

Photochromic properties of 4'-amino-substituted 2-hydroxychalcones

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Abstract

2-Hydroxychalcones with 4'-amino substituents undergo facile photochemical conversion into highly coloured flavylium ions on irradiation with 365–436 nm light in aqueous ethanol solution in the pH region 4–6. The coloured solutions are substantially stable against prolonged irradiation with visible light. The absorption coefficients of the flavylium ions around 530–560 nm are strong (approximately $5 \times 10^4 \text{ mol}^{-1} \text{ l m}^3 \text{ cm}^{-1}$) and well separated from those of the chalcones around 400 nm. Some of the derivatives feature good reversibility for repeated photochemical colouration and thermal reversion without significant fatigue in dilute solution, while others feature high thermal stability. Similar photochemical colouration occurs in many solid polymers, but irreversible thermal bleaching takes place. The photochromic properties are discussed in terms of the frontier orbital theory.

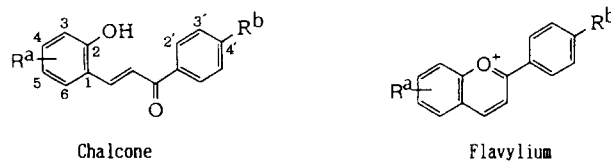
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1. Introduction

This study deals with a new and unique photochromic system involving chalcone–flavylium interconversions, as a simplified model of the naturally occurring anthocyanin pigments [1]. Although the photochromic properties are poor, at present, compared with those of well-developed systems [2], the system investigated has some unique features, e.g. it performs in aqueous as well as organic solvents without suffering from moisture and oxidizing impurities, and photochromic responses are strongly dependent on the acidity of the medium as well as on the substrate structure.

2-Hydroxychalcones with hydroxy or alkoxy substituents have been shown to undergo rapid photochemical conversion into highly coloured flavylium ions in strong acid solution [3]. However, the colour stability and photochemical response are usually low in neutral or weak acid at $\text{pH} > 3$ [3–5], in contrast with the natural anthocyanin pigments which are stable in essentially neutral medium conditions due to association or copigmentation [1]. We have attempted to improve the colour property and photochromic response in more neutral medium conditions by molecular modifications [6].

In the present work, the 4'-amino-substituted derivatives shown in Fig. 1 have been studied in detail, demonstrating significant improvements in the absorption spectra and photochromic performance compared with those of 4'-methoxy and 4'-methyl derivatives.



R ^a	R ^b	Chalcone	Flavylium
H	N(CH ₃) ₂	1 H	1 F
H	NHC ₈ H ₁₇	2 H	2 F
H	NHC(CH ₃) ₃	3 H	3 F
5,6-Benz o	NH ₂	4 H	4 F
5,6-Benz o	N(CH ₃) ₂	5 H	5 F
5,6-Benz o	NHC ₈ H ₁₇	6 H	6 F

Fig. 1. Structures of chalcones and flavylium ions.

photochromic performance compared with those of 4'-methoxy and 4'-methyl derivatives.

2. Experimental details

2.1. Materials

The flavylium perchlorates and chalcones were prepared according to the literature [7,8]. To a stirred mixture of 2-hydroxy-1-naphthaldehyde (6.9 g) and 4-dimethylaminoacetophenone (6.5 g) in formic acid (70 cm³), dry hydrogen

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Table 1
Yields and physical constants of chalcones and flavylum perchlorates ^a

