

Photochemistry of 2,3-dimethoxy-9H-xanthen-9-one: Generation and characterization of its radical cation

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ABSTRACT

Laser flash photolysis studies ($\lambda_{\text{exc}} = 355$ nm, 10 ns pulse, 16 mJ/pulse) were performed to investigate the reactivity of the triplet excited state of 2,3-dimethoxy-9H-xanthen-9-one (**1**) towards several quenchers, in acetonitrile. The triplet **1** ($\lambda_{\text{max}} = 380, 550$ and 630 nm; $\tau = 3.0$ μs , in acetonitrile) was efficiently quenched by 1,3-cyclohexadiene [$k_q = (5.84 \pm 0.18) \times 10^9$ Lmol⁻¹s⁻¹], 1,4-cyclohexadiene [$k_q = (7.15 \pm 0.21) \times 10^5$ Lmol⁻¹s⁻¹], and 1,4-diazabicyclo[2.2.2]octane (DABCO) [$k_q = (7.15 \pm 0.21) \times 10^5$ Lmol⁻¹s⁻¹]. In the case of DABCO, the anion radical derived from **1** was clearly observed ($\lambda_{\text{max}} = 410$ and broad absorption in the 600-710 nm region). In the presence of phenol and its derivatives containing polar substituents (4-OMe- and 4-CN), a value of $\sim 10^9$ Lmol⁻¹s⁻¹ was measured in all cases for the quenching rate constant. Photolysis ($\lambda = 266$ nm, 10 ns pulse, ~ 10 mJ/pulse) of **1** in 1:1 H₂O/acetonitrile solution leads to its photoionization, with the radical cation **2** formed showing absorption maximum at around 390 nm maximum

and a wide band in the 500 to 650 nm region of the spectrum and a lifetime of 18.7 μs . The chemical characterization of this radical cation was performed employing nucleophilic species such as chloride, bromide, and acetate ions.

KEYWORDS: 2,3-dimethoxy-9H-xanthen-9-one, laser flash photolysis, energy transfer, hydrogen transfer, electron transfer, radical cation.

INTRODUCTION

In nature, xanthenes are found as secondary metabolites in plants of the Clusiaceae, Gentianaceae, Moraceae, and Polygalaceae families, and in many species of fungi [1], lichen, and bacteria [2]. Recently, it has been demonstrated that xanthenes are a promising source of anticancer compounds with oral bioavailability [3]. Xanthenes can also be isolated from fossil fuels, suggesting considerable stability of their dibenzo- γ -pirone structure [2, 4].

In general, dimethoxylated xanthenes have been used as an interesting model for the synthesis of compounds with a wide variety of pharmacological and biological activities [5-14].

Among them, one can cite antifungal, antibacterial, antiviral, antimalarial, anti-inflammatory, antioxidant, vascular, antidiabetic, hepatoprotective, anticonvulsant, antipyretic, and antiulcerogenic activities, as well as enzymatic activation or inhibition [7].

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2,3-Dimethoxy-9H-xanthen-9-one (**1**) significantly affects the growth of three human cancer cell lines, namely MCF-7 (breast cancer), TK-10 (renal cancer), and UACC-62 (melanoma), as well as the proliferation of human T-lymphocytes, when compared to the unsubstituted xanthenone [15]. 2,3-dimethoxy-9H-xanthen-9-one also shows strong lipid reducing activity in zebrafish larvae *in vivo*. No toxicity was reported when it was employed to reduce the mRNA expression of fatty acid synthase [16]. However, it shows very low antioxidant properties as evaluated by its 2,2-diphenyl-1-picrylhydrazyl (DPPH) and peroxy radical scavenging effects, as well as its inhibitory effect on the prooxidant enzyme myeloperoxidase (MPO) [17].

Xanthenone, the parent compound, has a strong triplet-triplet absorption (T-T) in the 600-660 nm range [18, 19], with the maximum absorption varying according to the polarity of the solvent from 580 nm in water [20] to 615 nm in 2-propanol and 655 nm in CCl₄ [19]. Due to the change of its excited state configuration as a function of the polarity of the solvent, xanthenone has often been used as a polarity sensor of the micro heterogeneous environment in supramolecular complexes [20, 21]. Although the photochemistry of xanthenone has been thoroughly investigated by the laser flash photolysis technique, as far as we know, no studies have been performed on the photochemical behavior of methoxyxanthenes. In this work, we show the results on the reactivity of 2,3-dimethoxy-9H-xanthen-9-one (**1**) toward hydrogen and electron donors using laser flash photolysis and its ability to form the corresponding cation radical **2** (Figure 1).

MATERIALS AND METHODS

Materials

Acetonitrile (TEDIA), 2-propanol, toluene, ethanol, and methanol, all spectroscopic grade from Aldrich, were used as received. The quenchers 1,4-cyclohexadiene, phenol, 4-cyanophenol, 4-methoxyphenol, and 1,4-diazabicyclo[2.2.2]octane (DABCO) from Aldrich were used as received. 1,3-Cyclohexadiene (Aldrich) was distilled bulb-to-bulb before its utilization. Potassium chloride, potassium bromide, and sodium acetate from Aldrich were used as received.

