Photochromism of 4′-Methoxyflavylium Perchlorate. A "Write−Lock−Read−Unlock−Erase" Molecular Switching System

Fernando Pina,*,1a Maria João Melo,1a Mauro Maestri,*,1b Roberto Ballardini,1c and Vincenzo Balzani*,1b

Contribution from the Centro de Química Fina e Biotecnologia, Departamento de Química, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal, Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy, and Istituto FRAE-CNR, via Gobetti 101, 40134 Bologna, Italy

Received February 11, 1997[⊗]

Abstract: In aqueous solution (2 < pH < 8) the thermodynamically stable form of the 4′-methoxyflavylium ion ($\mathbf{AH^+}$) is its hydrated derivative *trans*-4′-methoxychalcone, $\mathbf{C_t}$. The $\mathbf{C_t}$ compound shows a broad absorption band with $\lambda_{max} = 350$ nm. In acid medium, irradiation of $\mathbf{C_t}$ with near-UV light causes strong spectral changes with five isosbestic points and appearance of a very intense band in the visible region with maximum at 435 nm, corresponding to the $\mathbf{AH^+}$ form. It has been shown that irradiation of $\mathbf{C_t}$ causes a *trans* → *cis* photoisomerization reaction ($\Phi = 0.04$ at $\lambda_{exc} = 365$ nm), which is followed by 100% conversion of the *cis*-chalcone form ($\mathbf{C_c}$) to the $\mathbf{AH^+}$ ion. The $\mathbf{AH^+}$ ion is photochemically inactive and thermally inert in acid medium (half-life of the back conversion at 25 °C in the dark is 815 days at pH 1.0 and 20 h at pH 4.3, respectively). At high temperature (>50 °C) and/or pH ≥3, however, $\mathbf{AH^+}$ can be quantitatively converted back to $\mathbf{C_t}$ (half-life of 15 min at pH 4.0 and 60 °C). Owing to this unique behavior, this represents a novel molecular system in which the color can be controlled by light and changes in temperature and/or pH. The ability to photochemically convert the stable and colorless $\mathbf{C_t}$ form to the kinetically inert and colored $\mathbf{AH^+}$ form, and the possibility to reconvert $\mathbf{AH^+}$ to $\mathbf{C_t}$ at high temperature or by a pH jump make the system well-suited as the basis for an optical memory device with multiple storage and nondestructive readout capacity through a write−lock−read−unlock−erase cycle.

Introduction

Great interest is currently devoted to bistable molecular or supramolecular species presenting two forms whose interconversion can be modulated by an external stimulus.[2−6] The design of such molecular-level switching devices is directly linked to the chemistry of signal generation, transfer, conversion, storage, and detection (semiochemistry).[2]

Typical bistable species are the so-called photochromic compounds, molecules that can be interconverted between two forms (**X** and **Y**) exhibiting different colors.[7,8] Most photochromic compounds change their color by photoexcitation and revert more or less slowly to their initial state when kept in the dark (Figure 1a). Compounds exhibiting this behavior are useless for information storage (or switching purposes) since the written information (switching state) is spontaneously erased (back converted) after a relatively short time.

Other photochromic compounds do not return to the initial state thermally, but can undergo reversible photoisomerization (Figure 1b).[9] Such compounds can be used for optoelectronic devices. However, they present a severe problem. The light used for reading the written data (detecting the switching state) causes the back-conversion of the sampled molecules and therefore the gradual loss of information (state definition). Several attempts have been made to overcome this difficulty, including the use of photochemically inactive infrared light to read the status of the system.[10]

A general approach to avoid destructive reading is to combine two reversible processes that can be addressed by means of two different stimuli (dual-mode systems).[11] The additional stimulus can be another photon,[12] heat,[13] an electron,[11,14] a proton,[15] or

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

(1) (a) Universidade Nova de Lisboa. (b) Università di Bologna. (c) Istituto FRAE-CNR.

(2) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives*; VCH: Weiheim, 1995.

(3) Feringa, L. B.; Jager, W. F.; de Lange, B. *Tetrahedron* **1993**, *49*, 8267.

(4) Balzani, V.; Scandola, F. "Photochemical and photophysical devices". In *Comprehensive Supramolecular Chemistry*, Reinhoudt, D. N., Ed.; Pergamon Press: Oxford, England, 1996; Vol. 10, p 687.

(5) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, 1991.

(6) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 146. (b) Credi, A.; Balzani, V.; Langford, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 2679.

(7) Dürr, H.; Bouas-Laurent, H., Eds. *Photochromism−Molecules and Systems*; Elsevier: Amsterdam, 1990.