Compound	Yield ^b (%)	Melting point (°C)	¹ H NMR (DMSO- <i>d</i> ₆) δ (ppm)	λ _{max} (nm)	UV-visible ε _{max} (M ⁻¹ cm ⁻¹)
1H	63	194.0–195.5	3.0 (s, 6H), 6.6–8.1 (m, 10H), 10.2 (s, 1H)	395	2.8
2H ^d	31	141.2–142.5	0.7 (t, 3H, <i>J</i> = 4 Hz), 1.1 (s, 12H) 2.9 (d, 2H, <i>J</i> = 6 Hz), 6.5–7.9 (m, 13H), 10.1 (s, 1H)	390	3.2
3H	13	175–176	1.4 (t, 9H), 2.5 (s, 1H), 6.6–8.2 (m, 10H), 9.2 (s, 1H)	385	2.0
4H ^e	16	120 (decomp.)	6.0 (s, 2H), 6.6 (d, 2H, <i>J</i> = 9 Hz), 7.1–8.2 (m, 10H), 10.3 (s, 1H)	395	2.7
5H ^f	55	189.0–191.2	2.8 (s, 6H), 6.6 (d, 2H, <i>J</i> = 9 Hz), 7.1–8.2 (m, 10H), 9.0 (d, 1H, <i>J</i> = 9 Hz)	410	3.2
6H ^g	28	118.0–119.5	0.8 (t, 3H, <i>J</i> = 4 Hz), 1.2 (s, 12H), 3.1 (d, 2H, <i>J</i> = 6 Hz), 6.6 (d, 3H, <i>J</i> = 9 Hz), 7.2–8.2 (m, 10H)	406	3.2
1F	70	259.0–260.0	2.7 (s, 6H), 2.9 (s, 4H), 6.5 (d, 2H, <i>J</i> = 9 Hz), 7.2–7.9 (m, 7H), 8.2 (d, 1H, <i>J</i> = 9 Hz)	535	4.8
2F	73	136.0–138.5	0.7 (t, 3H, <i>J</i> = 4 Hz), 1.1 (s, 12H), 3.1 (s, 2H), 6.6 (d, 2H, <i>J</i> = 9 Hz), 7.4–8.6 (m, 9H)	522	5.5
4F	21	Above 280	3.2 (br, 2H), 6.5 (d, 2H, <i>J</i> = 9 Hz), 7.4–8.3 (m, 9H), 9.0 (d, 1H, <i>J</i> = 9 Hz)	530	5.3
5F	62	273.0–274.5	2.7 (s, 6H), 3.1 (s, 3H), 6.4 (d, 2H, <i>J</i> = 9 Hz), 7.5–8.4 (m, 9H), 9.0 (d, 1H, <i>J</i> = 9 Hz)	558	5.6
6F	35	120.0–124.0	0.7 (t, 3H, <i>J</i> = 4 Hz), 1.1 (s, 12H), 3.0 (s, 2H), 6.6 (d, 2H, <i>J</i> = 9 Hz), 7.2–8.2 (m, 11H), 9.1 (d, 1H, <i>J</i> = 9 Hz)	548	5.7

^a Melting points were uncorrected.

^b Overall yields based on the substituted acetophenones.

^c Measured at pH 7 for chalcones and at pH 1 for flavylum ions, both in 1:1 aqueous ethanol.

^d Found: C, 78.53%; H, 8.31%; N, 3.98%. Calc. for C₂₃H₂₉NO₂: C, 78.59%; H, 8.32%; N, 3.99%.

^e Found: C, 78.84%; H, 5.34%; N, 4.83%. Calc. for C₁₉H₁₅NO₂: C, 78.87%; H, 5.23%; N, 4.84%.

^f Found: C, 79.26%; H, 6.05%; N, 4.45%. Calc. for C₂₁H₁₉NO₂: C, 79.47%; H, 6.03%; N, 4.41%.

^g Found: C, 81.11%; H, 7.83%; N, 3.49%. Calc. for C₂₇H₃₁NO₂: C, 80.76%; H, 7.78%; N, 3.49%.

DMSO, dimethylsulphoxide.

chloride was introduced for 6 h. After 15 min aeration to remove hydrogen chloride, aqueous perchloric acid (20%, 40 cm³) was added, followed by extraction with ether yielding a brown precipitate (62%, 10.0 g). Recrystallization from ethanol yielded violet fine needles of 4'-dimethylamino-5,6-benzoflavylum perchlorate (**5F**). Other flavylum salts were prepared by a similar treatment from the appropriate acetophenones and 2-hydroxyaldehydes.

