

Photochromism of the Synthetic 4',7-Dihydroxyflavylium Chloride

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Abstract: The synthetic compound 4',7-dihydroxyflavylium chloride shows an interesting photochromic effect at moderately acidic pH values. Pale yellow solutions of this compound, equilibrated in the dark at pH 3.4, become bright yellow upon irradiation with 313-nm light. Switching off the light, gives back the initial pale yellow solution. Photochemical methods, ¹H NMR, and molecular orbital calculations were used to elucidate this photochromic behavior. In solutions equilibrated in the dark (pH < 5.7), the existence of two main species in equilibrium is demonstrated: the colored flavylium cation and the colorless *trans*-chalcone. Freshly prepared solutions of this compound at pH 6.2 reveal the existence of another colored form, the quinonoidal base, which reacts thermally to yield *trans*-chalcone. An analogous reaction takes place in freshly prepared solutions at pH 3.4: the flavylium cation is partially converted into *trans*-chalcone. The extent of such conversion is pH dependent and nearly complete at pH 6.2. Irradiation of *trans*-chalcone at the wavelength of 313 nm partially gives back the initial colored form, with concomitant formation of small amounts of photodegradation products. The turnover of the photochromic reaction is greater at pH 3.4 than at pH 6.2. The photochromism is explained on the basis of a *trans*-*cis* photoisomerization. In fact the relative stability of the two chalcone isomers is reversed in the excited state, as predicted from molecular orbital calculations.

Introduction

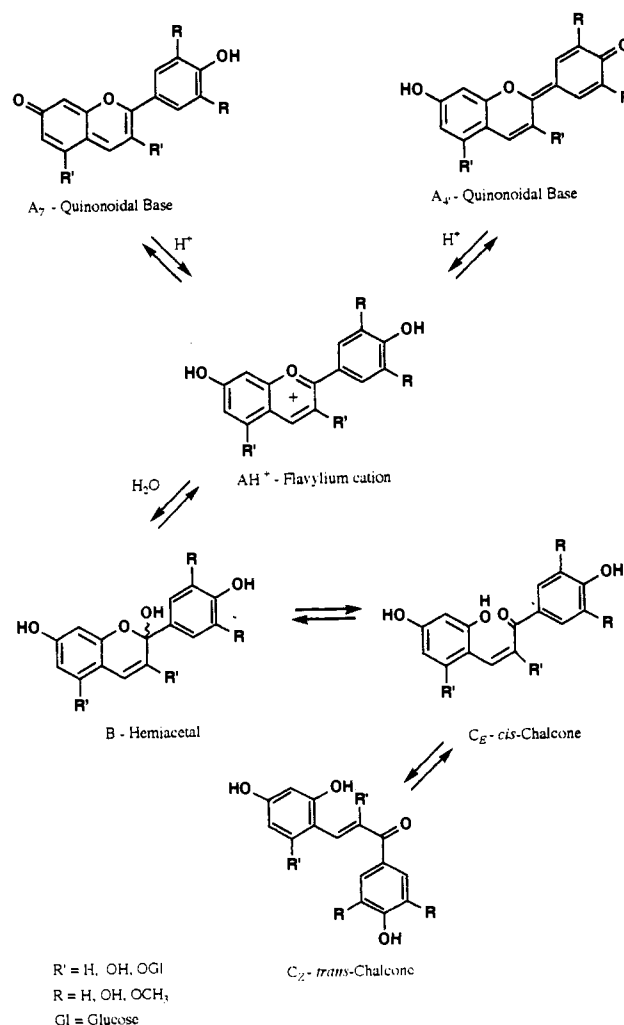
The most significant molecules with a flavylium structure, the anthocyanins, are very important plant pigments, conferring to many flowers and fruits their diverse colors.¹ In spite of the interest in natural or synthetic compounds of this family,² namely as food additives, less attention has been lent to their photochemical properties.

Natural or synthetic flavylium salts in slightly acidic aqueous solutions undergo structural transformations which result in the formation of quinonoidal bases, hemiacetal, and chalcone forms, as depicted in Scheme 1.³

Recently we studied at length the fluorescence spectra and decays⁴ of the natural anthocyanin malvin (3,5-diglucosylmalvidin) as well as its photodegradation.^{5,6} Moreover, the multiple equilibria of malvin in moderately acidic aqueous solutions were elucidated by one- and two-dimensional ¹H NMR.⁷ Using this technique, apart from the flavylium cation, two hemiacetal forms and both *cis* and *trans* forms of chalcone were firmly characterized.

The present work extends these studies to the synthetic compound 4',7-dihydroxyflavylium chloride (Chart 1). Unlike natural anthocyanins and its aglycons, this synthetic salt exhibits an intense photochromic effect, which was characterized using the *supra* mentioned techniques.