(8) Tsivgoulis, G. M.; Lehn, J.-M. *Chem. Eur. J.* **1996**, *2*, 1399 and references therein.

(9) (a) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803. (b) Buchholtz, F.; Zelichenok, K.; Krongauz, V. *Macromolecules* **1993**, *26*, 906. (c) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206. (d) Wals, J.; Ulrich, K.; Port, H.; Wolf, H. C.; Wonner, J.; Effenberger, F. *Chem. Phys. Lett.* **1993**, *213*, 321. (e) Saika, T.; Irie, M.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2123. (f) Coursan, M.; DEsvergne J.-P.; Deffieux, A. *Macromol. Chem. Phys.* **1996**, *197*, 1599.

(10) (a) Dvornikov, A. S.; Rentzepis, P. M. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 379. (b) Seibold, M.; Port, H. *Chem. Phys. Lett.* **1996**, *252*, 135.

(11) Kawai, S. H.; Gilat, S. L.; Posinet, R.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285.

(12) Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1993**, *115*, 6442.

(13) Irie, M. *Mol. Cryst. Liq. Cryst.* **1993**, *227*, 263.

(14) (a) Daub, J.; Salbeck, J.; Knöchel, T.; Fischer, C.; Kunkely, H.; Rapp, K. M. *Angew Chem., Int. Ed. Engl.* **1989**, *28*, 1494. (b) Iyoda, T.; Saika, T.; Honda, K.; Shimidzu, T. *Tetrahedron Lett.* **1989**, *30*, 5429. (c) Daub, J.; Fischer, C.; Salbeck, J.; Ulrich, K. *Adv. Mater.* **1990**, *8*, 366.

(15) Yokoyama, Y.; Ymamane, T.; Kurita, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1722.
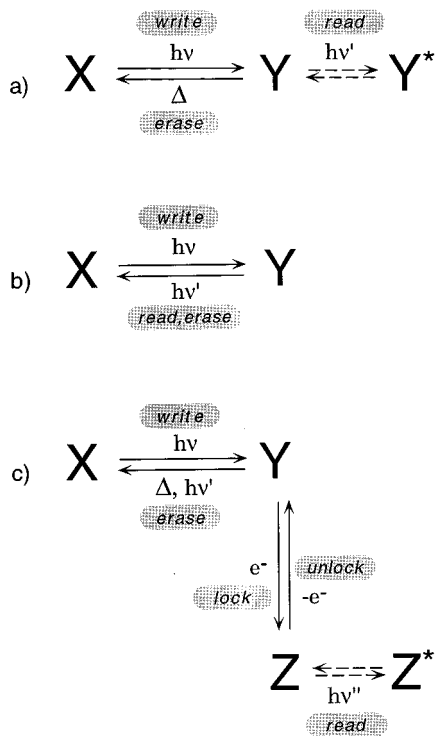
Figure 1. Schematic representation of the behavior of three types of photochromic systems. (a) The photochemical reaction of form **X** is thermally reverted in the dark. (b) The photochemical reaction of form **X** can be reverted only by light excitation of form **Y**. (c) Form **Y**, which goes back to **X** under light excitation, can be transformed by a second stimulus (e.g., a redox reaction) into another form, **Z**, which is stable toward light excitation and, when necessary, can be reconverted to **Y**. For more details, see text.

even something more subtle such as formation of a hydrogen bond.[16] In such systems (Figure 1c), light is used to convert **X** to **Y** (*write*), then a second stimulus (e.g., a reduction process as in Figure 1c) is employed to transform **Y** (which would be reconverted back to **X** by a direct photon reading process) into **Z**, another stable state of the system (*lock*), that can be optically detected without being destroyed (*read*). Through this process, the change caused by the writing photon is safeguarded. When the written information has to be erased, **Z** is reconverted back to **Y** (*unlock*; e.g., by an oxidation process as in the example of Figure 1c) and **Y** is then reconverted back to **X** (*erase*). Such a *write−lock−read−unlock−erase* cycle could constitute the basis for an optical memory system with multiple storage and nondestructive readout capacity.

In this paper we describe a photochromic system, based on a synthetic flavylium salt in aqueous solution, which can undergo such a *write−lock−read−unlock−erase* cycle. In such a system, as a stimulus for locking−unlocking the written information one can use temperature and/or pH. The behavior of the system has been characterized under a variety of experimental conditions, including continuous and pulsed excitation.