An acetone solution (400 cm³) containing **5F** (1.0 g) was neutralized with dilute aqueous sodium hydrogencarbonate solution (20 cm³), and stirred for 30 min. Removal of the solvent gave a yellow precipitate (90%, 0.71 g) which, on further crystallization from acetone, yielded pure orange plates of chalcone **5H**, showing a single spot on thin layer chromatography (TLC) over silica gel with benzene. Other chalcones were prepared by a similar treatment. Their yields and physical constants are summarized in Table 1, together with the UV-visible absorption and elemental analysis data.

2.2. Apparatus and procedure

The UV-visible absorption spectra were recorded on a Hitachi 200-10 spectrophotometer, while ¹H NMR spectra were obtained on a Hitachi R-24 spectrometer. The pH values of the solutions were measured before and after irradiation, with a Yanaco PH-7 pH meter. Melting points were measured

by a micro-melting point apparatus (Yanaco MP-S3, Yanagimoto).

The major light beams at 405 nm (with a small contribution at 436 nm) and 365–366 nm were obtained from a 400 W high-pressure mercury lamp (Riko Kagaku) by passing through filters. Quantum yields were estimated by the total absorption of incident light method [9] using a toluene solution of the furylfulgide actinometer by parallel irradiation in a merry-go-round irradiation apparatus. Solvents were distilled before use. All photochemical and thermal reactions were carried out without elimination of dissolved oxygen.

3. Results

3.1. Thermal stability of chalcone solutions

On standing at room temperature in the dark, chalcones **1H**–**3H** were substantially stable in the pH region 2–7 in 1:1 aqueous ethanol solution for several weeks, whereas solutions of chalcones **4H**–**6H** were subject to significant conversion into flavylum ions in the pH region below 5 on standing for over 24 h.

3.2. Photochemical colouration and thermal bleaching

Fig. 2 illustrates the spectral changes of photochemical colouration (PC) of **2H** at pH 4 (a) and **6H** at pH 6 (c) in 1:1 aqueous ethanol solution on irradiation with 405 nm light. Photostationary states (PSSs) were attained within 20–80 min, with the mole fraction of the coloured form (flavylium ion) in the range 0.7–0.9. The broken curve in Fig. 2(c) shows the thermal colouration of **6H** on standing in the dark at room temperature for over 1 h.

The absorption bands of the flavylium ions (around 520–560 nm) are well separated from the chalcone bands (around 380–400 nm), and their absorption coefficients are high ($\epsilon > 5 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) as listed in Table 1.

Chalcone **3H** exhibits a lower absorption coefficient (Table 1), implying inefficient conjugation of the π -electron system or poor coplanarity due to the bulky tert-butyl substituent.

The coloured solutions of **1F–7F** do not undergo photochemical bleaching on prolonged irradiation with visible light ($\lambda > 436 \text{ nm}$). In the dark at room temperature, the solution of **2F** is stable for 1 month in the region up to pH 4, while **5F** is moderately stable up to pH 6, thus showing improved thermal stability against hydration compared with the 4'-methoxyflavylium ions (**7F**), which are unstable in the region above pH 3. On heating at 50 °C, on the other hand, the coloured solution **2F** is very slowly (several weeks)

Table 2

Relative response rates for photochemical colouration (A_F) and thermal bleaching at 50 °C ($-A_F$) in solution^a

Medium pH	Colouration rate		Bleaching rate	
	Chalcone	$A_F \text{ min}^{-1}$	Flavylium	$-A_F \text{ h}^{-1}$
4.0	1H	0.0075	1F	0.0036
4.0	2H	0.037	2F	0.0032
4.0	3H	2.2 ^b	3F	0.8
5.3	4H	0.75	4F	15
5.3	5H	0.22	5F	5.9
5.3	6H	0.36	6F	6.1
6.2	6H	0.2	6F	14

^a In 1:1 aqueous ethanol solution containing $(1.3\text{--}1.5) \times 10^{-5} \text{ M}$.

