

Spectroscopy and photophysics of 4- and 7-hydroxycoumarins and their thione analogs

J. Seixas de Melo*, P.F. Fernandes

Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

Received 31 August 2000; revised 28 November 2000; accepted 28 November 2000

Abstract

Acid-base equilibria were studied for 4-hydroxycoumarin, 7-hydroxy-4-methylcoumarin and their thione derivatives in different media for their ground and lowest energy singlet and triplet excited states. The ethoxylated and/or methoxylated derivatives were also investigated. Characterization involves fluorescence spectra, quantum yields, lifetimes, phosphorescence spectra, lifetimes, and triplet–triplet absorption spectra. From their pK_a values it was found that 4 and 7-hydroxycoumarins are more acidic in their lowest excited singlet states than in S_0 . The origin and character of the lowest singlet and triplet excited states is discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Coumarins; Photophysics; Singlet state; Triplet state; Fluorescence; Phosphorescence

1. Introduction

Coumarins, in particular the hydroxycoumarins (HCs), are well-known natural products [1], but they also occur in areas as diverse as sun screen formulations [2], laser dyes [3], pesticides, etc [4]. Despite the enormous potential interest of these compounds there is no complete characterization of their photophysics.

In this work, we report the properties of 4 and 7-HCs, their ethers and their thione analogs in their S_0 , S_1 and T_1 states (Scheme 1). Ground and excited state acid-base behavior was studied, and absorption assigned to neutral, anionic and cationic forms. The absence of fluorescence for the thionecoumarins indicates very efficient radiationless deactivation. In some cases more complex tautomeric behavior was

observed [5–8]. This will be described in detail elsewhere [9].

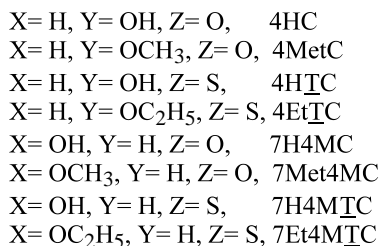
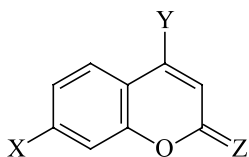
The overall excited state formation and deactivation pathways for the HC are summarized in Scheme 2. Depending on the HC considered, some of the pathways can be neglected.

2. Experimental

All used solvents were of spectroscopic grade and were purified by conventional methods. Millipore water was generally used. Glass compositions are given in volume:volume ratios. 4-Hydroxycoumarin and 4-methoxycoumarin were used as purchased (extra-synthesis). 7-Methoxy-4-methylcoumarin (Aldrich) and 7-hydroxy-4-methylcoumarin (Aldrich) were purified as reported elsewhere [10]. The thione coumarins were synthesized by conventional procedures [9,11]. Absorption and luminescence spectra were recorded on Shimadzu UV-2100, Olis-Cary 14, and Jobin-Ivon

* Corresponding author. Tel.: +351-39-852-080; fax: +351-39-827-703.

E-mail address: sseixas@ci.uc.pt (J. Seixas de Melo).



Scheme 1.

SPEX Fluorog 3-22 spectrometers, respectively. For phosphorescence studies, the 1934 D phosphorimeter accessory was used. Fluorescence and phosphorescence spectra were corrected for the wavelength response of the system. Oscillator Strengths were obtained from the experimental integrated intensities, according to equation: $f = 4.315 \times 10^{-9} \int \epsilon(\bar{\nu})d\bar{\nu}$.

Triplet–triplet absorption spectra and intersystem crossing (ISC) yields were obtained using an Applied Photophysics laser flash photolysis equipment pumped by a Nd:YAG laser (Spectra Physics) with excitation wavelength 355 nm or 266 nm [9]. First-

order kinetics was observed for the decay of the lowest triplet state. The transient spectra (300–700 nm) were obtained by monitoring the optical density change at 5–10 nm intervals and averaging at least 10 decays at each wavelength.

