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Light and pH switching between the various forms of the 4′-methylflavylium cation

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Abstract

In aqueous solution, the 4′-methylflavylium ion (**AH**$^+$) can be interconverted into several different forms by light excitation and/or pH changes. All the observed processes are fully reversible and accompanied by strong changes in absorption and emission spectra. At pH < 1, the stable form is the coloured cationic species (**AH**$^+$). By increasing pH, **AH**$^+$ is no longer stable and undergoes structural transformations that at pH > 3 lead to the uncoloured *trans*-chalcone (**Ct**) as a final product. This transformation occurs through the hemiacetal form (**B2**) and the *cis*-chalcone (**Cc**) isomer. This mixture is relatively inert due to the existence of a kinetic barrier that slows down the thermal isomerisation of **Cc** to the final **Ct** form. **Ct** is photosensitive and can be backconverted by light excitation into **Cc** which at low pH rapidly gives the **AH**$^+$ species. In basic solution, two more species were detected, the anionic forms (**Cc**$^-$ and **Ct**$^-$) of the *cis* and *trans*-chalcone. **Ct**$^-$ is a stable, not photosensitive species, whereas **Cc**$^-$ is not stable, being converted into **Ct**$^-$ in the dark. A detailed analysis of the chemical behaviour of 4′-methylflavilium ion from the viewpoint of molecular level device shows that this compound behaves as a *multistate/multifunctional* system. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: 4′-Methylflavylium salt; Thermal isomerisation; Photochromic compounds; Multistate/multifunctional systems

1. Introduction

The study of molecular or supramolecular species capable of existing in different forms that can be interconverted by external stimuli is a topic of great fundamental interest [1–7]. The design of such molecular-level switching devices is also very interesting for practical application since it is directly linked to the chemistry of signal generation, transfer, conversion, storage, and detection (semiochemistry) [3].

Photochromic compounds, which are typical bistable species where light can induce the reversible interconversion between the two forms exhibiting different absorption spectra, [8,9] may find application in the field of information processing at the molecular level [10,11], for relevant examples, see: [12–23]. Recently, it has also been shown that suitably designed photochromic compounds may (i) be used to obtain switchable quadratic non-linear optic properties [24], (ii) behave as logic gates [25–28], (iii) exhibit very complex patterns of chemical reactions [26–28] and (iv) be used as components of rudimental neuron-like networks [29].

Like anthocyanins [30,31], which are among the most important sources of colour in flowers and fruits, synthetic flavylium salts undergo various structural transformations, [32–35] often accompanied by colour changes, that can be driven by pH changes and light excitation. Several works concerning the thermodynamic as well as the kinetic aspects of the thermal reactions of flavylium-type compounds have since long been reported in literature [30–35], whereas the photochemical and photophysical aspects have been systematically examined more recently [26–28,36–43]. Previous studies have clearly shown that the thermal and photochemical behaviour of these compounds is strongly affected by the substituents (either nature or attached position) [28,38–43] and that some of these compounds can perform write-lock-read-unlock-erase cycles via a very interesting multistate/multifunctional behaviour [26,37,41].

Continuing the systematic study initiated some years ago 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 chemical and photochemical behaviour of the 4′-methylflavylium ion.

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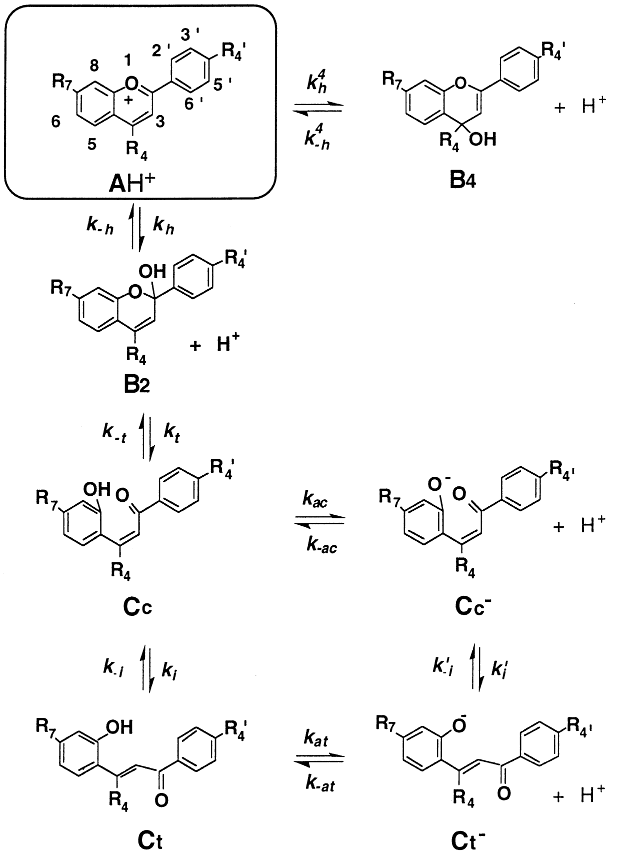
A kinetic investigation of the transformations undergone by this compound was originally performed by McClelland and Gedge [34]. These authors reported the values of the kinetic and thermodynamic constants of some processes connecting the various forms present in acidic and neutral aqueous solution. In this work, we have (i) re-examined the thermal reactions of the flavylium cation in acidic and neutral solution, (ii) extended the study to basic solutions, and (iii) investigated the effect of continuous and pulsed irradiation. The results have then been elaborated on the basis of a previously reported kinetic method [36,40] to obtain all the kinetic and thermodynamic parameters that control the complex network of observed reactions.