Synthesis

2,3-dimethoxy-9H-xanthen-9-one was synthesized in 61% yield according to a previously described procedure [22]. Briefly, 2-carboxyphenyl 3',4'-dimethoxyphenyl ether was obtained according to the method of Ullmann by condensation of *ortho*-bromobenzoic acid with 3,4-dimethoxyphenol in hot *n*-butyl alcohol, potassium carbonate, and copper turnings. The resulting diphenylether was initially dissolved in acetyl chloride and concentrated sulfuric acid, and most of the acetyl chloride was then removed by distillation. On addition of water to the residue, crude 2,3-dimethoxy-9H-xanthen-9-one was obtained. Recrystallization from acetone-*n*-hexane led to colorless needles, mp 166-167 °C (mp lit [23] 165-167 °C). Spectroscopic and spectrometric data for 2,3-dimethoxy-9H-xanthen-9-one are in full accord with the structure proposed [24, 25].

Spectroscopic data

The phosphorescence emission spectrum was obtained using a PTI model LS100 spectrofluorimeter

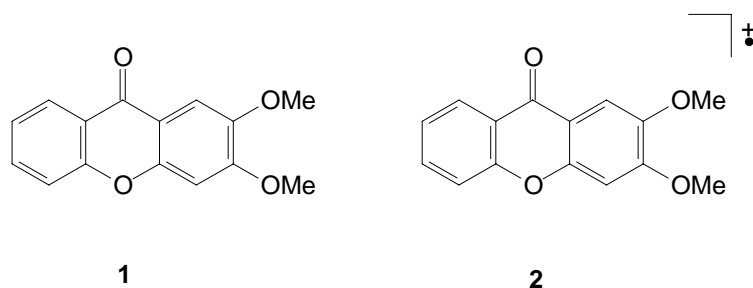


Figure 1. Structure of 2,3-dimethoxy-9H-xanthen-9-one (**1**) and its cation radical **2**.

in a rigid glass solution of ethyl ether:pentane:ethanol 5:5:2 (v:v:v) (EPA) [26], at 77 K, using liquid nitrogen. Fluorescence emission spectra and ultraviolet absorption spectra were recorded using a Jasco model J-815 spectrofluorimeter.

Laser flash photolysis

Laser flash photolysis experiments were carried out on a Luzchem system model mLFP 112. The samples contained in 10 x 10 mm quartz cells were degassed using nitrogen and irradiated using the third ($\lambda = 355$ nm, 10 ns pulse, ~ 40 mJ/pulse) or the fourth harmonic ($\lambda = 266$ nm, 10 ns pulse, ~ 10 mJ/pulse) of a Quantel Nd/YAG laser, model Brilliant B. The system is fully controlled by a Dell 4700 series computer using the Labview 4.1 software from National Instruments, which performs the acquisition, storage, and processing of the data.

Alternatively, experiments were carried out in an Edinburgh Instruments LP 980 system, using the fourth harmonic of a Quantel Nd/YAG laser, model Q-smart 450 ($\lambda = 266$ nm, 10 ns pulse, ~ 10 mJ/pulse), which was controlled by a Dell 4700 series computer using the Labview L900 software from Edinburgh Instruments.

RESULTS AND DISCUSSION

Spectroscopic studies: UV/Visible absorption and steady-state fluorescence and phosphorescence emission

The UV/Vis absorption spectrum for 2,3-dimethoxy-9H-xanthen-9-one (**1**) shows a band with $\lambda_{\max} = 245$ nm, which can be attributed to the $\pi\pi^*$ electronic transition of the xanthone aromatic rings (Figure 2). The high intensity of absorption, in this case, can be related to a symmetry-allowed transition of $\pi\pi^*$ type. The band with $\lambda_{\max} = 350$ nm (in *n*-hexane) refers to the $\pi\pi^*$ electronic transition of the 2,3-dimethoxy-9H-xanthen-9-one carbonyl, and it is possible to observe a bathochromic effect with increasing solvent polarity. The band from the $n\pi^*$ transition is symmetry forbidden and could not be observed due to its low absorption intensity. Probably it is superimposed by the $\pi\pi^*$ transition of higher intensity. The band with $\lambda_{\max} = 300$ nm can be attributed to a $\pi\pi^*$ transition related to the presence of the substituent in the 3-position, *i.e.*, the *para*-position of the aromatic ring relative to the carbonyl group. The attribution of the $\pi\pi^*$ character to the band at $\lambda_{\max} = 300$ nm was made because of the