Scheme 1



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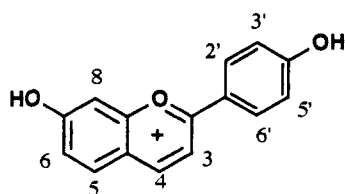
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Chart 1



4',7-dihydroxyflavylium cation

Experimental Section

Materials. The synthetic flavylium salt was prepared according to a published procedure.⁸ All other chemicals used were of analytical grade.

pH Measurements. The pH was measured with a Metrohm 713 pH meter. The pH of the solutions was adjusted by addition of HCl (pH < 2) or buffer solutions for higher pH values, except for NMR experiments where a different procedure was used (see below).

Absorption Spectroscopy. Spectra were recorded on a Perkin-Elmer $\lambda 6$ spectrophotometer. A constant temperature of 20 °C in the quartz cell ($d = 1$ cm) was obtained by use of a Haake water-thermostated bath.

Molecular Orbital Calculations. Calculations were performed in a MicroVax 3100 computer, using the AM1 method.⁹

Photochemical Experiments. Light excitation was carried out using a medium pressure Hg lamp; the irradiation wavelengths were isolated with interference filters (Oriel). The incident light intensity was measured by ferric oxalate actinometry.¹⁰ Estimated errors for quantum yields are 10%. Semipreparative irradiation for HPLC injection was performed in a 100-mL photochemical reactor from Applied Photophysics, equipped with a medium-pressure Hg lamp.

HPLC Apparatus. The HPLC equipment consisted of a L-6200 A Merck-Hitachi intelligent pump, with a Rheodyne 7125 injection valve, fixed volume loop of 20 μ L. The effluent was monitored by means of a diode array UV-visible detector Merck-Hitachi L-4500. Quantitative measurements were made with a Merck-Hitachi D-6000 interface connected to a computing integrator.

The chromatographic assays were performed with a LiChrospher 100 RP-8 column (E. Merck, Darmstadt), particle size 5 mm, 250 mm \times 4.6 mm i.d. The mobile phase was constituted by A (aqueous solution of HClO₄ pH = 1.5) and B (methanol) in a gradient mode: 2 min at B% = 2, in 10 min B% = 20, 15 min at B% = 20, in 60 min B% = 60, 8 min at B% = 60, in 10 min B% = 2, and 5 min at B% = 2. The flow was 1.3 mL/min. A LiChrosphere RP-18, 4 mm \times 4 mm, particle size 5 mm (E. Merck, Darmstadt) was used as a guard column.

Sample Preparation for NMR. 4',7-Dihydroxyflavylium chloride was dissolved in DCl (ca. 0.1 M) to a final concentration of 0.6 mM; the pH of the starting solution was typically 0.8 and, when required, was changed by addition of small aliquots of 1 or 0.1 M NaOD. pH measurements were performed in the NMR tube using an Ingold glass electrode, and quoted pH values are direct meter readings without correction for the isotope effect¹¹ and are denoted with an asterisk.

NMR Spectroscopy. One- and two-dimensional ¹H NMR spectra were obtained with either Bruker AMX-500 or AMX-300 spectrometers operating at 500.13 and 300.13 MHz, respectively. One-dimensional spectra were obtained with presaturation of the residual HDO resonance for 3 s. The following conditions were used: 50° flip angle, 7.3 s total recycle delay, and 64 K acquisition data points. Spectra were processed with 0.4 or 1 Hz line-broadening prior to Fourier transformation. Chemical shifts are referenced to the methyl resonance of ethanol (present in small amounts as contaminant) quoted at 1.2 ppm. Two-dimensional spectra were acquired over 10 ppm bandwidth, collecting 2048(t_2) \times 512(t_1) data points. Spectra were recorded in the phase-sensitive mode by the time-proportional phase incrementation method and transformed to produce real matrices consisting of 1024 \times 1024 data points. Nuclear Overhauser effect spectroscopy (NOESY) was performed according to

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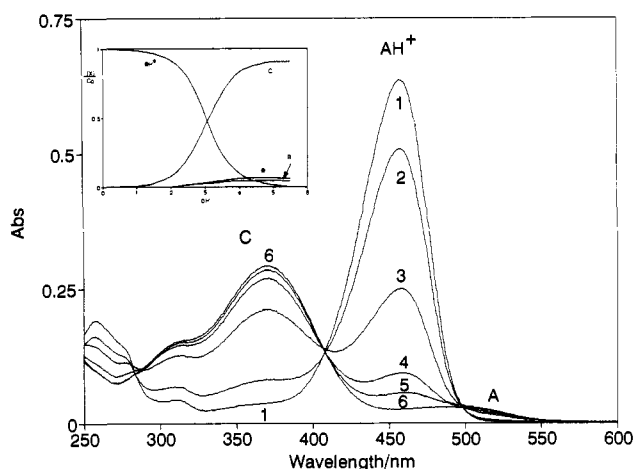


