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Dual Photochromic Properties of 4-Dialkylamino-2-hydroxychalcones

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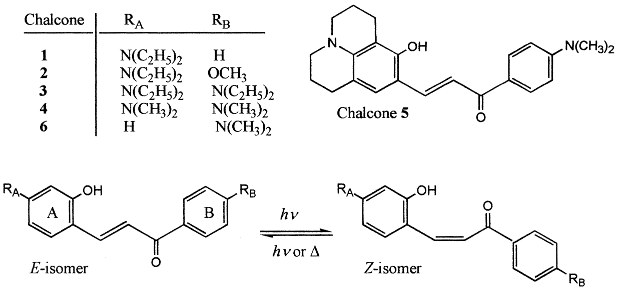
4-Dialkylamino-2-hydroxychalcones [3-(4-dialkylamino-2-hydroxyphenyl)-1-(substituted phenyl)-2-propen-1-ones] undergo reversible *E*/*Z*-photoisomerization in good quantum yields (0.2–0.4) in neutral aprotic solvents. The absorption bands of the photo-*Z*-isomers are significantly red-shifted from the *E*-isomers. By addition of acid, the photo-*Z*-isomers are converted to the flavylium ions with competitive reversion to the *E*-isomers. In aqueous ethanol solution, photochromic interconversion between chalcones and flavylium ions takes place rather slowly and less extensively.

In order to develop unique and environmentally suitable photochromic systems involving chalcone–flavylium interconversion, as a simplified model of the naturally occurring anthocyanin dyes,[1–3] we have undertaken to investigate a series of substituted 2-hydroxychalcones [3-(2-hydroxyphenyl)-1-(substituted phenyl)-2-propen-1-ones], and hitherto achieved good photochromism at least in fluid solution. The colored forms (flavylium ions) exhibit sharp and strong absorption bands in the yellow,[4,5] magenta,[6–9] and blue[10,11] regions (depending on the substituents) which are well separated from the chalcone bands. Among the 4′-dialkylamino-2-hydroxychalcones [3-(2-hydroxyphenyl)-1-(4-dialkylaminophenyl)-2-propen-1-ones] exhibit excellent photochromic reversibility and the flavylium ions exhibit favorable color properties (high color purity and strong intensity).[7] A novel photochemical process has been developed for the system, leading to a photon-mode erasable optical memory with nondestructive readout ability.[12,13]

Recently, it was found that 4-dialkylamino-2-hydroxychalcones (Scheme 1) exhibit dual photochromism depending on the medium conditions, and strong fluorescence in polar solvents.[10] The present paper reports on the dual photochromic properties as well as the fluorescence of these chalcones.



Chalcone	R_A	R_B
1	$N(C_2H_5)_2$	H
2	$N(C_2H_5)_2$	OCH_3
3	$N(C_2H_5)_2$	$N(C_2H_5)_2$
4	$N(CH_3)_2$	$N(CH_3)_2$
6	H	$N(CH_3)_2$

Scheme 1. Structures and photoisomerization of chalcones in neutral solution.

