The Interaction of Ground and Excited States of Lumichrome with Aliphatic and Aromatic Amines in Methanol

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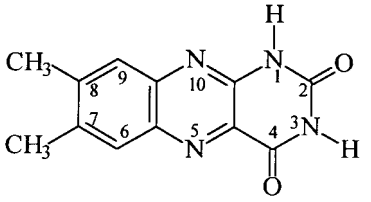
Dedicated to Prof. *André M. Braun* on occasion of his 60th birthday

The reaction of the ground and excited states of lumichrome (= 7,8-dimethylalloxazine = 7,8-dimethylbenzo[*g*]pteridine-2,4(1*H*,3*H*)-dione) with aliphatic and aromatic amines was investigated in MeOH. In the presence of aliphatic amines of high basicity, new bands are observed in the absorption and fluorescence spectra. These bands arise in a proton-transfer reaction from lumichrome, in the ground and in the singlet excited states, to the amine. On the other hand, amines with lower basicity such as triethanolamine (=2,2′,2″-nitrilotris-[ethanol]) and aromatic amines are not able to deprotonate lumichrome, and hence a quenching of the fluorescent emission takes place without changes in the spectral shape. In this case, bimolecular-quenching rate constants were determined for the excited singlet and triplet states. Based on laser-flash-photolysis experiments, an electron-transfer mechanism is proposed. Aliphatic amines yield lower rate constants than the aromatic ones for the same driving force. A notable difference arises in the limiting value reached by the singlet and triplet quenching rate constants by aromatic amines. For the singlet quenching, the limit is coincident with a diffusion-controlled reaction, while those for triplet quenching reach a lower constant value, independent of the driving force. This is explained by an electron-transfer mechanism, with a lower frequency factor for the triplet-state process.

Introduction. – The photoreactions of flavins (= 10-alkyl-7,8-dimethylisoalloxazines) have been of great interest due to their biological relevance [1][2]. Flavins are based upon the isoalloxazine ring system. One of the most important members of this family of compounds is riboflavin. The anaerobic photolysis of riboflavin affords, as the main product, lumichrome (= 7,8-dimethylalloxazine = 7,8-dimethylbenzo[*g*]pteridine-2,4(1*H*,3*H*)-dione) [3]. Lumichrome (LCH) is also generally found in biological materials associated with flavins, and it may participate in some biological processes. While a great number of publications deal with the excited-state reactions of flavins, in particular photoreduction *via* single-electron-transfer processes [2], much less is known concerning the reactivity of alloxazine excited states.



LCH

Alloxazines unsubstituted at N(1) can undergo an excited-state proton transfer from N(1) to N(10) to form the corresponding isoalloxazine in the presence of pyridine, carboxylic acids, and other compounds bearing proton donor and acceptor functions, such as primary amines [4][5]. This reaction has been postulated to proceed *via* a cyclic complex where H-bonding takes place at both N(1) and N(10) simultaneously, and involves a double-proton transfer. The phototautomerism proceeds *via* the excited singlet state and can be conveniently monitored by the appearance of the isoalloxazinic fluorescence and disappearance of the alloxazinic fluorescence. In the triplet state, this tautomerism has only been suggested in AcOH [6]. On the other hand, the emission spectra of anions of alloxazines are very similar to those of isoalloxazines [7]. This makes the separation of the phototautomeric and anionic species difficult in the singlet excited states.

Most of the work on the photochemistry of flavins and lumichrome has been performed in aqueous solution. However, the photoreactions in nonaqueous solvents are also of interest due the heterogeneous nature of biological systems and to the potential use of these natural pigments as photosensitizers [8]. We have previously shown that riboflavin and lumichrome may act as efficient photoinitiators of free-radical polymerization in the presence of triethanolamine (=2,2′,2″-nitrilotris[ethanol]) in MeOH [9]. The mechanism was explained in terms of a one-electron-transfer process from the amine to the flavin. Other aliphatic amines have also been shown to act as effective co-initiators of vinyl polymerization with riboflavin as photosensitizers [10]. However, in the presence of aliphatic amines of higher basicity, lumichrome suffers a proton-transfer process instead of the electron-transfer reaction of the isoalloxazine ring.

To obtain further information on the reaction of the excited states of lumichrome with amines in organic solvents, we undertook the present investigation. Here, we present results on the effect of aliphatic amines on the proton-transfer processes of the ground states and on the quenching of the excited states of lumichrome by aliphatic and aromatic amines.