Figure 1. Absorption spectra of dark equilibrated aqueous solutions of 4',7-dihydroxyflavylium chloride (2×10^{-5} M) as a function of pH: 1, pH 1.0; 2, pH 2.3; 3, pH 3.2; 4, pH 3.8; 5, pH 4.3; 6, pH 5.7. Inset: equilibrium distribution of the AH⁺, B, C, and A forms.

ref 12, using mixing times of 0.5 or 1 s. Correlation spectroscopy (COSY) was run according to the literature.^{13,14}

Results

Structural Transformation in the Ground State. (a) Equilibrated Solutions. Aqueous solutions of the synthetic flavylium salt 4',7-dihydroxyflavylium chloride, upon reaching the equilibrium in the dark, exhibit pH dependent absorption spectra (Figure 1), as previously reported.^{15,16} As the pH increases from 0 up to 5.7, the characteristic flavylium cation (AH⁺) absorption band (458 nm) decreases, while the absorption of the chalcone (C) at 370 nm increases as well as a small absorption band at 495 nm attributed to the quinonoidal base (A). The inset of Figure 1 shows the equilibrium distribution as a function of pH for the following four species detected in solution:¹⁷ (i) the two main species, flavylium cation and chalcone, and (ii) the two minor species, quinonoidal base and hemiacetal (B).

¹H NMR spectroscopy allows the assignment of the resonances due to the flavylium cation. A spectrum was performed on a sample at pH* ca. 0.8 where this is the only detectable form in solution (spectrum A in Figure 2). Resonances due to protons 2' + 6' and 3' + 5' at 8.37 and 7.16 ppm (Chart 1) are immediately recognized from the expected relative intensity of two protons. Resonance due to proton 6 is identified from the displayed coupling pattern to proton 5 ($J = 8.8$ Hz) and to proton 8 ($J = 2.3$ Hz); the observation of a 2.3-Hz splitting in the resonance at 7.53 ppm allows its assignment to proton 8. The full assignment of the spectrum was achieved by running COSY (Figure 3) and NOESY (not shown) spectra. In the NOESY spectrum there is a clear connectivity between the two proton doublet at 8.37 ppm and the single-proton intensity doublet at 8.23 and this identifies these resonances to protons 2' + 6' and 3, respectively. All the remaining assignments follow directly from the clear connectivities observed in the COSY spectrum (Figure 3) and are shown in Table 1.

(b) Nonequilibrated Solutions. Aqueous solutions of 4',7-dihydroxyflavylium chloride at pH 3.4 (immediately upon dissolution in the dark) undergo spectral modifications (Figure

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Table 1. Chemical Shifts (δ /ppm) and Scalar Couplings (J /Hz) of the Three Forms of 4',7-Dihydroxyflavylium Chloride by ^1H NMR in D_2O at 27 °C

	flavylium ^a		quinonoidal base ^b		<i>trans</i> -chalcone ^b	
	δ	J	δ	J	δ	J
H _{2'} + H _{6'}	8.37	8.9	8.13	8.9	7.99	8.8
H _{3'} + H _{5'}	7.16	8.9	7.05	8.9	7.02	8.8
H ₃	8.23	8.8	7.76 ^c	8.2	7.61	15.7
H ₄	9.03	8.8	8.42 ^c	8.2	7.94	15.7
H ₅	8.13	8.8	7.57	8.2	7.62	8.8
H ₆	7.46	8.8	6.97	8.2	6.54	8.8
		2.3		2.1		2.3
H ₈	7.53	2.3	6.84	2.1	6.45	2.3

^a pH* 0.8. ^b pH* 3.4. ^c Tentative specific assignments.

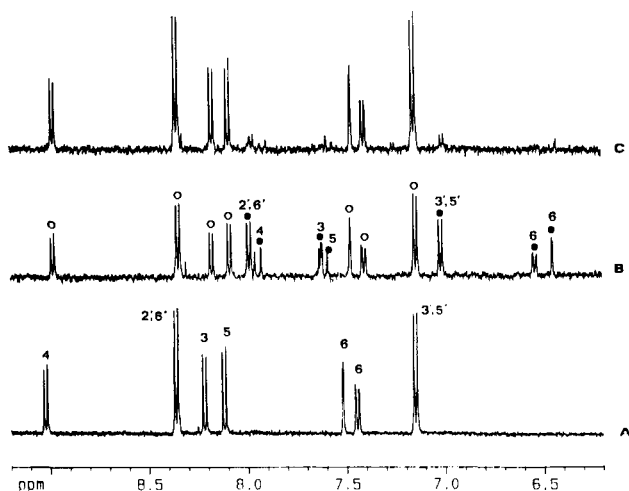


Figure 2. 500-MHz ^1H NMR spectra of 0.6 mM 4',7-dihydroxyflavylium chloride in D_2O at 27 °C: (A) pH* 0.8, (B) same solution with pH* adjusted to 3.4, spectrum acquisition started 3 h after the pH change; and (C) spectrum of the same sample of (B) acquired immediately after 30 min of illumination. Spectra were processed with 0.4 Hz line broadening prior to Fourier transformation. Resonances are indicated with the following symbols: (O) flavylium cation and (●) *trans*-chalcone.

