathbf{C_c}^- \xrightleftharpoons{K_i} \mathbf{C_t}^- \quad (16)$$

Photochemical Experiments

No spectral variation was observed upon 1 hour irradiation of solutions of flavylium ion at pH = 1.0, showing that $\mathbf{AH}^+$ is photochemically stable. The same result was obtained in the case of $\mathbf{C_t}^-$, whereas $\mathbf{C_t}$ and $\mathbf{C_c}$ were found to undergo a reversible photoisomerization reaction.

Continuous Irradiation: Continuous irradiation of $\mathbf{C_t}$ with 313 or 365 nm light causes spectral variations at all the pH values in the range 1−7. Figure 8 shows the absorbance changes observed at pH 2.0 and 5.2 under irradiation with 313 nm light. Such spectral changes are the reverse of those observed in the thermal reactions which follow the pH jumps of $\mathbf{AH}^+$ solutions from pH = 1 to the same pH of the irradiated solution (see, e.g., Figure 3).

As shown by the flash photolysis experiments described below, the primary product of the photochemical reaction of $\mathbf{C_t}$ is $\mathbf{C_c}$ (Scheme 1), which then undergoes the previously discussed thermal reactions leading in the second time scale to its pseudo equilibration with $\mathbf{B_2}$ and $\mathbf{AH}^+$. The relative concentrations of the photoproducts $\mathbf{C_c}$, $\mathbf{B_2}$, and $\mathbf{AH}^+$ are controlled by the pH of the solution (Figure 4, dashed lines). At pH < 1, the only photoproduct is $\mathbf{AH}^+$. At pH > 5 no $\mathbf{AH}^+$, is present in the mixture. Moreover, inspection of Figure 8**b** shows that at pH = 5.2 the systems reaches a photostationary state whose spectrum is different from that expected for the mixture $\mathbf{C_c}/\mathbf{B_2}$ at this pH (Figure 2). These results are consistent with an uncomplete photoconversion of $\mathbf{C_t}$, caused by the concomitant $\mathbf{C_c} \rightarrow \mathbf{C_t}$ back photoisomerization (see below) that takes place as the $\mathbf{C_c}$ concentration increases. The quantum yield of the $\mathbf{C_t} \rightarrow \mathbf{C_c}$ photoisomerization, measured after 1 minute of irradiation, is 0.05 at both pH 2.0 and 5.2.

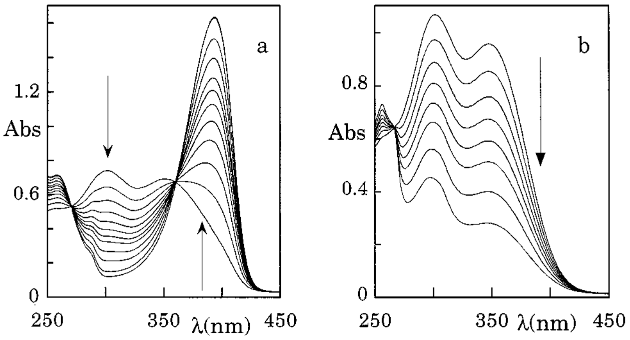


Figure 8. Spectral variations observed upon continuous irradiation (313 nm) of dark equilibrated aqueous solutions of $\mathbf{C_t}$ as a function of time (initial time increments = 30 s). (a) pH = 2.0, concentration 4.7×10^{-5} M; (b) pH = 5.2, concentration 8.0×10^{-5} M

As we have seen above, a pH jump from 1.0 to 5.2 on $\mathbf{AH}^+$ solutions leads immediately to an equilibrated mixture of $\mathbf{B_2}$ and $\mathbf{C_c}$ that lasts for a time period sufficiently long to allow the study of its photochemical behavior. Continuous irradiation of this mixture at 313 nm causes an absorbance increase at 302 and 345 nm, indicating the formation of $\mathbf{C_t}$. The apparent photochemical quantum yield for this reaction, based on the total light absorbed by the mixture, is ca. 0.1. According to Scheme 1 it is clear that only the $\mathbf{C_c}$ species can be responsible for the photoreaction leading to $\mathbf{C_t}$. Since at pH = 5.2 $\mathbf{C_c}$ constitutes about 6% of the mixture and presumably absorbs a comparable fraction of the total absorbed light, it follows that the actual quantum yield of the *cis→trans* photoisomerization is likely close to unity.