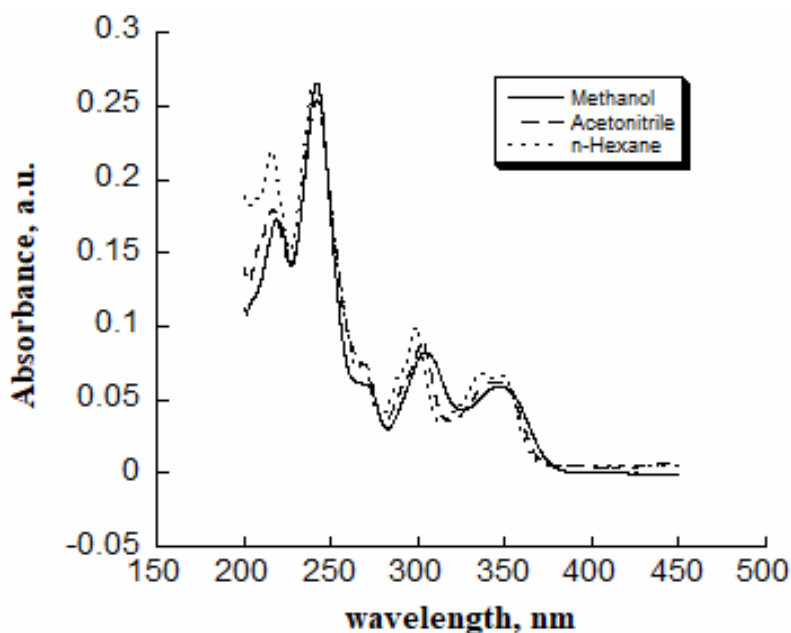


Figure 2. UV/vis absorption spectra for **1** (1.0×10^{-3} mol/L) in methanol, *n*-hexane and acetonitrile.

bathochromic shift observed with the increase of the solvent polarity, from *n*-hexane to methanol.

The fluorescence emission spectrum for 2,3-dimethoxy-9H-xanthen-9-one is very weak in methanol, *n*-hexane, and acetonitrile (Figure 3), showing a broad band at $\lambda_{\text{max}} = 420$ nm in methanol, $\lambda_{\text{max}} = 406$ nm in acetonitrile, and $\lambda_{\text{max}} = 388$ nm in *n*-hexane. It is important to note that the UV/vis absorption spectrum and the excitation spectrum for the 2,3-dimethoxy-9H-xanthen-9-one (Figure 3) are perfectly superimposable, confirming that the fluorescence emission observed for **1** in these solvents is not the result of the presence of impurities. It is known that photoexcited xanthenes have a very high intersystem crossing quantum yield (for xanthone, $\Phi_{\text{isc}} = 0.97$), with an intersystem crossing rate constant (k_{ISC}) in the order of 10^{12} s^{-1} [18, 19]. Consequently, its fluorescence quantum yield in most solvents is very low ($\sim 10^{-4}$).

The phosphorescence emission spectrum for 2,3-dimethoxy-9H-xanthen-9-one was recorded in a rigid glass solution of ethyl ether:*iso*-pentane:

ethanol (5:5:2, EPA) [26] at 77K. The phosphorescence spectrum obtained (Figure 4) showed a single band, without vibrational resolution, characteristic of aromatic ketones with a lower energy triplet excited state with $\pi\pi^*$ character [27]. The configuration of the triplet excited state to **1** can be explained by the presence of the two methoxyl groups in positions 2 and 3 of the aromatic ring. These groups act as electron donors to the conjugate system, resulting in an energetic stabilization of the *n* orbital of the carbonyl oxygen atom, together with a destabilization of the π^* orbital, making the $\pi\pi^*$ electronic transition of lower energy when compared to the $n\pi^*$.

The triplet energy of 2,3-dimethoxy-9H-xanthen-9-one was calculated considering the value of the wavelength at the beginning of the phosphorescence emission band, in nm, using equation 1 [26]. A triplet energy of $79.3 \text{ kcalmol}^{-1}$ was obtained. Under this condition, xanthone, the parent compound, has triplet energy of 74 kcalmol^{-1} with its lowest energy triplet excited state showing $n\pi^*$ configuration [18].

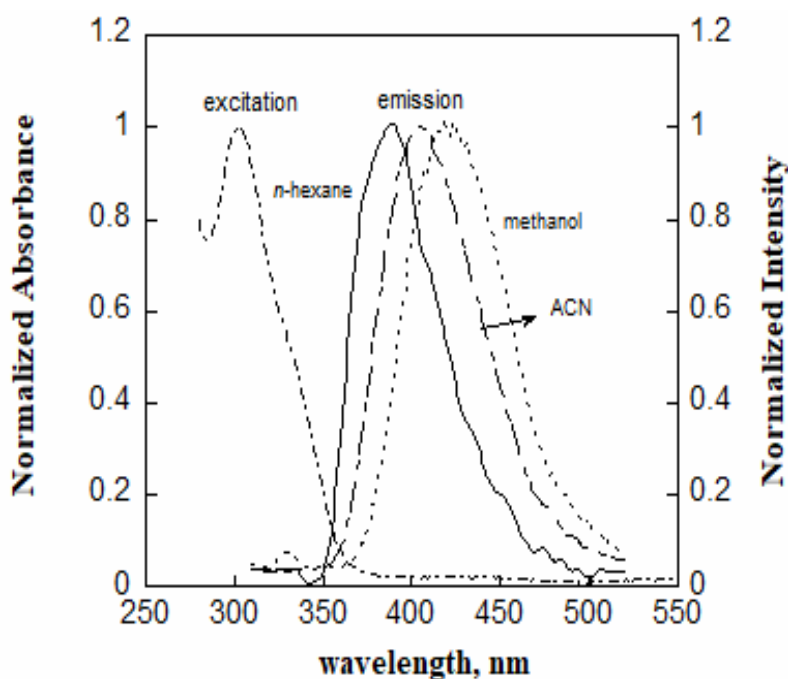


Figure 3. Normalized fluorescence emission spectra for **1** in *n*-hexane, acetonitrile, and methanol ($\lambda_{\text{exc}} = 380$ nm) and normalized fluorescence excitation spectrum monitored at $\lambda_{\text{emi}} = 430$ nm for **1**, in acetonitrile.