4a) which reflect predominantly the partial transformation of the flavylium cation into chalcone, until attaining the equilibrium concentration for this pH value, as depicted in the inset of Figure 1. An analogous experience carried out at pH 6.2 (Figure 4b) shows an initial spectrum due to the quinonoidal base absorption, which decreases to give a final absorption spectrum, characteristic of the chalcone form ($\lambda_{\text{max}} = 370$ nm). A residual absorption of the quinonoidal base ($\lambda_{\text{max}} = 495$ nm) reflects the partial conversion of A into C, according to the results shown in the inset of Figure 1.

These results were firmly confirmed by proton NMR. When the pH* of a sample containing flavylium cation is increased from 0.8 to 3.4 and spectra were run consecutively for approximately 3 h, the intensities of the peaks due to the flavylium cation decrease with time, and new resonances increase concomitantly. The last spectrum of the series is shown in Figure 2 trace B. It is clear that, in addition to the flavylium cation, only one other form is present in solution. Assignment of the resonances due to this second form is also straightforward from NOESY and COSY spectra following strategy identical to that used for the assignment of the flavylium form; the corresponding chemical shifts are also shown in Table 1. The NOESY spectrum of a similar sample equilibrated at pH* 3.4 revealed connectivities between the resonances belonging to each form, but no cross peaks due to interspecies chemical exchange were detected, a result indicating that the rate of interconversion is very slow in the NMR time scale. The resonances of the new form present in Figure 2 spectrum B were assigned to *trans*-chalcone based on the following reasoning: the scalar coupling constant between protons 3 and 4 is 8.8 Hz in the flavylium form and has a similar

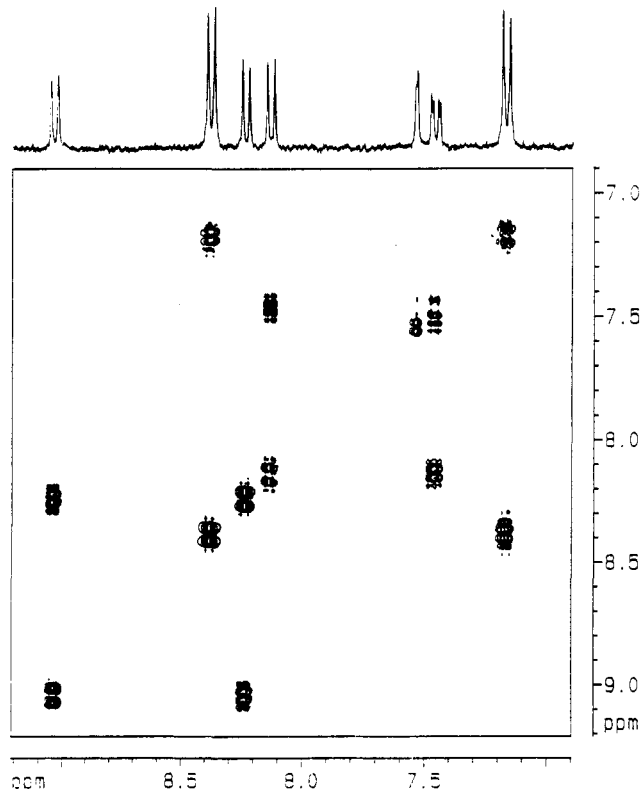


Figure 3. Phase-sensitive COSY spectrum (300 MHz) of a 0.6 mM 4',7-dihydroxyflavylium chloride in D_2O at 32 °C and pH* 0.8. Before transformation, the data were multiplied by sinebell window functions in both dimensions.

value (8.2 Hz) in the quinonoidal base (see below) but increases to 15.7 Hz in this new form; since it is well established that for unsaturated systems $^3J_{\text{trans}}$ is always higher than $^3J_{\text{cis}}$, it is concluded that there is a change in the configuration around the C₃-C₄ bond, going from *cis* to *trans*. Thus, NMR clearly shows that, upon increasing the pH* to 3.4, the flavylium form is converted in the dark into the *trans*-chalcone.

