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Photochromic properties of hydrolyzed benzopyrylium salts—the influence of substituents

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Abstract

A series of systematically modified benzopyrylium salts was hydrolyzed to study the influence of donor substituents in 4-, 7- and 4′-position of the benzopyrylium cation on photochromic systems. A photochromic behavior was observed at the 7- and 4′-substituted flavylium salts, whereas the insertion of 4-phenyl group prevents the formation of a photochromic system.

The photochemical quantum yield varies strongly depending on the substituents and the medium conditions. Good reaction quantum yields were found in highly viscous borax–glycerol mixtures. The exclusively OH- and OMe-substituted chalcones exhibit photochemical quantum yields up to 0.6, whereas the NR_2-substituted ones show quantum yields usually below 0.1. As a rule the latter ones fluoresce more intensively, indicating that the S_1 state of the *trans*-chalcone is the common precursor for the photochemical formation of flavylium cation. The differences in the reaction quantum yields can be referred to the different tendency of the formation of a highly polar state on the S_1 hypersurface, presumably a twisted intramolecular charge transfer state (TICT).

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

1. Introduction

2-Phenyl-1-benzopyrylium salts (flavylium salts) as derivatives of naturally occurring plant pigments are known to be involved in photochromic processes for long times [1–4]. The photochromic conversions occur between the often deeply colored flavylium salts and the colorless or yellow *trans*-2-hydroxychalcones. According to a number of mechanistical studies the thermal decoloration reaction is initiated by the formation of a 2-hydroxyflavene, a so-called pseudobase (Fig. 1). Being a hemiacetal, in acidic solutions this product undergoes a conversion to the tautomeric *cis*-2-hydroxychalcone. The latter one isomerizes acid-catalyzed to the *trans*-chalcone [1,5,6].

The photochemical coloration is initiated by a *trans–cis*-isomerization of the chalcone [1,4]. ^{1}H-NMR and mass spectroscopic data prove the formation of an acetal on irradiation of a *cis*-chalcone in alcohol. Thus, the formation of a 2-hydroxyflavene in the photochemical reaction can be concluded [7].

Recently, photochromic systems on the basis of flavylium–chalcone systems were shown to be favorable for the use as chemical actinometer [8,9]. Although, some properties are poor compared to well-developed systems, these systems are interesting because they work under environmental conditions where other systems are destroyed. Especially, they do not suffer from dissolved oxygen and work in aqueous solutions. Among the great number of known flavylium dyes it is likely to find systems with optimal properties. Especially interesting are such systems which involve a long-wavelength absorbing form and which can be excited by visible light. Thus, our studies are concerned with the influence of donor substituents in 4-, 7- and 4′-position at the flavylium salt on the photochromic properties (Fig. 2).

Code	R^1	R^2	R^3
a	–	–	–
b	–	Me	–
c	–	OH	–
d	–	OMe	–
e	–	NMe_2	–
f	OH	–	–
g	OH	OH	–
h	OH	OMe	–
i	OMe	–	–
k	OMe	Me	–
l	OMe	OH	–
m	OMe	OMe	–
n	OMe	OMe	Ph
o	OMe	NMe_2	–
p	NMe_2	OMe	–
q	NMe_2	NMe_2	–
r	NEt_2	OMe	–
s	NEt_2	NMe_2	–

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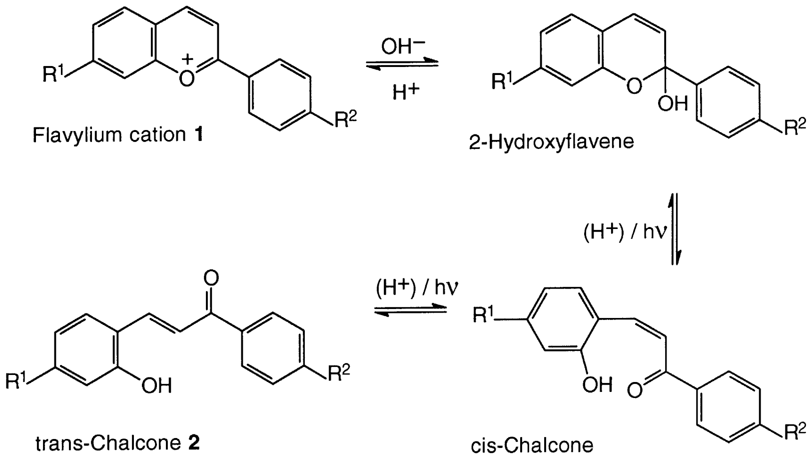

Fig. 1. Reaction pathways for the photochemical coloration and thermal conversion.