$$E_T = 2.862 \times 10^4 / \lambda \text{ (nm) kcalmol}^{-1} \quad (\text{Equation 1})$$

Nanosecond laser flash photolysis

Laser flash photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of a $10^{-3} \text{ molL}^{-1}$ solution of 2,3-dimethoxy-9H-xanthen-9-one (**1**) in acetonitrile led to the formation of a transient with maximum absorption at 380, 550 and a broad absorption at 630 nm (Figure 5), with a lifetime of about 3.0 μs . The decay for this transient observed at 620 nm (Figure 5, *inset*) showed first-order kinetics with the contribution of second-order kinetics, resulting from a deactivation process by triplet-triplet annihilation, common to triplet excited states that exhibit a long lifetime [27, 28].

The quenching rate constants by triplet-triplet energy transfer, hydrogen abstraction, or electron transfer can be obtained from the Stern-Volmer analysis of the kinetics of photochemical reactions [29], in which the decay rate constant (k_{obs}) is related to the quenching rate constant (k_q) according to the Stern-Volmer equation (Equation 2) [28]:

$$k_{\text{obs}} = k_0 + k_q[Q] \quad (\text{Equation 2})$$

where: k_0 is the decay rate constant of the triplet excited state in the absence of the quencher; k_q is the decay rate constant of the triplet excited state in the presence of the quencher; $[Q]$ is the quencher concentration.

Since the k_{obs} values are directly measured by the laser flash photolysis technique as a function of a known quencher concentration $[Q]$, using the Stern-Volmer equation one can then calculate the quenching rate constant k_q for the various quenchers used. In equation 2, the quenching rate constant is the slope k_q of the plot k_{obs} versus $[Q]$. In all cases, linear plots were obtained in the quenching experiments.

The triplet characteristic of the transient generated in the photolysis of 2,3-dimethoxy-9H-xanthen-9-one in acetonitrile was confirmed by the quenching with 1,3-cyclohexadiene ($E_T = 52.4 \text{ kcalmol}^{-1}$) [26], an efficient triplet quencher through energy transfer [28].

The absorption spectrum for the transient generated by photolysis ($\lambda_{\text{exc}} = 355 \text{ nm}$) of **1**, in the presence of excess 1,3-cyclohexadiene, shows a considerable decrease in the absorption bands corresponding to the dimethoxylated xanthone triplet. No new absorption bands appeared in the spectrum, even when it was recorded at times as long as 20.0 μs after the laser pulse. Furthermore, the evident change in the decay profile of triplet **1**, in the absence and presence of 1,3-cyclohexadiene, clearly shows the existence of a quenching process. From a Stern-Volmer plot obtained by successively adding aliquots of a 1,3-cyclohexadiene solution to the xanthone solution, a quenching rate

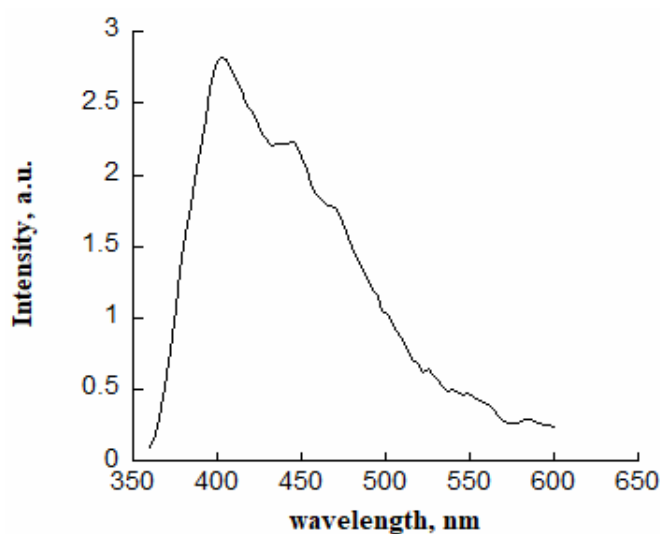


Figure 4. Phosphorescence emission spectrum for **1** in EPA rigid glass, at 77 K, $\lambda_{\text{exc}} = 350 \text{ nm}$.