Experimental

Fluorescence spectra were measured on a Hitachi 204 fluorescence spectrometer, and fluorescence quantum yields were estimated by using aqueous acid solutions of quinine sulfate as a standard.[14] Electronic absorption spectra were recorded on a Hitachi U-3000 spectrophotometer, while ^1H NMR spectra were obtained on a EX-90 FT-NMR spectrometer (90 MHz). Melting points were measured with a micro-melting point apparatus (Yanaco MP-3S, Yanagimoto). The light source was a 400-W high-pressure mercury lamp (Riko). Its monochromatic 405 nm beam was selected through an interference filter (Hitachi B420), or 405 and 436 nm beams were selected through a cut-off glass filter (Toshiba C-39B). Photoreaction quantum yields were estimated from the plots of the consumption of *E*-chalcones as a function of irradiation time, by using the potassium tris(oxalate)ferrate(III) solution as a chemical actinometer under conditions that the absorbance of each solution of the incident light was around 2.[15,16] The concentration of each chalcone was estimated from its molar absorption coefficient and maximum absorbance. Reactions were carried out without elimination of the dissolved oxygen, while fresh solvents of guaranteed grade (Wako Chemicals) were used as received. 3-(4-Diethylamino-2-hydroxyphenyl)-1-phenyl-2-propen-1-one (chalcone **1**) was prepared from 7-diethylaminoflavylium perchlorate (**1F**) as follows.[7] To a mixed solution containing **1F** (26.5 mmol), ethanol (100 mL) and *N*,*N*-dimethylformamide (40 mL), 0.1 M aqueous sodium hydroxide solution (20 mL) was slowly added, and the mixture was stirred for a day at room temperature under nitrogen atmosphere. The mixture was condensed and extracted with ethyl acetate (150 mL) and water (150 mL). By removal of the solvent from the extracts, a black oil was obtained; this was subjected to column chromatography on silica gel with hexane–ethyl acetate, giving orange needles of chalcone **1** (13%): mp 126–132 °C; ^1H NMR (90 MHz, in DMSO-d_6) δ 1.12 (t, 6H, J = 7.0 Hz), 3.34 (q, 4H, J = 7.0 Hz), 6.17 (sd, 1H, J = 2.4 Hz), 6.26 (dd, 1H, J = 8.8 Hz, J = 2.4 Hz), 7.49–7.62 (m, 5H), 7.96–8.02 (m, 3H), 9.94 (s, 1H). By an essentially similar method,[17,18] other chalcones **2–5** were prepared starting from the corresponding flavylium perchlorates: namely, 7-diethylamino-4′-methoxyflavylium perchlorate (**2F**), 7-diethylamino-4′-dimethylaminoflavylium perchlorate (**3F**), 4′,7-bis(dimethylamino)-flavylium perchlorate (**4F**), and 6-(4-dimethylaminophenyl)-julolido[8,9-*b*]pyrylium perchlorate (**5F**), respectively. Recrystallization from ethyl acetate yielded dark blue plates of chalcone **2**: mp 136 °C (decomp.); ^{1}H NMR (90 MHz, in DMSO-d_6) δ 1.12 (t, 6H, J = 7.0 Hz), 3.34 (q, 4H, J = 7.0 Hz), 3.85 (s, 3H), 6.17 (sd, 1H, J = 2.4 Hz), 6.24 (dd, 1H, J = 8.8 Hz, J = 2.4 Hz), 7.05 (d, 2H, J = 8.8 Hz), 7.53 (d, 1H, J = 15.1 Hz), 7.61 (d, 1H, J = 8.8 Hz), 7.94 (d, 1H, J = 15.6 Hz), 8.03 (d, 2H, J = 9.3 Hz), 9.96 (s, 1H), orange needles of chalcone **3**: mp 182 °C (decomp); ^{1}H NMR (90 MHz, in DMSO-d_6) δ 1.12 (t, 6H, J = 7.0 Hz), 3.02 (s, 6H), 3.33 (q, 4H, J = 7.0 Hz), 6.17 (sd, 1H, J = 2.4 Hz), 6.24 (d, 1H, J = 8.8 Hz), 6.75 (d, 2H, J = 9.3 Hz), 7.52 (d, 1H, J = 15.6 Hz), 7.58 (d, 1H, J = 8.8 Hz), 7.88 (d, 1H, J = 15.6 Hz), 7.93 (d, 2H, J = 9.3 Hz), 9.80 (s, 1H), respectively, while recrystallization from ethanol gave orange granules of chalcone **4**: mp 210–212 °C; ^{1}H NMR (60 MHz, in DMSO-d_6) δ 2.98 (s, 2H), 3.05 (s, 2H), 6.21–8.00 (m, 10 H). The ^{1}H NMR (DMSO-d_6) spectra of the flavylium perchlorates **1F**–**3F** and **5F** were also satisfactory. However, recrystallization of chalcone **5** was unsuccessful, and its crude yellow powders were used without further purification.