Flash Photolysis: As pointed out in previous papers, flash photolysis experiments can be most useful to confirm and complement the results obtained by the pH jump measurements.[16]

Dark equilibrated solutions of flavylium ion were irradiated with a flash lamp (lifetime ca. 0.1 s) and the changes in absorbance were monitored as a function of time. In Figure 9 the traces obtained at 394 nm (absorption maximum of $\mathbf{AH}^+$) are shown for the pH values 2.0 and 5.2. Like in the case of 4′-methoxyflavylium,[7] the absorbance decay traces clearly show the presence of three consecutive kinetic processes. The first one, that can be better seen at pH = 5.2, occurs within the flash and is too fast to be monitored with our apparatus. It may be assigned to the reaction of $\mathbf{C_t}$ to give $\mathbf{C_c}$ in equilibrium with $\mathbf{B_2}$. The second process ends in a few seconds and can be assigned to the formation of $\mathbf{AH^+}$ from the equilibrated $\mathbf{C_c/B_2}$ mixture. The third process (not shown in Figure 9), falls into the time domain of hours and leads back to $\mathbf{C_t}$ since it completely restores the absorbance values observed before irradiation. The decay trace taken at 394 nm (Figure 9**a**) shows that the formation of $\mathbf{AH^+}$ at pH = 2.0 occurs via a first order process, whose rate constant was found to be pH dependent. The rate constant value obtained at pH = 2.0, 2.4 s^{-1}, is in excellent agreement with the rate constant found by McClelland and Gedge[5] upon the assumption that the rate determining step of the process leading from $\mathbf{C_c}$ to $\mathbf{AH^+}$ is the tautomerization reaction that transform $\mathbf{C_c}$ into $\mathbf{B_2}$.

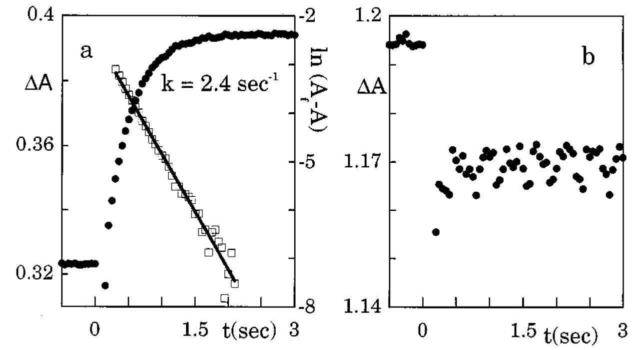


Figure 9. Spectral variations at 394 nm obtained under flash irradiation of dark equilibrated aqueous solutions of $\mathbf{C_t}$ (8.0×10^{-5} M) as a function of time. (a) pH = 2.0; (b) pH = 5.2. The right hand scale in (a) refers to the kinetic treatment of the decay as a first order process

Differential time-resolved spectra were obtained from traces as those reported in Figure 9 by plotting the difference between the initial absorbance and the absorbance at different delay times. These results show that the $\mathbf{C_c}$ formed by light excitation is an unstable species in acid medium (Figure 10a) since it disappears by a fast pH-controlled reaction to give $\mathbf{AH^+}$, whereas it is relatively inert at pH>5 (Figure 10b) since it can only give a slow back reaction yielding *trans*-chalcone.