^b Quantum yield, ≈ 0.11 .

bleached at pH 4, while **6F** is rapidly bleached at pH 6, as illustrated in Figs. 2(b) and 2(d) respectively. Relative response rates for the PC and thermal bleaching (TB) reactions are numerically compared in Table 2, showing remarkable structural effects. Particularly notable is the large difference in the PC rates of **1H–3H** under similar reaction conditions, implying a remarkable effect of the bulky (alkyl) substituents in R^b. A similar difference in the PC rates was also observed in acetic acid solution and in a solid polymer of methacrylic acid (PMA), as shown in Figs. 3(a) and 3(b). In a copolymer of styrene and maleic anhydride (SMA),

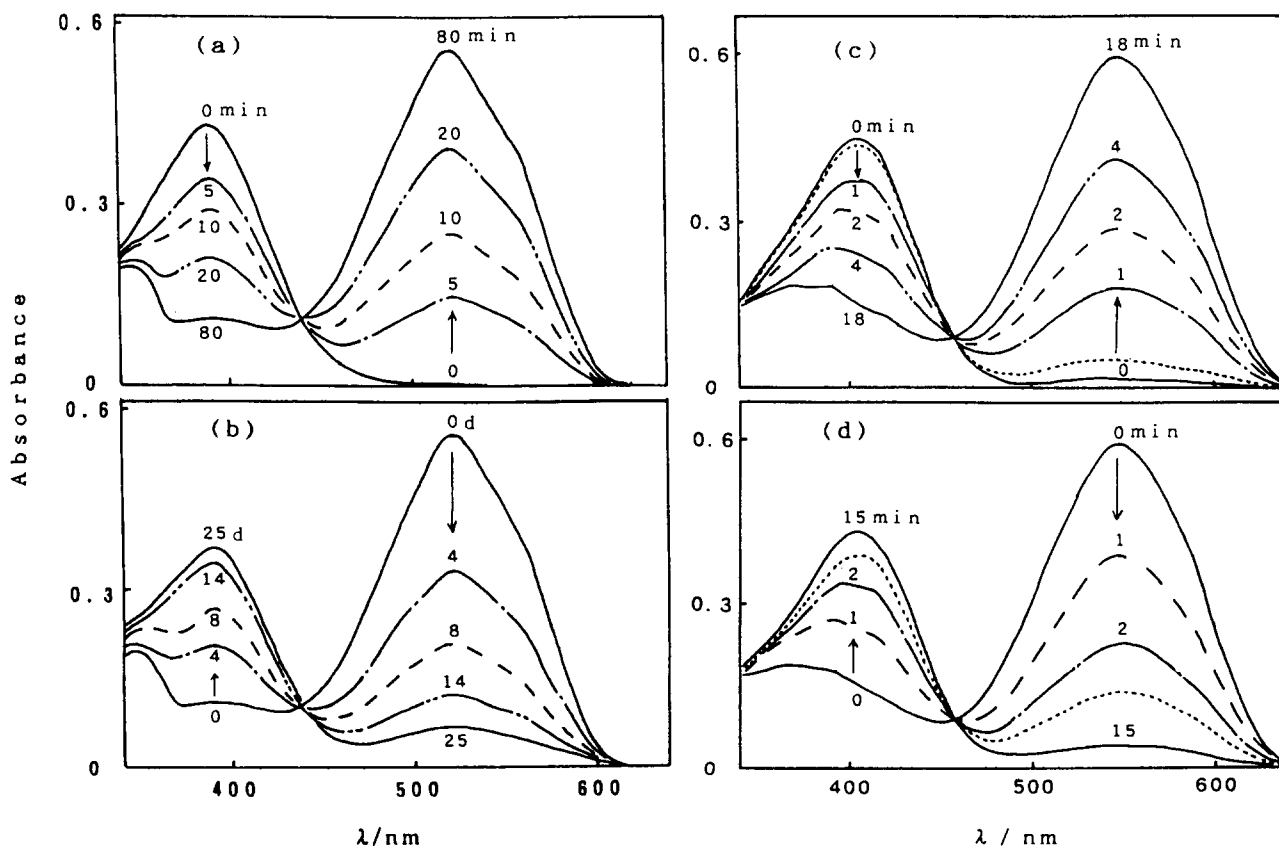


Fig. 2. Photochemical colouration of chalcone **2H** at pH 4 (a), followed by thermal reversion at 50 °C (b), and chalcone **6H** at pH 6 (c), followed by thermal reversion at 50 °C (d) ($1.5 \times 10^{-5} \text{ M}$ in 1:1 aqueous ethanol solution).