Experimental – *General*. Lumichrome (LCH) was purchased from *Sigma* and was used without further purification. The amines $BuNH_2$, Bu_2NH, $(i\text{-}Bu)_2NH$, Pr_3N, Bu_3N, triethanolamine (TEOHAm), methyldiethanolamine (MDEOHAm), aniline (An), *N*-methylaniline (MAn), *N*,*N*′-dimethylaniline (DMAn), 4-methylaniline (*p*MAn) and 2-chloroaniline (*o*ClAn) obtained from various commercial sources were purified by vacuum distillation just before use. 4-Methoxyaniline (*p*MOAn), 3,4-dimethylaniline (3,4-DMAn), Ph_2NH, and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD) were purified by sublimation. MeOH, HPLC grade, was from *Merck*.

Absorption spectra were recorded with a *HP8453* diode-array spectrophotometer. Steady-state fluorescence experiments were carried out at r.t. in air-equilibrated solns. ($25 \pm 1°$) with a *Spex Fluorolog* spectrofluorometer. Fluorescence-lifetime measurements were carried out by the time-correlated single-photon-counting technique with an *Edinburg Instrument OB-900* instrument. Transient absorption spectra and triplet quenching were determined by laser flash photolysis. A *Spectron SL400* Nd : YAG laser generating 355-nm laser pulses (*ca*. 18 ns pulse width) was the excitation source. The laser beam was defocused in order to cover the entire path length (10 mm) of the analyzing beam from a 150-W Xe lamp. The experiments were performed with rectangular quartz cells with right-angle geometry. The detection system comprises a *PTI* monochromator coupled to a *Hamamatsu R666 PM* tube. The signal was acquired by a digitising scope (*Hewlett-Packard 54504*) where it was averaged and then transferred to a computer. Samples were deoxygenated prior to use by Ar bubbling.

Results and Discussion. – Absorption spectrum of lumichrome in MeOH exhibits two bands in the near-UV region with maxima at 342 and 384 nm, which have been assigned to the two independent $\pi\pi^*$ transitions [11][12]. The addition of mM concentrations of NaOH caused considerable changes in the shape of the spectrum. Shifts in the position of both maxima are observed, and a new band as a shoulder at the 425–480 nm region appeared, with well-defined isosbestic points at 311 and 398 nm. This spectrum is similar to that reported in basic aqueous solution and has been assigned to the emission to the anionic form of the lumichrome [7].

The emission spectrum in MeOH showed only a broad band with a maximum at 450 nm, which is similar to that previously reported in organic solvents [4][11]. The addition of NaOH decreases the intensity of the emission band at 450 nm, and a new broad band appears at 532 nm, which increases in intensity with the increase of the NaOH concentration. A well-defined isoemissive point was observed at 492 nm. These luminescence features are also in agreement with those reported for the mono-anionic form of lumichrome in aqueous solution [7].

The spectral characteristics of lumichrome in MeOH solution in the presence of amines depend on the basicity of the amine as measured by their pK_a in H_2O. The spectral changes upon addition of amines of high basicity ($pK_a > 9$ in H_2O) are similar to those found in the presence of NaOH. The absorption spectrum shows a new band as a shoulder at the region 420–480 nm and two isosbestic points (*Fig. 1*). The

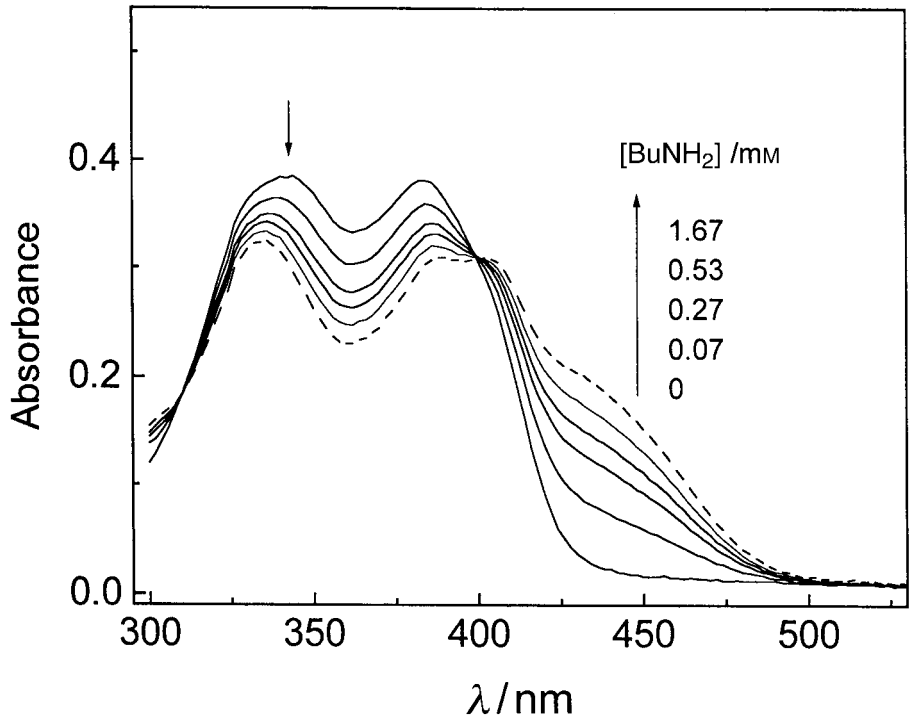


Fig. 1. *Absorption spectra of LCH in MeOH.* Effect of the addition of $BuNH_2$ (——) and 1 mM NaOH (– – –).