Results and Discussion

Photochromism in Neutral Apolar Solvents. Chalcones **1**–**5** (Scheme 1) exhibit electronic absorption bands around 410–420 nm. The ^{1}H NMR coupling constants (J = 15–16 Hz) for the enone vinyl protons imply the *E*-conformation in the unirradiated form (X-ray structural analysis of chalcone **1** also revealed an *E*-isomer, though data not shown here). These chalcones undergo facile photochemical color changes (red shifts) upon irradiation in neutral aprotic solvents, as illustrated with chalcone **3** in toluene (red shift from 408 to 471 nm) on irradiation with 405 nm light for one minute (Fig. 1a). While the new band of the photoisomer reverts slowly in the dark at 30 °C (Fig. 1b), photochemical reversion can be more clearly observed on irradiation with light of $\lambda > 460$ nm (Fig. 1c) at a low temperature below 5 °C where thermal reversion is substantially depressed (Fig. 1d). Similar photochromic reactions were found with other chalcones **1**, **2**, and **5**, as summarized in Table 1. The photochemical red-shifts are ascribable to photochemical *E*/*Z* isomerization around the enone double bond, as will be discussed later. The quantum yields for the photochemical reaction are relatively high and less variable, while the half-lives ($\tau_{1/2}$) of the photoisomers strongly vary with the structure. The half-lives $\tau_{1/2}$ also varied with temperature. Thus, from the Arrhenius plots for the thermal reversion of **3**, the value for the apparent activation energy was estimated to be around 65 kJ mol^{-1}.

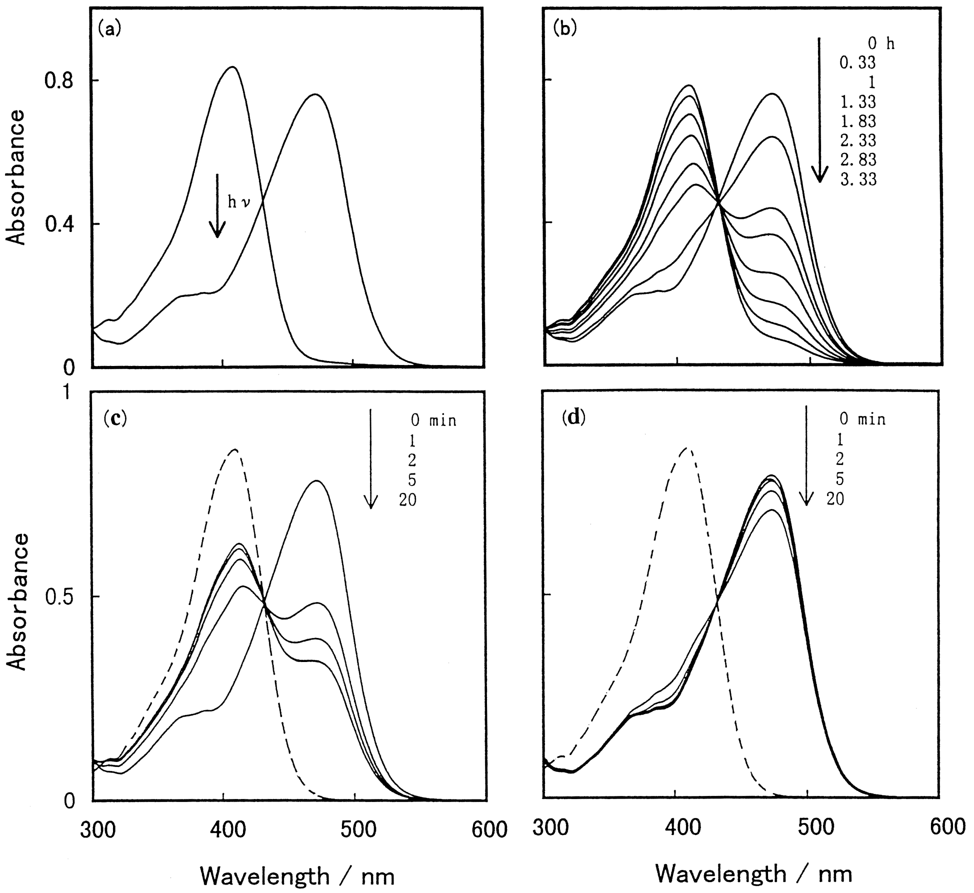


Fig. 1. Photochemical isomerization of chalcone **3** in toluene solution (30 μM) on irradiation with 405 nm light for one minute (a), followed by thermal reversion at 30 °C (b), and photochemical reversion with light of $\lambda > 460$ nm 4 °C (c) where thermal reversion is substantially depressed (d).