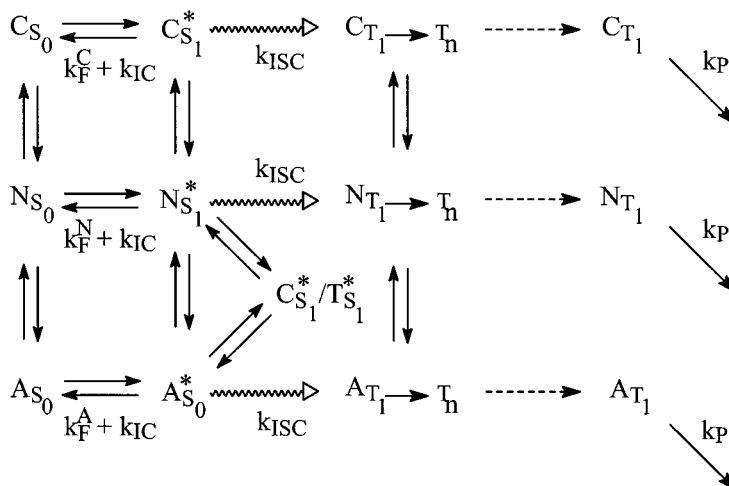
Fluorescence decays were measured using a home-built TCSPC apparatus with an N₂ filled IBH 5000 coaxial flashlamp as excitation source, Jobin–Ivon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA. Alternate measurements (1000 c.p.c.) of the pulse profile at 337 nm and the sample emission were performed until $1 - 2 \times 10^4$ counts at the maximum were reached. The fluorescence decays were analyzed using the modulating functions method of Striker with automatic correction for the photomultiplier “wavelength shift” [12].

The semi-empirical quantum mechanical calculations were performed with the ZINDO/S Hamiltonian [13] using HYPERCHEM (release 3, for Windows). Up to 201 singly excited configurations were used in the configuration interaction (CI) calculations.

3. Results

3.1. 4HC and 4MetC

Fig. 1A presents the absorption, fluorescence and



Scheme 2.

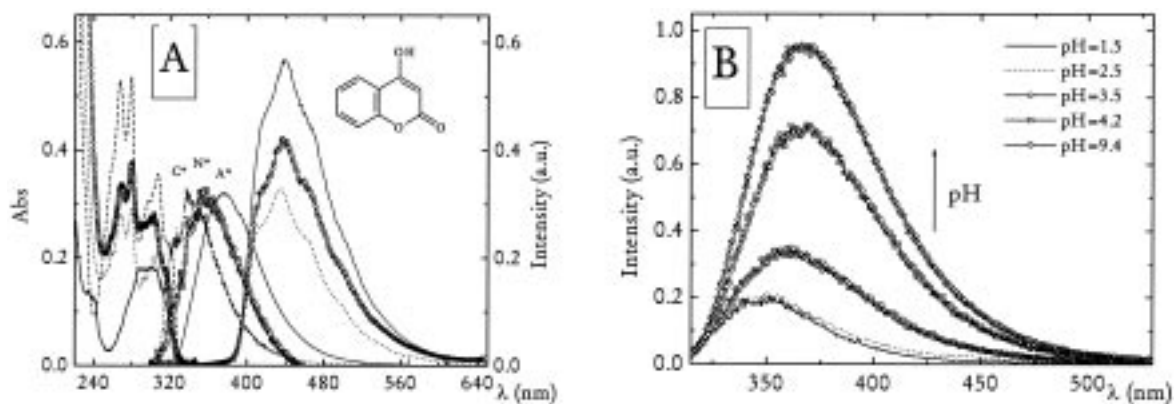


Fig. 1. (A) Left-hand panel, absorption spectra of 4HC, middle-hand panel, fluorescence spectra of and right-hand panel, phosphorescence spectra of 4HC in ethanol (-O-), ethanol:HCl (...), ethanol: diethyl ether:NH₃ (—) and dioxane [only for absorption (- - -)]. (B) Fluorescence spectra of 4HC as a function of pH.

phosphorescence spectra of 4-hydroxycoumarin (4HC) in the solvents: ethanol, ethanol:HCl (37% in water) 19:1 (v:v) and ethanol: diethyl ether: NH₃ (28% in water) 10:9:1. In water (figure not shown), for pH < 4 the spectra presents two vibrationally resolved bands at 280 and 300 nm. For pH > 4 new bands appear at 286 and 298 nm. In aprotic solvents (e.g. dioxane) the absorption spectra of 4HC is equal in shape and has similar maxima to these obtained for water at pH < 4. This absorption was therefore attributed to a neutral species. The other absorbing form,

also obtained in basic ethanolic mixtures, was attributed to the anionic form of 4HC.

The emission spectrum of 4HC in water (Fig. 1B) lacks structure, and for pH < 3 has a maximum at $\lambda_{em}^{max} = 350$ nm. The emission maximum shifts to 360 nm ($3 < \text{pH} < 4$) and for pH ≥ 4 , the maximum is at $\lambda_{em}^{max} = 370$ nm. The observed pH dependent maxima probably imply the presence of three different species: a cation, C*, with $\lambda_{em}^{max} = 350$ nm, a neutral form, N*, $\lambda_{em}^{max} = 360$ nm, and an anion, A*, $\lambda_{em}^{max} = 370$ nm.

