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Photochromic properties of hydrolysed benzopyrylium salts—the influence of bridging

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Abstract

A series of systematically modified benzopyrylium salts was hydrolysed to study the influence of structural factors on a photochromic behaviour. It was found that photochromic systems can be created from most of the studied non-bridged flavylium salts and such ones which contain a $(CH_2)_2$-bridge between the 3- and 2′-position. However, all investigated CH_2-bridged benzopyrylium cations undergo an irreversible hydrolysis reaction, and do not show photochromism. On the basis of semiempirical AM1 calculations the behaviour can be explained with the instability of the 2-hydroxyflavene in comparison with the *cis*-chalcone. The latter one can be referred to ring tensions caused by the CH_2-bridge. Studies on the solvent dependence of the photochemical reaction and flash photolysis studies indicate that the mechanisms of the photochemical colouration reaction of non-bridged benzopyrylium ions can be applied also to the $(CH_2)_2$-bridged ones. The insertion of a CH_2- or $(CH_2)_2$-bridge causes a decrease of the hydrolysis speed of the benzopyrylium salts.

Comparing the behaviour of the 7,4′-dimethoxyflavylium perchlorate and the respective $(CH_2)_2$-bridged flavylium salt (3,10-dimethoxy-5,6-dihydrobenzo[c]-xanthylium perchlorate) it was found that the reversibility of the photochromic conversions can be improved introducing a $(CH_2)_2$-bridge.

Keywords: Benzopyrylium salts; 2-Hydroxychalcones; Photochromism; Bridging

1. Introduction

2-Phenyl-1-benzopyrylium salts (flavylium salts) occur in nature as essential component of plant pigments and are responsible for the yellow, red and blue colour of most flowers and fruits. They are easily hydrolysed and form *trans*-2-hydroxychalcones. On irradiation with visible or UV light the initial flavylium salts can be reformed, thus constituting a photochromic system.

The photochromic behaviour of these dyes was discovered for long times [1]. By now a number of photochromic systems derived from differently coloured flavylium salts is known. The conversions occur usually between the deeply coloured flavylium salts and the colourless or yellow *trans*-2-hydroxychalcones. The colours of the flavylium salts and chalcones strongly depend on the substituents. Subsequent studies on the mechanism of the thermal and the photochemical interconversions [1–13] give evidence for a quite complicated reaction sequence (Fig. 1).

Some of these systems can be applied as actinometers [18,22]. Surprisingly, our studies show that a bridging between the 3- and 2′-position at the flavylium ion decisively influences the photochemical reformation of the flavylium ion and thus the photochromic behaviour. The insertion of a CH_2-bridge disturbs the photochromism, while a $(CH_2)_2$-bridge seems to improve it. Therefore, our studies are concerned with the dependence of the photochromic behaviour on the bridging. The aim is an understanding of the different behaviour (Fig. 2).

2. Experimental details

2.1. Materials

The pure chalcones were prepared from the corresponding benzopyrylium perchlorates as follows: 100 ml of a 1 M aqueous sodium acetate solution were added slowly to 20 ml of a cold-saturated solution of the benzopyrylium perchlorate in ethanol. After standing for at least 3 days in the dark the hydrolysis product was separated and recrystallized from methanol.

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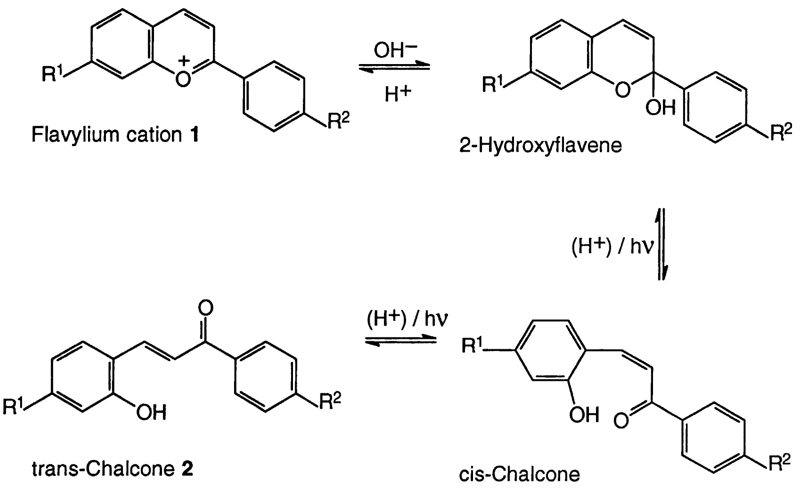
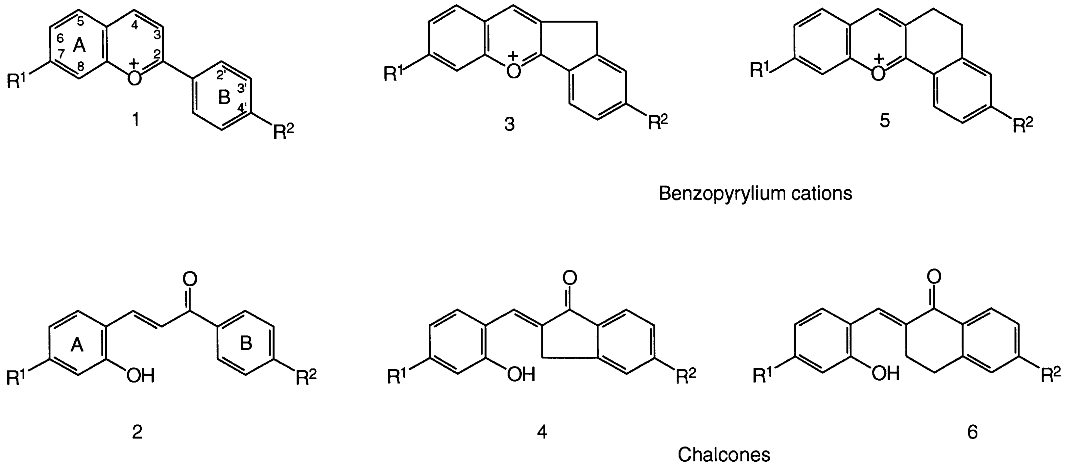


Fig. 1. Reaction pathways for the photochemical colouration and thermal conversion.



Code	R^1	R^2
a	H	H
b	H	OMe
c	OMe	OMe
d	NEt_2	OMe

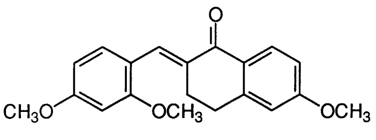


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Fig. 2. Structures of benzopyrylium ions and chalcones.