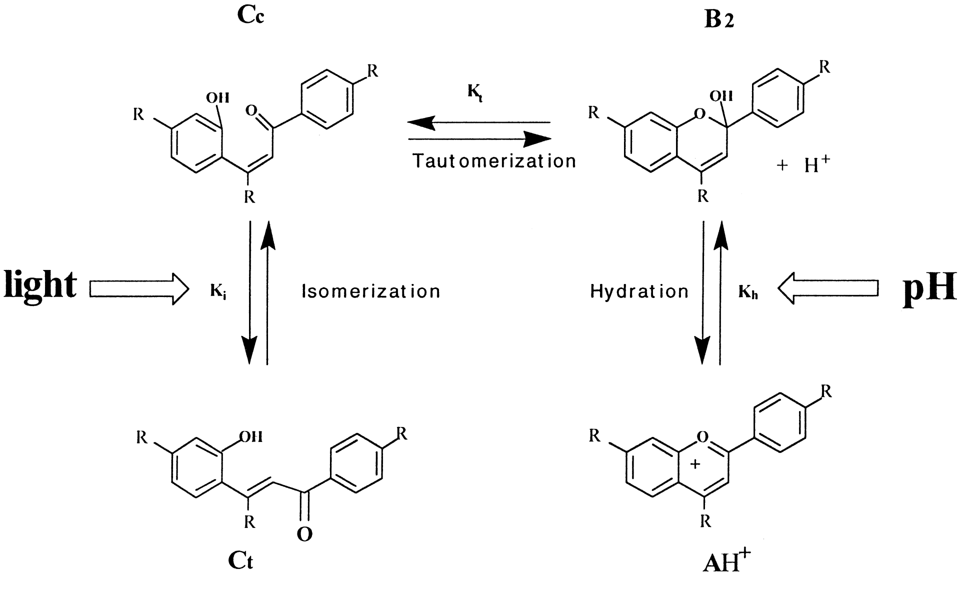
2. Nature of the species involved in the chemistry of flavylium compounds

The basic scheme to discuss the structural transformations of flavylium-type compounds is that shown in Scheme 1 [30–35]. In moderately acidic or neutral solution, the thermodynamically stable form is generally the neutral *trans*-2-hydroxychalcone species **Ct**, which is formed from **AH**$^+$ through the two intermediate compounds **B2** and **Cc**. **B2** is a hemiacetal species, obtained by hydration in the 2 position of the flavilyium cation, and **Cc** is a *cis*-2-hydroxychalcone, formed from the hemiacetal **B2** through a tautomeric process. The interesting feature of these systems is that the **AH**$^+$ and **B2** forms can be reversibly interconverted by pH changes, [32–35] whereas **Cc** and **Ct** can be interconverted by photoexcitation [26–28,36–47]. Since the **B2** and **Cc** forms are in tautomeric equilibrium, it follows that pH and light stimulations can be used to cause interconversion of the four fundamental forms (Scheme 2).



Scheme 1. Structural transformations of the flavylium-type compounds.

Furthermore, the **AH**$^+$ form exhibits acid properties not only in the 2-, but also in the 4-position, to give the **B4** basic species. Usually the **B4** species has a negligible role in the global process, being always present in very low quantity



Scheme 2. Structural transformations of the flavylium-type compounds.

($\leq$1%), and thus will not be considered in the following. In their turn, in basic solution **Cc** and **Ct** can undergo deprotonation to give the respective **Cc**$^-$ and **Ct**$^-$ monoanions which, being *cis–trans* isomers, can in principle be interconverted by light excitation. Depending on the nature of the substituents, other acid–base equilibria and *cis–trans* couples may be present.