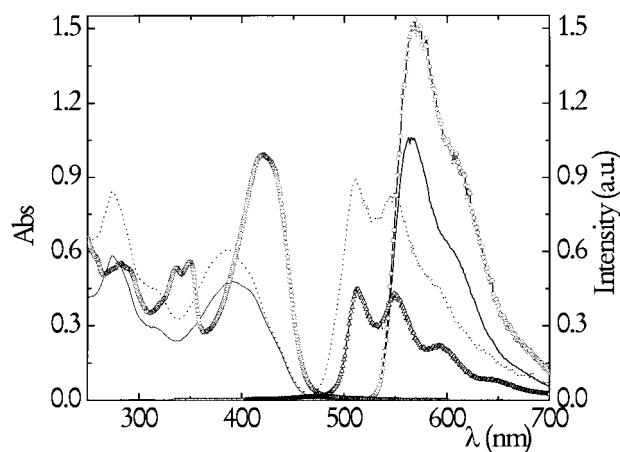


Fig. 2. Left-hand panel, absorption spectra of 4HTC and right-hand panel, phosphorescence spectra of 4HTC in ethanol (—), ethanol:HCl (- - -) and ethanol:diethyl ether:NH₃ (-O-). In right-hand panel also presented is the phosphorescence spectrum of 4Et7C in ethanol (-Δ-).

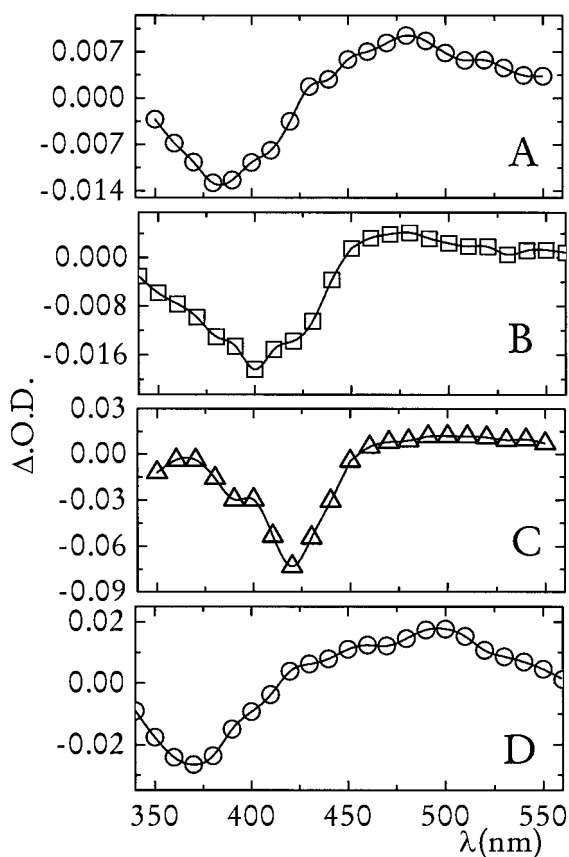


Fig. 3. Triplet–triplet spectra of 4H7C in (A) benzene collected 0.2 μ s after the flash, (B) ethanol collected 0.3 μ s after the flash, (C) ethanol: diethyl ether: NH_3 collected 1 μ s after the flash and of 4Et7C in (D) benzene collected 0.3 μ s after the flash.

The obtained $\text{p}K_a^* = 3.7$, for the $\text{N}^* \longleftrightarrow \text{A}^*$ equilibrium was determined by fluorimetric titration. Comparison of the emission spectra in aqueous solution (Fig. 1B) and in the ethanolic mixtures (Fig. 1A) shows a blue shift of the emission band for all three species: C^* ($\lambda_{\text{em}}^{\text{max}} = 340$ nm), N^* ($\lambda_{\text{em}}^{\text{max}} = 355$ nm) and A^* ($\lambda_{\text{em}}^{\text{max}} = 375$ nm). Also, in the ethanolic mixtures C^* and N^* emission presents vibrational structure. In the three ethanolic mixtures (figure not shown), the parent compound 4MetC shows a similar emission with $\lambda_{\text{em}}^{\text{max}} = 350$ nm, identified with the neutral form of 4HC. This suggests the cationic form of 4HC being protonated at the hydroxylic rather than carbonyl oxygen.

3.2. 4H7C and 4Et7C

Fig. 2 presents the absorption and phosphorescence spectra of 4-hydroxythionecoumarin (4H7C) in three different ethanolic solvents, together with the phosphorescence of 4Et7C in ethanol. For 4Et7C, a single vibrationally resolved band is observed with $\lambda_{\text{em}}^{\text{max}} = 550$ nm independent of solvent. Fig. 3 shows the triplet–triplet spectra of 4H7C and 4Et7C in different solvents.