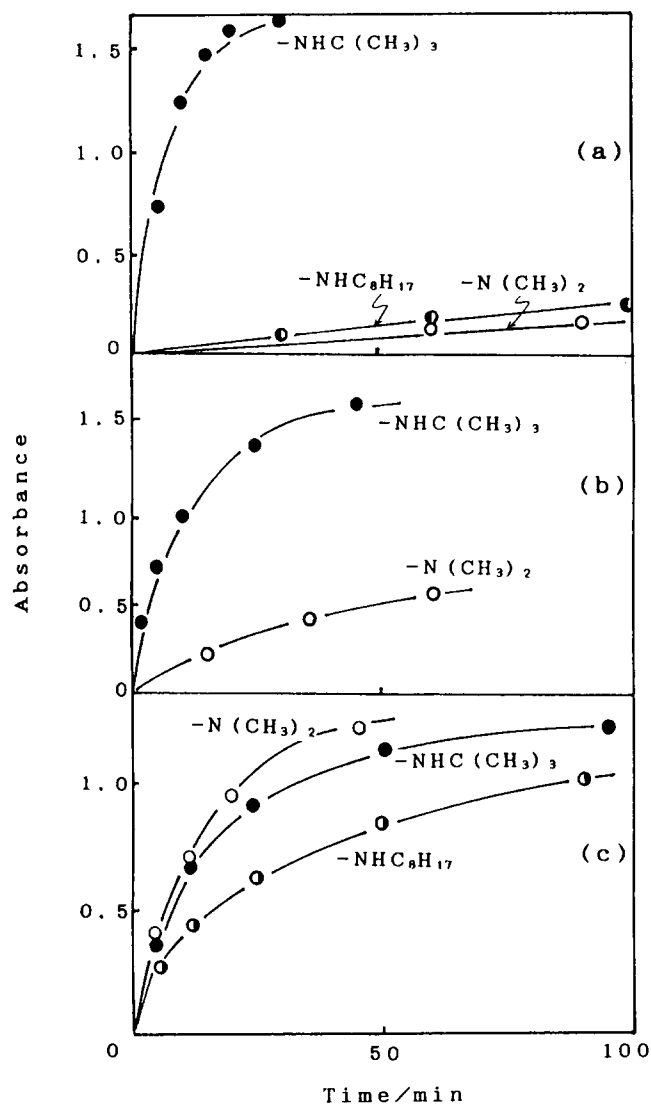


Fig. 3. Photochemical colouration of chalcones **1H** (○), **2H** (●) and **3H** (●) in acetic acid (a), poly(methacrylic acid) film (b) and copolymer of styrene with maleic anhydride (c).

however, similar rates were found (Fig. 3(c)). These differences in the PC rate may be ascribable to the different conformations, and/or intermolecular association and solute-solvent interactions, which are currently under investigation.

3.3. Recyclizability for colouration and bleaching

Under the limited pH conditions, the PC and TB interconversions can be repeated many times without significant fatigue, as illustrated in Fig. 4 with chalcone **4H** at pH 5 (a) and **6H** at pH 6 (b). After ten cycles of interconversion, the absorption spectra of both coloured and bleached solutions are almost superimposable on those of the initial solutions (data not shown), indicating a high reversibility, or cleanliness, of the interconversions. Thus chalcone **6H** demonstrates a smooth photochromic performance at pH 6 which is almost neutral. Its long alkyl substituent also serves to improve its solubility in many organic solvents as well as polymers,