Trans-2-hydroxy-4,4′-dimethoxychalcone (**2c**) was prepared from 4′,7-dimethoxyflavylium perchlorate (**1c**) and gave pale yellow needles or powder, m.p.: 147–149, 150 °C [1]. MS, *m/z* (%): 284 (7) [M^+], 57 (100). ^{1}H-NMR (DMSO), δ (ppm): 8.08 [d, $^3J = 8.3$ Hz, 2H]; 7.98 [d, $^3J = 15.6$ Hz, 1H]; ca. 7.76 [dd 2H, $^3J = 13.4$ and 15.6 Hz]; 7.07 [$J = 8.3$ Hz, 2H]; 6.49 [s, 2H]; 3.85 [s, 3H]; 3.75 [s, 3H].

Trans-2-(2-hydroxy-4-methoxy-benzylidene)-6-methoxy-3,4-dihydro-2H-naphthalen-1-one (**6c**) was prepared from 3,10-dimethoxy-5,6-dihydrobenzo[c]xanthylium perchlorate (**5c**), giving pale yellow needles and plates, m.p.: 163–165 °C. MS, *m/z* (%): 310 (23) [M^+], 293 (100). ^{13}C-NMR, ^{1}H-BB-decoupled ([D_6]DMSO), δ (ppm): 185.53; 163.04; 161.14; 158.20; 145.75; 132.33; 131.40; 130.87; 129.77; 126.65; 115.44; 113.51; 112.25; 104.88; 101.17; 55.47; 55.08; 28.48; 27.08. ^{1}H-NMR ([D_6]DMSO), δ (ppm): 10.07 [s, 1H]; 7.90 [d, $^3J = 7.2$ Hz, 1H]; 7.79 [s, 1H,]; 7.25 [d, $^3J = 8.4$ Hz, 1H]; 6.91 [d, $^3J = 8.8$ Hz, 1H]; 6.85 [s, 1H]; 6.49 [s, 1H]; 6.45 [d, $^3J = 8.4$ Hz, 1H]; 3.82 [s, 3H]; 3.72 [s, 3H]; 2.96 [m, 2H]; 2.85 [m, 2H].

A coupling between $\delta = 2.96$ ppm (CH_2) and $\delta = 7.25$ ppm (aromatic) in the NOESY experiment established the *trans*-geometry.

2-(2-Hydroxy-4-methoxy-benzylidene)-6-methoxy-3-hydro-2H-inden-1-one (**4c**) was synthesized from 2,7-dimethoxy-11*H*-indeno[b]-1-benzopyrylium perchlorate (**3c**). A dark yellow powder, m.p.: 188–190 °C was obtained. MS, *m/z* (%): 296 (47) [M^+], 279 (100). ^{13}C-NMR, ^{1}H-BB-decoupled ([D_6]DMSO), δ (ppm): 191.70; 173.44; 164.415; 161.94; 160.55; 152.57; 131.141; 130.74; 130.51; 126.83; 125.06; 115.22; 115.07; 110.13; 105.53; 101.16; 55.71; 55.08; 32.13; 23.56. ^{1}H-NMR ([D_6]DMSO), δ (ppm): 7.86 [s, 1H]; 7.675 [d, $^3J = 8.4$ Hz, 2H]; 7.59 [d, $^3J = 8.7$ Hz, 2H]; 7.15 [s, 1H]; 7.00 [d, $^3J = 8.36$ Hz, 1H]; 6.54 [s, 1H]; 6.47 [d, $^3J = 9.7$ Hz, 1H]; 4.0–2.8 [m].

Trans-2-(2,4-dimethoxy-benzylidene)-6-methoxy-3,4-dihydro-2H-naphthalen-1-one (**7**) has been synthesized by a base-catalysed aldol condensation of 2,4-dimethoxybenzaldehyde and 6-methoxy-1-tetralone as described in [1] giving pale yellow crystals, m.p.: 114 °C. Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06%; H, 6.21%. Found: C, 73.76%; H, 6.51%. MS, *m/z* (%): 324 (2) [M^+]; 293 (100). ^{13}C-NMR, ^{1}H-BB-decoupled ([D_6]DMSO), δ (ppm): 185.40; 163.08; 161.48; 159.35; 145.80; 133.26; 130.77; 129.78; 126.51; 116.55; 113.53; 112.24; 104.88; 98.30; 55.463 [m]; 39.28 [m]; 28.43; 27.03. ^{1}H-NMR ([D_6]DMSO), δ (ppm): 7.90 [d, $^3J = 8.6$ Hz, 1H]; 7.75 [s, 1H]; 7.29 [d, 1H, $^3J = 8.5$ Hz]; 6.91 [dd, $^3J = 8.8$ Hz, $J = 2.5$ Hz, 1H]; 6.86 [d, $^3J = 2.4$ Hz, 1H]; 6.63 [d, $^3J = 2.4$ Hz, 1H]; 6.58 [d, $J = 2.3$ Hz, 1H]; 6.56 [dd, $J = 8.4$, 2.3 Hz, 1H]; 3.79 [m, 6H]; 3.75 [m, 3H]; 2.94 [m, 2H]; 2.85 [m, 2H].

The *trans*-geometry was verified by a NOESY experiment which shows a coupling between the signals $\delta = 2.94$ ppm (CH_2) with $\delta = 7.29$ ppm (aromatic).

Borax–glycerol mixtures were prepared by dissolving 40 g borax in 50 g glycerol for 5 min cooking. Acetonitrile was distilled twice before use. All solvents were spectroscopic grade. All studies were performed without elimination of dissolved oxygen.

2.2. Apparatus and procedures

Fluorescence spectra were recorded on a Perkin Elmer LS 50 at an absorption of 0.05. The quantum yield of the fluorescence was determined from the fluorescence spectra which were corrected using an apparatus specific function. A solution of quinine bisulphate in 0.1 N aqueous sulphuric acid served as fluorescence standard ($\Phi_f = 0.55$, $n_d^{20} = 1.333$).

^{1}H- and ^{13}C-NMR spectrum were obtained in DMSO by means of a Bruker AMX 400 using TMS as internal standard. GC–MS spectra were detected with a Trio 2000 (Carlo Erba) at an electronic energy of 70 eV.

The melting points were determined by means of a Kofler apparatus and are uncorrected. Reaction spectra of the photochemical colouration and the thermal degradation of the benzopyrylium salts were obtained by means of the Carl Zeiss M 400 UV/Vis spectral photometer which is equipped with an irradiation unit B 400. In this arrangement, the irradiation light is directed perpendicularly to the measurement light so that irradiation and measurement can be performed inside the sample holder of the spectrometer without breaks. The irradiation light is supplied by a mercury high pressure lamp HBO 200. The irradiation intensity I_0 was determined at 20 °C using α,β-di-*p*-anisilfulgide as secondary actinometer [14–16]. The heats of formation of the ground state were obtained from semiempirical MNDO-AM1 calculations by means of VAMPC 4.56 [17].