3. Thermal reactions of the 4′-methylflavylium ion

The transformations undergone by the 4′-methylflavylium ion in aqueous solutions were spectroscopically investigated in the pH range 1–12 by means of the pH-jump technique. We have collected five different absorption spectra (see Fig. 1) depending on pH and time elapsed from the pH jump assigning each of them to the species shown in Scheme 1. The solution obtained dissolving the starting flavylium salt in HCl 0.1 M gives the spectrum I ($\lambda_{\max} = 408$ nm, $\varepsilon = 36\,500$ M^{-1} cm^{-1}) in Fig. 1(a). In the same figure, the spectrum II was obtained immediately after a pH jump to 5.8 of the starting (pH = 1) solution. This spectrum undergoes very slow changes (half-life ca. 13 h) and in 3 days gives the stable spectrum III ($\lambda_{\max} = 304$ nm, $\varepsilon = 15\,500$ M^{-1} cm^{-1}) (Fig. 1(a)). In agreement with McClelland and Gedge [34] and following Scheme 1, we assign spectrum I to the flavylium cation (**A**H$^+$), spectrum II to the equilibrated tautomeric mixture of **B2** and **Cc**, obtained by hydration of **A**H$^+$ and spectrum III to the **Ct** species, formed by isomerisation of **Cc**.

The solution obtained immediately upon a pH jump to 11.5 of the starting (pH = 1) solution exhibits spectrum IV (Fig. 1(b)) that slowly (half-life = 1.65 h) turns to spectrum V (Fig. 1(b)). Spectrum V can be immediately converted to spectrum III (Fig. 1(a) and (b)) by a pH jump to pH = 6.0 (or pH = 1) of the related (pH = 11.5) solution. The behaviour of the 4′-methylflavylium ion in basic solutions can be accounted for by assigning the spectrum IV and V to **Cc**$^-$ and **Ct**$^-$ anions, respectively (see Scheme 1).

3.1. Acidic and neutral solutions

The complex equilibria involving the species present in acidic or neutral solutions can be described in terms of a single acid–base equilibrium between the acid species **A**H$^+$ and a conjugated base "**CB**" having concentration equal to the sum of the concentrations of the species **B2**, **Cc** and **Ct**

$$\mathbf{A}\mathrm{H}^+ \overset{K'_a}{\rightleftharpoons} \text{“}\mathbf{CB}\text{”} + \mathrm{H}^+$$

where, following a kinetic treatment illustrated in previous papers [42,43] $K'_a = K_h + K_h K_t + K_h K_t K_i$. When, as in this case, the isomerisation reaction rate is much slower than the hydration and tautomerisation reaction rates, a pseudo-equilibrium is attained. The pseudo-equilibrium constant is $K_a = K_h + K_h K_t$ and "**CB**" is equal to the sum of the concentrations of the species **B2** and **Cc**.

In order to characterize the equilibria, a series of pH jumps from 1.0 to higher pH values (range 1–7) was carried out. The results show a continuous decrease and then a disappearance of the band characteristic of the **A**H$^+$ species (Fig. 2). These spectra are due to the contemporary presence of the three species **A**H$^+$, **B2**, and **Cc**, whose relative amounts depend on the final pH of the solution. The spectral variations at 408 nm allow us to plot the molar fraction distribution of **A**H$^+$ as a function of pH (inset of Fig. 2). A best fitting procedure on this plot gives a pK_a value of 3.57 for the dissociation equilibrium of **A**H$^+$ to give the **B2** and **Cc** species. All the solutions exposed to a pH jump undergo a slow equilibration process assigned to the conversion of **A**H$^+$ into the thermodynamically stable product **Ct** through the **Cc**/**B2** mixture (Scheme 1). Fig. 3 shows that the conversion at pH = 3.3 follows a first order kinetics. A similar behaviour is observed at any other pH value in the acid