Photochemical Reactivity. Solutions of 4',7-dihydroxyflavylium chloride at pH 1.0 are stable upon standing for several months. Irradiation of these solutions with incident light of 313 nm results in the disappearance of the flavylium cation with a quantum yield of 1.5×10^{-4} . The photodegradation kinetics is followed by HPLC. The initial chromatogram shows a peak attributed to the flavylium cation (retention time 42 min); this peak decreases with irradiation time, while three new peaks appear. Those peaks are identified as (i) 4-hydroxybenzoic acid (retention time 14 min), (ii) 4-hydroxybenzaldehyde (retention time 15 min), and (iii) 2,4-dihydroxybenzaldehyde (retention time 17 min).

The photodegradation of 4',7-dihydroxyflavylium chloride shows a similar behavior to that observed for the aglycons of natural anthocyanins.⁵ The molecule is cleaved into two moieties, one with the structure of ring A, 2,4-dihydroxybenzaldehyde,

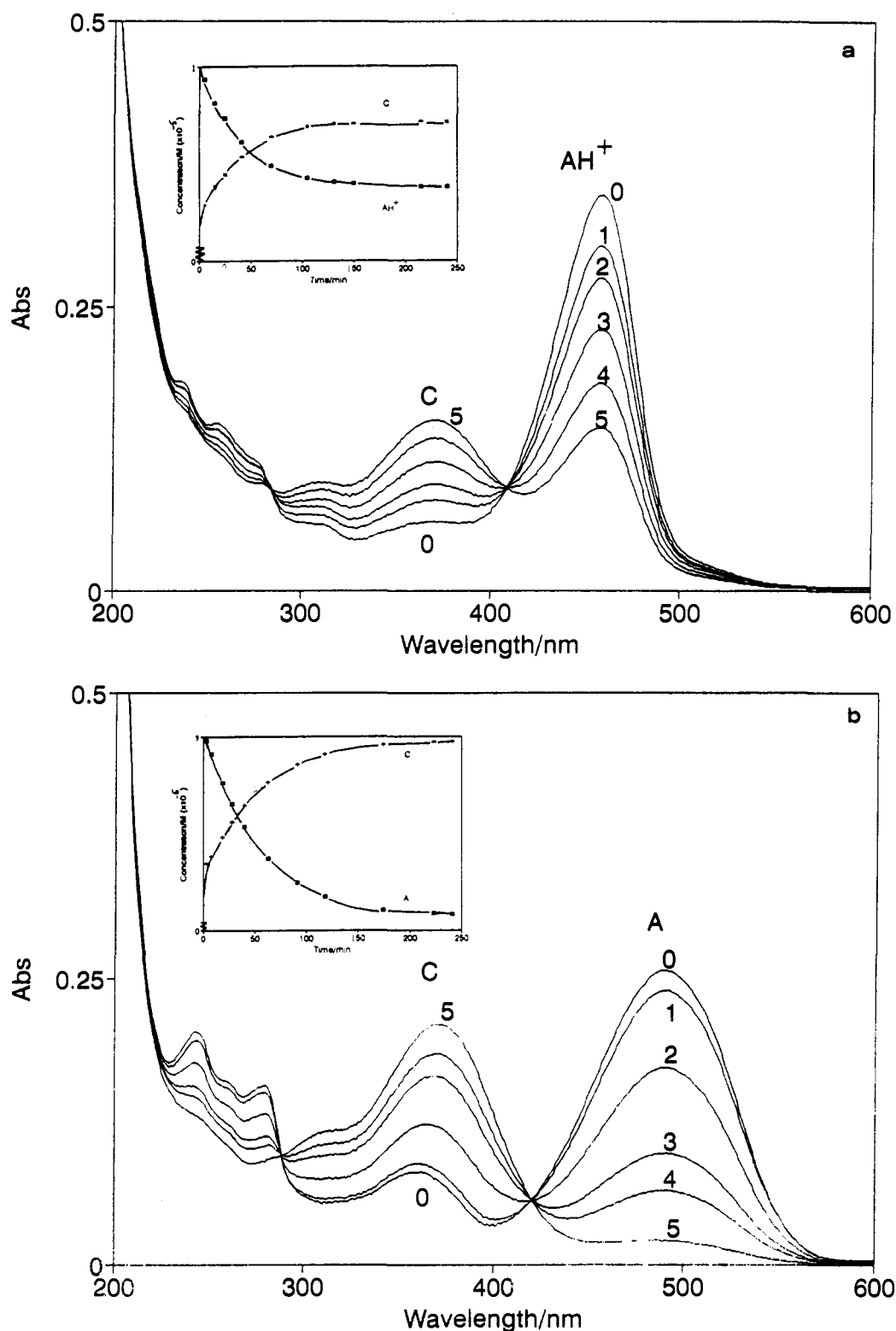


Figure 4. (a) Thermal evolution of 4',7-dihydroxyflavylium chloride (10^{-5} M, pH 3.4, $T = 20$ °C). 0, 5 min; 1, 15 min; 2, 25 min; 3, 41 min; 4, 70 min; and 5, 240 min. Inset: plot of the concentration vs time for the thermal reaction. (b) Thermal evolution of 4',7-dihydroxyflavylium chloride (10^{-5} M, pH 6.2, $T = 20$ °C). 0, 3 min; 1, 8 min; 2, 28 min; 3, 63 min; 4, 91 min; and 5, 241 min. Inset: plot of the concentration vs time for the thermal reaction.