Table 1. Photochemical Isomerization and Thermal Reversion of Chalcones in Toluene Solution[a)]

Chalcone	Before irradiation		After irradiation[b)]		Quantum yield[c)]	Half-life of isomer[d)]	Reversibility[e)]
No.	λ_{max}/nm	$\varepsilon_{max}/10^4\,M^{-1}\,cm^{-1}$	λ_{max}/nm	$\varepsilon_{max}/10^4\,M^{-1}\,cm^{-1}$	ϕ_{EZ}	$\tau_{1/2}$/min	A_{10}/A_0
1	410	3.74	476	3.34	0.30	3.5	0.78
2	406	3.28	471	2.88	0.37	11	0.69
3	408	2.85	471	2.58	0.37	93	0.85
5	424	2.98	493	3.13	0.17	15	0.39

a) Initial concentration of chalcones were 8–10 × 10^{-5} (1 M = 1 mol dm^{-3}), irradiated with 405 nm light from a 400-W high-pressure mercury lamp. b) Absorption maximum and appropriate molar absorption coefficient obtained from the PSS solution immediately after irradiation. c) Quantum yield for the photochemical consumption of the initial *E*-chalcone, by using the potassium tris(oxalate)ferrate(III) solution as chemical actinometer under conditions that the absorbance of each solution of the incident light was around 2. d) Half-life for the thermal reversion of the photoisomer at 30 °C. e) A_0 and A_{10} refer to the absorbances of the photoisomer at the initial and after 10 cycles of the repetition.

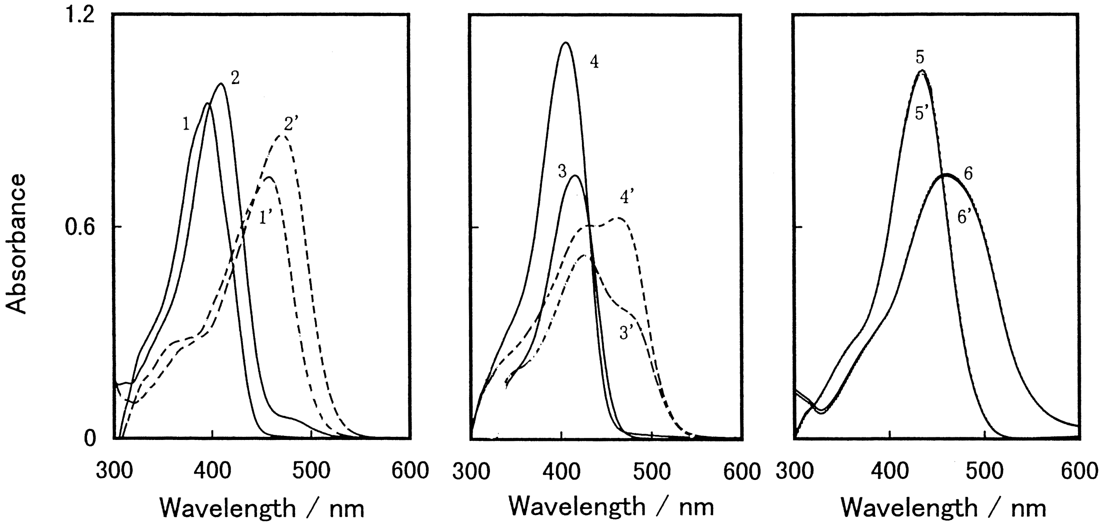


Fig. 2. Photochemical isomerization of chalcone **3** in hexane (1,1'), toluene (2,2'), acetone (3,3'), ethyl acetate (4,4'), ethanol (5,5'), and water (6,6'). Solid curves: before irradiation, broken curves: after irradiation with sunlight for one minute. Each solution contained 8.5% of 1,2-dimethoxyethane.