3. Results and discussion

3.1. Thermal bleaching and photochemical colouration

All studied benzopyrylium salts undergo a thermal decolouration reaction in aqueous solution or borax–glycerol media usually forming *trans*-2-hydroxychalcones (Fig. 3(a)). A number of them is reconverted to the initial benzopyrylium salts on irradiation, so that a photochromic system results (Fig. 3(b)). The formation of 2-hydroxychalcones is evident from the comparison of the UV/Vis spectra of the hydrolysis products with spectra of known *trans*-2-hydroxychalcones which were synthesized independently [1–3,5,12]. The spectral data of the hydrolysis products are summarized in Table 1. Furthermore, the absorption bands are shifted long-wavelength when these hydrolysis products are treated with NaOH to achieve pH > 5. The latter effect indicates the deprotonation of a phenolic OH group in the molecule.

The structure of the final hydrolysis products of the bridged benzopyrylium salts **3c** and **5c** were confirmed by means of ^{1}H- and ^{13}C-NMR spectroscopy. For this purpose, the hydrolysis products of these benzopyrylium salts were

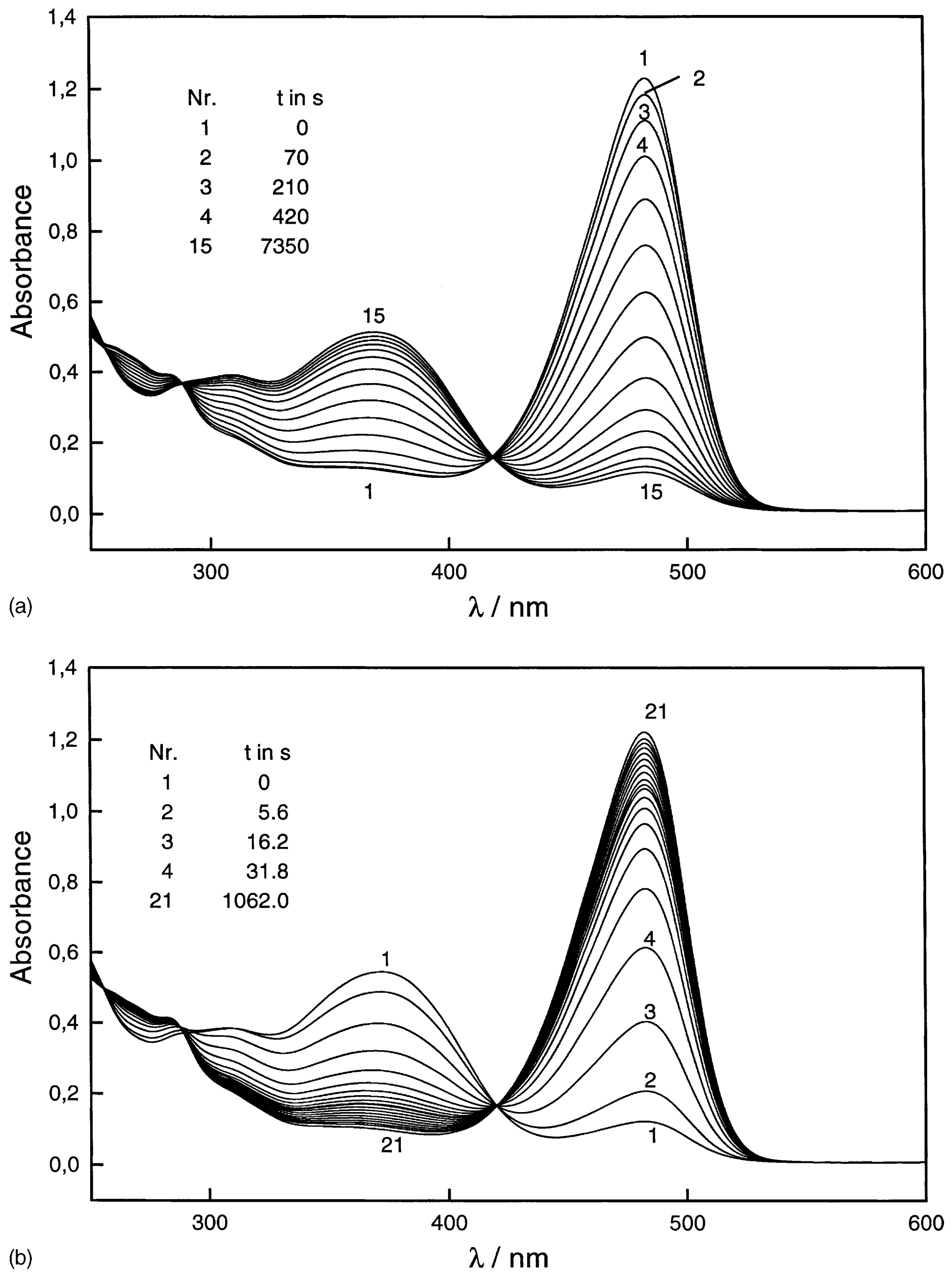

Fig. 3. Thermal bleaching of **5c** at 20 °C (a), followed by photochemical colouration in 1:1 aqueous acetonitrile (pH = 4.7) on irradiation with 366 nm light.

Table 1
The UV/Vis spectral data, $\lambda_{\max}$ in nm ($\varepsilon_{\max}$ in $\mathrm{l\,mol^{-1}\,cm^{-1}}$), of the hydrolysis products in aqueous solution, usually *trans*-2-hydroxychalcones

	2	**4**	**6**
a	352 (13,000)	[a]	[a]
b	356 (17,000)	327 (17,700)[b]	[a]
c	371 (26,000)	377 (30,200)	354 (21,000)
d	448 (38,000)	456 (43,000)	446 (17,000)

[a] Several products.

[b] Probably a *cis*-chalcone.

precipitated by the addition of an aqueous buffer solution to a cold-saturated solution of the benzopyrylium salts in ethanol. The ^{13}C-NMR spectra of the products **4c** and **6c** give characteristic signals at $\delta = 191.70$ and 185.53 ppm, respectively, indicating the structure of a chalcone in both cases. Additionally, the structure of the chalcone **6c** was verified by the synthesis of the respective 2-methoxy-chalcone (**7**) via a base-catalysed aldol condensation in accordance to the literature [1]. As demonstrated in Fig. 4 both products have identical UV/Vis spectra.

In order to get knowledge about the stereochemistry of the bridged chalcones a NOESY experiment was performed.