Results and Discussion

Nature of the Species Involved and Their Thermal Interconversion. Flavylium salts have basically the chemical structure of anthocyanins, the natural pigments responsible for a variety of fruit and flower colors. Like the anthocyanins, the flavylium salts can undergo various structural transformations,
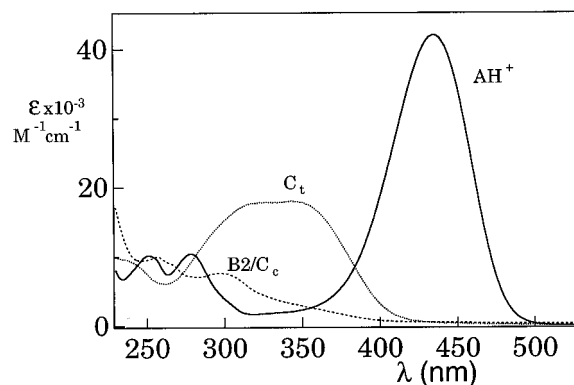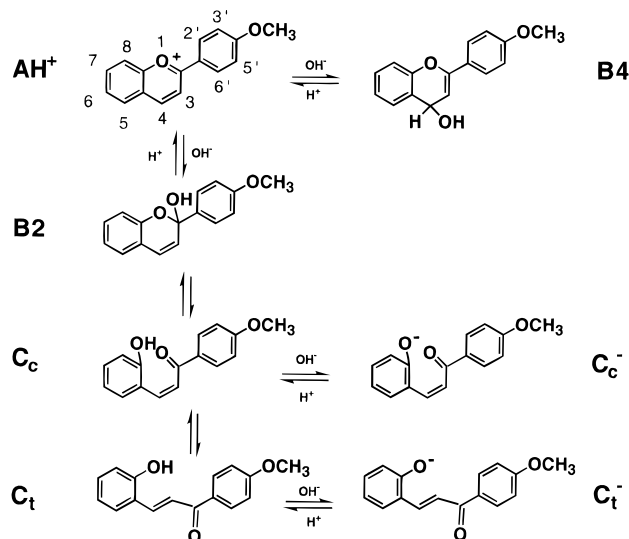

Figure 2. Absorption spectra in aqueous solution at 25 °C of **AH**⁺ at pH 1.0, **C_t** at pH 4.0, and a **B2/C_c** mixture at pH 7.0.

Scheme 1

often with quite dramatic color changes or color disappearance,[17−22] as in the case of the yellow 4′-methoxyflavylium ion which loses its color when dissolved in a neutral or basic solution.

A very careful spectral and kinetic investigation of the transformations undergone by the 4′-methoxyflavylium ion was performed by McClelland and Gedge.[19] By using the pH-jump technique, they found that as many as seven different species are involved, as transient or equilibrium compounds, depending on the experimental conditions (Scheme 1). The most important forms, as we will see later, are the strongly colored 4′-methoxyflavylium ion **AH**⁺ (λ_{max} = 435 nm, ϵ = 42000 M⁻¹ cm⁻¹) and the colorless *trans*-4′-methoxychalcone **C_t** (λ_{max} = 350 nm, ϵ = 18000 M⁻¹ cm⁻¹), whose absorption spectra are shown in Figure 2, together with the spectrum of the **B2** and **C_c** mixture (*vide infra*).

We have calculated the molar fraction distribution of the various species in aqueous solution at 25 °C as a function of pH by using the results obtained by McClelland and Gedge[19] and a previously described method for the elaboration of data

(16) Irie, M.; Miyatake, O.; Uchida, K.; Eriguchi, T. *J. Am. Chem. Soc.* **1994**, *116*, 9894.

(17) Brouillard, R.; Dubois, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 1359.

(18) Brouillard, R.; Delaporte, J. *J. Am. Chem. Soc.* **1977**, *99*, 8461.

(19) McClelland, R. A.; Gedge, S. *J. Am. Chem. Soc.* **1980**, *102*, 5838.

(20) (a) Brouillard, R. In *The Flavonoids, Advances in Research*; Harborne, J. B., Ed.; Chapman and Hall: London 1988; p 525. (b) Brouillard, R. In *Anthocyanins as food colors*; Markakis, P., Ed.; Academic Press: New York, 1982; Chapter 1.

(21) Figueiredo, P.; Lima, J. C.; Santos, H.; Wigand, M.-C.; Brouillard, R.; Pina, F. *J. Am. Chem. Soc.* **1994**, *116*, 1249.