3.3. 7H4MC, 7H4M7C and their parent compounds 7Met4MC and 7Et4M7C

The absorption spectra of 7H4MC consist of two different bands, attributed to the neutral and anionic forms, N and A, respectively [5,7,8]. In fluorescence, an additional band with $\lambda_{\text{em}}^{\text{max}} \approx 480$ nm is also observed [5,6]. The nature of this new band as been extensively discussed, but must be considered to be a neutral tautomer [5,6]. Triplet–triplet spectra of 7H4MC, 7Met4MC, 7H4M7C and 7Et4M7C in different solvents are shown in Fig. 4.

Fig. 5A presents the absorption and phosphorescence spectra of 7H4M7C in different ethanolic solvents, while Fig. 5B presents the pH dependence of the absorption spectra.

4. Discussion

The only previous reports on the spectroscopy and photophysics on these systems are for the S_1 state of 7H4MC [3,5–8] and transient spectra for 4HC at 77 K and 7H4MC at room temperature [14–16].

The following discussion will focus on: (a) the assignment of the lowest singlet and triplet states (n,π^* vs π,π^*); (b) the influence of solvent on the emission; (c) the nature of the coupling mediating S_1 – T_1 ISC and (d) the number and type of species existing in S_0 , S_1 and T_1 .

4.1. Acidity in the S_0 and S_1 states

Table 1 presents the $\text{p}K_a$ and $\text{p}K_a^*$ values for the studied compounds. Substitution in the 4 and 7 positions induces different behavior relative to the parent thiones. With 4HC vs 4H7C an increase of three $\text{p}K_a$ units is obtained. However, for 7H4MC vs 7H4M7C

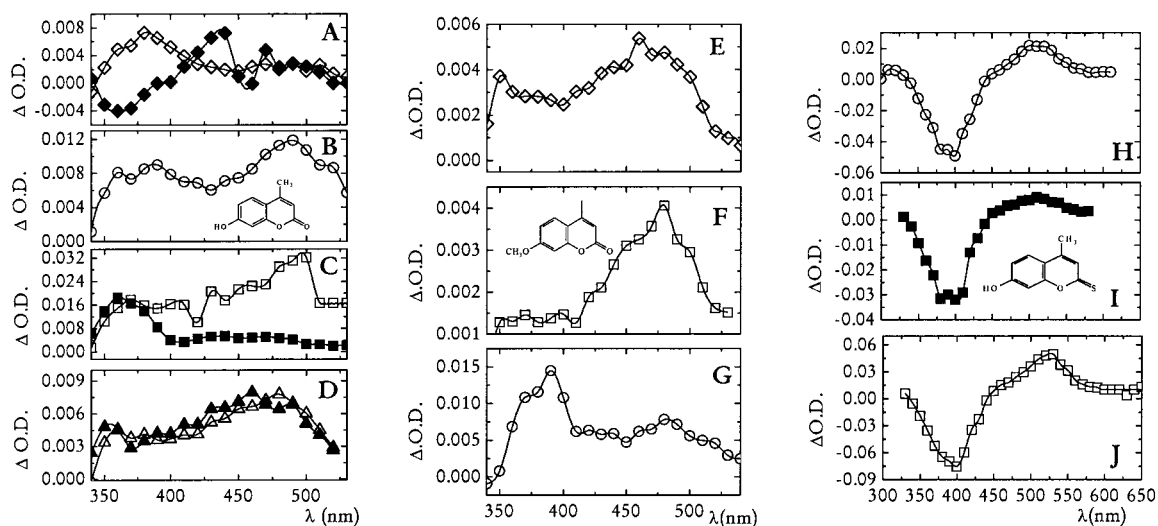


Fig. 4. Left-hand panel, triplet–triplet spectra of 7H4MC in (A) ethanol (—◇—) collected 0.5 μ s after the flash and water at pH = 11.5 (—◆—) collected 1.5 μ s after the flash, (B) ethanol:HCl collected 1.5 μ s after the flash, (C) dioxane:water mixture 4:1 (—□—) and dioxane:water mixture 1:4 (—■—) collected 2.5 μ s after the flash, (D) dioxane (—▲—) collected 8 μ s after the flash and acetonitrile (—△—) collected 1.5 μ s after the flash. Middle-hand panel, triplet–triplet spectra of 7Met4MC in (E) dioxane collected 1.5 μ s after the flash, (F) dioxane:water mixture 4:1 collected 7 μ s after the flash and (G) dioxane:water mixture 1:4 collected 0.2 μ s after the flash. Right-hand panel, triplet–triplet spectra of (H) 7HMTC in methanol collected 0.1 μ s after the flash, (I) 7HMTC in benzene collected 0.1 μ s after the flash and (J) 7Et4MTC in benzene collected 0.1 μ s after the flash.