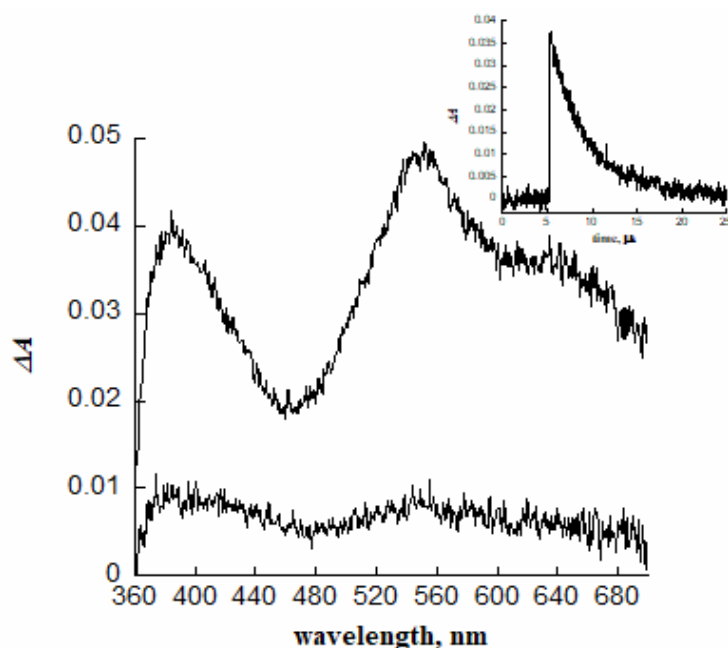


Figure 5. Absorption spectra for the transient generated upon excitation of **1** ($\lambda_{\text{exc}} = 355$ nm), in acetonitrile, at different times after the laser pulse. *Inset:* Decay for the transient generated on excitation of **1**, monitored at 620 nm, in acetonitrile.

constant (k_q) of $(5.84 \pm 0.18) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$ was calculated. This value is in agreement with the fact that the quenching rate constant for an exothermic energy transfer process must be diffusion-controlled in the solvent used (acetonitrile). These results confirm the nature of this transient as the triplet excited state of **1**.

Absorption spectrum for the transients generated by photolysis of 2,3-dimethoxy-9H-xanthen-9-one ($\lambda_{\text{exc}} = 355$ nm) in the presence of excess 1,4-cyclohexadiene as a quencher, in acetonitrile, was recorded at 0.3 and 2.4 μs after the laser pulse. By comparing these two spectra, it was not possible to observe any new absorption in the transient spectrum shown in Figure 6. However, a change in the ratio between the intensities of the absorption bands in the 380 nm and 500 nm regions is clearly seen. Thus, in the spectrum obtained at the longer lifetime (2.4 μs after the laser pulse), it is observed that the band in the 380 nm region is substantially more intense than that at 550 nm, an opposite trend compared to what was observed in the absence of the quencher. This is clear evidence of the formation of a new transient that absorbs at this wavelength.

In addition, the decay monitored at 380 nm after 1,4-cyclohexadiene addition revealed that this new transient has a much longer lifetime than triplet **1**. As the allyl radical from 1,4-cyclohexadiene is transparent in the 350 and 700 nm region, this new transient showing absorption maximum at 380 nm can be attributed to the ketyl radical **3** derived from 2,3-dimethoxy-9H-xanthen-9-one, whose formation can be represented by Scheme 1.

A Stern-Volmer plot for the triplet excited state quenching process of **1** by 1,4-cyclohexadiene allowed us to obtain the corresponding hydrogen abstraction rate constant ($k_q = 7.15 \pm 0.21) \times 10^5 \text{ Lmol}^{-1}\text{s}^{-1}$. In general, in the process of hydrogen abstraction by excited aromatic ketones, the rate constant for the reaction of a triplet state with $n\pi^*$ configuration is usually much higher than for the $\pi\pi^*$ character [28]. 1,4-Cyclohexadiene is an excellent hydrogen donor as it can generate a doubly allylic free radical after hydrogen transfer, as shown in Scheme 1. For this reason, it has often been used to define the $n\pi^*$ or $\pi\pi^*$ character of a carbonyl triplet. In this case, hydrogen transfer rate constants of the order of $10^8 \text{ Lmol}^{-1}\text{s}^{-1}$ for carbonyl compounds showing $n\pi^*$ triplet

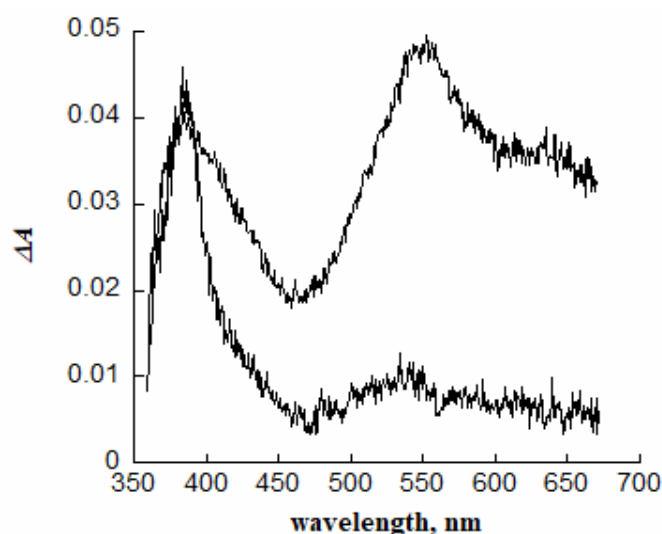
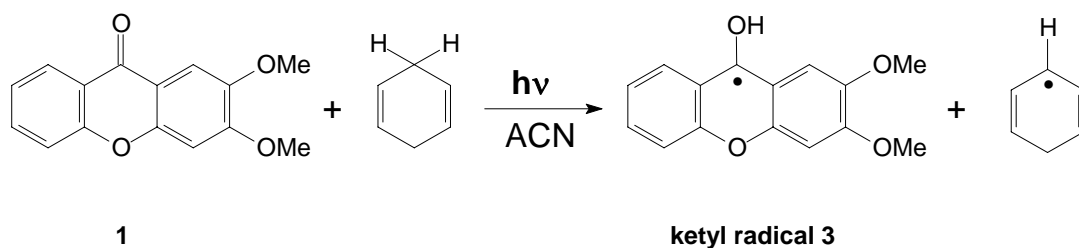


Figure 6. Absorption spectra for transients generated by photolysis of **1** ($\lambda_{\text{exc}} = 355 \text{ nm}$) with an excess of 1,4-cyclohexadiene as a quencher, in acetonitrile, and recorded at different times after the laser pulse.