Fluorescence Spectra: An equilibrated solution at pH = 1.0, where the predominant species is $\mathbf{AH^+}$, excited at 394 nm yields an emission band with maximum at 446 nm, similar to that previously observed for substituted flavylium ions.[8] Excitation at 300 nm of an equilibrated solution at pH = 5.0, where the stable species is $\mathbf{C_t}$, gave a weak emission with maximum at 443 nm. The large Stokes shift with respect to the absorption band suggest that the geometry of the excited state is different from that of the ground state. Finally, a weak emission band with maximum at 625 nm was observed on excitation at 430 nm of an equilibrated solution at pH = 11.0, where the stable species is the $\mathbf{C_t}^-$ anion.

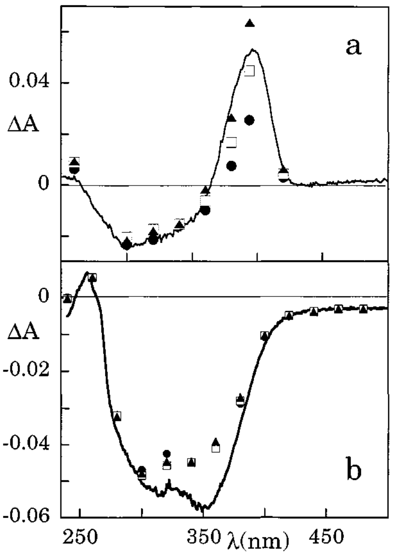


Figure 10. Differential time-resolved spectra of dark equilibrated aqueous solutions of $\mathbf{C_t}$ (5.0×10^{-5} M) at 0.5 (●), 1.0 (□), 3.0 (▲) seconds after the flash. a) pH = 2.0. b) pH = 5.2. Full lines are the final differential spectra obtained in continuous irradiation.

Write−Lock−Read−Unlock−Erase Cycles

It has been previously shown[7−10] that substituted flavylium ions can be taken as a basis for an optical memory system with multiple storage and nondestructive readout capacity through a *write−lock−read−unlock−erase* cycle. Such a cycle, schematized in the shaded area of Figure 11, combines two reversible processes that can be driven by means of two different stimuli (dual-mode systems). Photoexcitation (*write*) converts the stable $\mathbf{C_t}$ species into the $\mathbf{C_c/B_2}$ mixture. A pH change (*locks*) converts the $\mathbf{C_c/B_2}$ mixture to the kinetically inert $\mathbf{AH^+}$ form, that can be read without being erased. An opposite pH change (*unlock*) reconverts $\mathbf{AH^+}$ into the $\mathbf{C_c/B_2}$ mixture, that can be driven back (*erase*) by a photochemical or thermal reaction to $\mathbf{C_t}$. Working at a suitable pH value (vide infra), locking would occur spontaneously, thus simplifying the operation of the system.

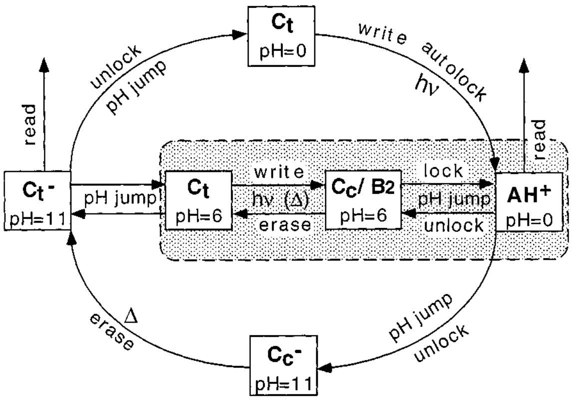


Figure 11. *Write-lock-read-unlock-erase* cycles for the flavylium ions. For more detail, see text

The thermal and photochemical behaviour of the unsubstituted flavylium cation examined in this paper suggests that also this compound can be used in a cycle like that described above. In order to check the reversibility of this system, a series of light/dark cycles has been performed on a 5.0×10^{-5} M aqueous solution of $\mathbf{C_t}$ at 60°C, at the autolocking pH = 2.2. The results obtained are reported in Figure 12. As it can be seen, the reversibility of the system is not fully satisfactory.