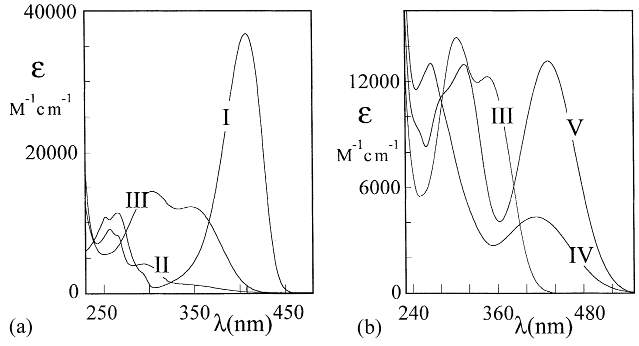


Fig. 1. Absorption spectra of the 4′-methylflavylium ion under different experimental conditions. (a) Acidic or neutral solutions: I, solution at pH = 1; II, pseudoequilibrated solution obtained immediately after a pH jump to pH = 5.8; III, equilibrated solution after 3 days from a pH jump to pH = 5.8. (b) Basic solutions: III, see above; IV, pseudoequilibrated solution obtained immediately after a pH jump from 1.0 to 11.5; V, equilibrated solution obtained after 4 h from pH jump from 1.0 to 11.5.

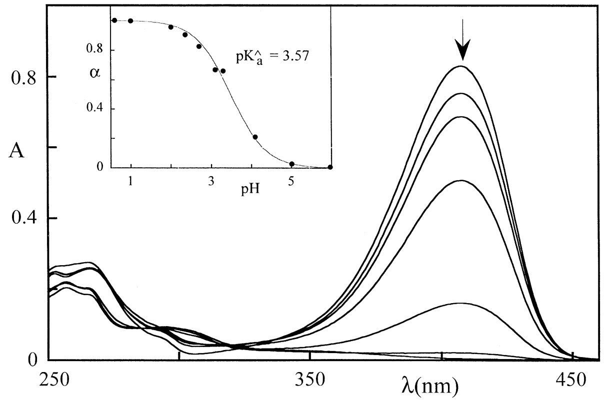


Fig. 2. Absorption spectra of aqueous solutions of the flavylium cation (2.2×10^{-5} M) as a function of pH (range 1–7), few minutes after the pH jumps. The inset shows the molar fraction of **A**H$^+$ as a function of the final pH, calculated from the absorbance changes at 407 nm.

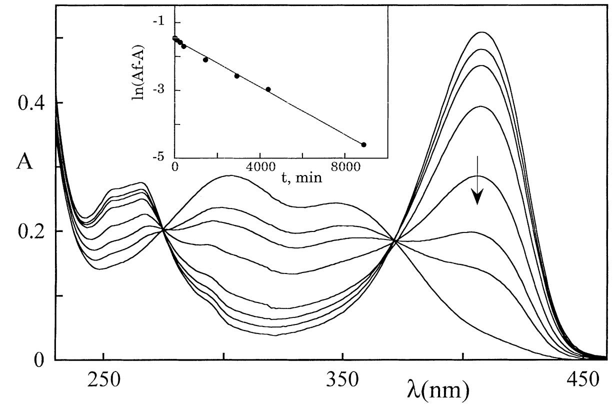


Fig. 3. Spectral variations observed in the dark for an aqueous solution of the flavylium cation (1.9×10^{-5} M) upon a pH jump from 1.0 to 3.3 as a function of time. The inset shows that the change in absorbance at 407 nm, i.e. the conversion of the $\mathbf{AH}^+$, **Cc**, and **B2** mixture to **Ct**, follows a first order kinetics.

region. The values of the rate constants are $2.8 \times 10^{-6}\,\mathrm{s}^{-1}$ at pH = 2.7; $5.8 \times 10^{-6}\,\mathrm{s}^{-1}$ at pH = 3.3; $1.06 \times 10^{-5}\,\mathrm{s}^{-1}$ at pH = 5.0; $1.38 \times 10^{-5}\,\mathrm{s}^{-1}$, at pH = 5.6 and $1.50 \times 10^{-5}\,\mathrm{s}^{-1}$ at pH = 7.0 showing that the rate of formation of **Ct** is pH dependent. This reaction is also temperature dependent and shows an activation energy of $87\,\mathrm{kJ\,mol}^{-1}$ at pH = 5.8.

The concentration of **Ct** present at the final equilibrium at the various pH values allow us to calculate the equilibrium constant between $\mathbf{AH}^+$ and **Ct** ($\mathrm{p}K'_\mathrm{a} = 1.55$).

By applying the previously reported kinetic treatment [42,43] to our and McClelland's results, we were able to evaluate the following thermodynamic constants $K_\mathrm{h} = 2.3 \times 10^{-4}$, $K_\mathrm{t} = 0.16$, $K_\mathrm{i} = 800$ (see Scheme 1). Using these constants we plotted the energy-level diagram shown in Fig. 4 that could be useful to explain the behaviour of the system in the pH range 0–7.