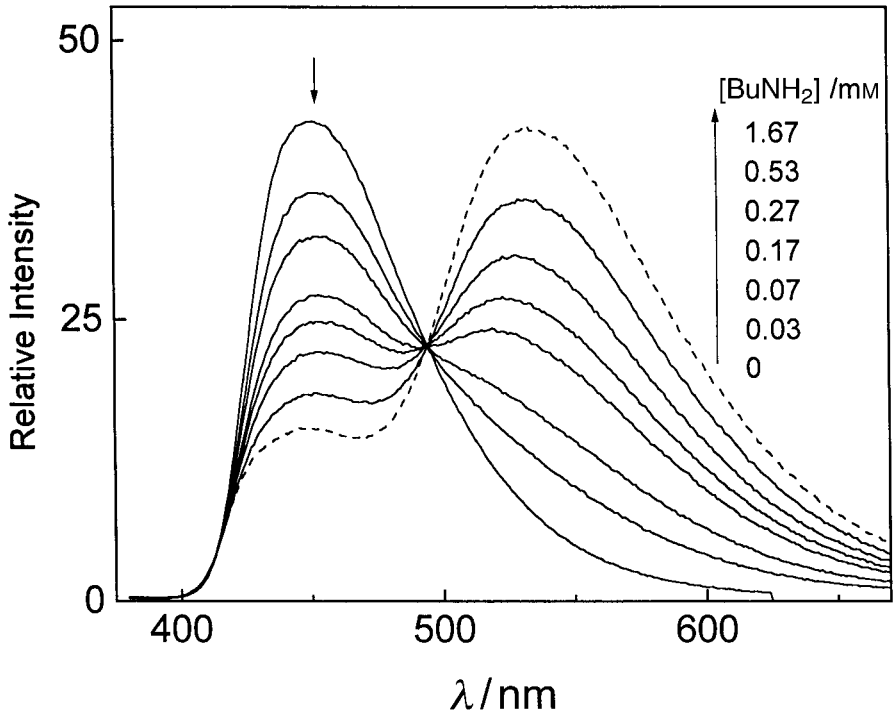


Fig. 2. *The fluorescence spectra of LCH in MeOH* ($\lambda_{exc} = 340$ nm). Effect of the addition of $BuNH_2$ (—) and 1 mM NaOH (– – –).

fluorescence spectrum shows a new band at longer wavelengths. The intensity of this new emission centered at 535 nm increases as the concentration of the amine is increased with simultaneous decrease in the 450 nm peak as shown in *Fig. 2*. *Fig. 3* shows the effect of equimolar concentration (1.5 mM) of butylamines on the fluorescence spectrum. It can be seen that $BuNH_2$ is more efficient at enhancing the emission at 535 nm, reflecting the greater basicity of the primary amine. The less-basic Bu_3N produces only a minor increase of the band of the anionic form. The isoemissive points observed with all amines of high basicity indicate two excited species in equilibrium, the neutral and anionic forms.

The excitation spectrum depends on the emission wavelength. The spectra in the presence of aliphatic amines are very similar to that obtained in the presence of NaOH. The spectrum monitored at 530 nm presents two bands at 335 and 435 nm. On the other hand, when the monitoring wavelength is 450 nm, the excitation spectrum closely resembles that in pure MeOH. All these observations show that basic amines (Am; $pK_a > 9$ in H_2O) abstract a proton from LCH in the ground and the singlet excited states, as depicted in the *Scheme*.

Proton transfer from excited-singlet states has been described in several compounds, such as naphthols [13] and acridinedione [14]. It is also well-known that the singlet excited state of alloxazines without substituents at N(1) undergoes proton transfer in the presence of compounds bearing proton donor or acceptor functions that