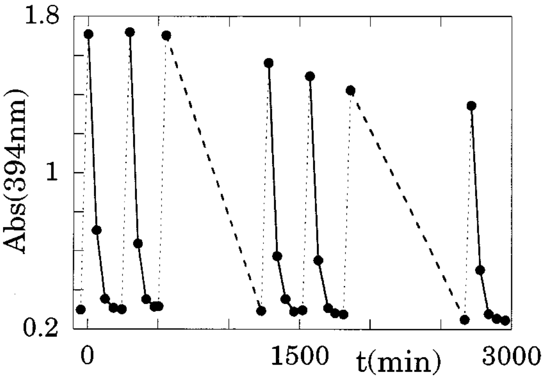


Figure 12. Changes in the absorbance at 394 nm (corresponding to the maximum of the $\mathbf{AH^+}$ form) observed for a 5.0×10^{-5} M aqueous solutions of $\mathbf{C_t}$ at pH = 2.2 and 60°C under 313 nm light excitation (dashed lines) followed by dark periods (full lines). Heavy dashed lines correspond to overnight dark periods.

A different cycle can be designed involving the anionic species present in basic media (Figure 11). This cycle starts at pH = 11 with the $\mathbf{C_t}^-$ form that, being not photosensitive, can be read without writing. Then, two different paths can be followed. The first one begins with a pH jump to pH = 6 which leads to $\mathbf{C_t}$ and goes on as described above (shaded area in Figure 11). The second path starts with a pH jump from 11 to 0, leading to $\mathbf{C_t}$ that can be photochemically written (and locked because of the low pH) to $\mathbf{AH^+}$. In this form, the information can be stored permanently and read without erasing since $\mathbf{AH^+}$ is thermally and photochemically stable. When necessary, $\mathbf{AH^+}$ can be unlocked by a pH jump to 11 and thermally erased to give back $\mathbf{Ct^-}$. An advantage of this cycle lies in the possibility of reading the system in both the initial (nonwritten) and final (written) states without writing or erasing. Moreover, $\mathbf{C_t}^-$ is more stable than $\mathbf{C_t}$, so that durability of the system could increase. A disadvantage is given by the fact that in this cycle auto-locking (and auto-unlocking) cannot occur so that two pH changes per cycle are needed.

Substituent Effects

The thermodynamic and kinetic constants for the structural transformations of the flavylium compounds investigated in this and previous papers are collected in Table 1. Inspection of these data shows that the substituents in the 4′ or 7 positions have a noticeable effect on some of the constants.

It is interesting to compare the properties of the four compounds from the viewpoint of the *write–lock–read–unlock–erase* cycle initiated by light excitation of $\mathbf{C_t}$. In a previous paper[9] we have shown that substitution in the 7-position lowers the kinetic barrier of the *cis→trans* thermal isomerization (compare the k_i values in Table 1). This causes autoerasing of the written information and therefore the 7-substituted compound is unsuitable for memory-storage purposes. In the following, only the two 4′-flavylium derivatives and the unsubstituted flavylium ion will be considered.

As mentioned above, in such a *write–lock–read–unlock–erase* cycle "autolocking" takes place when irradiation of $\mathbf{C_t}$ is performed at a sufficiently low pH value (see also Figure 5). If the chosen pH value is too low, however, the starting $\mathbf{C_t}$ form is already in equilibrium with a substantial amount of the $\mathbf{AH^+}$ form where the written information has to be stored. The best compromise between these two opposite requirements is that offered by the pH value of the crossing point between the curves describing the molar fractions of $\mathbf{C_t}$ at the final equilibrium conditions and of $\mathbf{AH^+}$ at the pseudoequilibrium conditions (see Figure 4). In the case of unsubstituted-, 4′-hydroxy-, and 4′-methoxyflavylium ions such a crossing occurs at pH 2.2, 3.2, and 3.0, respectively. Therefore the comparison among the properties of the three compounds will be made considering the properties of each system at the pH of that crossing point, which in the following will be called autolocking pH value.