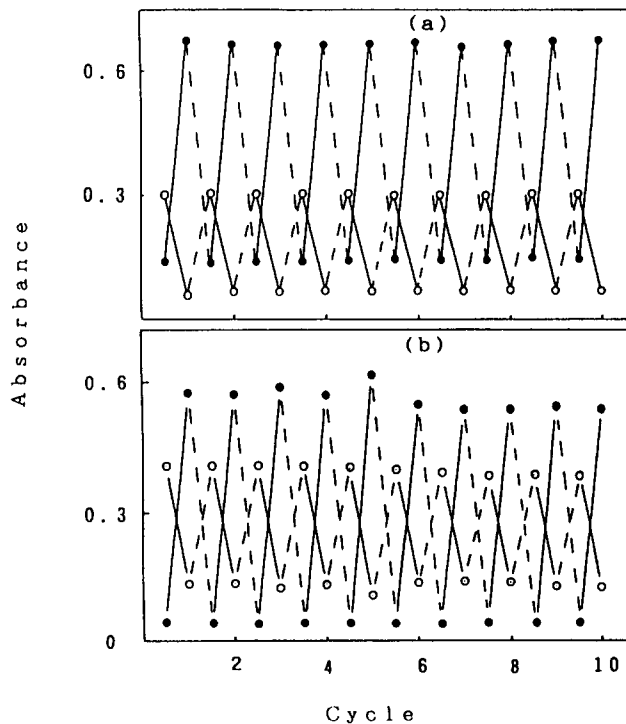


Fig. 4. Reversibility of successive photocoloration (full line) and thermal reversion at 50 °C (broken line) for chalcone **4H** at pH 5 (a) and chalcone **6H** at pH 6 (b). (○) and (●) refer to the absorbances at λ_{\max} of the chalcones and flavylium ions respectively.

whereas **4H** and **5H** exhibit poor solubility often preventing experiments in polymer films.

3.4. Photochromic properties in solid polymers

A solid polymer film containing 1 wt.% of chalcone or flavylium perchlorate was spin coated on a slide cover glass, which was then subjected to photochromic reactions. In a PMA film, the PC rate of chalcone **1H** was moderate, while the coloured film of **1F** was stable and remained unchanged at room temperature for over 3 years. In an SMA film, chalcones **1H**–**3H** underwent rapid PC, much more rapidly than in acetic acid solution. However, the coloured films underwent irreversible TB (not accompanied by chalcone formation). A solid polymer of poly(methyl methacrylate) containing chalcone **6H** showed a rapid PC response to give a highly coloured film at the PSS, which underwent substantial bleaching on heating at 80 °C. However, subsequent photoirradiation of the bleached film led to a poor colouration (only one-half of its initial value at the PSS).

4. Discussion

4.1. Photochemical reaction

With regard to the photoreaction mechanisms, we initially assumed (expected) a two-photon process which would provide a favourable threshold to control the PC reactions.

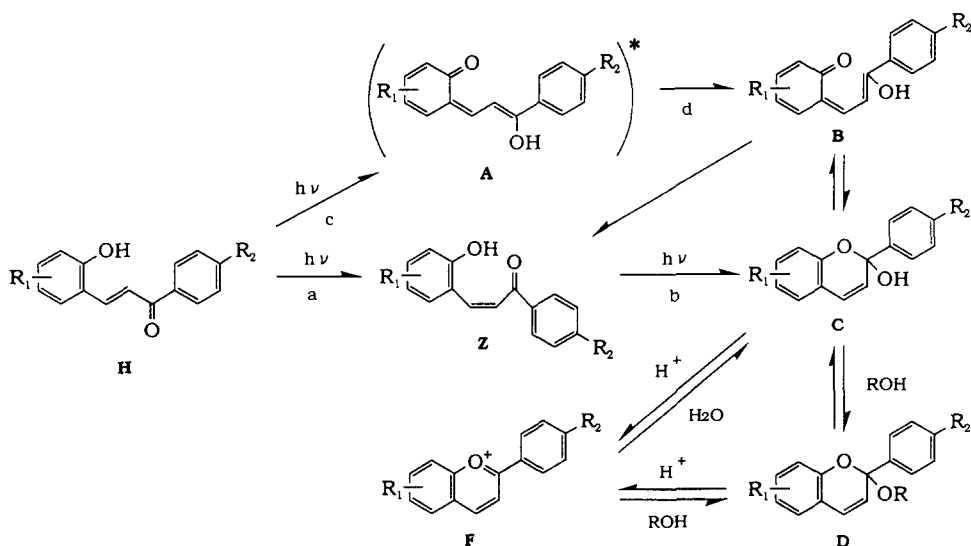


Fig. 5. Reaction pathways for photochemical colouration and thermal reversion.