this difference is reduced to one unit, and the thione now has lower pK_a than the oxygen derivatives. The change is more dramatic for the pK_a values of 7H4MC where a difference of ca. eight orders of magnitude is found when going from S_0 to S_1 . In

the literature identical pK_a and pK_a^* are given for 4HC [17]. The lack of significant difference between ground and excited state pK_a s, for 4HC, may explain why tautomerism is observed in the S_1 state of 7H4MC but not in 4HC.

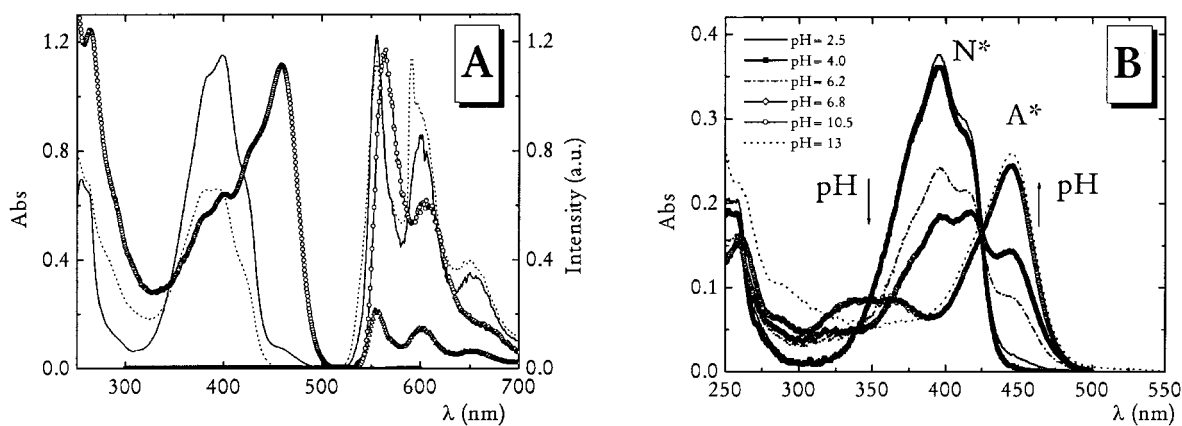


Fig. 5. (A) Left-hand panel, absorption spectra of 7H4MTC and right-hand panel, phosphorescence spectra of 7H4MTC in ethanol (—), ethanol:HCl (---) and ethanol:diethyl ether:NH₃ (···). In right-hand panel also presented is the phosphorescence spectrum of 7Et4MTC in ethanol (—△—). (B) Absorption spectra of 7H4MTC as a function of pH.

Table 1
Values of pK_a and pK_a^* for the different HCs

Compound	pK_a	pK_a^*
4HC	$4.2 \leq pK_a \leq 4.3$	$3.6 \leq pK_a^* \leq 3.7$
4HTC	$7.3 \leq pK_a \leq 7.5$	–
7H4MC	$7.7 \leq pK_a \leq 7.8$	$pK_a^* = 0.74$
7H4MTC	$6.8 \leq pK_a \leq 7.0$	–

4.2. Triplet states

4.2.1. Nature of the lowest triplet state, T_1

Assignment of triplet state configurations [18] is based upon: (1) the relatively large gap, ΔE_{ST} , between the lowest singlet and emitting triplet when T_1 is n, π^* ; and (2) characteristic phosphorescence lifetimes ($\tau_{ph} < 0.01$ s, for n, π^* states and seconds for π, π^* states).

From the observed phosphorescence lifetimes (Table 2), T_1 has π, π^* character for all the carbonyl compounds whilst for the thiones it is n, π^* . This appears to be independent of the state of protonation. Also, the relatively large energy gap between the lowest singlet and the emitting triplet, ΔE_{ST} , suggests a $^3(\pi, \pi^*)$ state. Smaller values for ΔE_{ST} are associated with $^3(n, \pi^*)$ states. Exceptional behavior was observed for 7H4MTC, where the short τ_{ph} clearly shows $^3(n, \pi^*)$ character for T_1 but ΔE_{ST} is relatively large. This may be due to the small T_1 – T_2 gap, lending some π, π^* character to T_1 , according to ISC **I** in Scheme 2 (see next section).