(22) Pina, F.; Benedito, L.; Melo, M. J.; Parola, A. J.; Bernardo, M. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1693.
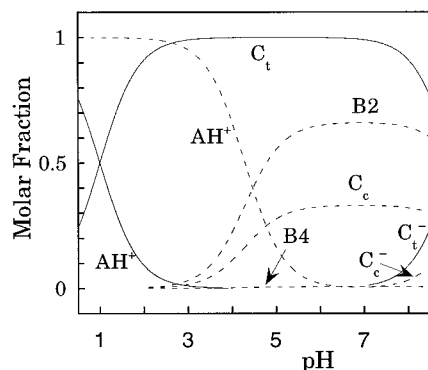
Figure 3. Molar fraction distribution in aqueous solution at 25 °C as a function of pH. The structures of C_t, C_t^-, C_c, C_c^-, **B2**, **AH**$^+$, and **B4** are shown in Scheme 1. Solid lines refer to the species obtained at the thermodynamic equilibrium. Dashed lines refer to species obtained by bringing **AH**$^+$ solutions from pH 1 to higher pH values by the pH-jump technique or by exciting C_t solutions by flashlight. Such species reach a pseudoequilibrium in the second time scale and then undergo a very slow thermal reaction to C_t. The molar fractions were calculated by using the equilibrium constants reported and/or estimated in ref 19. For more details, see text.

concerning interconnected equilibria.[22] The thermodynamically stable form in the pH range 2–8 is the *trans*-4′-methoxychalcone, C_t, which, at higher pH, is transformed into its anion, C_t^- (Figure 3, solid lines). In strongly acidic solutions, **AH**$^+$ becomes thermodynamically stable; however, C_t cannot be converted to **AH**$^+$ because of the very large activation barrier which involves isomerization of C_t to the intermediate compound C_c (Scheme 1). Furthermore, a solution of **AH**$^+$ (as perchlorate salt), which can be easily prepared from the solid compound obtained through the acid condensation of salicylaldehyde and the 4′-methoxyacetophenone,[23] is almost indefinitely stable at room temperature below pH 3. Under such conditions a very large kinetic barrier prevents conversion of **AH**$^+$ to the thermodynamically stable C_t form via the hydrated (pseudobase) species **B2** and the C_c isomer (Scheme 1).

At higher pH, however, **AH**$^+$ is very reactive.[19] For example, starting from an aqueous solution of **AH**$^+$ at 25 °C and pH 1, a pH jump to pH 4.29 leads within a few seconds to a pseudoequilibrium consisting of 50% **AH**$^+$, 33.2% **B2**, 0.3% **B4** (which is a 4-hydroxy product), and 16.5% C_c (Figure 3, dashed lines). A much slower reaction follows (half-life 19.7 h), resulting in complete conversion to the thermodynamically stable form C_t.

At pH 8, **AH**$^+$ reacts mainly with solvent water[19] (half-life 0.44 s) to produce 64% **B4**, 24% **B2**, and 12% C_c, the last two being in equilibrium with each other (half-life of the equilibration, 7×10^{-5} s). This is followed by another fast reaction (half-life 66 s) in which **B4**, a product of kinetic control of the initial neutralization of **AH**$^+$, is converted via **AH**$^+$ to **B2** and C_c, yielding a pseudoequilibrated mixture of 66.3% **B2**, 33.1% C_c, and 0.6% **B4** (Figure 3, dashed lines). A much slower reaction (half-life 9.9 h) then occurs, resulting in complete conversion to C_t.

Photochemical Behavior. As described above, in the pH range 2–8 the colorless *trans*-4′-methoxychalcone (C_t) is the thermodynamically stable species, and therefore it is the final product of the transformations of the strongly colored 4′-methoxyflavylium ion (**AH**$^+$).

(23) Michaelis, C.; Wizinger, R. *Helv. Chim. Acta* **1951**, *34*, 1761.
(24) Maestri, M.; Ballardini, R.; Pina, F.; Melo, M. J. *J. Chem. Educ.* In press.
(25) Pina, F.; Melo, M. J.; Flamigni, L.; Maestri, M.; Ballardini, R. *New. J. Chem.* In press.
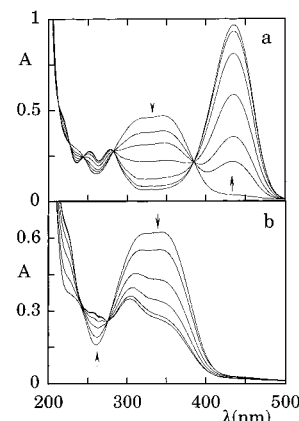

Figure 4. Spectral changes caused by continuous irradiation of an aqueous solution of C_t with 365-nm light: (a) pH 1.0, $[C_t] = 2.5 \times 10^{-5}$ M—the curves correspond to the irradiation times 0, 0.5, 1, 2, 4, 7, and 12 min; (b) pH 7.0, $[C_t]$ 3.2×10^{-5} M—the curves correspond to the irradiation times 0, 0.25, 1.5, 3, 6, and 10 min.