Unfortunately, however, on the basis of the first-order dependence of the rate on the incident light intensity, it appeared that the PC reaction of chalcone **7H** involved a proton-transferred tautomer **A** via a one-photon process (path

c) [10], rather than a two-photon process (paths a, b), as shown in Fig. 5. The tautomer **A** may undergo conformational rotation to give **B** (path d) followed by a 6π -electrocyclic closure to give an acetal **C**, without further excitation. Subsequent dehydration and acetal exchange processes etc. are acid-catalysed reactions. Tentatively, we assume a similar mechanism for the reactions of chalcones **1H–6H**, although this assumption has not been proved directly as yet.

The molecular orbitals of some chalcones and flavylium ions were calculated by the MNDO-PM3 algorithm with full structure optimization [11]. The C2-aryl ring of chalcone is twisted out of plane by about 30° , while the flavylium ion is essentially planar. In Fig. 6, the pertinent coefficients (Pz) of the lowest unoccupied molecular orbital (LUMO) (a) and highest occupied molecular orbital (HOMO) (b) of **5H** are illustrated, where coefficients whose absolute values are less than 0.1 are omitted. In the LUMO, the magnitude of the coefficient on the phenolic oxygen (O7) is smaller while that on the carbonyl oxygen (O1) is larger, contrary to the reverse features in the HOMO. Also, the bonding/antibonding properties are reversed in the LUMO relative to the HOMO: thus the C3–C4 bond features a strong antibonding character, while the C4–C5 and C2–C3 bonds feature bonding character. These results are essentially consistent with the adiabatic path (c) in Fig. 5 involving proton-transferred tautomerization in the excited state.

4.2. Thermal bleaching

In terms of the frontier orbital theory, hydration (or ROH addition) of the flavylium ion can be depicted as orbital interactions between the HOMO of the nucleophile (H_2O or ROH) and the LUMO of the flavylium ion. The smaller the HOMO–LUMO energy gap, the more effective the orbital interaction, and hence the faster the reaction, according to the theory [12]. The calculated LUMO levels of **1F** and **5F**, -5.45 and -5.32 eV respectively, are significantly higher

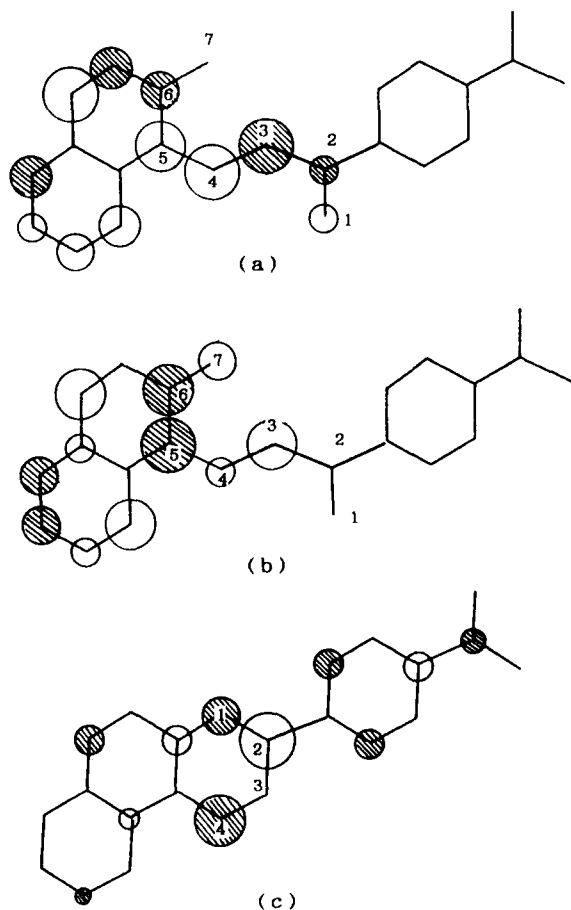


Fig. 6. Frontier orbital coefficients of LUMO (a) and HOMO (b) of chalcone **5H** and LUMO (c) of the flavylium ion **5F**, calculated by the MOPAC-PM3 program.