3.2. Basic solutions

A series of pH jumps from 1.0 to pH values in the range 8–12 show at pH > 9 the formation and increase of the band characteristic of the $\mathbf{Cc}^-$ species (Fig. 5).

The spectral variations at 415 nm allow us to plot the molar fraction distribution of $\mathbf{Cc}^-$ as a function of pH (inset of Fig. 5). A best fitting procedure on this plot gives a $\mathrm{p}K_\mathrm{ac}$ value of 9.61 for the dissociation equilibrium of **Cc** to give the $\mathbf{Cc}^-$ species. All the solutions exposed to a pH jump

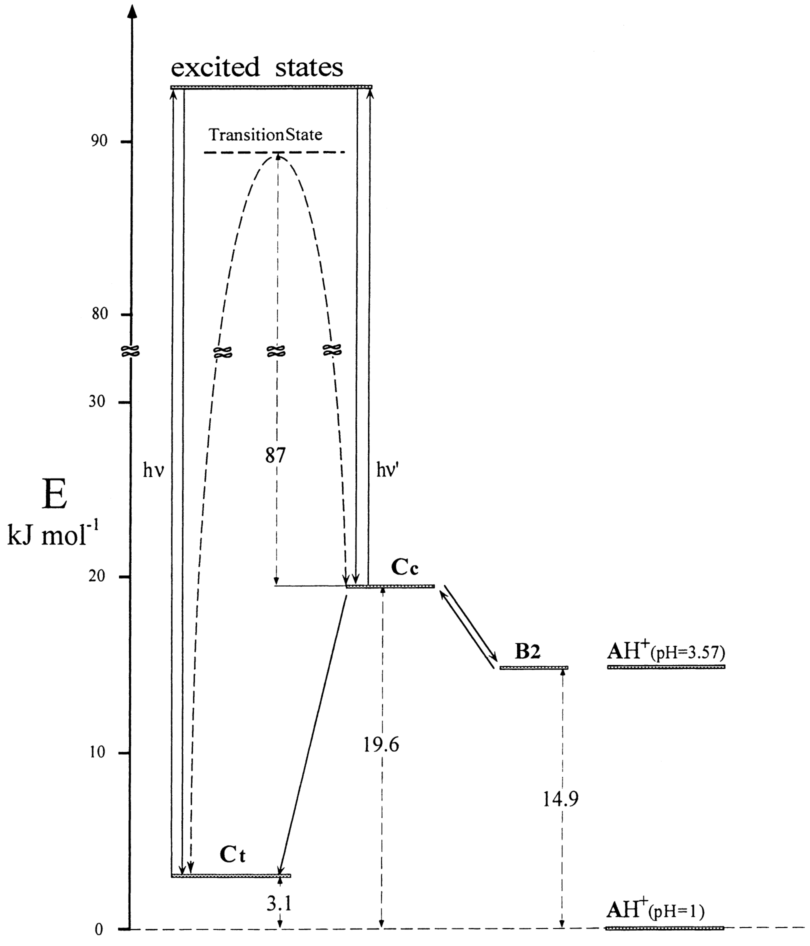


Fig. 4. Energy-level diagram for the species involved in the transformation of the flavylium cation in acidic or neutral solutions.

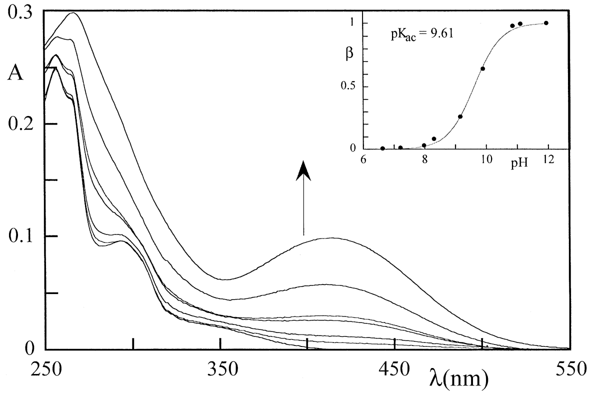


Fig. 5. Absorption spectra of aqueous solutions of the flavylium cation (2.5×10^{-5} M) as a function of pH a few minutes after the pH jumps from1 to basic pH values (range 8–12). The inset shows the molar fraction of **Cc**$^-$ as a function of the final pH, calculated from the absorbance changes at 415 nm.

undergo a slow equilibration process assigned to the conversion of **Cc**$^-$ into **Ct**$^-$ (Scheme 1). At pH = 11.5 this reaction follows a first order kinetics with rate constants of 1.2×10^{-4} s^{-1}. A similar behaviour is observed at any other pH value in the range 9–12.