Scheme 1

configuration, such as for benzophenone [30] and 10,10-dimethylantrone [31], can be obtained. On the other hand, for ketones with an excited state of $\pi\pi^*$ characteristic hydrogen abstraction rate constants of the order of $10^5 \text{ Lmol}^{-1}\text{s}^{-1}$ are commonly observed [32]. Since for the triplet state of 2,3-dimethoxy-9H-xanthene-9-one a hydrogen abstraction rate constant from 1,4-cyclohexadiene of $(7.15 \pm 0.21) \times 10^5 \text{ Lmol}^{-1}\text{s}^{-1}$ was obtained, a $\pi\pi^*$ configuration was assigned to the triplet excited state of **1**. This result fully agrees with the phosphorescence emission result described above, which showed that **1** has a triplet excited state with $\pi\pi^*$ configuration.

The transient absorption spectrum observed when photolysis of 2,3-dimethoxy-9H-xanthene-9-one was performed in the presence of phenols (phenol, 4-methoxyphenol, and 4-cyanophenol) as a

quencher, in acetonitrile, revealed in all cases an appreciable decrease in the absorptions at longer wavelengths (550 and 640 nm). In the case of phenol, the spectrum obtained at 19.0 μs after the laser pulse shows an absorption with a maximum at 400 nm region. At the same time, the absorptions at 580 and 640 nm corresponding to the excited state triplet of **1** practically disappeared. The signal at 400 nm is clear evidence of the formation of a new transient, which can be attributed to the phenoxyl radical ($\lambda_{\text{max}} = 400 \text{ nm}$) with some contribution from the ketyl radical **3** [33, 34]. Similar behavior was observed when 4-methoxyphenol ($\lambda_{\text{max}} = 400 \text{ nm}$ for the 4-methoxyphenoxyl radical) and 4-cyanophenol ($\lambda_{\text{max}} = 440 \text{ nm}$ for the 4-cyanophenoxyl radical) were used as hydrogen donors [35, 36]. A representative transient spectrum for the case

where 4-methoxyphenol was employed as a quencher is shown in Figure 7. The *inset* in Figure 7 shows decays for triplet **1** in the absence and presence of 4-methoxyphenol monitored at 620 nm, in acetonitrile.

From Stern-Volmer plots for the hydrogen abstraction reaction of these phenols by the 2,3-dimethoxy-9H-xanthen-9-one triplet, the corresponding phenolic hydrogen transfer rate constants were obtained, whose values are: phenol, $(1.95 \pm 0.10) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$; 4-methoxyphenol $(2.56 \pm 0.12) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$, and 4-cyanophenol $(1.64 \pm 0.04) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$. It is important to point out that, regardless of the type of the substituent, the abstraction rate constants of phenolic hydrogen are practically identical and almost as fast as the diffusion-controlled rate constant. It can be considered that this high reactivity of 2,3-dimethoxy-9H-xanthen-9-one triplet towards phenols is due to both the lower bond dissociation energy of the O-H bonding and the lower oxidation potential of phenols. In addition, it is well known that the reaction with phenols is faster for ketones whose lowest excited triplet state shows $\pi\pi^*$ configuration, such as 2,3-dimethoxy-9H-xanthen-9-one, than those that

have $n\pi^*$ character for its triplet state [32, 37]. In the phenolic hydrogen abstraction reaction by the carbonyl triplet, the involvement of a mechanism in which there is the formation of the hydrogen-bonded triplet exciplex followed by a proton-coupled electron transfer has been proposed, resulting in the formation of the radical pair ketyl/aryloxyl [33, 37-47].

The spectrum recorded 10 μs after the laser irradiation of a 2,3-dimethoxy-9H-xanthen-9-one (**1**) solution in acetonitrile, in the presence of an excess of the tertiary amine 1,4-diazabicyclo [2.2.2] octane (DABCO), clearly shows the disappearance of the absorption in the 550-700 nm region, corresponding to the triplet excited state of **1** (Figure 8). However, a new absorption at 410 nm can be observed. The kinetics associated with this absorption shows that this transient presents a slow decay. This is clear evidence of the formation of a new transient, which can be attributed to the radical anion **4** derived from the dimethoxyxanthone. This anion radical is probably formed through an electron transfer process from the DABCO donor to the excited ketone, leading to the formation of an ion-radical pair (Scheme 2) [48, 49]. Under the