Figure 2 illustrates the photochemical color changes of chalcone **3** in different solvents, showing large shifts in hexane or toluene solution (Fig. 2a), but moderate one in acetone or ethyl acetate (Fig. 2b) and no shift in hydroxylic solvents (Fig. 2c). Similar solvent effects were found with chalcones **1**, **2**, and **5**. On addition of a small amount of ethanol to the photostationary state (PSS) solution in toluene (2' in Fig. 2a), the 471 nm band rapidly disappeared to reform the 408 band of **3**. Therefore, the apparent nil spectral change in the protic solvents (Fig. 2c) might be the result of either the rapid reversion of the photoisomer if formed or may be due to the nil photoisomerization.

Figure 3 illustrates the reversibility in neutral toluene solution toward the repeated cycles for the photochemical color change and thermal reversion at 30 °C. Chalcones **1** and **3** revealed fairly good reversibilities (ca. 80% retainment after 10 cycles), while chalcone **5** revealed poor reversibility (last column in Table 1) partially because of its impurity. The thermal reversion curves in Fig. 3 become steeper (faster rate) in order of the number of the cycles. The unusual behaviors might be related to the complicated phenomena such as intermolecular association and/or complexation.

We assume that the red-shifted photoisomers have the *Z*-conformation about the enone double bond (Scheme 2), which is supported by the observation that the PSS solution of **3** gave a mixture of the flavylium ion and chalcone **3** (*E*-isomer) upon addition of a strong acid. Thus, as illustrated in Fig. 4, the 471 nm band of the photoisomer disappeared and a new band around 600 nm (flavylium band) appeared with competitive reversion to the *E*-isomer **3** (408 nm), by addition of trifluoroacetic acid (50 μM) (1 M = 1 mol dm^{-3}). No such spectral change was observed by addition of the acid to the solution before irradiation. The flavylium-ion formation is explained by the reaction sequences in Scheme 2 involving photochemical *E*/*Z*-isomerization followed by acid-catalyzed cyclization to hemiacetals (second step) and dehydration to give flavylium ions (last step), in analogy to the reaction sequence for the majority of other 2-hydroxychalcones in the presence of acid.[4–9]

Photochromism in Acid Media. Figure 5 illustrates the photochromism of chalcone **4** in a 1 : 1 aqueous ethanol solution at pH 6.0. Chalcone **4** was substantially converted into blue-colored flavylium ion upon irradiation with 405–436 nm light, according to the assumed reaction sequence shown in Scheme 2,[4–9] while it was fairly stable in the dark. On heating

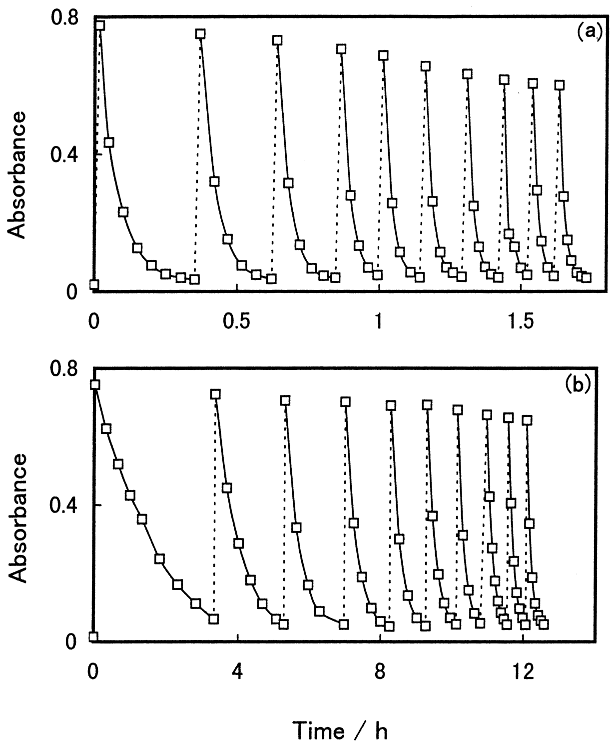
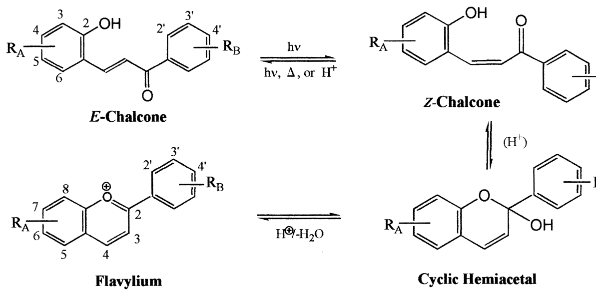