4.2.2. Mechanisms of intersystem crossing

The following ISC pathways can be observed (Scheme 3), for the different studied coumarins, depending on the nature of the S_1 and T_1 states. For the thionecoumarins, since S_1 and T_1 both are n, π^* , the pathway of ISC should occur via the spin orbital coupling (H_{SO}) and vibrational coupling operators (H_{Vib}), **I**. For the carbonyl compounds two mechanisms can operate, **II** or **III** in Scheme 3.

4.3. Nature of the lowest singlet excited state, S_1

Generally if a carbonyl or a thiocarbonyl-containing molecule has a lowest S_{n, π^*} state, it will only be weakly fluorescent. The absence of fluorescence of thiones is generally accepted to be due to very efficient radiationless deactivation [19], where T_1 is populated with close to unit efficiency, but also with some efficient internal conversion from S_1 . For 6-methylthionecoumarin and thionecoumarin, which has lowest n, π^* singlet states, values of $\phi_T = 0.75$ and 1.0, respectively, were obtained in benzene [11,20].

For the carbonyl compounds, the origin of the lowest singlet excited state strongly depends on the nature of the solvent. With 7H4MC and its methoxylated compound a S_1 n, π^* state is observed in nonpolar solvents, but S_1 is π, π^* in polar solvents [10]. For 4HC, based on τ_F and ϕ_F data it is also n, π^* . In dioxane:water mixtures quenching of the neutral form is observed, with lifetimes changing from 0.83 ns

Table 2
Phosphorescence lifetimes, τ_{ph} , in seconds, in four different solvents for the coumarins studied. Also presented is the nature of the T_1 state and the singlet-triplet splitting

Compound	Ethanol	Ethanol:HCl	Ethanol:ether:NH ₃	MCH	ΔE_{ST}^a (cm ⁻¹)
4HC	1.43 π, π^*	1.53 π, π^*	0.61 π, π^*	– ^(b)	≈ 4000
4MetC	1.27 π, π^*	1.41 π, π^*	1.31 π, π^*	1.12 π, π^*	
4HTC	0.0052 n, π^*	0.0023 n, π^*	0.0053 n, π^*	– ^(b)	≈ 900
4Et7C	0.001 n, π^*	0.0012 n, π^*	0.00124 n, π^*	0.00083 n, π^*	
7H4MC	1.65 π, π^*	1.69 π, π^*	2.26 π, π^*	– ^(b)	≈ 6000
7Met4MC	1.41 π, π^*	1.77 π, π^*	1.49 π, π^*	1.47 π, π^*	
7H4MTC	0.0006 n, π^*	0.0009 n, π^*	0.01 n, π^*	– ^(b)	≈ 2700
7Et4MTC	0.00045 n, π^*	0.00041 n, π^*	0.00054 n, π^*	0.00056 n, π^*	

^a Obtained by taken the energy of the on set of the absorption and phosphorescence bands. For the methoxylated or ethoxylated parent compounds identical values were found.

^b Not soluble in this solvent.

(ethanol), 1.53 s (ethanol:HCl) and 0.61 s (ethanol:ether:NH₃) suggest that in basic media either a different species might be present, or these are quenched by NH₃. With the parent 4MetC a single phosphorescent band is observed with $\lambda_{em}^{max} = 445$ nm and $\tau_{ph} = 1.3 \pm 0.1$ s independent of solvent/mixture (Table 2).

For the cationic species in S₁, protonation is possible at three different sites. Since the spectrum of the methoxylated compound is independent of solvent matrix, protonation is most probably at the hydroxyl oxygen. Literature data exists on the presence of three species in S₀ and S₁ [21,22]. However, the assignment of the emitting species is questionable, since it is suggested that at pH = 2.4 a neutral excited species exists, while the cationic species is only reported for very strong acidic media [21]. Comparison with our data shows that the species attributed to N* may actually be considered the excited cation, C*. Also the same authors suggest that their cationic excited species ($\lambda_{em}^{max} = 386$ nm) is formed by protonation of the carbonyl group. It is possible that under the strong acid conditions used a new cationic excited species arises, which is different from ours. Although the likely protonation site of 4HC in S₁ is the carbonyl oxygen, the hydroxyl and lactone oxygens cannot be excluded.

Although difficulties exist in detailed analysis of the triplet–triplet spectra of 4HC (figure not shown) because of low absorption, and solvent influence, studies of 4MetC allow assignment of the neutral triplet state, and this is supported by phosphorescence lifetimes.