We have found that, as previously shown for other flavylium derivatives,[21,22] C_t can be converted into **AH**$^+$ by a photochemical reaction. As expected from the thermal behavior of the system, the photoreaction causes a transient or an almost permanent effect depending on temperature and pH of the irradiated solution. The results obtained by continuous and pulsed irradiation are described below.

(a) Continuous Irradiation. Continuous irradiation of 2.3 $\times 10^{-5}$ M aqueous solutions of C_t at pH 1.0 with 365-nm light was found to cause strong spectral changes, with five isosbestic points and formation of a very intense band in the visible region with maximum at 435 nm (Figure 4a). Analysis of the spectral changes showed that the photoreaction converts C_t into **AH**$^+$, without formation of sizable amounts of other products. The quantum yield of the photoreaction is 0.04, independent of the presence of dioxygen in solution. At pH 1.0, no back reaction takes place and irradiation with 434-nm light, corresponding to the maximum of the absorption band of **AH**$^+$ (Figure 2), does not cause any effect.

When irradiation of C_t was carried out at pH 4.0, the quantum yield of the photoreaction leading from C_t to **AH**$^+$ was unchanged, but the expected thermal back reaction of **AH**$^+$ to C_t was observed. The rate of the back reaction was found to increase with temperature, its activation energy determined to be 93 kJ mol^{-1} from an Arrhenius plot, at pH 4.0 and in the temperature range between 30 and 65 °C. Irradiation at pH 7.0 caused the spectral changes shown in Figure 4b. At this pH the disappearance of C_t does not cause any increase of absorbance in the visible spectral region, showing that **AH**$^+$ is not formed. Furthermore, the back reaction is very fast and complete disappearance of C_t cannot be observed. This is in full agreement with the expectations based on the data shown in Figure 3, which indicate that at pH 7.0 the pseudoequilibrated mixture of products is constituted essentially by the open C_c and closed **B2** *cis* forms. Their absorption spectrum, as is always the case for aromatic derivatives of ethylene,[26] is less intense and slightly blue-shifted compared to the spectrum of the *trans* form (Figure 2). Under such conditions, irradiation of the mixture with 313-nm light was found to cause the reverse *cis* → *trans* photoisomerization reaction with an apparent quantum yield of ca. 0.5 (based on the total light absorbed by C_c and **B2**).

We have also found that C_t and **AH**$^+$ exhibit intense fluorescence bands with λ_{max} at 430 and 530 nm, respectively

(26) Saltiel, J.; Sun, Y.-P. In *Photochromism—Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 3.
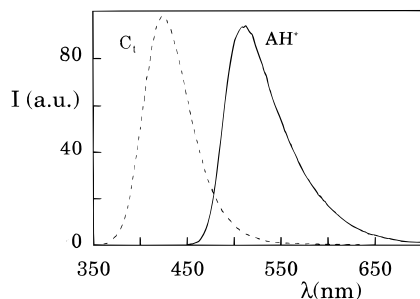
Figure 5. Fluorescence spectra in aqueous solution at 25 °C of **AH**$^+$ (pH 1.0) and **C$_t$** (pH 4.0).
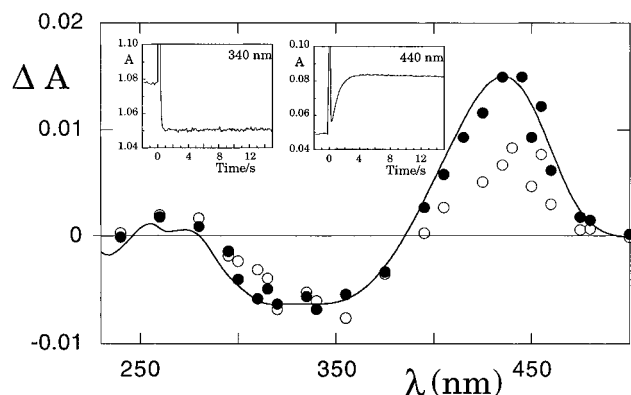

Figure 6. Differential spectra recorded after flash excitation of a 5.0 × 10^{-5} M aqueous solution of **C$_t$** at pH 3.0. The delay times are 1 (○) and 3 s (●). The full line is the final differential spectrum obtained after continuous irradiation. The insets show the absorbance *vs* time traces obtained at λ = 340 nm (where **C$_t$** shows a maximum and **AH**$^+$ a minimum) and at λ = 440 nm (where **C$_t$** shows a minimum and **AH**$^+$ a maximum).