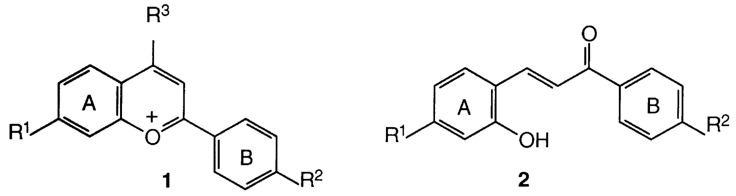

Fig. 2. Structures of benzopyrylium ions and *trans*-2-hydroxychalcones.

2. Experimental details

2.1. Materials

Borax–glycerol mixtures were prepared by solving 40 g borax in 50 g glycerol during 5 min cooking. The highly viscous borax–glycerol mixtures exhibit a defraction index of 1.444 and a pH of 5.9–6.9 at 30 °C. Highly viscous mixtures with pH = 3 were prepared from glycerol/borax/boric acid in a mass ratio 2:2:1. On the basis of UV–VIS data it can be assumed that borax–glycerol mixtures exhibit a considerably lower polarity than water. All solvents were spectroscopic grade. Acetonitrile was distilled twice before use. The flavylium salts were synthesized according to the literature [10–13].

The *trans*-2-hydroxy-4,4′-dimethoxychalcone (**2m**) was prepared from the 4′,7-dimethoxyflavylium perchlorate (**1m**) 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 recrystallyzed from methanol.

Pale yellow needles or powder, mp: 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, $^3J = 13.4$ Hz and $^3J = 15.6$ Hz]; 7.07 [$J = 8.3$ Hz, 2H]; 6.49 [s, 2H]; 3.85 [s, 3H]; 3.75 [s, 3H].

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 using the corrected fluorescence spectra. A solution of quinine bisulfate in 0.1N aqueous sulfuric acid served as fluorescence standard ($\Phi_\mathrm{f} = 0.55$, $n_\mathrm{D}^{20} = 1.333$).

^{1}H- and ^{13}C-NMR-spectra 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.

To study spectra and quantum yields of the photochromic systems a stock solution of the benzopyrylium perchlorate in acetonitrile was prepared which was mixed with a warm borax–glycerol solution. While standing for at least 10 h in the dark at 60 °C, the colored flavylium form was converted to the hydrolyis product. Since borax–glycerol solutions can not be stirred during irradiation, the concentration was adjusted that way that the absorption of the chalcone ranges between 0.05 and 0.1 at the irradiation wavelength.

The irradiation of the chalcones was performed at 20 °C using the Carl Zeiss M 400 UV–VIS spectral photometer which is equipped with an irradiation unit B 400. The irradiation light is directed perpendicularly to the measurement light. This arrangement makes possible that irradiation and measurement can be carried out inside the sample holder of the spectrometer without breaks. The major light beams 365, 405, and 436 nm are supplied by a mercury high pressure lamp HBO 200. The quantum yield was determined using the formula (1):

$$\phi_{\mathrm{r}} = \frac{1}{I_0 t \varepsilon_{\mathrm{C}} d} \log\left(\frac{10^{A(0)}-1}{10^{A(t)}-1}\right) \qquad (1)$$

where A represents the absorption at the irradiation wavelenth, ε_{C} the molar absorption coefficient of the chalcone at the irradiation wavelength, t the time of irradiation, and d the length of the cell. The irradiation intensity I_0 was determined at 20 °C using α,β-di-*p*-anisilfulgid as secondary actinometer [14–16].

All studies were performed without elimination of dissolved oxygen.