and the other with the structure of ring B, 4-hydroxybenzaldehyde, and its oxidation product 4-hydroxybenzoic acid.

At this pH value no postphotochemical dark reactions were observed.

Excitation at the irradiation wavelength of 436 nm (first singlet of the flavylium cation) gives no spectral modifications, as reported for natural anthocyanins.⁶

Photochromic Properties. Irradiation of preequilibrated solutions of 4',7-dihydroxyflavylium chloride (pH 3.4), at the

wavelength of 313 nm, gives rise to an increase in the flavylium absorption (Figure 5a). The quantum yield for flavylium recovery, calculated on the basis of the light absorbed by the *trans*-chalcone, decreases with irradiation time, as depicted in the inset of Figure 5b. Extrapolation for the initial irradiation time allows to estimate a quantum yield of 0.1 for this reaction. The photochemical recovery of the colored flavylium cation form competes with the thermal conversion of flavylium into chalcone, which explains the decrease of quantum yield with time. The sequence of photo-

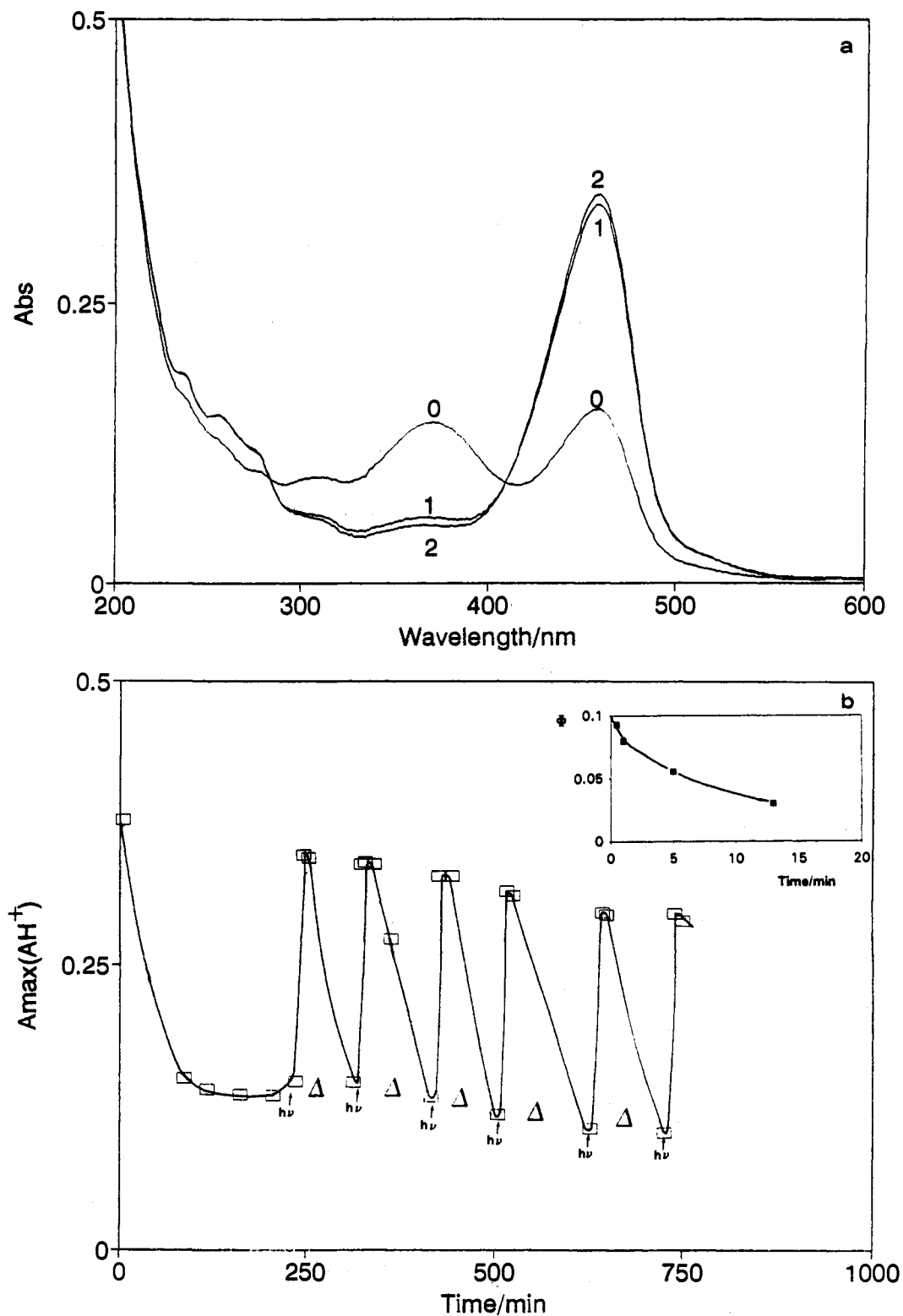


Figure 5. (a) Changes in the absorption spectra of 4',7-dihydroxyflavylium chloride (10^{-5} M, pH 3.4, $T = 20$ °C) reflecting the effect of photoisomerization from C_{trans} to C_{cis} . Since C_{cis} is in fast equilibrium with the hemiacetal form, which is also in fast equilibrium with the colored flavylium form, the result of the irradiation is an increase in the flavylium cation absorption (for details see text and Figure 2, curve C). 0, upon equilibration in the dark at pH = 3.4; 1, the same solution upon 8 min of irradiation; and 2, upon 16 min of irradiation. (b) Photochromic cycles consisting in the sequences of thermal equilibration followed by irradiation at 313 nm (10^{-5} M, pH 3.4, $\lambda_{irr} = 313$ nm, $T = 20$ °C).