Figure 7. Differential spectrum obtained 1 s after the flash for a 5.0 × 10^{-5} M aqueous solution of **C$_t$** at pH 7.0. The insets show the absorbance *vs* time traces obtained at λ = 340 nm (where **C$_t$** shows a maximum and **AH**$^+$ a minimum) and at λ = 440 nm (where **C$_t$** shows a minimum and **AH**$^+$ a maximum).

Figure 8. Behavior of a 1.0 × 10^{-5} M aqueous solution of **C$_t$** at pH 3.0 and 60 °C under 365 nm light excitation (dashed lines) followed by dark periods (full lines).

(Figure 5). The fluorescence lifetime is shorter than 1 ns in both cases. It is worth noting that the occurrence of the above-described thermal and photochemical reactions can also be followed by fluorescence measurements.

(b) Pulsed Irradiation. Previous work showed that flash photolysis is a powerful technique for investigating the kinetics of conversion of the various forms of flavylium ions.[24,25] Kinetic data were obtained by using a simple flash photolysis apparatus as previously decribed[24] and used to complement and/ or replace those available with a more traditional pH-jump technique.[19]

Flash photolysis experiments were performed on a 6.0 × 10^{-5} M aqueous solution of **C$_t$** at 25 °C and pH 3.0 or 7.0 by excitation through a previously described[24] apparatus with a time resolution of the order of 0.5 s. After flash excitation, absorbance *vs* time traces were recorded at several wavelengths in the spectral region 250−500 nm. The differential spectra obtained after 1 and 5 s for the solution at pH 3.0 are shown in Figure 6. The bleaching in the 300−400-nm region corresponds to the disappearance of **C$_t$**, and the strong absorbance in the 400−500-nm region corresponds to the formation of **AH**$^+$. As is better shown by the absorbance *vs* time traces reported in the two insets of Figure 6, **C$_t$** disappears within the time scale of the flash, but such disappearance of **C$_t$** does not lead directly to **AH**$^+$. One or more intermediate products are formed (**C$_c$** and **B2** according to Scheme 1), which convert completely to **AH**$^+$ in a few seconds. The differential spectrum observed after 1 s for a pH 7.0 solution is shown in Figure 7. Under these conditions the decrease of absorbance in the 300−400-nm region, corresponding to the disappearance of **C$_t$**, is not accompanied by an increase in absorbance in the visible region
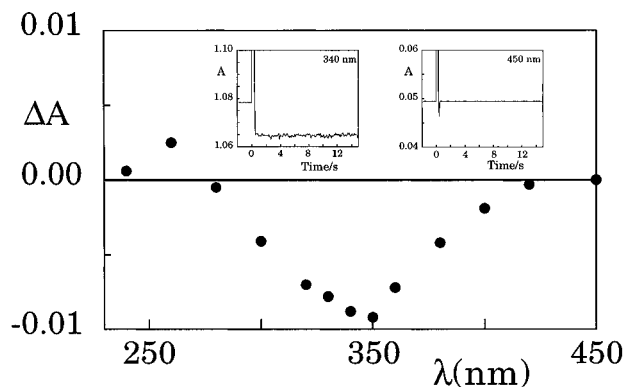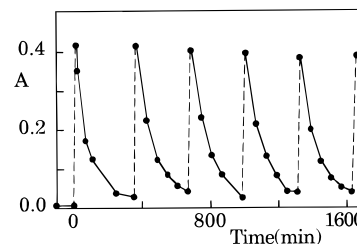
because at pH 7.0 **AH**$^+$ is not stable and the main products of the photoreaction are **B2** and **C$_c$** (Figure 3).

None of the thermal and photochemical processes observed are affected by the presence of oxygen in the solution, within our experimental conditions. In order to check the degree of reversibility of the observed reactions, a 1.0 × 10^{-5} M aqueous solution of **C$_t$** at pH 3.0 and 60 °C was irradiated at 365 nm. After 20 min of irradiation, which causes the formation of the colored form **AH**$^+$, the solution was kept in the dark, at 60 °C, until a practically complete bleaching of the visible absorption of **AH**$^+$ had occurred. Then, light excitation was again performed. The changes in absorbance at 435 nm obtained by repeating these light/dark cycles five times are shown in Figure 8. As one can see, the degree of reversibility of the system is quite satisfactory.