3. Results

3.1. Spectral data of the benzopyrylium salts and their hydrolysis products

In weak acidic or neutral solutions the colored flavylium salts are converted to *trans*-2-hydroxychalcones often forming a photochromic system. The structural conversions of the flavylium salts are accompanied by a color change or the decoloration of the solutions. Spectral data of the benzopyrylium salts and their final hydrolysis products obtained in borax–glycerol are given in Table 1.

Because of the relatively large pH (5.9–6.9), in borax–glycerol the chalcones **2a**, **b**, **d**, **i**, **k**, **m** form colorless species on irradiation which may be *trans*- and *cis*-chalcones and 2-hydroxyflavenes (pseudobases). In order to study the photochromism of these chalcones, aqueous solutions with an individual pH were, therefore, preferred which was between 2 and 4. Spectral data are given in Table 2.

Table 1
The UV–VIS spectral data of the photochromic systems in borax–glycerol-mixtures

Substitution	Flavylium ion		Chalcone	
	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ ($\mathrm{l\,mol^{-1}\,cm^{-1}}$)	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ ($\mathrm{l\,mol^{-1}\,cm^{-1}}$)
c	508	40000[a]	356	22100
e	540	39500	406	28000
f	486	27000[a]	386	17100
g	506	39000[a]	382	21900
h	494	40000[a]	380	23300
l	519	41000[a]	379	22500
m[b]	467	52600	379	26000
o	566	57000	413	33600
p	537	31700	448	40900
q	603	75900	447	49300
r	536	33000	456	41600
s	608	68000	461	44500

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

Table 2
The UV–VIS spectral data of the benzopyrylium compounds and their hydrolysis products in water

Substitution	Flavylium ion		Hydrolysis product	
	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ ($\mathrm{l\,mol^{-1}\,cm^{-1}}$)	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ ($\mathrm{l\,mol^{-1}\,cm^{-1}}$)
i	426	23900	371	16700
k	438	37100	371	20500
m	459	53000	371	26000
n	461	48600	228[a]	18500[a]

[a] Probably a 2-hydroxyflaven.

As revealed by the position of the longest-wavelength absorption band the final hydrolysis products can normally be identified as *trans*-2-hydroxychalcones. However, comparing the spectral data of the hydrolysis products of **1m** and **1n** (Table 2), the product of **1n** exhibits a considerably short-wavelength shifted absorption maximum. The formation of a chalcone can, therefore, be ruled out. This is supported by the observation that the hydrolysis product of **1n** does not undergo the typical coloration reaction in basic media which indicates the phenolic OH-group in the 2-hydroxychalcones. It is, thus, assumed that a 2-hydroxyflavene is formed from the 4-phenyl-substituted flavylium salt. In accordance, no photochromic reaction was recognized at **1n** in contrast to the analogue without a 4-phenyl group (**1m**) which forms a photochromic system.

As seen in Tables 1 and 2, the longest-wavelength absorption maxima of the studied benzopyrylium cations range between 400 and 600 nm depending on the substituents in R^1- and R^2-position and cover nearly the whole spectrum of visible light [17]. The corresponding chalcones absorb between 350 and about 460 nm. The system of **1**/**2o** achieves with $\Delta\lambda = 127\,\mathrm{nm}$ ($\Delta\tilde{\nu} = 6553\,\mathrm{cm^{-1}}$) the largest band separation of all studied flavylium cation-chalcone systems.

The strong shift of the maxima of the benzopyrylium cations by increasing the donor strength of the substituents is characteristic for the transformation of a charge transfer system to a polymethine-like system [12]. The insertion of donor substituents in R^1- and R^2-position causes increasing HOMO and decreasing LUMO orbital energies. Since the longest-wavelength absorption bands are mainly determined by the transition between the frontier orbitals, a strong bathochromic shift results with growing donor strengths of these substituents. The shift is more pronounced in R^2- than in R^1-position.

In the borax–glycerol-mixtures, the OH groups of the flavylium salts **1c**, **1f**, **1g**, **1h**, **1l** deprotonate, i.e. the strong donor O^- is formed. The longest-wavelength absorption band of these benzopyrylium compounds (anhydrobases) is, therefore, considerably red-shifted and broad compared to the cationic forms. For **1l** the absorption band is strongly

Table 3
Absorption and fluorescence maxima, λ_{max} and λ_{f}, of **1s**

Solvent	λ_{max} (nm)	ε_{f} (nm)
$CHCl_3$	613	632
CH_2Cl_2	610	634
Acetonitrile	596	637
Ethanol	601	634
Borax–glycerol	608	635

structured. Since the chalcones are not deprotonated in the borax–glycerol mixtures, an improved band separation is obtained in the anhydrobase–chalcone system compared with the respective systems involving cationic flavylium forms.