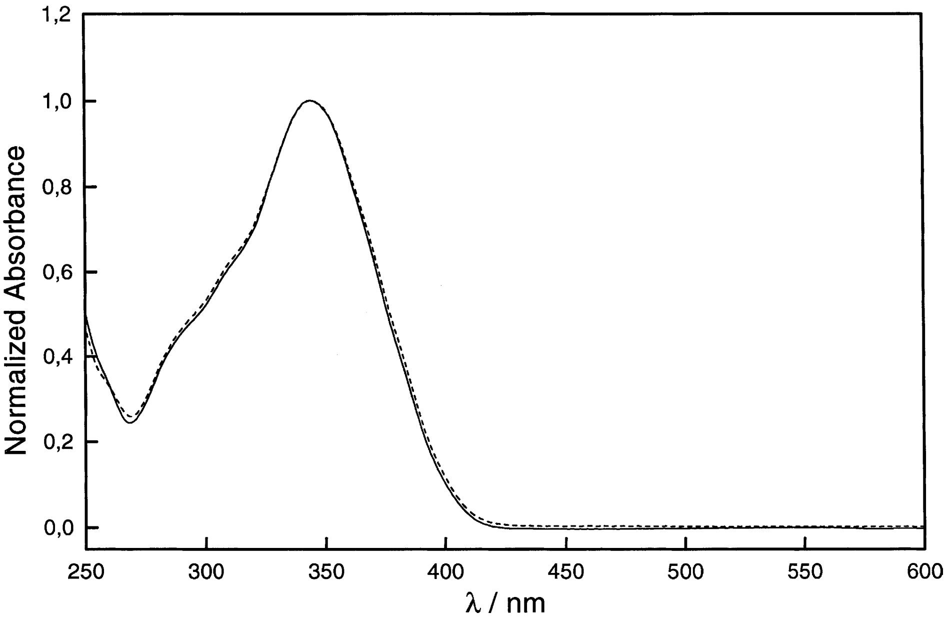

Fig. 4. UV/Vis spectra of **6c** and **7** in acetonitrile: solid line, **6c**; dashed line, **7**.

The spectrum of the chalcone **6c** shows a characteristic cross peak between the ^{1}H signals at $\delta = 7.25$ and 2.97 ppm. As these signals belong to the phenyl ring and the bridge, respectively, this coupling indicates a *trans*-isomer.

Due to impurities of the hydrolysis product **4c** the NOESY experiment does not provide evident results. However, the high melting point and the long-wavelength shifted UV/Vis absorption band indicate a *trans*-isomer as well.

Despite the similar structure of the final hydrolysis products it was found quite a different behaviour regarding the photochemical reaction. Only non-bridged and $(CH_2)_2$-bridged *trans*-chalcones show a photochemical colouration in borax–glycerol media or aqueous acetonitrile (1:1) (Fig. 3(b)), while all CH_2-bridged benzopyrylium cations (**3**) cannot be formed by a photochemical reaction of the respective chalcones. The irradiation of the CH_2-bridged chalcone leads only to a decrease of the absorption at the chalcone absorption maximum and the appearance of absorption bands in the long-wavelength tail of the band (Fig. 5).

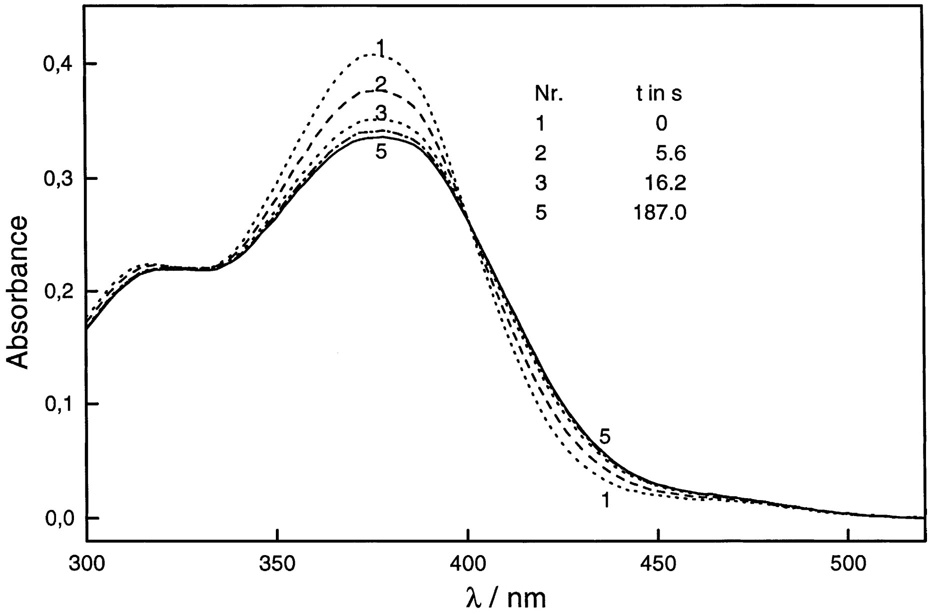

Fig. 5. Photochemical reaction ($\lambda' = 365$ nm, $I_0 = 8.5 \times 10^{-9}$ mol s^{-1} cm^{-2}) of the chalcone **4c** in 1:1 aqueous acetonitrile (pH = 5.7).