In conclusion, the photochemical behavior is in very good agreement with the behavior observed by pH-jump experiments. Although **C$_c$** is obviously the primary product of flash excitation, the observed species and their survival time *(from seconds to years)* before going back to the thermodynamically stable form **C$_t$** depend on temperature and pH.

"Write−Lock−Read−Unlock−Erase" Cycle. The thermal and photochemical behavior of the system under examination can be summarized by using the energy level diagram of Figure 9. The rate constants of the thermal reactions are those measured by McClelland and Gedge.[19]

As happens in general for the *trans* isomers of substituted ethylene-type compounds[26] and as previously found for other *trans*-chalcone derivatives,[24,25] the thermodynamically stable form of the system, **C$_t$**, undergoes a *trans* → *cis* photoisomerization. Since we do not detect quenching by dioxygen, the photoisomerization reaction must proceed trough a short-lived excited state, presumably a singlet state. The **C$_c$** isomer, which is the primary photoproduct, undergoes a slightly downhill ring closure process which leads to the pseudobase **B2** (Figure 9,
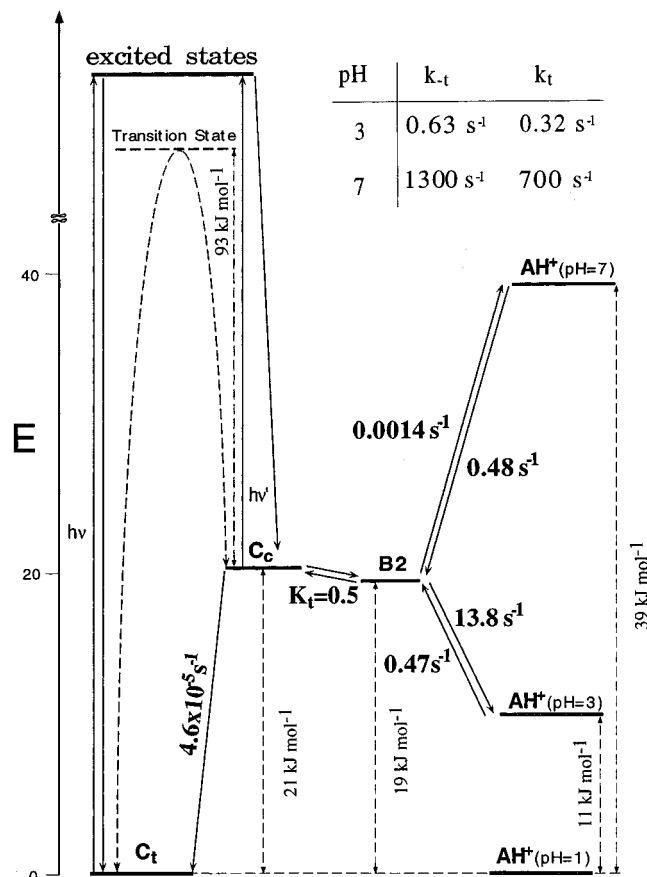
Figure 9. Energy level diagram for the species involved in the photochromic behavior of C_t at pH 1.0, 3.0, and 7.0. The energies of C_t, C_c, and **B2** do not depend on pH. The species C_t^- and C_c^- (Scheme 1) are not shown because they are not formed in the pH range 1−7 (Figure 3). The species **B4** is also ignored since it is a product of kinetic control of the initial neutralization of AH^+ which reversibly reconverts back to AH^+. The energy difference between C_t and C_c was calculated on the basis of a lower limit of 5000 for the equilibrium constant of the thermal isomerization reaction.[19]

Scheme 1). Since the thermodynamic stabilization of **B2** *vs* C_c is only 2 kJ/mol, at 25 °C the equilibrium $[C_c]/[B2]$ ratio has a value of about 1/2. At this stage, the behavior of the system depends on the pH of the solution. At pH > 7, **B2** is stable toward OH^- elimination, and the C_c and **B2** mixture goes back to C_t by a slow thermal reaction (rate constant *ca.* 0.07 h^{-1}, activation energy 93 kJ/mol). Under such conditions, the *cis* → *trans* back photoisomerization can also be performed. In acid medium, **B2** reacts to give the strongly colored 4′-methoxyflavylium ion (AH^+, Figure 9 Scheme 1). At pH 1.0, the stabilization of AH^+ *vs* **B2** amounts to ca. 19 kJ/mol, so that the thermal back conversion to the thermodynamically stable C_t form becomes extremely slow ($t_{1/2}$ = 815 days at 25 °C). At the same time, the *cis* → *trans* back photoisomerization cannot be observed because the concentration of C_c is negligibly low.