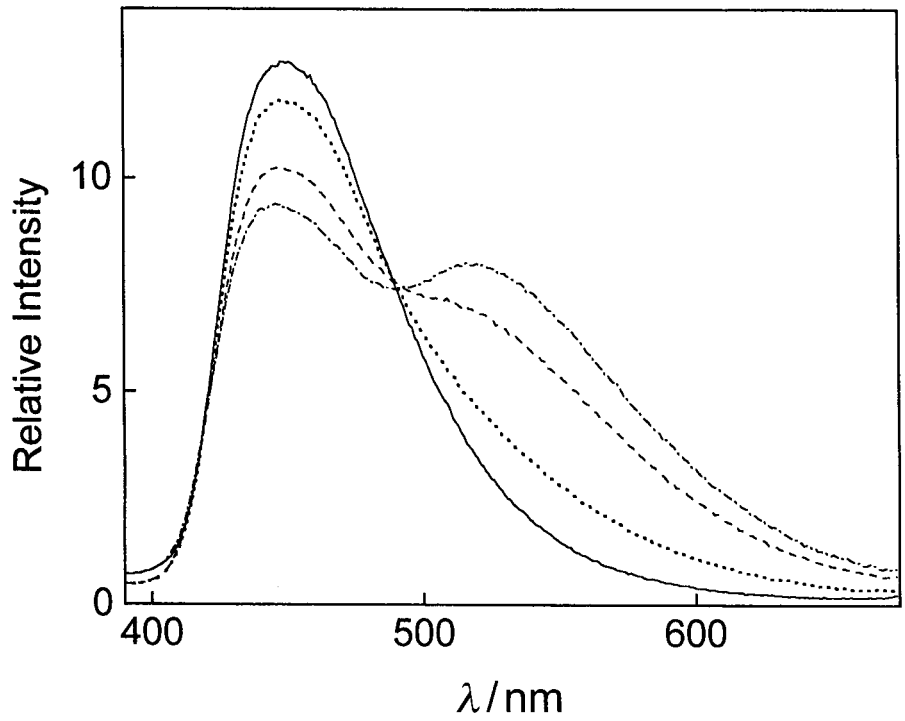
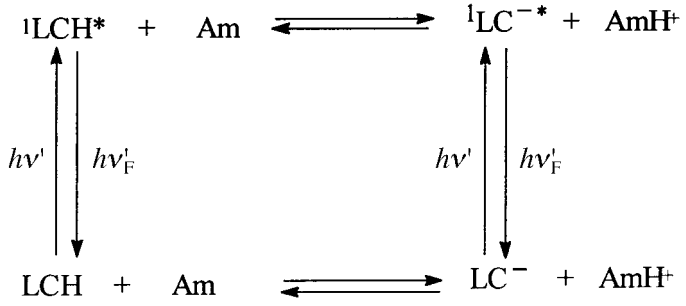


Fig. 3. *Effect of equimolar concentration* (1.5 mM) *of butylamines of different basicity on the emission of LCH in MeOH* ($\lambda_{exc} = 340$ nm). In the absence of amine (—) and in the presence of Bu_3N (·····); Bu_2NH (– – –); and $BuNH_2$ (–·–·– ·).

Scheme



are able to form H-bonds with the alloxazine ring system [15]. These proton-transfer processes lead to phototautomerization to give the corresponding isoalloxazine. The latter species shows a broad emission in the 500–600-nm region, but the absorption spectrum is very similar to that of alloxazines. The broad-band emission found here in the presence of amines could be due to the presence of a phototautomeric equilibrium. However, the similarity of the absorption and emission spectra of lumichrome in the presence of amines with those in the presence of NaOH reveals that the new emission is

due to the deprotonated form of the alloxazine singlet excited state. Further support for this assumption is the coincidence between the excitation and the absorption spectra in the presence of amines and shows that basic amines in MeOH lead almost exclusively to the ionic dissociation of lumichrome.

1. *Singlet Quenching*. Fluorescence lifetime (τ°) of LCH was determined in neutral (450 nm) and basic (535 nm) MeOH. In both cases, the decay could be fitted by a mono-exponential function. The decay times were 1.04 ± 0.03 and 4.88 ± 0.05 ns in the absence and the presence of 2 mM NaOH, respectively.

The fluorescence of LCH was quenched by amines of low pK_a, such as hydroxy-alkylamines and aromatic amines, without changes of the spectral shape. In addition, ground-state absorption spectra do not show any change in the presence of the quenchers at the concentrations used here. Thus, ground-state complex formation can be disregarded. Bimolecular-quenching rate constants were determined from the *Stern-Volmer* (*SV*) plots of I°/I or τ°/τ *vs.* amine concentration $[Q]$, where I° and I stand for the florescence intensity at the wavelength of the maximum, and τ° and τ the fluorescence lifetimes, in the absence and the presence of amine, respectively.

$$\frac{I^\circ}{I} \text{ or } \frac{\tau^\circ}{\tau} = 1 + K_{SV}[Q] = 1 + {}^1k_q\tau^\circ[Q] \quad (1)$$

For low quencher concentrations, the *SV* plots determined from the fluorescence intensity at 450 nm gave linear relationships. However, for the strongest quencher, steady-state *SV* plots showed small positive deviations, indicating some contribution of static quenching. Nevertheless, in these cases *SV* plots based on lifetime measurements were linear, and from the slopes the quenching rate constants were obtained. The ${}^1k_q$ values and redox potentials for the different quenchers are collected in *Table 1*. Values of ${}^1k_q$ for aromatic amines are in the diffusional-controlled limit, 1.2×10^{10} M^{-1} s^{-1} in MeOH [16], the values for hydroxy-alkylamines being slightly lower.