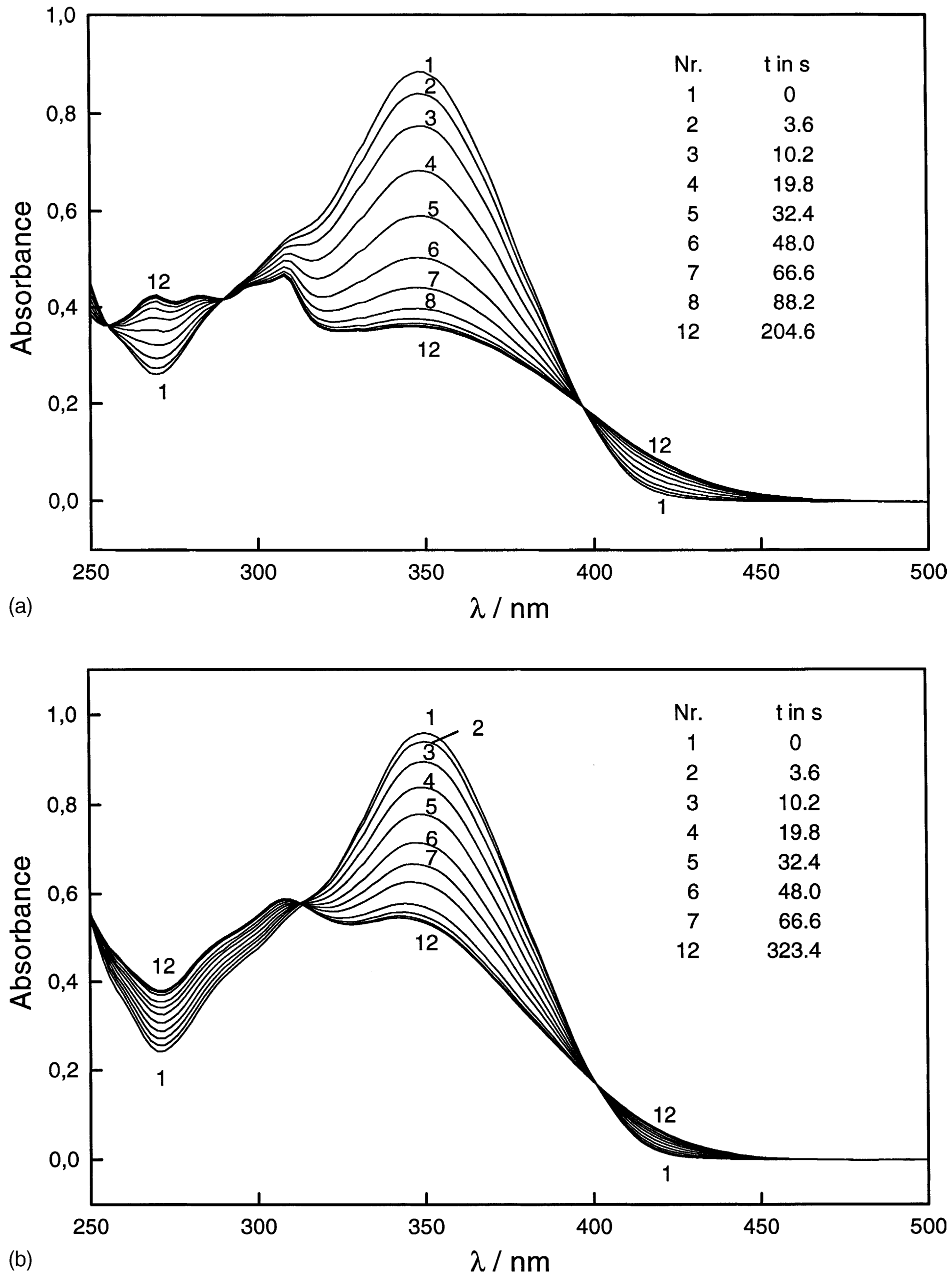

Fig. 6. Photochemical reaction of **6c** (a) and **7** (b) in propylene carbonate at 20 °C. Irradiation with light of 365 nm wavelength.

3.2. Mechanistic studies

In order to understand the different behaviour of the $(CH_2)_2$- and the CH_2-bridged chalcones the behaviour of the $(CH_2)_2$-bridged *trans*-2-hydroxychalcone (**6c**) on irradiation in several acid-free solvents was studied. In these media the conversion of the intermediates to the benzopyrylium cation is prevented, as its formation requires acid. For comparison, the behaviour of the 2-OMe-substituted analogue **7** was investigated under the same conditions. In the latter one the cyclization of the *cis*-chalcone and a keto–enol tautomerism are blocked. Thus a photochemical reaction of **7** (Fig. 6(b)) can be referred to a *trans–cis* isomerization. The addition of acids after the photochemical reaction results in a quantitative formation of the initial *trans*-chalcone indicating that subsequent reactions do not happen.

Similar to **7**, the irradiation of **6c** in propylene carbonates leads to a decrease in the absorption of the long-wavelength band and growing absorptions at about 270 and 400 nm until a photostationary state is attained (Fig. 6(a)). The three isosbestic points obtained with **6c** have a similar position as observed with **7** (255, 290, and 397 nm with **6c** and 251, 313, and 401 with **7**).

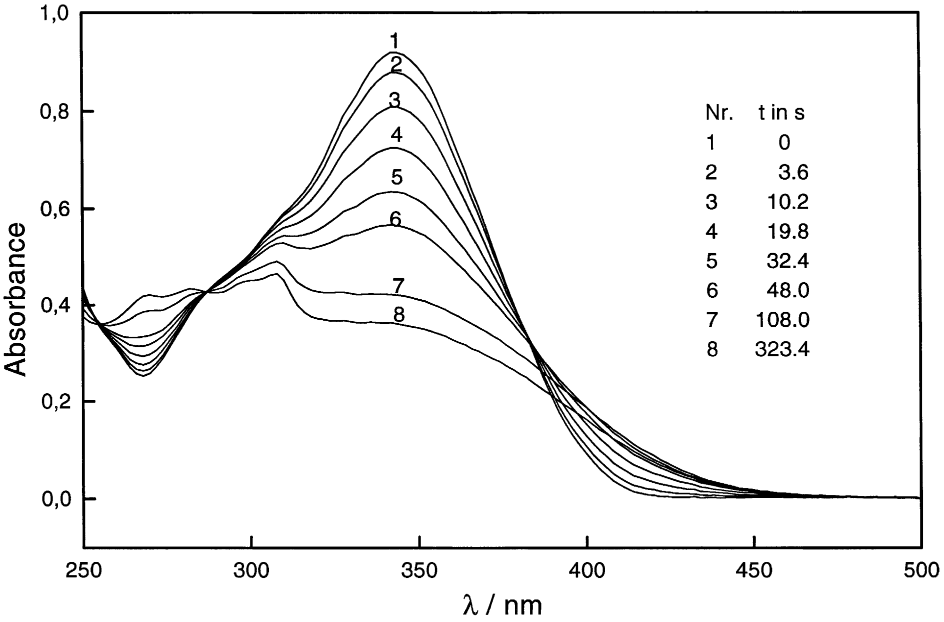

Fig. 7. Photochemical reaction of **6c** in acetonitrile on irradiation with 365 nm light.

Because of the similar behaviour of the 2-hydroxy- and the 2-methoxychalcone, the photochemical reaction of **6c** can be attributed to a *trans–cis* isomerization. This is supported by linear curves in the AD diagrams of the reaction spectra which indicate a uniform reaction. The formation of an enol in the S_1 state, as proposed in [3], can be ruled out.

In acetonitrile, the reaction spectra of **6c** during the first reaction period (spectra 1–6, Fig. 7) resemble Fig. 6(a) and isosbestic points occur (at 254, 287 and 386 nm). This first reaction step can thus be referred to a *trans–cis* isomerization. However, on prolonged irradiation a subsequent photochemical reaction takes place which can be concluded from the disappearance of the isosbestic point at 386 nm. This subsequent reaction step is not found with the respective 2-OMe chalcone **7**. It can, therefore, be assumed that a ring closure of the *cis*-2-hydroxychalcone to the 2-hydroxyflavene happens on irradiation of **6c**.