As far as the writing function is concerned, its effectiveness depends on: i) light absorption by $\mathbf{C_t}$; ii) quantum yield

Table 1. Thermodynamic and kinetic constants for some structural transformations of synthetic flavylium compounds[a]

Substituent	7-OH [b]	none[c]	4′-OH [d]	4′-OMe [e]
K'_a	2.0×10^{-3}	2.3×10^{-2}	1.26×10^{-2} [f]	8.0×10^{-2}
K_a	2.8×10^{-4}		3.16×10^{-6}	
K_h	8.0×10^{-6}	9.8×10^{-4}	3.6×10^{-6}	3.4×10^{-5}
K_t	-	0.06	1	0.50
K_i	500	400	3500	ca 100
k_h	$0.48\ s^{-1}$ [a]	$4.6\ s^{-1}$	$8.9 \times 10^{-2}\ s^{-1}$	$0.47\ s^{-1}$
k_{-h}	$3 \times 10^4\ s^{-1}M^{-1}$ [g]	$4.7 \times 10^3\ s^{-1}M^{-1}$	$2.5 \times 10^4\ s^{-1}M^{-1}$ [g]	$1.38 \times 10^4\ s^{-1}M^{-1}$
k_i	$0.57\ s^{-1}$ [g]	$4.1 \times 10^{-4}\ s^{-1}$	$3.7 \times 10^{-5}\ s^{-1}$	$5.8 \times 10^{-5}\ s^{-1}$
k_{-i}	$8.3 \times 10^{-4}\ s^{-1}$	$1.1 \times 10^{-6}\ s^{-1}$	$< 10^{-7}\ s^{-1}$	$< 10^{-6}\ s^{-1}$

[a] Measured by means of pH jump techniques at 25°C, unless otherwise noted. – [b] Ref.[9] – [c] Ref.[5] and this work. – [d] Refs.[6,8] – [e] Refs.[5,7] – [f] At 60 °C. – [g] Measured by flash photolysis.

of the *trans→cis* photoisomerization; iii) rate of the locking process. Concerning the first point, the best wavelength for writing is that corresponding to the maximum difference between the molar absorption coefficients of the $\mathbf{C_t}$ and $\mathbf{AH^+}$ species. Comparison of the absorption spectra (Figure 1; Figure 1 of ref.[8]; Figure 2 of ref.[7]) shows that the best region for writing is around 310 nm for each compound and that the difference between the molar absorption coefficients of $\mathbf{C_t}$ and $\mathbf{AH^+}$ is about 15000 M^{-1} cm^{-1} in all cases (ca. 12000 M^{-1} cm^{-1} for the title compound). The quantum yield of the *trans→cis* photoisomerization is very similar for the three compounds. As far as the locking process is concerned, its rate depends on the rates of two consecutive steps, ring closure and dehydration (Scheme 1, Figure 5). The rate determining step is the ring closure and its rate constants, at the respective autolocking pH values, are 2.4 s^{-1}, 0.22 s^{-1}, and 0.63 s^{-1} for unsubstituted-, 4′-hydroxy-, and 4′-methoxyflavylium, respectively (Table 1).

The best wavelength for the reading function is that corresponding to the highest difference between the molar absorption coefficients of $\mathbf{AH^+}$ and $\mathbf{C_t}$. Such a wavelength is 394 nm ($\Delta\varepsilon = 30800$) for the unsubtituted flavylium ion, 426 nm ($\Delta\varepsilon = 39000$) for the 4′-hydroxy derivative, and 435 nm ($\Delta\varepsilon = 41000$) for the 4′-methoxy derivative.