The spectral data of **1m** and **1n** are identical within the experimental error (Table 2). Obviously, the 4-phenyl group forms a separate chromophore system (y-chomophore) and, thus, it hardly influences the longest-wavelength absorption band [18].

The solvatochromism of the flavylium salts is well-studied [12,17,18]. As a rule, the flavylium salts exhibit a hypsochromic shift of the longest-wavelength absorption band with increasing solvent polarity which is due to their extensive charge shift during the excitation and the delayed reorganization of the solvent molecules. For the same reason the fluorescence maximum is shifted long-wavelength with increasing solvent polarity. Since the absorption maximum of the benzopyrylium salt **1s** in borax–glycerol is shifted long-wavelength and the fluorescence short-wavelength compared to ethanol (see Table 3), it can be assumed that borax–glycerol mixtures exhibit a considerably lower polarity than ethanol.

The longest-wavelength absorption maximum of the chalcones shows positive solvatochromism. Therefore, this maximum can be classified as a π–π* transition which is in accordance with the large absorption coefficient. However, since the chromophore is more polyen-like, the absorption maxima of the chalcones achieve only wavelengths up to about 460 nm and the influence of the donor strength of the substituents on the spectral data is much smaller.

3.2. *Thermal bleaching and photochemical coloration*

An example of the photochromic conversions is demonstrated in Fig. 3. Despite the complex reaction mechanism of the thermal and photochemical reaction, clear isosbestic points are characteristic for the spectral changes.

Studies of the pH dependent thermal reactions show that the decoloration rate of the flavylium cation grows with an increasing pH [5,6]. Therefore, the participation of OH^- as nucleophile has been concluded. Second order rate constants can, thus, be given (Table 4). Comparing the rate constants of the NR_2-substituted flavylium salts **1e**, **1o**–**1r** with the non-substituted, alkyl and methoxy substituted flavylium salts, one can state that the rate constants decrease with a growing donor strength of the substituents indicating a decreasing tendency of the benzopyrylium cations to interact with OH^-.

Table 4
Second order rate constants of hydrolysis of benzopyrylium cations in 1:1 aqueous acetonitrile, k_2, at 20 °C[a]

	k_2 ($\mathrm{mol\,l^{-1}\,s^{-1}}$)	η (eV)[a]
1a	$\geq 3.9 \times 10^7$	3.54
1e	1.7×10^3	3.02
1m	3.4×10^7	3.26
1o	7.3×10^2	3.07
1q	3.7×10^2	2.92
1r	7.0×10^2	3.07

[a] Absolute hardness, η, was calculated using PM3 Hamiltonian.

The effect of the substituents in R^1- and R^2-position can qualitatively be explained in terms of Pearsons HSAB-principle which proposes that hard–soft bases prefer to coordinate with hard–soft acids, whereas the combination hard–soft is quite instable [19]. It has been shown that the absolute hardness of a molecule η is approximately half the energy difference between the ionization potential I and the electron affinity A [20].

$$\eta = \tfrac{1}{2}(I - A)$$

As seen in Table 4 an increasing donor strength of substituents in R^1- and R^2-position causes an decreasing hardness of the flavylium cations as an expression of the growing polarizability of the delocalized π-system. As OH^- belongs to the hard bases, the interaction with the colored flavylium salts decreases with increasing donor strength of substituents, thus, leading to a decrease in the decoloration rate.

The hydrolysis of the flavylium salts is often reversible on acidification or on exposure to light.