than that of the 4'-methoxyflavylium ion (**7F**), -5.86 eV. Because of the larger HOMO–LUMO energy gap, flavylium **1F** (and **5F**) will undergo hydration more slowly than **7F**. This explains the higher thermal stability of the 4'-amino-substituted flavylium ions (**1F**–**6F**) in the more neutral pH region, where hydroxylated or alkoxyated flavylium ions are subject to rapid hydration. The site selectivity of hydration is also explained as follows.

The pertinent LUMO (ψ_{57}) coefficients of **5F** are illustrated in Fig. 6(c). Qualitatively similar results were obtained on calculation with **1F** and **7F**. While the magnitude of the LUMO coefficient is largest at the 2-position and next largest at the 4-position, attack on the 2-position will suffer from significant steric hindrance by the 2-aryl ring. Therefore nucleophilic additions on these two positions are assumed to be competitive.

It has been implied by kinetic analysis of some flavylium ions that the hydration (or TB) reaction occurs either directly at the 2-position or via initial addition predominantly at the 4-position followed by rapid migration to the 2-position [4,5]. This is consistent with the above prediction from frontier orbital theory and steric considerations.

With regard to the possibility of photochemical hydration, two frontier orbitals, upper SOMO and lower SOMO', should be considered for interaction with the HOMO of the nucleophile. Of the two, the lower SOMO' is more important because of the smaller energy gap [12]. Thus photochemical hydration of the flavylium ions (if it occurs) should involve orbital interaction of the lower SOMO' with the HOMO of the nucleophile. However, the lower SOMO' coefficients of **1F**–**7F** are vanishingly small at the 2- and 4-positions, and hence no reactive interactions are expected at these positions. This may be one of the reasons why the flavylium ions are stable against prolonged irradiation with visible light. Another reason may be that flower colours should not bleach in sunlight!

4.3. Miscellaneous discussions

Although the photochromic properties are poor, at present, compared with those of well-studied photochromic systems [2], the system investigated has some unique features: it is soluble and functions in aqueous and/or organic media without suffering from moisture and oxidizing impurities. Under such environmental conditions, some photochromic systems may be subject to degradation [13]. Since the basic skeleton of the present system is essentially similar to that of the naturally occurring anthocyanin dyes, we expect it to be relatively harmless to living things and their environment. The photochromic responses are, however, slow in nature, since stable intermediates (acetals) are involved in the process.

Therefore it may be suitable for wider conventional uses in photochromic inks, clothes, cosmetics, toys, etc., as well as in photosensitive dyes for resists and printing processes. For example, a PMA film of **2H** exhibits a high thermal stability and a moderate PC response, while the coloured form **2F** is stable both thermally and photochemically (with visible light), and is thus feasible for a non-destructive optical memory of "write-once" type. Since the colour stability of the flavylium ions can be changed by the acidity (pH) of the medium, a secret memory (which will disappear in a certain time when required) can be made by suitable adjustment of the medium acidity. The compounds can be prepared by simple reactions from cheap starting materials, e.g. salicylaldehydes and acetophenones.

5. Conclusions

2-Hydroxychalcones with 4'-amino substituents undergo reversible, clean photochromic reactions in aqueous ethanol solution in the pH region 4–6, whereas reversible photochromism has not yet been successful in solid polymers. Relative response rates for PC and TB are strongly dependent on both the A ring and B ring substituents as well as the medium conditions. Some of these photochromic properties can be explained in terms of frontier orbital considerations.

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