On the other hand, when highly basic amines are added, the fluorescence at 450 nm is quenched (*Fig. 2*). However, *SV* plots at this wavelength present a rapid initial linear

Table 1. *Singlet and Triplet Quenching Rate Constants* ([10^9 M^{-1} s^{-1}]) *for Neutral Form of LCH*

Amine ([V])[a])	Singlet quenching[b])		Triplet quenching[c])	
	${}^1\Delta G^\circ$/eV	${}^1k_q$	${}^3\Delta G^\circ$/eV	${}^3k_q$
MDEOHAm (n.a.)	–	4.8	–	0.084
TEOHAm (0.90)	−0.78	8.6	−0.26	0.3
An (1.08)	−0.60	14.0	−0.08	1.7
MAn (1.03)	−0.65	12.0	−0.13	4.0
Pr_2NH (0.83)	−0.85	10.6	−0.33	3.7
DMAn (0.78)	−0.90	13.1	−0.39	6.4
*o*ClAn (0.74)	−0.94	10.8	−0.42	5.3
*p*MAn (0.54)	−1.14	13.0	−0.62	2.8
3,4-DMAn (0.5)	−1.18	12.5	−0.66	4.3
*p*MOAn (0.34)	−1.34	9.7	−0.82	4.9
TMPD (0.13)	−1.55	16.0	−1.03	4.1

[a]) Oxidation potential in V *vs.* SCE in MeCN. From [17]. [b]) Estimated error ±5%. [c]) Estimated error ±10%.

portion with a slope incompatible with an excited-state quenching and afterwards a downward curvature is observed (*Fig. 4*). This behavior can be explained by the deprotonation process in both ground and excited states, as previously discussed.

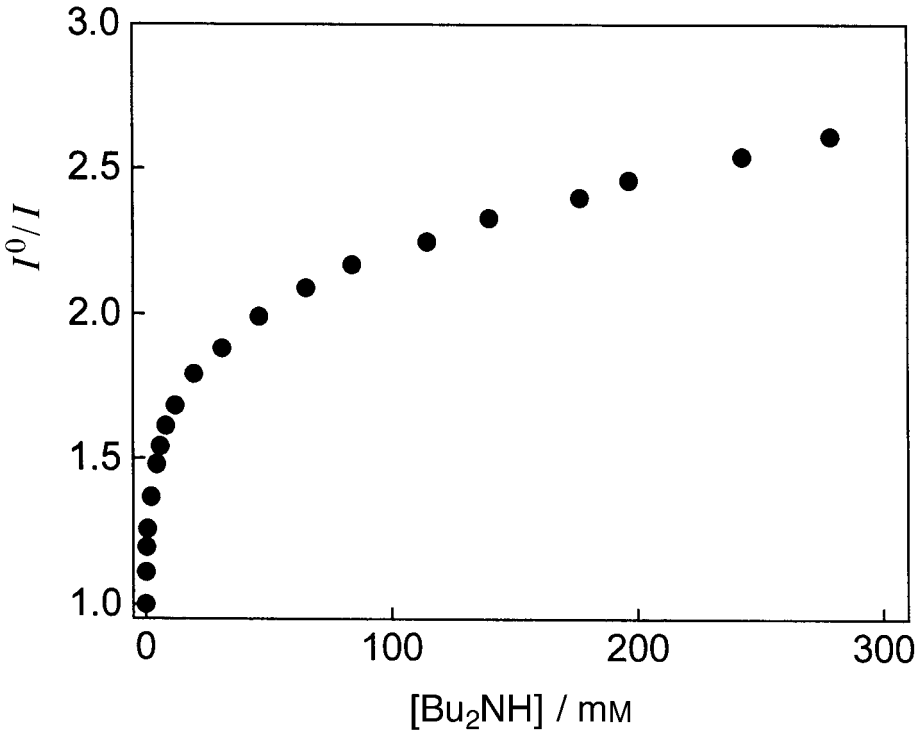


Fig. 4. Stern-Volmer *plot for the fluorescence quenching of LCH neutral singlet by* Bu_2NH. Emission wavelength 440 nm.