To perform comparative studies on the spectra and quantum yields of the photochromic conversions borax–glycerol mixtures proved to be appropriate, because all flavylium salts (except **1n**) can be hydrolyzed and most of the studied systems show a photochromic behavior in these solutions. With the exception of **1a** and **1d** the hydrolysis products are stable on standing in the dark at room temperature over several days. The quantum yield of the photochemical reaction was determined as long as the absorbance of the benzopyrylium dye can be neglected at the irradiation wavelength. In order to minimize the errors, a high density of measurement points were gathered at the beginning of the photoreaction. The benzopyrylium compounds are usually stable on irradiation. On prolonged irradiation **1a** and the anhydrobases of **1f** and **1g** are, however, decomposed.

It was found that the reaction quantum yield strongly depends on the reaction medium. Interestingly, it decreases going from the highly viscous borax–glycerol media to the liquid aqueous solvent mixtures. The medium effect is especially remarkable, as *trans*–*cis*-isomerization requires considerable molecular motions. For example, the NMe_2- and NEt_2-substituted chalcones do not undergo any

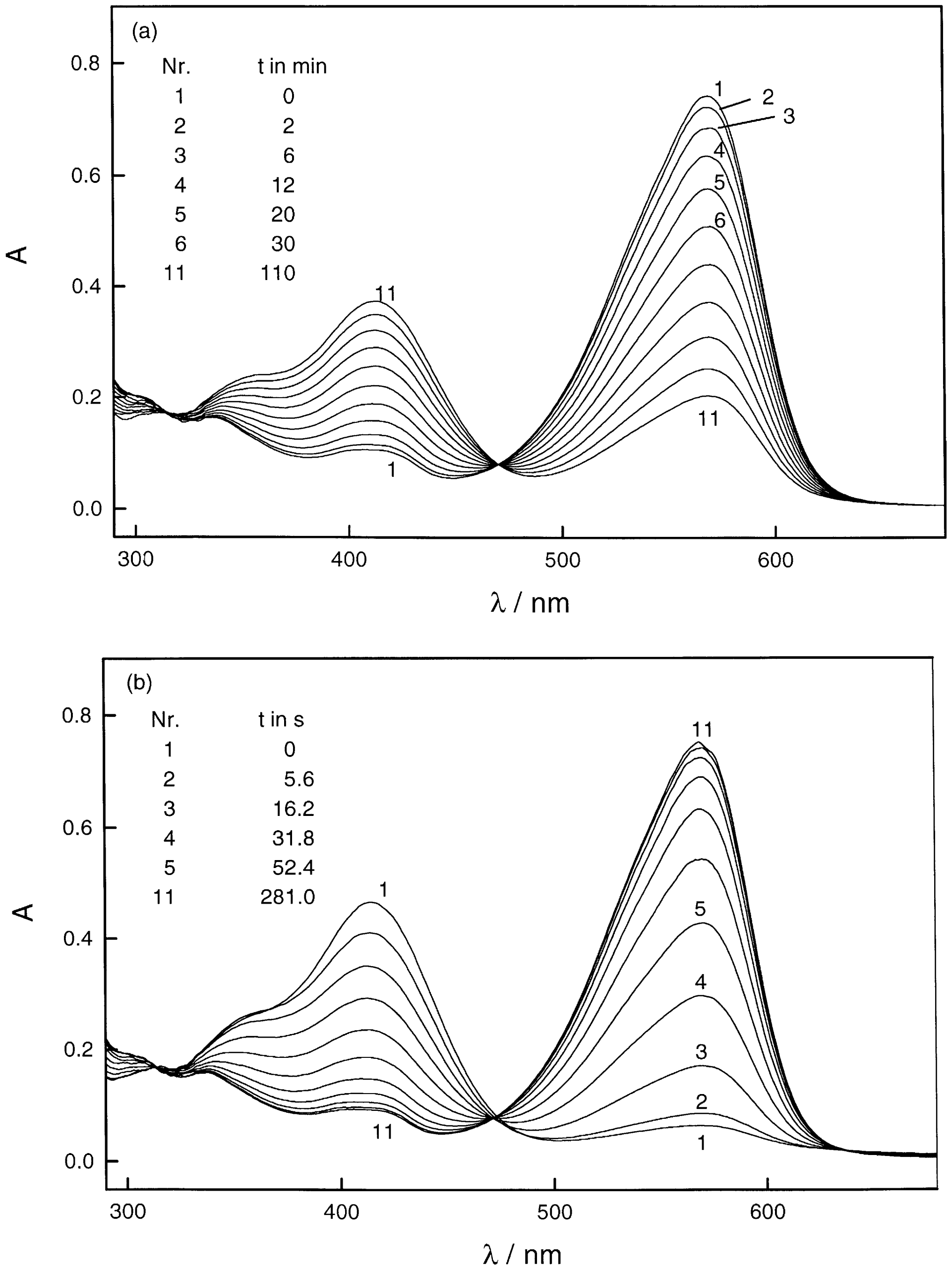

Fig. 3. Reaction spectra of the thermal bleaching of **1o** at 50 °C in borax–glycerol (a), followed by photochemical coloration of chalcone **2o** on irradiation with 436 nm light (b).

photochemical reaction in water and 1:1 aqueous acetonitrile, while they show a photochemical reaction in highly viscous borax–glycerol medium (4:5). Even on dilution of the borax–glycerol mixtures with a small amount of water, which causes a fluid consistence, no photochemical reaction has been observed for these chalcones. The analogous behavior was found comparing the quantum yield of **2m**. It was 0.59 in highly viscous glycerol:borax:boric acid (2:2:1) and 0.29 in the aqueous solvent mixture.

Furthermore, the photochemical quantum yields of the chalcones differ considerably depending on their substituents. Chalcones which only contain OMe- and/or OH-substituents (**2c**, **f–h**, **l**, **m**) can achieve photochemical quantum yields up to 0.6, whereas the NR_2-substituted chalcones exhibit photochemical quantum yields ≤ 0.2 (Table 5).

3.3. Deactivation of the chalcones

To discuss the photochemical quantum yield several competitive radiative and non-radiative deactivation channels from the S_1 must be considered. Investigations of several