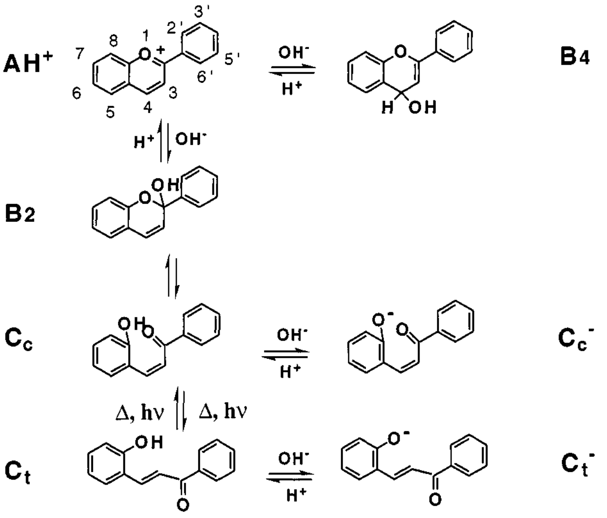
The erase function is performed in all cases at high temperature (60°C) in order to overcome the activation energy for the *cis→trans* isomeritation. The rate constants for $\mathbf{AH^+}$ disappearance, at the respective autolocking pH values, are 5.3×10^{-4} s^{-1}, 1.1×10^{-4} s^{-1} and 2.0×10^{-4} s^{-1} for unsubstituted-, 4′-hydroxy-, and 4′-methoxy-flavylium, respectively.

In conclusion, the unsubstituted flavylium cation, compared to the 4′-derivatives, exhibits higher locking and erasing rates, whereas the other properties are not substantially different.

Conclusions

We have investigated the structural transformations of the unsubstituted flavylium ion in aqueous solutions caused by pH jumps and continuous and flash photolysis excitation. The rate constants and equilibrium constants of the various processes have been obtained and compared with those previously reported for some flavylium derivatives. It is shown that substituents in the 4′ or 7 positions have a strong influence in determining the thermal and photochemical reactivity.

Write−lock−read−unlock−erase cycles starting from the *trans*-chalcone ($\mathbf{C_t}$) form and based on pH jumps and light excitation can be designed for each flavylium compound. The cycle based on the 7-OH derivative undergoes autoerasing. The cycle based on the unsubstituted flavylium ion shows some advantages compared with the analogous cycles based on 4′ derivatives. For the unsubstituted flavylium ion, a series of light/dark cycles has shown that the reversibility of the system is not fully satisfactory



Experimental Section

Flavylium perchlorate was prepared according to a published procedure.[17] All other chemicals were of analytical grade. The experiments were carried out in water at 25°C. The pH of the solutions was adjusted by addition of HCl (pH < 2) or buffer,[18] and measured by a Metrohom 713 pH meter. For ^{1}H-NMR spectroscopy experiments, the flavylium salt was dissolved in DCl ca. 0.5 M. When required, the pH was changed by addition of small aliquots of NaOD 1.0 or 0.1 M. pH measurements were made in the NMR tube using an Ingold glass electrode. The reported pH values, denoted with an asterisk, are direct readings without correction for the isotope effect.[19]

NMR spectroscopy[14,15a] and flash photolysis[16a,b] experiments were performed as previously described. Absorption and emission spectra were recorded by a Perkin−Elmer lambda 6 spectrophotometer and a Perkin−Elmer LS 50 spectrofluorimeter. Photoexcitation in continuous irradiation experiments was performed by using a medium pressure mercury lamp equipped with interference filters (Oriel) to isolate a narrow excitation band. The incident light intensity was measured by ferrioxalate actinometry.[20]

The NMR spectrum at pH = 1.0 was in perfect agreement with the proposed structure, proving the purity of the flavylium salt. A spectrum taken several minutes after a pH jump from 1 to 6 (pseudo-equilibrium) did not allow to distinguish the several forms probably because they are in fast equilibrium. The NMR spectrum taken 2 days after a pH jump from 1 to 6 (final equilibrium) was compatible with that of the *trans*-chalcone form, but did not permit (a straightforward assignment) an unequivocal identification of the several peaks due to their notable overlap; there are two multiplets which can be attributed to hydrogens 4, 2′, 6′ and 3, 5, 4′ respectively.

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