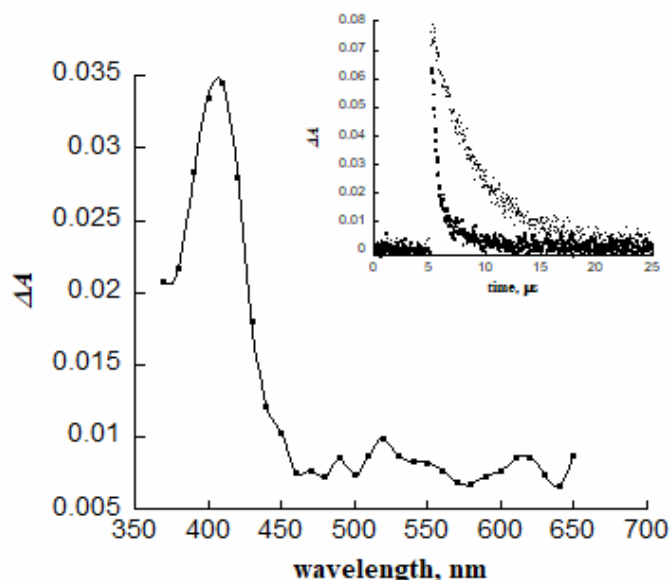


Figure 7. Absorption spectra for transients generated by photolysis of **1** ($\lambda_{\text{exc}} = 355 \text{ nm}$), with excess 4-methoxyphenol as a quencher, in acetonitrile, and recorded at different times after the laser pulse. *Inset:* Decays for the triplet **1** in the absence and presence of 4-methoxyphenol monitored at 620 nm, in acetonitrile.

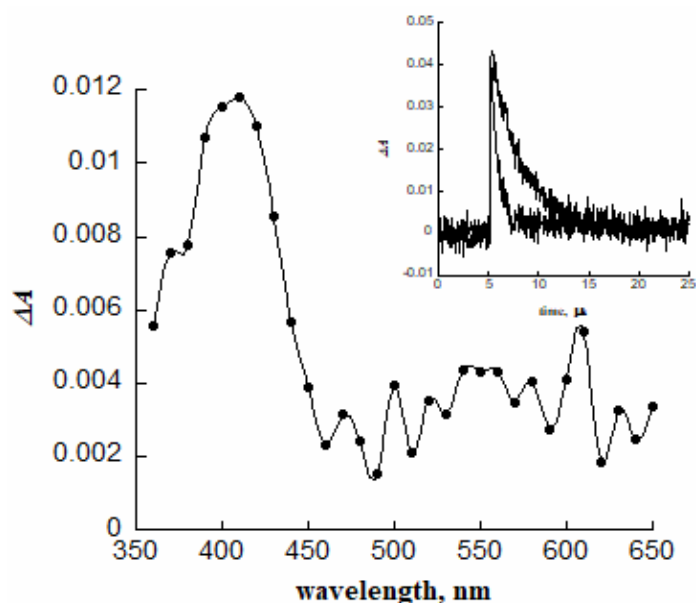
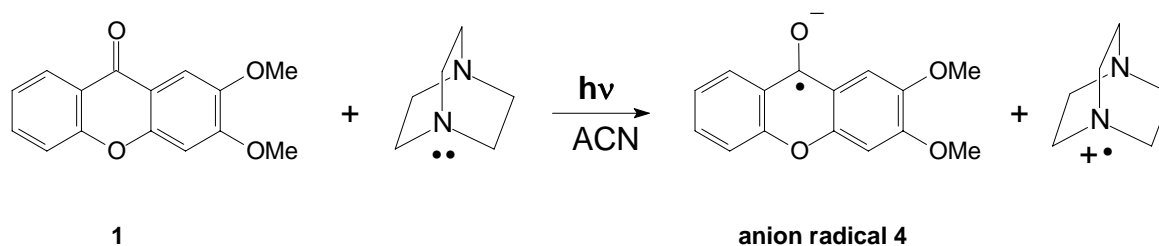


Figure 8. Absorption spectrum for the transients generated by photolysis of **1** ($\lambda_{\text{exc}} = 355 \text{ nm}$), with excess DABCO as a suppressor, in acetonitrile, and recorded at $10 \mu\text{s}$ after the laser pulse. *Inset:* Decays for triplet **1** in the absence and presence of DABCO monitored at 620 nm , in acetonitrile.



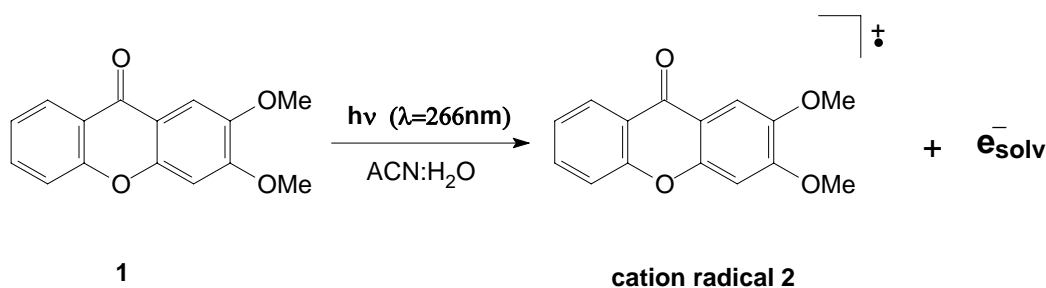
Scheme 2

experimental conditions employed in this work, the DABCO cation radical cannot be observed since it has a non-detectable absorption band in the visible region of the spectrum [50]. Figure 8, *inset* shows the decay for triplet **1** in the absence and presence of DABCO monitored at 620 nm , in acetonitrile.