Table 5
Photochemical quantum yields Φ_r in borax–glycerol at 20 °C

	Φ_r	λ' (nm)
2e	0.20	405
2f	0.51	366
2g	0.35	366
2h	0.31	366
2l	0.51	366
2m	0.59[a]	366
2o	0.07	436
2q	0.03	436
2r	0.02	436
2s	0.002	436

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

authors show, however, that dissolved oxygen does not influence the photochemical reaction of the *trans*-chalcones [21,22]. Therefore, deactivation processes via triplet states can be neglected. A reaction path via the excited singlet state has, thus, been concluded.

In order to get knowledge about the S_1 state, the fluorescence behavior of the chalcones has been investigated. Despite the high viscosity of the borax–glycerol mixtures in most cases a low fluorescence quantum yield ϕ_f was found (Table 6). Among the studied chalcones **2q**, **2r** and **2s** fluoresce, however, most intensively and show at the same time the smallest Stokes shift $\Delta\tilde{\nu}$ which is defined as the difference between the longest-wavelength absorption maximum and the respective fluorescence maximum. Both effects indicate smaller geometric changes between the S_0 and the S_1 state which can be referred to a stronger fixing of the substituents in the highly viscous matrix.

Consequently, the fluorescence life time of **2s** decreases from $\tau_f = 2.12$ ns in the highly viscous borax–glycerol mixtures to $\tau_f < 1$ ns in fluids [23]. Furthermore, the fluorescence quantum yield considerably decrease in fluid media (acetonitrile and 1:1 aqueous acetonitrile), while the Stokes shift increases (Table 7).

Since fluorescence and photochemical reaction are competetive deactivation processes from S_1, a high photochemical quantum yield is obtained in the chalcones with a low fluorescence quantum yield. The presence of additional deactivation processes must, however, taken into consideration, since the sum of the quantum yields of fluorescence and photoreaction ranges considerably below unity in all cases.

Table 6
Absorption and fluorescence data in borax–glycerol at 20 °C

	λ_{max} (nm)	λ_f (nm)	ϕ_f	$\Delta\tilde{\nu}$ (cm^{-1})
2e	406	503	0.07	4750
2g	382	478	0.16	5258
2l	379	480	0.05	5552
2m	379	485	≈0.06	5767
2o	413	512	0.05	4682
2q	447	542	0.40	3921
2r	456	549	0.27	3715
2s	460	541	0.56	3255

Table 7
Absorption and fluorescence data in acetonitrile at 20 °C

	λ_{max} (nm)	λ_f (nm)	ϕ_f	$\Delta\tilde{\nu}$ (cm^{-1})
2m	353	454	0.0015	6302
2r[a]	440	554	0.0016	4677
2s	423	508	0.09	3956

[a] In acetonitrile:water (1:1).