The quenching of the excited anionic LCH was further investigated by monitoring the decrease of the emission intensity at 550 nm (excitation at 450 nm) by addition of the amine to a solution containing 2 mM NaOH. In all cases, linear *SV* plots were obtained. From the slopes and the lifetime in the presence of NaOH, bimolecular quenching rate constants were obtained and are collected in *Table 2*. It can be observed that the rate constants are lower than the diffusion-controlled limit and depend on the oxidation potential of the amines, decreasing when the amine oxidation potential increases. This behavior indicates that the process takes place through a charge-transfer mechanism. In all cases, the quenching of excited singlet of the anionic form of LCH is very much less efficient than the quenching of the neutral form.

2. *Triplet Quenching*. When solutions of LCH are laser-flash-irradiated at 355 nm, a transient species absorbing in the region 350–700 nm is formed. The initial absorption spectrum presents a sharp maximum at 370 nm and broad absorption in the region 420–700 nm. This spectrum is similar to that previously reported by *Grodowski et al.* [20] in EtOH, and to that reported for 1,3-dimethyllumichrome in neutral aqueous solution [6] and assigned to the T-T absorption of the neutral triplet state. The transient

Table 2. *Singlet Quenching Rate Constant* ($[10^9\ M^{-1}\ s^{-1}]$) *for the Anionic Form of LCH*

Amine ([V])[a])	^1k_q
$BuNH_2$ (1.6)[b])	0.016
Bu_2NH (1.17)[b])	0.52
$(i\text{-}Bu)_2NH$ (1.17)[b])	0.48
Pr_3N (0.94)[b])	0.90
Bu_3N (0.92)[b])	0.92
MDEOHAm (n.a.)	1.1
TEOHAm (0.90)[c])	1.4
An (1.08)[c])	6.5
MAn (1.03)[c])	8.4
DMAn (0.78)[c])	10.3
*p*MOAn (0.34)[c])	9.4

[a]) Oxidation potential in V *vs.* SCE in MeCN. [b]) From [18]. Corrections for reference electrode when necessary, from [19]. [c]) Refs. as in *Table 1*.

absorption spectrum is shown in *Fig. 5* at 2, 20, and 90 μs after the laser pulse. At longer times, the bands at 360 and 550 nm are reduced, while an absorption remains at 450 nm. This long-lived band can be ascribed to the radicals derived from LCH [20].

In the presence of 1 mM NaOH, the laser-flash irradiation of LCH produces a somewhat different initial transient absorption. The maximum is shifted to 520 nm, and a considerable decrease in the absorption at 370 nm is observed (inset *Fig. 5*). The comparison of this spectrum with those reported by *Heelis* and *Phillips* [6] for 1-methyl- and 3-methyllumichrome in aqueous solution indicates that the spectrum observed in MeOH in the presence of 1 mM NaOH corresponds to the triplet of the anionic form of LCH. As discussed above, in basic MeOH solution, the ground and singlet excited states correspond mainly to the anionic form, hence the excitation at 355 nm leads to the anionic triplet.

As discussed above, basic aliphatic amines are able to abstract a proton from LCH in the ground and excited singlet states. Therefore, in the presence of these amines, the triplet-state absorption spectrum should be similar to that in the presence of NaOH. In fact, this is found, when LCH is laser-flash-irradiated in the presence of $BuNH_2$; however, the triplet decay is very much faster than that in the presence of NaOH. From the triplet lifetime as a function of high amine concentration, a second-order quenching rate constant of $1.8 \times 10^6\ M^{-1}\ s^{-1}$ was determined for $BuNH_2$. This value is very much lower than the corresponding rate constant for singlet quenching in basic MeOH, in agreement with the expectation for an electron-transfer process of the triplet state.

In the presence of aromatic amines and TEOHAm at concentrations such that the excited singlet is not quenched, a shortening of the triplet lifetime is observed, while an increase in the intensity and a different time profile is observed in the region of 400–450 nm. These changes are shown in *Fig. 6* for the case of 3,4-DMAn. The absorption in the region of 420 nm increases with a time constant that parallels the triplet decay in the presence of the amine. Similar spectral features were obtained, when the spectrum was recorded at 2 and 40 μs. This spectrum presents a main absorption at 450 nm, which corresponds fairly well with the spectrum of the anion radical of LCH [21]. Moreover, it