A Stern-Volmer plot for the quenching of the triplet excited state of the dimethoxyxanthone by DABCO provided a value for the quenching rate constant of $(2.71 \pm 0.13) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$. The value obtained for this constant, close to diffusional control, demonstrates that the process is highly efficient, being of the same order of magnitude compared to other data in the literature [51].

Generation and characterization of the cation radical

The radical cation **2** was generated by direct photolysis ($\lambda_{\text{exc}} = 266 \text{ nm}$) of 2,3-dimethoxy-9H-xanthen-9-one (**1**) in a solution of H_2O :acetonitrile (1:1, v/v) saturated with oxygen gas (Scheme 3). The presence of oxygen in the reaction medium aimed to quench the formation of the solvated electron, whose absorption band (wide band from 640 nm to 750 nm) overlaps those of other possible transients formed (Figure 9) [52]. From this figure it was possible to visualize the absorption bands relative to the radical cation **2**, which shows a maximum at 390 nm and a wide band in the 500 to 650 nm region of the spectrum.



Scheme 3

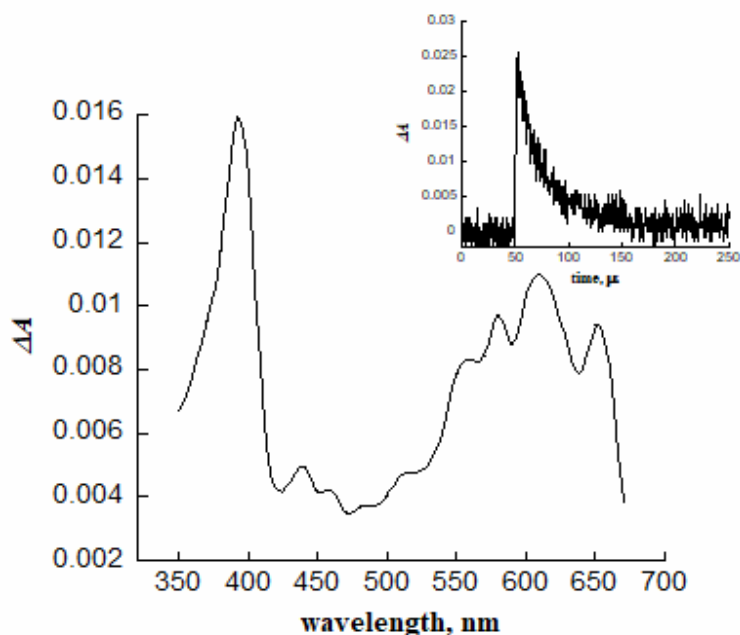


Figure 9. Absorption spectrum for the transient generated in the excitation of 2,3-dimethoxy-9H-xanthen-9-one (**1**) in a solution of H₂O:acetonitrile (1:1 v/v) and saturated with oxygen gas, using the 4th harmonic of a Nd/YAG laser ($\lambda_{\text{exc}} = 266$ nm). *Inset:* Decay for this transient monitored at 390 nm, under the same conditions.

All these absorptions show the same kinetics, with a decay rate constant of $(5.34 \pm 0.26) \times 10^4 \text{ s}^{-1}$ ($\tau = 18.7 \mu\text{s}$). Figure 9, *inset* shows the kinetic trace obtained for this transient, monitored at 390 nm.

The chemical characterization of the radical cation **2** was performed using the nucleophilic quenchers potassium chloride, potassium bromide, and sodium acetate, which are more susceptible to reactions with radical cations, since they are electrophilic species. In all cases, there was efficient quenching of the radical cation **2**, with the quenching rate constants (chloride: $(5.37 \pm 0.27) \times 10^9 \text{ Lmol}^{-1}\text{s}^{-1}$;

bromide: $(1.78 \pm 0.20) \times 10^{10} \text{ Lmol}^{-1}\text{s}^{-1}$; acetate: $(1.36 \pm 0.32) \times 10^{10} \text{ Lmol}^{-1}\text{s}^{-1}$) obtained showing that the process is diffusion-controlled in the solvent used, which is in agreement with results from the literature [52-54].

CONCLUSION

In conclusion, laser flash photolysis results show that the triplet excited state of 2,3-dimethoxy-9H-xanthen-9-one (**1**) ($\lambda_{\text{max}} = 380, 550$ and 630 nm; $\tau = 3.0 \mu\text{s}$, in acetonitrile. $E_{\text{T}} = 79.3 \text{ kcalmol}^{-1}$) was efficiently quenched by energy transfer, hydrogen

abstraction, and electron transfer. Hydrogen abstraction quenching leads to the formation of the ketyl radical derived from **1**, whereas by electron transfer the anion radical derived from **1** was clearly observed. A photoionization process was observed when 2,3-dimethoxy-9H-xanthen-9-one was photolyzed at 266 nm, in ACN:H₂O, with the formation of the corresponding radical cation **2**. The high reactivity of **2** toward nucleophilic agents confirms the electrophilicity of this species.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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