4. Discussion

In our study the photochemical reaction of the chalcones was investigated depending on simple substituents with a different donor strength and solvents with a different polarity and viscosity. Remarkably, it was found that the photochemical quantum yield is lower in aqueous solutions than in borax–glycerol mixtures although a *trans*–*cis*-isomerization is characterized by torsional motion and should thus be hindered by a viscous medium. The reaction is also suppressed in diluted borax–glycerol media with a liquid consistence. That means, not only the torsion around the double bond is essential for the deactivation of the chalcones, but also additional motions, presumably of the substituents. The latter assumption is supported by studies in acetic acid which show a considerably faster photochemical coloration for a chalcone with a bulky substituent ($R^2 = NHC(CH_3)_3$) than for less space consuming ones ($R^2 = NHC_8H_{17}$ and $N(CH_3)_2$) [3].

Furthermore, a strong dependence of the photochemical quantum yields on the donor strength of the substituents was found. While chalcones with NR_2-substituents exhibit low photochemical quantum yields, chalcones which bear exclusively OH- and OCH_3-groups show high quantum yields in borax–glycerol.

An explanation of the dependence on the substituents of the reaction quantum yield and the medium dependence can be given involving the presence of a highly polar excited state as a competitive deactivation channel of the S1 state. The formation of the latter one is reasonable, because in the chalcones a strong donor is connected with an acceptor unit (Ph–C=O) and a charge transfer from the donor to the acceptor unit can take place. The occurrence of a highly polarized excited state is supported by earlier studies which gave a decreasing rate of the photochemical coloration of chalcones with increasing solvent polarity in a number of liquid solvents [9]. The fast photochemical reaction of the chalcone with a bulky substituent gives rise to the conclusion that torsional motions of the substituents are involved in the deactivation of the chalcones. That is why it can be assumed that the model of the twisted intramolecular charge transfer (TICT) with a radiationless deactivation to the ground can be applied to explain the deactivation behavior of the chalcones

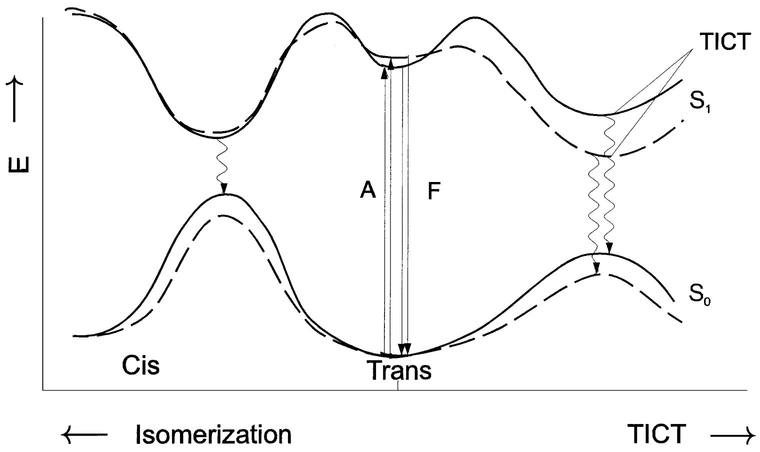

Fig. 4. Pothential surface of a NR_2-substituted chalcone. Solid line, in borax–glycerol matrix; dashed line, in aqueous solution.

[24–27] (Fig. 4). The TICT state is characterized by a charge transfer from the donor to the acceptor moiety leading to a radical ion pair which is stabilized by polar solvents [28,29].

As can be assumed that the polarity of the borax–glycerol media is considerably smaller than that one of aqueous solutions, a decreasing force for the formation of the TICT can be expected in borax–glycerol. Furthermore, a decoupling of the donor and acceptor molecule part takes place by a twisting of a substituent by 90°. Therefore, the activation barrier increases with increasing viscosity of the medium and, thus, the rate constant for the formation of the decoupled geometry in the S_1 state should decrease. This is in accordance with the observed growing fluorescence life time in borax–glycerol which corresponds to the life time of the planar S_1 state.