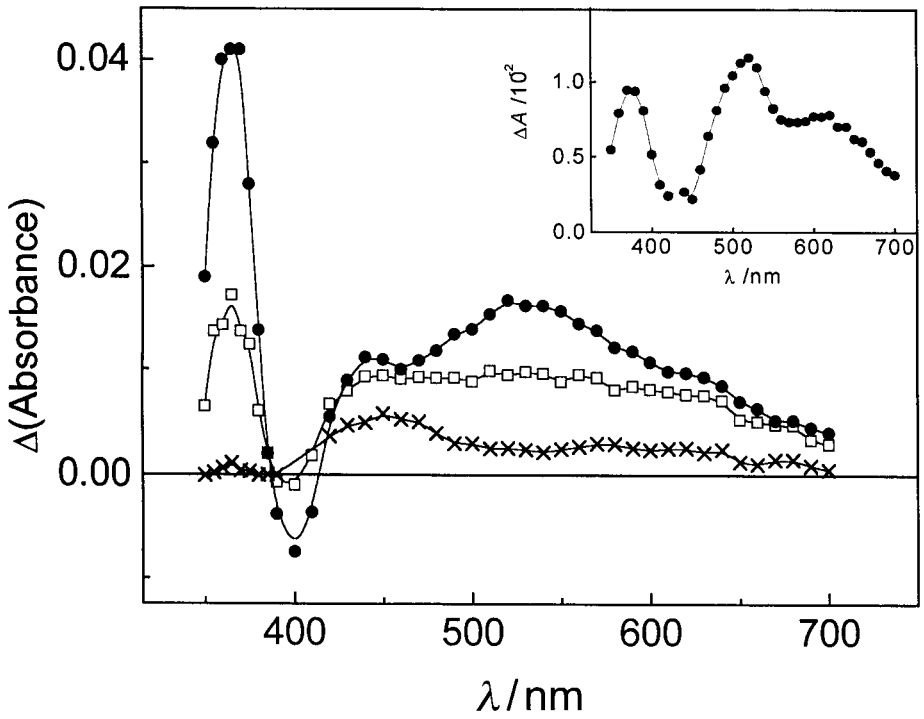


Fig. 5. *Transient absorption spectrum of LCH in MeOH at 2* (●), *20* (□), *and 90* (×) μs *after laser-pulse excitation at 355 nm*. Inset: *Transient absorption of LCH in MeOH in the presence of 1 mM NaOH at 2* μs *after the laser pulse.*

is known that the radical cation of aniline and its derivatives also absorbs in the wavelength range 400 – 500 nm. Thus, the triplet quenching of LCH by aromatic or low pK_a aliphatic amines can be described by an electron-transfer process. Bimolecular quenching rate constants ^3k_q, were obtained from a plot of the pseudo-first-order-decay rate constants at 550 nm as function of the amine concentrations [Q], *Eqn.*(2):

$$k_{obs} = k^o + {}^3k_q[Q] \tag{2}$$

^3k_q Values are included in *Table 1.*

3. *Kinetics of Electron-Transfer Quenching.* The rate constants for singlet and triplet quenching in *Table 1* may be understood in terms of an electron-transfer mechanism:

$$LCH^* + Am \rightarrow (LCH^{-\bullet} + Am^{+\bullet}) \tag{3}$$

The amine acts as an electron donor, and this is reflected in the trend observed in the rate constants with the redox potential of the amine. In their classic work on electron-transfer fluorescence quenching, *Rehm* and *Weller* [22] demonstrated that the rate constant depends on the free-energy change involved in the electron-transfer process.