4.5.2. 4HTC and 4EtTC

The absorption spectrum of 4HTC in basic ethanol show a band ($\lambda_{max} = 420$ nm) attributed to the anion that is only observed at very high pH (Fig. 2). Also, note that the absorption band in the acidified mixture ($\lambda_{max} = 385$ nm) has a different maximum from the one in neutral ethanol ($\lambda_{max} = 390$ nm), again showing a new cationic species. This compound did not fluoresce. Peculiar phosphorescence behavior was observed for 4HTC with spectra and lifetimes suggesting that two species exist in T₁ (Fig. 2). Most probably, neutral (N_{T₁}^{*}) and anion (A_{T₁}^{*}) forms are present. Phosphorescence lifetimes, for each solvent,

were collected at different wavelengths and first order decays were always obtained (Table 2).

Comparison with the phosphorescence spectra of the ethoxylated thione compound shows that the vibrational structure, found for 4HTC in ethanol:HCl, is present for all solvents in 4EtTC, although small differences, in intensity, were found (Fig. 2). This suggests that with 4HTC in ethanol and basic ethanol the same A* species is present and that no cation is found for 4HTC in T₁.

The triplet–triplet absorption spectrum of 4HTC (Fig. 3) shows singlet depletion in addition to the T₁ → T_n absorption signal. For 4HTC, in both benzene and ethanol, the spectra are similar in shape and maxima to that obtained for 4EtTC in benzene. This is compatible with a neutral triplet transient. However, in basic ethanol a new band appears in addition to singlet depletion at ≈ 420 nm, equal to the absorption observed in the ground-state absorption (Fig. 2), suggesting therefore that the new band should be attributed to this species, A_{T₁→T_n}.

4.5.3. 7H4MC, 7H4MTC and their parent compounds 7Met4MC and 7Et4MTC

The complex excited state kinetics of 7H4MC in S₁, involving three excited species, was previously considered [5]. For 7Met4MC we have obtained τ_F values of 0.48, 0.46 and 0.68 ns in ethanol, acidified ethanol and basic ethanol, respectively. We cannot clearly establish, based on the fluorescence lifetimes, if the cation (ethanol:HCl mixture) actually has a different value than the neutral and anionic species.

The triplet–triplet absorption spectra of 7H4MC in dioxane (Dx) and acetonitrile (MeCN) consist of single bands with maxima at 460 and 480 nm, respectively (Fig. 4D). The transient spectra obtained in these conditions can be attributed to a neutral form, N_{T₁→T_n}, obtained via the N_{S₀} → N_{S₁} ^{ISC} N_{T₁→T_n} pathway. This is confirmed by comparison with the similar triplet–triplet spectrum of 7Met4MC (Fig. 4E and F). In ethanol, acidified ethanol and in dioxane: water 4:1 (Dx:H₂O 4:1), the T₁ → T_n absorption spectra of 7H4MC is different from those obtained in Dx and MeCN, indicating that although the same neutral form is present, there are some differences in the spacing of the T_n states. The similarity between the T₁ → T_n absorption spectra of 7H4MC and 7Met4MC in Dx:H₂O (1:4), (Fig. 4C and G), suggests that similar

neutral species are present and that the differences between dioxane and acetonitrile are due to solvent effects on the $T_1 \rightarrow T_n$ transitions. The spectrum obtained at pH = 11.5 (Fig. 4A) is different, indicating a triplet of the anion, $A_{T_1 \rightarrow T_n}$. In the transient behavior of 7H4MC, no tautomeric triplet, $T_{T_1 \rightarrow T_n}$, was observed. However, we cannot discard the formation of a small amount of $T_{T_1 \rightarrow T_n}$.

The phosphorescence data clearly shows that only two emissive species, $N_{T_1}^*$ and $A_{T_1}^*$ (Table 2), are observed. In the acidified ethanolic mixture the fluorescence spectrum shows emission from N^* and T^* species, whereas in phosphorescence only neutral is observed. An acid-base equilibrium between $N_{T_1 \rightarrow T_n}$ and $A_{T_1 \rightarrow T_n}$ should exist. Although transient absorption data exists for 7H4MC [16], the solvent was not defined, and therefore the nature of the transient cannot be ascertained. However, comparison of the band reported at 510 nm [16] with our triplet–triplet spectra suggests this is the same as in our mixture of ethanol:HCl 19:1 and Dx:H₂O 4:1 (Fig. 4). The triplet–triplet absorption spectrum of 7H4MTC in methanol and benzene (Fig. 4H and I), displays a maximum at 510–520 nm. Comparison with the triplet–triplet absorption spectrum of 7Et4MTC (Fig. 4J) supports the idea that the absorbing species should be the neutral, $N_{T_1 \rightarrow T_n}$. The depletion at 300–450 nm, with a maximum at 390–400 nm, equal to the one observed in the ground-state absorption (Fig. 5), strongly supports the idea that the transient spectrum obtained in these conditions is the one of a neutral form, $N_{T_1 \rightarrow T_n}$, obtained via $N_{S_0} \rightarrow N_{S_1} \xrightarrow{ISC} N_{T_1 \rightarrow T_n}$.