From the above discussion it is clear that at pH > 7 C_t behaves as a (poor) photochromic system of the type schematized in Figure 1b, as is the case for many *trans−cis* isomer couples.[26] At lower pH values, however, the situation is much more interesting since the system follows the scheme of Figure 1c with C_t, $C_c/B2$, and AH^+ playing the roles of **X**, **Y**, and **Z**, respectively, and an acid−base stimulus playing the role of the redox stimulus. Therefore C_t can form the basis for an optical memory system with multiple storage and non-destructive readout capacity through a write−lock−read−unlock−erase cycle.
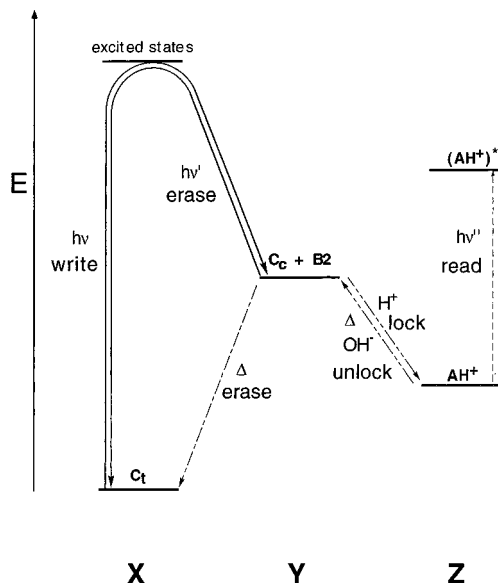

Figure 10. Schematic energy level diagram for the species involved in the *write−lock−read−unlock−erase* system.

For a simple description of the device-like behavior of the system, we can make reference to the scheme in Figure 10 (which refers to a solution at pH 3.0), and to Figure 1c: (i) a stable form ($C_t \equiv X$) can be photochemically converted (*write*) into a form ($C_c/B2 \equiv Y$) that can be reconverted back either thermally or on optical reading; (ii) by a second stimulus (addition of acid, which can also be present from the beginning without perturbing the behavior of the system), $C_c/B2 \equiv Y$ can be converted into a kinetically inert form $AH^+ \equiv Z$ (*lock*); (iii) the $AH^+ \equiv Z$ form shows a spectrum clearly distinct from that of $C_t \equiv X$ and is photochemically inactive, so that it can be optically detected (*read*) without being erased; (iv) by addition of base, $AH^+ \equiv Z$ can be reconverted into $C_c/B2 \equiv Y$ (*unlock*); and (v) $C_c/B2 \equiv Y$ can be thermally or photochemically reconverted into the initial $C_t \equiv X$, form (*erase*).

Although the resistance to fatigue has yet to be more deeply explored and the locking time of the written information bit is not indefinite (at 25 °C and pH 3.0, the half-life of the back reaction from AH^+ to C_t is *ca.* 8 days), this system is interesting. It is also likely that, among the great number of the known flavylium ions, one can find a species displaying even better properties.

Experimental Section

Materials. The synthetic 4′-methoxyflavylium (AH^+) perchlorate[23] and *trans*-4′-methoxychalcone (C_t)[27] were prepared according to methods described in the literature. All other chemicals used were of the best available commercial grade.

A useful procedure for preparing a solution of C_t is the following. A solution of AH^+ perchlorate is dissolved in water, 1 M NaOH is added until the pH reaches 12, and the solution is kept in the dark for 2 days. Under these conditions, AH^+ is completely converted into C_t^-. Solutions of C_t at the desired pH are then obtained by addition of the necessary amount of $HClO_4$ or proper buffer solution (citrate). A solution of C_t at pH 3.0 was also obtained by dissolving AH^+ perchlorate at pH 3.0 and keeping the solution at 60 °C for 7−8 h. The transformation of AH^+ into C_t was followed by absorption spectroscopy in the UV/vis region.

Photochemical Experiments. In continuous irradiation experiments, light excitation was performed by a medium-pressure mercury lamp. Interference filters (Oriel) were used to select a narrow spectral range with λ_{max} 313, 365, or 434 nm. The irradiated solution was contained

(27) Herstein, F.; von Kostanecki, S. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 318.

in a 1-cm spectrophotometric cell. The intensity of the incident light $(1.1 \times 10^{-7}$ einstein/min at 313 nm, 5.1×10^{-7} einstein/min at 365 nm, and 2.0×10^{-6} einstein/min at 434 nm) was measured by the ferrioxalate actinometer.[28]

The flash spectroscopy apparatus capable of acquiring 10 absorbance values per second has been described elsewhere.[24]

(28) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

JA9704646