Flash photolysis experiments were performed with the non-bridged chalcone (**2c**) and the respective $(CH_2)_2$-bridged one (**6c**). The experiments provide no hint for the appearance of triplets or radicals. In both cases the formation of the benzopyrylium cations passes an induction period of about 0.5 s and takes several seconds (Fig. 8). This is in accordance with studies of other non-bridged chalcones [12]. The induction period before the colouration gives evidence for a photochemically initiated formation of the benzopyrylium cation in the case of **1c** and **5c**. Both absorption–time curves can neither be fitted using a monoexponential nor a biexponential function. As the thermal decolouration of **5c** can be neglected during the first second after the flash, the occurrence of a more complex sequence of thermal reactions can be concluded.

The similar behaviour of the non-bridged and the $(CH_2)_2$-bridged chalcones in the flash photolysis experiments and the behaviour of **6c** on irradiation in acid-free media indicate that the mechanism of the interconversions of the non-bridged benzopyrylium–chalcone systems can be applied also to the $(CH_2)_2$-bridged ones. The stability of intermediates was studied using semiempirical MNDO-AM1 calculations (Table 2).

The heat of formation supplies a measure of the stability of species with the same molecular formula. According to the finding that *trans*-chalcones (*t*C) are formed on hydrolysis of benzopyrylium salts, one can expect that the heats of formation decrease to achieve the *trans*-chalcones. In the calculations, it was found to be really true for most of the bridged

Table 2
Heats of formation of the most important intermediates of the benzopyrylium–chalcone interconversions in kcal mol^{-1}, calculated using the MNDO-AM1 Hamiltonian

	$[F^+][ClO_4^-]$[a]	PB2	*c*C	*t*C
1a	75.14	−12.39	−8.50	−10.63
1b	33.59	−50.49	−46.82	−49.07
1c	−6.62	−88.37	−84.30	−87.54
1d	21.19	−53.54	−50.28	−52.62
3a	82.46	−5.47	−5.45	−7.38
3b	41.12	−43.41	−43.76	−45.95
3c	1.33	−81.30	−82.39	−84.10
3d	29.74	−46.35	−47.43	49.04
5a	63.78	−19.46	−16.76	−19.32
5b	22.52	−57.49	−55.22	−57.87
5c	−19.66	−95.37	−93.25	−96.25
5d	10.75	−61.29	−58.94	−61.14

[a] ClO_4^- was calculated using the MNDO-PM3 Hamiltonian ($\Delta_f H = -128.05$ kcal mol^{-1}).

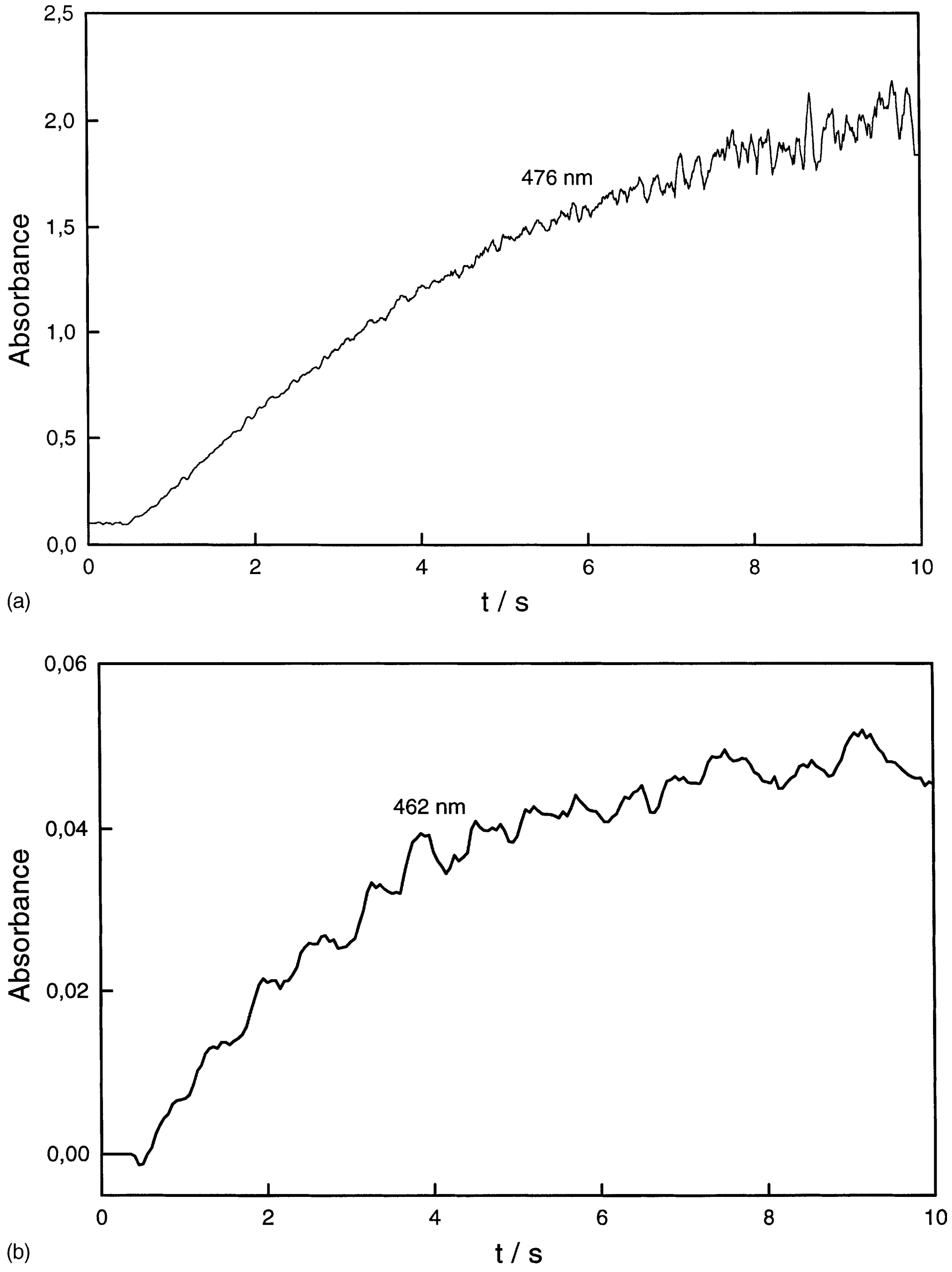

Fig. 8. Photochemical colouration of benzopyrylium cations. **5c** in 1:1 aqueous acetonitrile at pH 6.32 (a) and **1c** in 1:1 aqueous ethanol at pH 6.13 (b).

trans-chalcones, however, in the non-bridged systems the 2-hydroxyflavenes (PB2) are calculated to be always more stable than the corresponding *trans*-2-hydroxychalcones. In these cases, the hydrolysis should be finished after the formation of PB2 in contrast to the experimental data. However, due to different strength of interactions of the water molecules in the reaction media with the phenolic OH group in *t*C and the alcoholic one in PB2 a stronger stabilization of the chalcones can arise which explains the preference of the *trans*-chalcones. This is supported by the observation that the non-bridged 2-hydroxychalcone is not formed in tetrahydrofuran (THF) [18].