Fig. 5B shows the ground-state acid-base equilibrium between the neutral and anionic forms of 7H4MTC. Significant differences are observed between phosphorescence in basic ethanol and the other two mixtures, (Fig. 5A, Table 2), indicating that in T_1 two species (neutral and anion) are present.

5. Conclusions

Significant differences are observed between spectroscopy and photophysics of HCs and their thione analogs: red-shift in the absorption spectra, quenching of fluorescence, increased triplet–triplet absorption, suggesting increased $S_1 \sim \rightsquigarrow T_1$ ISC and a decrease in the phosphorescence lifetime. The long phosphor-

escence lifetimes observed for the carbonyl compounds indicate that emission is from a triplet π, π^* state, whilst for the thione compounds the shorter lifetimes indicate that the T_1 state has n, π^* character. For the thionyl compounds, the singlet state S_1 is always n, π^* whereas for the carbonyl compounds, where some degree of mixing with $S_2(\pi, \pi^*)$ or exchange in the energetic order can occur, it depends on the media. Depending upon pH and solvent, the compounds can exist in four forms: a cation, a neutral form, an anion and a tautomer (quinone-like canonical form).

Acknowledgements

The authors acknowledge financial support from Fundação para a Ciência e Tecnologia/Lisbon (PrAXIS/QUI/10137/98). JSM acknowledges Dr H.D. Burrows a critical review of this work.

References

- [1] B.E. Nielsen, Coumarins patterns in the Umbelliferae, in: V.H. Heywood (Ed.), *The Biology and Chemistry of the Umbelliferae*, Academic Press, London, 1971, pp. 325–336.
- [2] G. Lazarova, I. Kostova, H. Neychev, *Fitoterapia* 64 (1993) 134.
- [3] S.C. Haydon, *Spec. Lett.* 8 (1975) 815.
- [4] G. Matolcsy, M. Nádasy, V. Andriská, *Pesticide Chemistry, Studies in Environmental Science*, vol. 32, Elsevier, Budapest, 1988.
- [5] J. Seixas de Melo, A.L. Maçanita, *Chem. Phys. Lett.* 204 (1993) 556.
- [6] E. Bardez, P. Boutin, B. Valeur, *Chem. Phys. Lett.* 191 (1992) 142.
- [7] T. Moriya, *Bull. Chem. Soc. Jpn* 61 (1988) 1873.
- [8] P.E. Zinsli, *J. Photochem.* 3 (1974) 55.
- [9] J. Seixas de Melo, P.F. Fernandes, J.C. Lima, A.L. Maçanita, in preparation.
- [10] J. Seixas de Melo, R.S. Becker, A.L. Maçanita, *J. Phys. Chem.* 98 (1994) 6054.
- [11] R.S. Becker, S. Chakravorti, C. Gartner, M.G. Miguel, *J. Chem. Soc. Faraday Trans.* 89 (1993) 1007.
- [12] G. Stricker, V. Subramaniam, C.A.M. Seidel, A. Volkmer, *J. Phys. Chem. B* 103 (1999) 8612.
- [13] M.C. Zerner, in: K.B. Lipkowitz, D.B. Boyd (Eds.), *Semiempirical Molecular Orbital Methods, Reviews in Computational Chemistry*, VCH, New York, 1991, pp. 313–365.
- [14] B.R. Henry, R.V. Hunt, *J. Mol. Spec.* 39 (1971) 466.
- [15] P.T. Chou, M.L. Martinez, S.L. Studer, *Chem. Phys. Lett.* 188 (1992) 49.
- [16] T.G. Pavlopoulos, *IEEE J. Quantum Elec.* 9 (1973) 510.

- [17] O.S. Wolfbeis, G. Uray, *Monatsh. Chem.* 109 (1978) 123.
- [18] R.S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley-Interscience, New York, 1969.
- [19] A. Maciejewski, R.P. Steer, *Chem. Rev.* 93 (1993) 67.
- [20] K. Bhattachayya, P.K. Das, V. Ramamurthy, V.P. Rao, *J. Chem. Soc. Faraday Trans. 2* (82) (1986) 135.
- [21] D.W. Cho, S.G. Kang, Y.H. Kim, M. Lee, D. Kim, M. Yoon, *J. Photoscience* 2 (1995) 13.
- [22] G.J. Yakatan, R.J. Juneau, S.G. Schulman, *J. Pharm. Sci.* 61 (1972) 749.