Attempts were made to measure the dissociation constant of **Ct** by means of a series of pH jumps from an equilibrated solution at pH = 6 (containing the **Ct** species) to higher pH in the range 7–12. From the spectral variation at 431 nm we obtained the molar fraction distribution of **Ct**$^-$ as a function of pH shown in Fig. 6. From this plot we gained a value of 8.75 for the pK_{at} for the dissociation equilibrium of **Ct** to give **Ct**$^-$.

By means of all the thermodynamic constants evaluated here, we calculated the molar fraction distributions of the various species present at 20°C in aqueous solution in the pH range 0–12, reported in Fig. 7.

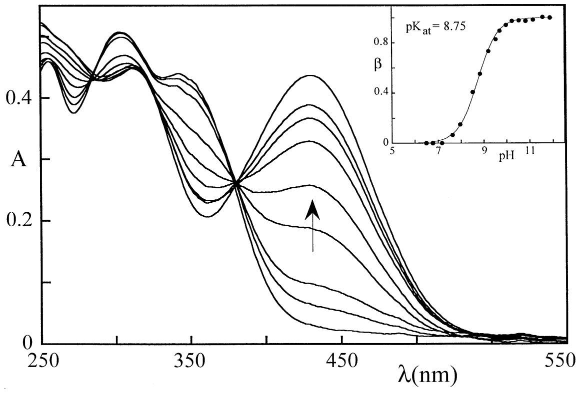


Fig. 6. Absorption spectra of aqueous solutions of the flavylium cation (3.5×10^{-5} M) as a function of pH a few minutes after the pH jumps from 6.0 to basic pH values (range 7–12). The inset shows the molar fraction of **Ct**$^-$ as a function of the final pH, calculated from the absorbance changes at 431 nm.

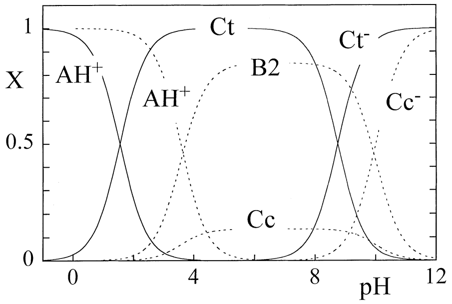


Fig. 7. Molar fraction distributions of the species involved in the transformation of the flavylium cation in the pH range 1–12. Solid lines refer to the species involved in the thermodynamic equilibrium. Dashed lines refer to the pseudoequilibrium obtained by pH jump from pH = 1 to higher pH values or by exciting **Ct** by flash light.

As it can be seen, the thermodynamically stable species at pH < 1 is the strongly coloured 4′-methylflavylium ion **AH**$^+$, while in the pH range 2–8 the colourless *trans*-4′-methylchalcone **Ct** is the thermodynamically stable species and, therefore, it is the final product of the transformations of **AH**$^+$ in acidic or neutral region. **B2** and **Cc** can exist as transient species between pH 2 and 9, while between 9 and 12 they are substitued by **Cc**$^-$. **Cc**$^-$ is again a transient species, since it is (slowly) converted into **Ct**$^-$ that is the thermodynamically stable species at pH > 9.

Even at pH = 1, where **AH**$^+$ is the thermally stable species, **Ct** can be maintained for some time since it is kinetically stable because of the energy barrier involved in its transformation to **Cc**.

4. Photochemical behaviour of the 4′-methylflavylium ion

In agreement with previously investigated flavylium compounds [36–47] we have found that **Ct** and the **B2**/**Cc** mixture are photosensitive. In the following we report the photochemical behaviour of these species under continuous and pulsed irradiation.

4.1. Continuous irradiation

Continuous irradiation of 7.0×10^{-6} M aqueous solutions of **Ct** at pH = 1.3 with 313 nm light causes strong spectral changes (Fig. 8(a)). The formation of the intense band centred at 407 nm shows that the photoreaction completely converts **Ct** into **AH**$^+$. The quantum yield of the photoreaction is 0.15. At this pH no back reaction takes place and irradiation with 404 nm light, corresponding to the absorption band of **AH**$^+$ (Fig. 1), does not cause any effect.