chemical reaction, followed by thermal dark reaction, defines a photochromic system, whose efficiency is depicted in Figure 5b.

The same photochromic effect was detected for irradiation with light of 436 nm, although the quantum yield of flavylium recovery is substantially lower (10^{-3}). At the irradiation wavelength of 546 nm the quantum yield for the same reaction is smaller than 10^{-4} .

The effect of irradiation at 313 nm was also monitored by NMR. Upon illumination of a solution thermally equilibrated in the dark, at pH* 3.4, the *trans*-chalcone (Figure 2, trace B) is converted into flavylium as demonstrated in spectrum C of Figure 2. Once in the dark, slow transformation of flavylium back into *trans*-chalcone occurs, and again no additional form was detected by NMR under these experimental conditions.

Table 2. Thermodynamic Constants for the *C_{cis}* and *C_{trans}* Isomers of 4',7-Dihydroxyflavylium Chloride Obtained by Modulation with the AM1 Method

	DH _f ⁰ <i>C_{cis}</i> (kcal·mol ⁻¹)	DH _f ⁰ <i>C_{trans}</i> (kcal·mol ⁻¹)	DH ⁰ _{isom} (kcal·mol ⁻¹)	K _{isom}	% <i>C_{cis}</i>	% <i>C_{trans}</i>
ground state	-68.1	-71.3	-3.2	407	0.25	99.75
excited state	15.0	16.5	1.6	0.7	58	42

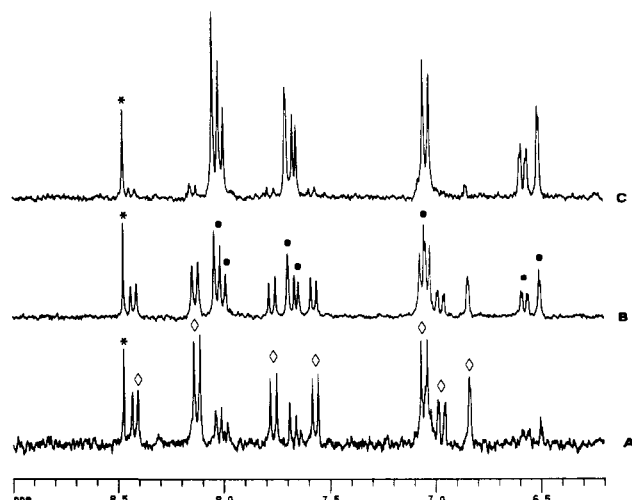


Figure 6. 300-MHz ¹H NMR spectra of 4',7-dihydroxyflavylium chloride in D₂O at 32 °C. The compound was dissolved in approximately 0.1 M DCl, and the pH* of this solution quickly increased to 5.9 with 1 M NaOD. Spectra were acquired at different times following this pH shock: (A) spectrum acquired for 9 min and starting immediately after the pH change, (B) acquisition started 17 min following pH shock, and (C) acquisition started at approximately 2.5 h following pH shock. Resonances due to the quinonoidal base are indicated with \diamond and those due to *trans*-chalcone are labeled with \bullet ; degradation product *.