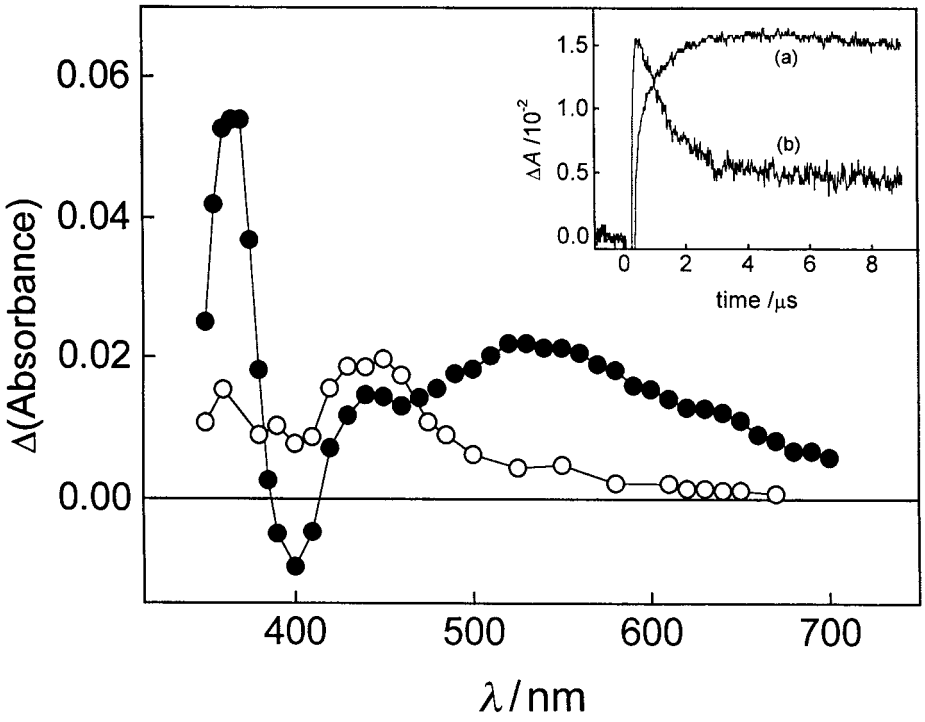


Fig. 6. *Transient absorption spectra of LCH in MeOH in the absence* (●) *and in the presence of* 0.18 mM *of 3,4-DMAn* (○) *5* μs *after the laser flash.* Inset: *Absorption profiles at 420* (a) *and 550* (b) *nm in the presence of 0.18 mM 3,4-DMAn.*

The latter is normally calculated from the redox potential of the donor $E(D/D^+)$ and acceptor $E(A/A^-)$ and the energy of the excited state involved

$$\Delta G^o = E(D/D^+) - E(A/A^-) - E^* + \frac{z_1 z_2}{D r_{12}} \quad (4)$$

where E^* is the energy of the excited state, and the last term represents the coulombic energy necessary to form an ion pair with charges z_1 and z_2 in a medium of dielectric constant D for a distance r_{12}. Taking r_{12} as 0.7 nm and with $+1$ and -1 as the charge of the ions formed, a value of 0.06 eV is calculated for the coulombic term.

The lumichrome redox potential was measured as 1.3 V with a SCE reference electrode in MeCN[1]). The oxidation potentials of the amines in MeCN *vs.* SCE are given in *Table 1*. The excited singlet energy of LCH was taken as 2.92 eV in both solvents [16]. Similarly, for the triplet energy, we used 2.40 eV [16]. In this way, ΔG^o was estimated in MeCN and assumed to be the same in MeOH on the basis of the similar polarity of the two solvents. The ΔG^o values for the quenching of the neutral form of LCH are collected in *Table 1*.

[1]) Measured in our laboratory by cyclic voltammetry.

For the anionic form, the redox potential is not known. However, it can be seen from comparison of the values in *Tables 1* and *2* that, in this case, the rate constants are lower. This is in agreement with a lower electroaffinity of the singlet excited state of the anionic form, which can be expected from the negative charge of the molecule. Moreover, also in this case the rate constants correlate with the oxidation potential of the amine.

Data in *Table 1* show that the singlet- and triplet-state rate constants reach a different limit at high negative values of ΔG^{o}. The most striking feature of the results for the quenching by aromatic donors and hydroxy-alkylamines is the different limit reached by the rate constants for very exergonic reactions. A diffusional limit 1.2×10^{10} M^{-1} s^{-1} in MeOH is commonly accepted for bimolecular rate constants at room temperature, in agreement with the *Smoluchowski-Stokes-Einstein* approximation at 298 K [16]. This is corroborated by numerous experimental studies, especially of bimolecular fluorescence-quenching rate constants. Our data for singlet quenching result in a mean value of $(12.0 \pm 1.2) \times 10^{9}$ M^{-1} s^{-1}. On the other hand, for the triplet quenching the rate constants a mean value of $(4.7 \pm 1.2) \times 10^{9}$ M^{-1} s^{-1} is obtained. A similar difference was previously found for the quenching of the excited states of the synthetic dye safranine T by phenols and aromatic amines in MeOH [23], and for the quenching of polycyclic aromatic hydrocarbons by quinones in polar solvents [24]. This remarkable effect is probably due to a lower matrix element related to the frequency factor for the unimolecular rate constant of the triplet state process in a *Rehm-Weller*-type mechanism.

Moreover, it can be seen in *Table 1* that the rate constant for the triplet quenching by the amine of low basicity TEOHAm is lower than the corresponding value for aromatic amines of similar ΔG^{o}. The same difference is found for singlet quenching of the anionic form of LCH (*Table 2*) where it can be observed that aliphatic amines of similar oxidation potential are less efficient quenchers than aromatic amines. Similar results have been reported for electron-transfer quenching of excited states for other systems [25][26]. Several explanations were offered for this contrast, including differences in the reorganization energy, steric factors [25], and exciplex formation [26].

In summary, these studies show that basic amines are able to abstract a proton from LCH in the ground and in the singlet excited states. On the other hand, less basic amines such as TEOHAm and aromatic amines are not able to deprotonate LCH, and, hence, the only change caused by these molecules is the quenching of the emission without changes in the spectral shape. The quenching in this case can be explained by an excited-state electron-transfer mechanism. A notable difference arises in the limiting value reached by the singlet- and triplet-state quenching rate constants.

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