When irradiation of **Ct** (8.5×10^{-6} M) is carried out at pH = 5.4 we observe the spectral changes shown in Fig. 8(b). At this pH the disappearance of **Ct** does not cause any increase of absorbance in the visible spectral region, showing that **AH**$^+$ is not formed. This is in full agreement

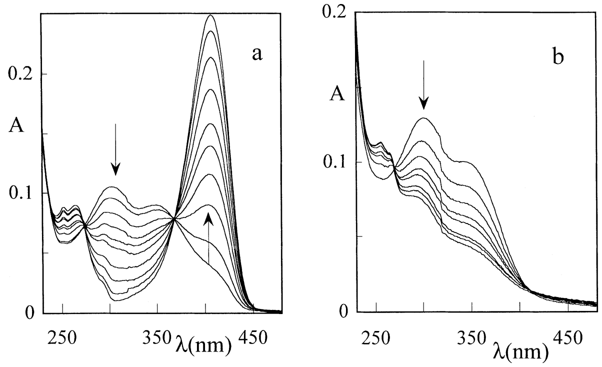


Fig. 8. Spectral variations observed upon continuous irradiation (313 nm) of dark equilibrated aqueous solutions of **Ct** as a function of time (initial time increments = 30 s): (a) pH = 1.3, concentration 7.0×10^{-6} M; (b) pH = 5.4, concentration 8.5×10^{-6} M.

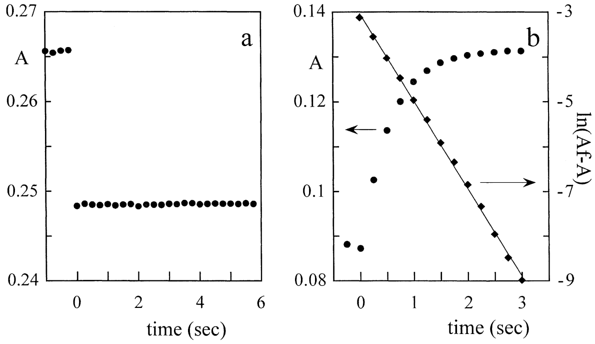


Fig. 9. Spectral variations obtained under flash irradiation of dark equilibrated aqueous solutions of **Ct** as a function of time: (a) pH = 5.4, concentration 1.7×10^{-5} M, 310 nm; (b) pH = 2.7, concentration 5.0×10^{-5} M, 407 nm. The right hand scale in (b) refers to the kinetic treatment of the decay as a first order process.

with the expectations based on the data shown in Fig. 7, which indicate that around pH = 6.0 the pseudo-equilibrated mixture of products is constituted essentially by **Cc** and **B2**. Irradiation of this mixture with 313 nm light causes the reverse *cis* → *trans* photoisomerisation reaction with an apparent quantum yield of ca. 0.22 (based on the total light absorbed by **Cc** and **B2**).

Interestingly, among the various species here identified, only **AH**$^+$ exhibit intense fluorescence bands with $\lambda_{\max}$ at 460 nm. The fluorescence lifetime, measured by phase shift methods, is 0.5 ns. It is worth noting that the formation or disappearance of the **AH**$^+$ species, i.e. the occurrence of the above-described thermal and photochemical reactions pattern, can also be followed by fluorescence measurements.

4.2. Pulsed irradiation

We have shown that a simple flash-photolysis apparatus [48] with a time resolution of ca. 0.2 s can be used to investigate the kinetics of conversion of the various forms of flavylium ions to obtain kinetic data that can complement and/or replace those obtainable by the pH jump technique.

Flash excitation [48] of aqueous solutions of **Ct** at 25°C in the pH range 1.3–5.4 causes a bleaching in the 300–400 nm region, that can be assigned to the disappearance of **Ct** (Fig. 9(a)). At pH 1.3–2.7, a strong increase in absorbance around 410 nm is observed (Fig. 9(b)), as expected for the formation of **AH**$^+$. The absorbance versus time traces show that **Ct** disappears within the time scale of the flash (Fig. 9(a)), but its disappearance does not lead directly to **AH**$^+$ (Fig. 9(b)). One or more intermediate products are initially formed (**Cc** and **B2** according to Schemes 1 and 2) which then completely convert to **AH**$^+$ in a few seconds ($k = 5.5$ and $1.7\,\mathrm{s}^{-1}$ at pH = 1.3 and 2.7, respectively). At pH = 5.4, the decrease of absorbance in the 300–400 nm region, corresponding to the disappearance of **Ct**, is not followed by an increase in absorbance in the visible region because the initially formed products of the photoreaction, **B2** and **Cc** do not convert to **AH**$^+$ at this pH (Figs. 7 and 8).