Fig. 3. Reversibility toward the repeated cycles for the photochemical isomerization (broken curves) and thermal reversion (solid curves) of chalcones **1** (a) and **2** (b) in toluene solution at 30 °C. The vertical axes refers to the absorbance of the photoisomers.



Flavylium	7- R_A	4'- R_B
1F	$N(C_2H_5)_2$	H
2F	$N(C_2H_5)_2$	OCH_3
3F	$N(C_2H_5)_2$	$N(CH_3)_2$
4F	$N(CH_3)_2$	$N(CH_3)_2$
6F	H	$N(CH_3)_2$

Scheme 2. Interconversions among *E*/*Z*-isomers of chalcones and flavylium ions.

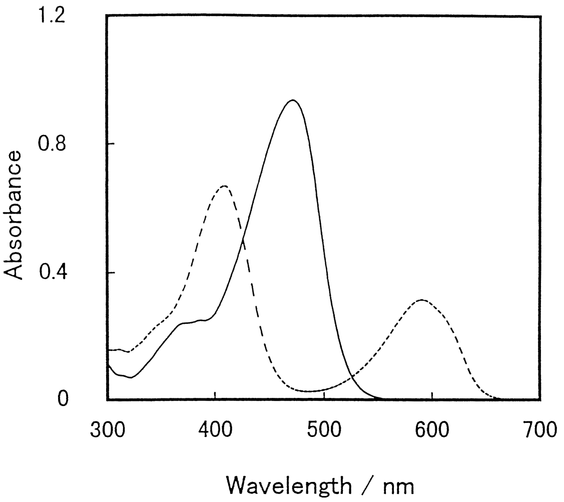


Fig. 4. Absorption spectra of the photoisomer (PSS solution) of chalcone **3** in toluene immediately after irradiation with 405 nm light (solid curve), and spectra after addition of 50 μM trifluoroacetic acid (broken curve). No such spectral change was observed by addition of the acid to the solution before irradiation.

at 60 °C for 100 min the blue-colored solution substantially bleached to the chalcone. An isosbestic point is seen around 500 nm during the reaction. The interconversion could be repeated several times, as illustrated in Fig. 5 b. Under similar conditions, chalcone **3** revealed much slower responses for both photochemical conversion into flavylium ion (4 h) and thermal reversion (12 h), while in PMMA film containing tannic acid it underwent more facile photoreaction to give flavylium ion, as illustrated in Fig. 6. The absorption spectra of the flavylium ion around 600 nm is accompanied by a new shoulder or peak around 570 nm, implying an intermolecular association or complexation of the flavylium ion at a higher concentration in thin film. Similar spectral features, as well as large deviations from the Beer–Lambert law, have been observed with many flavylium ions in solution,[19] often preventing accurate estimation for their molar absorption coefficients. The absorption maxima (λ_{max}) and approximate molar absorption coefficients ($\varepsilon_{max}/10^4$ M^{-1} cm^{-1} in parentheses) of the separately prepared flavylium perchlorates were **1F**: 522 nm (2.0), **2F**: 534 nm (3.3), **3F**: 600 nm (8.9), **4F**: 597 nm (9.0 in aqueous ethanol), and **5F**: 613 nm (7.3), respectively, in 30 μM in ethanol solution. Thermal reversion of the flavylium ion **3F** in the PMMA film was very slow and substantially not irreversible.