Regarding the photochemical colouration, the excitation of the *trans*-chalcone is necessary to achieve the *cis*-chalcone which is calculated to be 3–4 kcal mol^{-1} less stable in the ground state than the respective *trans*-isomer. As seen in Table 6, the non-bridged and the $(CH_2)_2$-bridged *cis*-chalcone can undergo either a downhill ring closure to the 2-hydroxyflavene or can reform the initial *trans*-chalcone. In contrast, the ring closure of the CH_2-bridged *cis*-chalcones is calculated to have usually a positive reaction enthalpy, i.e. a positive free reaction enthalpy since entropy changes can be neglected. For this reason, the formation of the 2-hydroxyflavene does not occur. The reaction spectra of the photochemical reaction of **4c** are thus similar to that of **6c** in propylene carbonate (Fig. 6(a)) and concludingly they can be attributed to the formation of the *cis*-chalcone. The instability of the 2-hydroxyflavene is probably due to enhanced ring tensions within the 5-membered ring in this arrangement.

Contrary to the non-bridged *trans*-chalcones the $(CH_2)_2$-bridged ones are calculated to be sometimes the most stable hydrolysis products (systems **5**/**6b** and **5**/**6c**), i.e. the formation of chalcones does not require the stabilizing effect of the water molecules. Hence, it can be expected that these $(CH_2)_2$-bridged photochromic systems work also in organic solvents with a minimum water content. This is welcome as a high water content usually decreases the reaction quantum yield [18].

3.3. Reaction quantum yield

Concerning the quantum yield of the photochemical reaction one must consider that the photochemical colouration of the benzopyrylium cations is initiated by a *trans*–*cis* isomerization. However, the subsequent reaction of the *cis*-chalcone proceeds fast and the benzopyrylium cations are stable on irradiation (except **1a**, **3a** and **5a**). The photochemical quantum yield Φ_r can therefore be estimated using the formula (2) as long as the absorption of the benzopyrylium dye is negligible at the irradiation wavelength:

$$\Phi_r = \frac{1}{I_0 t \varepsilon' d} \log \frac{10^{A'(0)} - 1}{10^{A'(t)} - 1} \qquad (1)$$

where I_0 represents the light intensity, d the path length of cell and $A'(0)$ and $A'(t)$ the absorption of the *trans*-chalcone at the irradiation wavelength at the beginning of the photochemical reaction and at the irradiation time t, respectively. The molar absorption coefficient at the irradiation wavelength ε' cannot be given accurately for borax–glycerol media. It was, therefore, estimated from the data in aqueous solution. Because of the viscosity of the borax–glycerol media, it was not possible to stir the probes during irradiation. Thus, the absorption at the irradiation wavelength was adjusted to about 0.05 which allows to neglect the decrease of the light intensity along the cell. Under these conditions, Φ_r can be determined approximately according to the following equation:

$$\Phi_r = \frac{1}{I_0 t \varepsilon' d} \log \frac{A'(0)}{A'(t)} \qquad (2)$$

In order to minimize the errors, a high density of measurement points were gathered at the beginning of the photoreaction. The reaction quantum yields are given in Table 3. The experimental error is estimated to be around ±20% in aqueous acetonitrile and ±30% in borax–glycerol.

From Table 3 several effects are obvious: (i) the increase of the quantum yield going from the aqueous acetonitrile to the viscous borax–glycerol media and (ii) the low quantum yield of the NEt_2 substituted chalcones. Both effects can be referred to the decreasing tendency of the excited chalcones to deactivate via a twisted intramolecular charge transfer (TICT) in borax–glycerol [19].

Table 3
Photochemical quantum yields, Φ_r, of some chalcones in (1:1) aqueous acetonitrile (a) and in borax–glycerol (bg) at 20 °C

	λ' (nm)	Φ_r (a)	Φ_r (bg)
2c	365	0.29[a]	0.59[b]
2d	436	0	0.02
6c	365	0.24[a]	0.42
6d	436	0	[c]

[a] At 0 °C.

[b] In a mixture consisting of glycerol:borax:boric acid in a mass ratio of 2:2:1.

[c] Not measurable because the chalcone is not formed.

The difference in the reaction quantum yields between **2c** and **6c** is not significant within the experimental error. It can thus be concluded that rotational motions of the 2-phenyl group are not effectively involved in the deactivation of the excited chalcone. This is supported by the fluorescence data which show an extremely low fluorescence quantum yield for the bridged chalcone **6c** (Table 4).

3.4. Thermal bleaching

The insertion of a $(CH_2)_2$- or a CH_2-bridge in the benzopyrylium cations causes a considerable decrease of their velocity of the hydrolysis reaction. In accordance with earlier studies [4,8], a first-order reaction kinetics was found at the beginning of the decolouration reaction. The rate constants were determined by adding 2 ml of a temperated stock solution of the benzopyrylium salt in acetonitrile to a stirred and temperated buffer solution in a cuvette which was measured in the UV/Vis spectrometer as quick as possible. In all cases the chalcone band does not overlap the benzopyrylium band over the whole area. Thus, at the long-wavelength flank of the benzopyrylium absorption band, the absorption is proportional to the concentration of the benzopyrylium cation. The first-order rate constant k' was determined from

$$\ln A(t) = \ln A(0) - k't$$

where A represents the absorption at time t and $A(0)$ the absorption at $t = 0$.

The first-order rate constant grows with increasing pH. With respect to the mechanism given in Fig. 1, it can be concluded that OH^- is involved in the reaction as a nucleophile.