Both, the smaller solvent polarity and the viscosity contribute to a decreasing tendency to form a polarized excited state and explain the preference of alternative deactivation channels, such as photochemical reaction.

The large photochemical quantum yield of the exclusively OH- and OMe-substituted chalcones can be understood on the basis of their smaller tendency to form a high polar excited state which arises from the smaller donor strength of the substituents. Furthermore, the smaller size of the substituents leads to a smaller fixing of the molecule which facilates the photochemical reaction and reduces the fluorescence quantum yields.

5. Conclusions

Based on 4′- and/or 7-substituted flavylium salts it is possible to create photochromic systems which allow the excitation with visible light and show usually a good band separation.

However, the photochemical quantum yield of the NR_2-substituted chalcones is often poor. Because of the importance of the medium conditions, the behavior of these systems should be studied as a function of the solvent. An improved photochemical quantum yield can be expected in media with a small polarity and an optimum of viscosity.

References

[1] L. Jurd, Tetrahedron 25 (1969) 2367.
[2] R. Matsushima, M. Suzuki, Bull. Chem. Soc. Jpn. 65 (1992) 39.
[3] R. Matsushima, H. Mizuno, H. Itoh, J. Photochem. Photobiol. A: Chem. 89 (1995) 251.
[4] F. Pina, M.J. Melo, M. Maestri, R. Ballardi, V. Balzani, J. Am. Chem. Soc. 119 (1997) 5556.
[5] R.A. McClelland, S. Gedge, J. Am. Chem. Soc. 102 (1980) 5838.
[6] R.A. McClelland, G. McGall, J. Org. Chem. 47 (1982) 3730.
[7] D. Dewar, R.G. Sutherland, J. Chem. Soc., Chem. Commun. (1970) 272.
[8] R. Matsushima, H. Mizuno, A. Kaijura, Bull. Chem. Soc. Jpn. 67 (1994) 1762.
[9] R. Matsushima, N. Suzuki, T. Murakami, M. Morioka, J. Photochem. Photobiol. A: Chem. 109 (1997) 91.
[10] P. Czerney, Dissertation, Technische Universität Dresden, 1982.
[11] B. John, Diplomarbeit, Friedrich-Schiller-Universität Jena, 1989.
[12] P. Czerney, Habilation, Friedrich-Schiller-Universität Jena, 1995.
[13] P. Czerney, H. Hartmann, J. Prakt. Chem. 325 (1983) 161.
[14] H.-D. Ilge, R. Paetzold, Z. Chem. 23 (1983) 419.
[15] H.-D. Ilge, J. Photochem. 33 (1986) 333.
[16] H.-D. Ilge, M. Kaschke, D. Khechinashvili, J. Photochem. 33 (1986) 349.
[17] G. Haucke, P. Czerney, C. Igney, H. Hartmann, Ber. Bunsen-ges. Phys. Chem. 93 (1989) 805.
[18] G. Haucke, P. Czerney, F. Cebulla, Ber. Bunsenges. Phys. Chem. 7 (1992) 880.
[19] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
[20] R.G. Pearson, J. Chem. Educ. 64 (1987) 561.
[21] R. Matsushima, K. Miyakawa, M. Nishihata, Chem. Lett. (1988) 1915.
[22] H. Lietz, Diplomarbeit, Friedrich-Schiller-Universität Jena, 1993.
[23] U. Kurzer, Diplomarbeit, Friedrich-Schiller-Universität Jena, 1991.
[24] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley, W. Baumann, Nouv. J. Chim. 3 (1979) 443.
[25] W. Rettig, Angew. Chem. 98 (1986) 969.
[26] W. Rettig, Angew. Chem. Int. Ed. Engl. 25 (1986) 971.
[27] J. Lu, J. Shoulian, X. Yunbao, Jingou, Anal. Chim. Acta 349 (1997) 17.

[28] W. Rettig, V. Bonacic-Koutecky, Chem. Phys. Lett. 62 (1979) 115.
[29] E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, L.A. Miehe, Adv. Chem. Phys. 68 (1987) 1.

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