Discussion on the Structures and Electronic Spectra. MOPAC-PM3 calculations[20] with full structure optimization implied that the most stable *E*-isomers were essentially planar, whereas the *Z*-isomers were nonplanar with substantially twisted benzoyl moiety (while the cinnamoyl moiety was almost planar). For the *Z*-isomers of chalcones **1**–**4**, intramolecular hydrogen bonding between the phenolic proton and carbonyl oxygen (with the H···O bond distance of 1.8–2.1 Å) was implied by the optimized structures. On the other hand, bimolecular hydrogen bonds between head-to-tail pairs have been implied for the *E*-isomers, which were confirmed at least in the X-ray crystal structures of 2-hydroxychalcone [3-(2-hydroxyphenyl)-1-phenyl-2-propen-1-one] and 4′-methoxy-2-hydroxychalcone [3-(2-hydroxyphenyl)-1-(4-methoxyphenyl)-2-propen-1-one]. Taking these results into account, PPP-CI calculations for the *E*-isomers were carried out by using the parameters for the hydrogen-bonded phenolic group, whereas calculations for the *Z*-isomers were carried out by using both the hydrogen-bonded and non-hydrogen-bonded parameters.[21] Table 2 lists the calculated π,π* electronic transitions for the first bands of the *E*- and *Z*-isomers, showing fair consistency with the experimental results listed in Table 1. The cal-

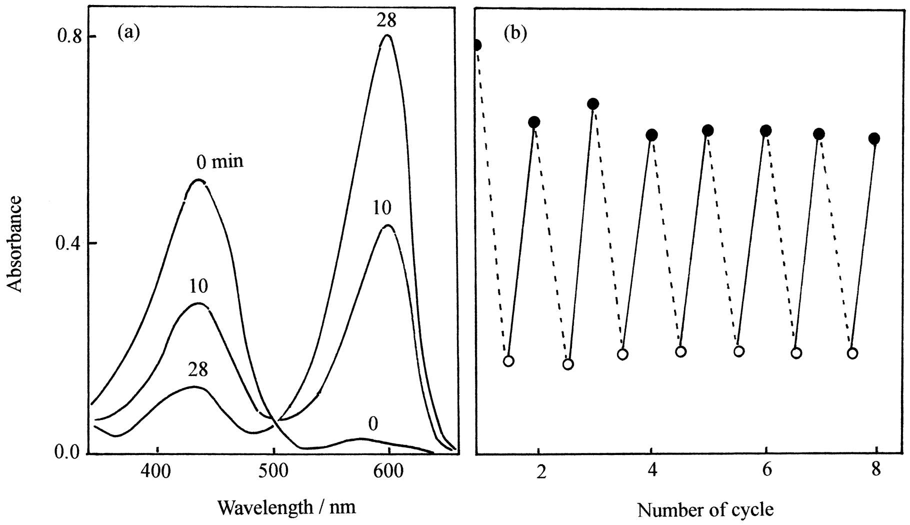


Fig. 5. Photochromism of chalcone **4** (10 μM) in a 1 : 1 aqueous ethanol solution at pH 6.0. (a) Photochemical conversion into flavylium ion on irradiation with 405 and 436 nm beams from a 400-W high-pressure mercury lamp. (b) Photochromic reversibility toward repeated cycles of photocoloration for 25 nm (solid lines) and thermal reversion on heating at 60 °C for 100 min (broken lines).

Table 2. PPP-CI Calculations for the First Bands of the *E*- and *Z*-isomers[a)]

Calcone	E-isomer with H-bond[b)]		*Z*-isomers with H-bond[b)]		*Z*-isomers without H-bond	
No.	λ_{max}/nm	*f*-value	λ_{max}/nm	*f*-value	λ_{max}/nm	*f*-value
1	396	1.05	445	0.56	442	0.55
2	389	1.09	413	0.29	434	0.59
3	384	1.22	427	0.74	423	0.73
6[c)]	350	0.98	357	0.93	348	0.99

a) Standard parameters were used unless otherwise noted. b) Hydrogen-bonded parameters were used for the 2-hydroxy group. c) Chalcone **6** revealed λ_{max} at 370 nm (ε_{max} 3.27 × 10^4 M^{-1} cm^{-1}) while its *Z*-isomer had λ_{max} around 390 nm, in toluene solution.