Table 4
Fluorescence data, λ_f, ϕ_f and $\Delta\tilde{\nu}$ of **6c** at 20 °C

Solvent	λ_f (nm)	ϕ_f
Ethanol	418	0.0008
Trichloromethane	434	0.0006

Table 5
Second-order rate constant, k (in $\mathrm{l\,mol^{-1}\,s^{-1}}$) of hydrolysis of benzopyrylium cations in 1:1 aqueous acetonitrile at 20 °C

	1	2	3
a	$\geq 3.9 \times 10^{7}$	4.8×10^{7}	9.1×10^{6}
b	$\geq 1.2 \times 10^{7}$	$\geq 8.4 \times 10^{6}$	3.7×10^{8}
c	3.4×10^{7}	7.7×10^{4}	4.1×10^{5}
d	7.0×10^{2}	5.5×10^{2}	2.0×10^{2}

Table 6
Difference between the heats of formation of the benzopyrylium salt and the 2-hydroxyflavene, $\Delta E = \Delta H^\circ(\mathrm{PB2}) - \Delta H^\circ([F^+][\mathrm{ClO_4}^-])$. ΔH° calculated using the MNDO-AM1 Hamiltonian

	1	5
a	−87.53	−83.24
b	−84.08	−79.47
c	−81.75	−75.71
d	−74.73	−72.04

Accordingly, second-order rate constant k can be given as follows:

$$k = \frac{k'}{[\mathrm{OH^-}]} \qquad (3)$$

For the model substance, the second-order rate constant was confirmed to be independent of the pH (in the studied range between 4.0 and 5.6). The second-order rate constants obtained in 1:1 aqueous acetonitrile are given in Table 5. The data of **1a** and **1b** are by more than two orders of magnitude larger than in 0.1 N HCl at 25 °C [4]. The acceleration of the reaction in aqueous acetonitrile is due to the decrease in the solvation of the $\mathrm{OH^-}$ ion. Concludingly, the desolvation of the nucleophile during the formation of the activated complex is facilitated which increases the strength of the nucleophile.

Table 5 shows that a $\mathrm{CH_2}$- and as well as a $(\mathrm{CH_2})_2$-bridging diminish the tendency of the benzopyrylium cations to a nucleophilic addition of $\mathrm{OH^-}$. However, the effect decreases with a growing number and donor strength of the substituents. During the nucleophilic attack at the benzopyrylium cation the hybridization of the C2 atom changes from sp^2 to sp^3. Due to the considerable loss of flexibility, especially by $\mathrm{CH_2}$-bridging, the resulting geometric changes are hindered. Consequently, the formation of the $\mathrm{CH_2}$-bridged 2-hydroxyflavene is made more difficult and a slower decolouration rate of these species results in comparison to the non-bridged ones.

The $(\mathrm{CH_2})_2$-bridging allows, however, stronger geometric changes in the molecule. Thus, the loss of flexibility does not explain the kinetic stability of the $(\mathrm{CH_2})_2$-bridged flavylium cations. As shown in Table 6, the decrease of the rate constant on insertion of the $(\mathrm{CH_2})_2$-bridge is associated with a decrease in the energy difference between the benzopyrylium cation and the 2-hydroxyflavene (ΔE) which is a measure of the reaction enthalpy for the formation of PB2 from $\mathrm{F^+}$. A less negative ΔE means a more endotherm reaction, an energetic increase of the transition state usually occurs [20]. Concludingly, a more positive energy difference means an increasing activation barrier which finally leads to a decrease in the rate constant of the reaction.

3.5. Reversibility

As mentioned above, the insertion of a $\mathrm{CH_2}$- and a $(\mathrm{CH_2})_2$-bridge between the 3-position of the benzopyrylium unit and the 2′-position of the phenyl moiety decisively af-

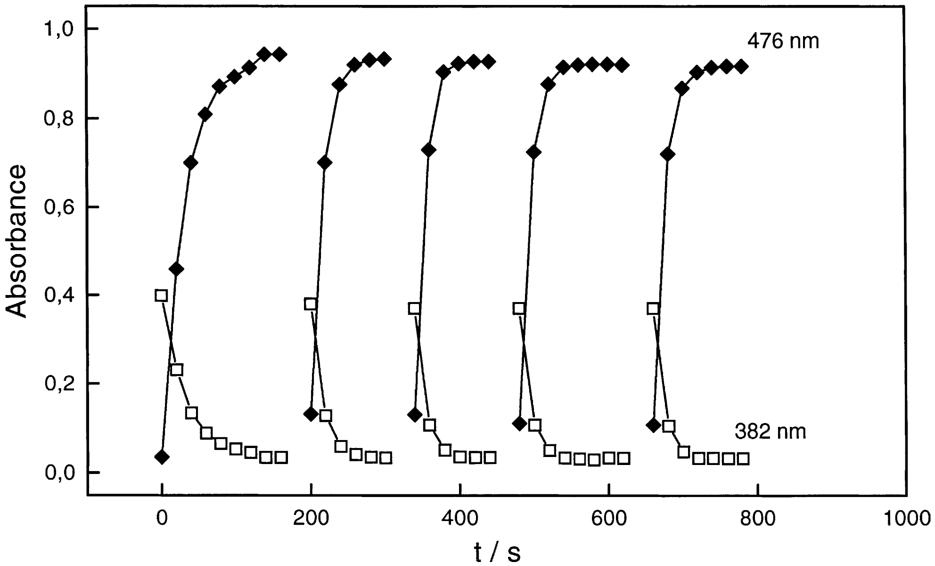

Fig. 9. Irradiation cycles of **6c** in 1:1 aqueous ethanol solution on irradiation with light of 365 nm wavelength, pH = 5.9 at 19 °C.

fects the reversibility of the benzopyrylium–chalcone interconversions. In most cases, the non-bridged and the $(CH_2)_2$-bridged chalcones show reversible structural changes in the presence of acids [21] and on irradiation, whereas the decolouration of all studied CH_2-bridged chalcones was found to be irreversible.

Studies on the influence of external factors on the reversibility of the photochromic conversions of **5**/**6c** show the lowest loss per cycle using an aqueous ethanol solution (1:1) with an acetic acid/acetate buffer and a relatively high light intensity (about 8×10^{-9} einstein s^{-1} cm^{-1}). However, the pH does not significantly affect the reversibility of the system in the studied range $(4.9 < pH < 6.4)$.

Comparing the benzopyrylium–chalcone interconversions of the non-bridged and the analogous substituted $(CH_2)_2$-bridged systems **1**/**2c** and **5**/**6c** a different reversibility was found. Using a 1:1 aqueous ethanol mixture containing a 0.1 M acetic acid/sodium acetate buffer, a fair reversibility was found in **5**/**6c** with a loss of about 0.7% performance per cycle (Fig. 9). Under similar conditions the respective non-bridged system **1**/**2c** exhibits a significant lower reversibility with a loss of 1.5% per cycle.

The fair reversibility of the system **5**/**6c** is in accordance with pronounced clean isosbestic points in the reaction spectra of the thermal and photochemical reaction and linear curves in the AD diagrams in both processes which account for a clean reaction sequence. Concludingly, further studies concerning the photochromic properties should be focussed on $(CH_2)_2$-bridged benzopyrylium salts.

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