4.3. Write-lock-read-unlock-erase cycles

As discussed in the introduction, photochromic systems represent potential molecular-level memory devices. A number of problems, however, must be solved for practical applications. A most challenging one is to find systems with multiple storage and non-destructive readout capacity, i.e. where the record can be erased when necessary, but is not destroyed by the readout. The previously studied 4′-hydroxyflavylium [26], 4′-methoxyflavilium [37], and unsubstituted flavylium [41] ions can operate through the write-lock-read-unlock-erase cycle illustrated in Fig. 10 and, therefore, they can be taken as a basis for optical memory systems with multiple storage and non-destructive readout capacity.

The thermal and photochemical study of the 4′-methylflavilium ion described in this paper clearly shows that this

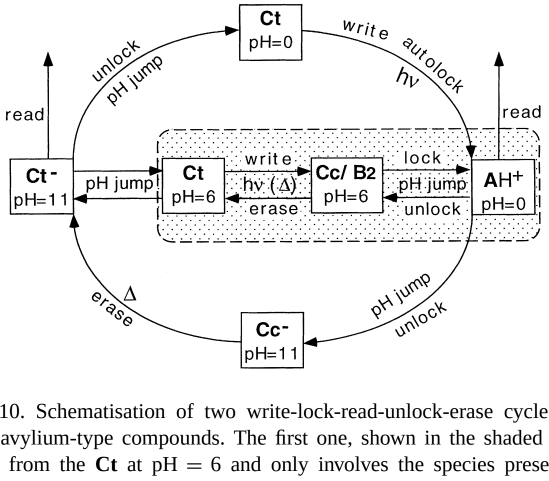


Fig. 10. Schematisation of two write-lock-read-unlock-erase cycles for the flavylium-type compounds. The first one, shown in the shaded area, starts from the **Ct** at pH = 6 and only involves the species present in acidic pH. On the contrary, the elliptic cycle makes use of the anionic species and starts from **Ct**$^-$ at pH = 11.

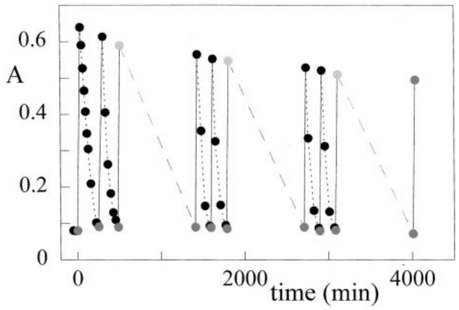


Fig. 11. Changes in the absorbance at 407 nm (corresponding to the maximum of the **A**H$^+$ form) observed for a 1.8×10^{-5} M aqueous solutions of **Ct** at pH = 2.6 and 60°C under 313 nm light excitation (full lines) followed by dark periods (dashed lines). Light dashed lines correspond to overnight dark periods. Nine light/dark cycles are shown.

compound behaves as a multistate/multifunctional system since it can exist in several forms that can be interconverted by more than one type of external stimuli (light and pH). A detailed analysis of the behaviour of 4′-methylflavilium ion from the viewpoint of molecular level device reveals that the chemical properties are not substantially different from those exhibited by the previously studied synthetic flavylium compounds [26,37,41].

Nevertheless, among the 4’-substituted flavylium ions, this compound exhibits the lowest energy barrier for the *cis–trans* isomerisation reaction; lowering the activation energy of the *cis–trans* isomerisation reaction favours auto-erasing, which discourages its use for an optical memory system.

To the same conclusion lead the results of a series of light/dark cycles at pH = 2.6 (the “autolock” pH [41] of this system) performed to check the reversibility of the system. As it can be seen in Fig. 11, that shows the absorbance changes at 407 nm (corresponding to the maximum of the **A**H$^+$ form) upon repeated light excitation (313 nm)/dark cycles, the absorbance reached after the irradiation periods continuosly decreases with the progressive increase of the irradiation cycle showing that the chemical stability of the system is not good even at the first light/dark cycles.

5. Experimental section

The 4′-hydroxyflavylium chloride was prepared according to a published procedure [49]. All other chemicals used were of analytical grade. The experiments were carried out in water at 25°C. The pH of the solutions was adjusted by addition of $HClO_4$ (pH $<$ 2) or Universal buffer Theorell–Stenhagen (0.04 M), and measured by a Metrohom 713 pH meter. Flash photolysis experiments were performed as previously described [36]. Absorption spectra were recorded on a Perkin-Elmer lambda 6 spectrophotometer. Photoexcitation in continuous irradiations experiments was performed by using a medium pressure mercury lamp, and interference filters (Oriel) to isolate the excitation bands. The incident light intensity was measured by ferrioxalate actinometry [50]. The estimated error on quantum yield values is +10%.

Acknowledgements

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