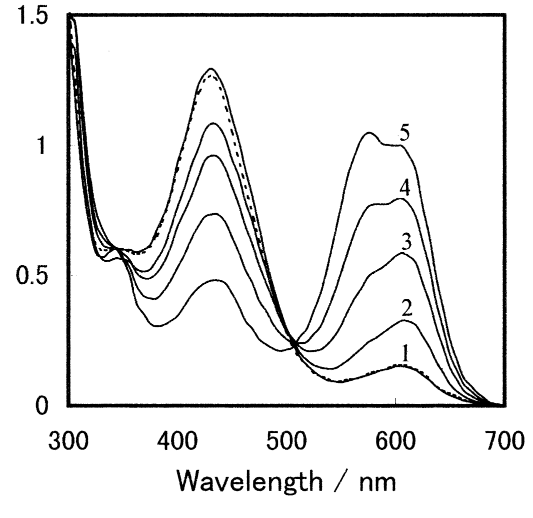


Fig. 6. Photochemical conversion of chalcone **3** (5 wt%) into flavylium ion in PMMA film in the presence of 10 wt% tannic acid, on irradiation with 405 and 436 nm beams from a 120-W high-pressure mercury lamp. Irradiation time/min: (1) 0, (2) 10, (3) 30, (4) 60, and (5) 120, respectively. Broken curve refers to the thermal change on standing at room temperature for 24 h.

culated red shifts (Δλ) from the *E*- to *Z*-isomers (H-bonded) are in the range of 25–50 nm for chalcones **1**–**3** (Table 2), being comparable to the shifts observed around 65 nm (Table 1). By contrast, the majority of 2-hydroxychalcones with R_A = H revealed blue shifts upon change from *E*- to *Z*-isomers, though the absorption wavelength of chalcone **6** was sensitive to the nature of the solvents. Thus, on irradiation of the *E*-isomer, chalcone **6** revealed a blue shift (from 369 to 350 nm) in tetrahydrofuran (THF) whereas a small red shift (from 370 to 390 nm) was found in toluene. It is tentatively speculated that the photochemically formed *Z*-isomer would form an intramolecular hydrogen bond in toluene which is neither proton-donating nor -accepting, but not in THF solution, where the solvent features a good proton acceptor and hence inhibits the hydrogen bonding of the *Z*-isomer. Interestingly, chalcones **1**–**5** are significantly fluorescent in solution, whereas the majority of other 2-hydroxychalcones with R_A = H are generally nonfluorescent. This implies that the amino substituents in the A-ring play a crucial role in the electronic transitions and/or the excited state properties. The INDO/S as well as the PPP-CI calculations implied strong intramolecular charge transfer character (mainly in the cinnamoyl plane) in the lowest π,π* excited states of chalcones **1**–**4**, as compared to the much less polar nature of other 2-hydroxychalcones with R_A = H. Increase in the charge transfer character in the excited states, by either structural or solvent polarity changes, tends to enhance the fluorescence efficiency: thus, the fluorescence quantum yields (ϕ_f) of chalcones **1**, **2**, and **3** were 0.091 (λ_F 520 nm), 0.15 (535 nm), and 0.22 (515 nm), respectively, on excitation at 405 nm in *t*-butyl alcohol. The ϕ_f value of chalcone **3** varied with solvent: 0.25 in *N*,*N*-dimethylformamide, 0.13 in THF, 0.076 in ethanol, 0.014 in methanol, and 0.03 in diethyl ether. Strong charge transfer interaction between the amino and carbonyl groups would help to retain the planarity of the cinnamoyl moiety, thus depressing the radiationless deactivation via twisting motions. While ϕ_f values are usually low in ethanol and methanol, relatively high values are obtained in *t*-butyl alcohol, whose viscosity is sufficiently high to retard the twisting motions of the chromophores.

In summary, 4-dialkylamino-2-hydroxychalcones undergo reversible photochemical *E*/*Z* isomerization in neutral aprotic solvents but not in neutral protic solvents, while they are significantly fluorescent in some polar and protic solvents. The photo-*Z*-isomers, which exhibit significantly red-shifted absorption bands, are converted to the blue-colored flavylium ions in competition with reversion to the *E*-isomers upon addition of small amounts of acid. In aqueous ethanol solution at pH around 6, photochemical chalcone → flavylium conversion and thermal reversion can be repeated with low rates.

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