At pH 6.2 the photochromic system is once more operative. Irradiation of the thermally equilibrated solutions at pH 6.2 with light of 313 nm, produces a recovery of the quinonoidal base, with a quantum yield of the order of 10⁻³. The turnover of the cycle at this pH value is much smaller than at the former. Upon irradiation at the wavelength of 546 nm no recovery reaction was observed.

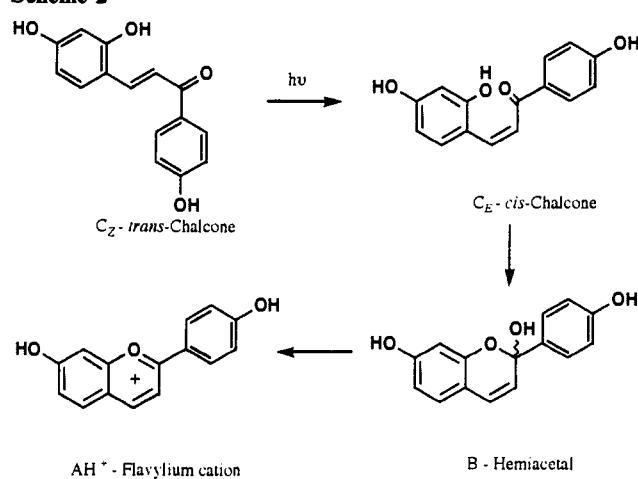
This different pattern is confirmed by NMR. When the pH* of a sample of flavylium cation was rapidly increased from 0.8 to 5.9 (Figure 6), significant precipitation occurs, but the first spectrum run after the pH shock (spectrum A in Figure 6) is dominated by resonances assigned to the quinonoidal base (Table 1), which decrease with time to originate the resonances due to the *trans*-chalcone form (spectra B and C in Figure 6). Assignment of resonances due to the quinonoidal base is made by comparison with the firm assignments made for the other two forms.

Discussion

Molecular Orbital Calculations. In order to rationalize the above described photochromic effect, the formation enthalpies for the *cis*- and *trans*-chalcones in the ground and excited states were calculated using the AM1 method (Table 2). Assuming no significant changes in the solvation enthalpy for the two isomers, an approximate value for the *cis*-*trans* isomerization enthalpy was obtained, both for the ground and excited states (Table 2).

This result predicts a much more stable ground state for the *trans* isomer (more than 99% according to Table 2), in agreement with the NMR observation of only one chalcone isomer (*trans*) in contrast with the results for two natural anthocyanins [malvin⁷ and oenin (3-glucosylmalvidin), Houbiers, C.; Santos, H. *unpublished results*] where both the *trans* and *cis* isomers coexist. For the excited state an inversion of the relative stability of the two isomers was calculated. On the other hand, using the experimental value of the *cis*-*trans* isomerization entropy obtained

Scheme 2



for malvin,⁷ 3.5 cal mol⁻¹ K⁻¹, an approximate value for the *cis*-*trans* equilibrium constants in the ground and excited states can be calculated as well as the relative concentrations of the two isomers with respect to the total amount of chalcone (*cis* and *trans*), also shown in Table 2.

These data show an important change in the relative concentration of the chalcone isomers when the ground state and the first excited singlet state are compared, with the *cis* isomer existing in significant amounts only in the excited state.

The photochromic effect can thus be explained on the basis of a photoisomerization of *trans*- to *cis*-chalcone, which rapidly cyclizes to give the pyrylium ring structure characteristic of the flavylium cation. A simplified scheme showing the interference of light in the conversion of *C_{trans}* to *C_{cis}* and then to AH⁺ is given in Scheme 2. This reaction is reversed thermally in the dark, reaching an equilibrium, since the *trans*-chalcone, which is the only existing isomer on the ground state (Table 2) cannot undergo the direct ring closure reaction.

The turnover of this photochromic system (Figure 5b) is lowered by the existence of the photochemical degradation path above described for very acidic pH values, which is also operative at mildly acidic pH values.

The work here described constitutes a novel photochromic system based on *trans*-*cis* isomerization of a C=C bond. Nature often employs this type of system.¹⁸ An important example is the isomerization of rhodopsin, the shift base of 11-*cis*-retinal.

Conclusions

Three different forms of 4',7-dihydroxyflavylium in aqueous solution were detected and assigned by NMR spectroscopy: the flavylium cation, the *trans*-chalcone, and the quinonoidal base. The color enhancement observed upon illumination of moderately acidic solutions of the compound is due to a *trans*-to-*cis* photoisomerization followed by ring closure to give the colored flavylium cation. The color enhancement reaction is reversed in the dark, owing to a thermal reaction which converts back the flavylium cation into *trans*-chalcone.

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