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COMPETITIVE ONE-POT REACTIONS: SIMULTANEOUS SYNTHESIS OF DECAHYDROACRIDINE-1,8-DIONES AND 1,8-DIOXO-OCTAHYDROXANTHENES AND PHOTOPHYSICAL CHARACTERIZATION

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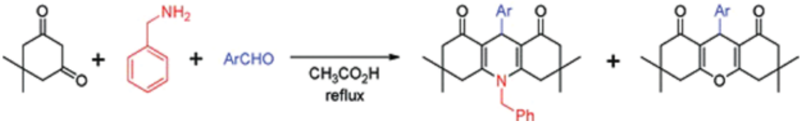
GRAPHICAL ABSTRACT



Abstract *A simple and convenient one-pot method for simultaneously obtaining decahydroacridine-1,8-diones and 1,8-dioxo-octahydroxanthene derivatives is described. A high conversion yielding both products was obtained under the reaction conditions. To understand the optical behavior of the model compounds and their potential use as antenna moieties in bichromophoric systems, the photophysical properties of all samples were studied using ultraviolet–visible absorption and steady-state fluorescence spectroscopy in methanol solutions. For the case of the acridinediones, the fluorescence spectra were found to exhibit the typical emission profile of the locally excited state, whereas, contrary to previous published experimental results, reliable fluorescence emission spectra for the xanthenes derivatives could not be obtained. On the other hand, the poor quantum yields of the synthesized decahydroacridine-1,8-diones were explained based on the benzene-like substitution effect, which favors the intersystem crossing relaxation mechanism.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Acridinediones; one-pot-synthesis; photophysical characterization; xanthenes

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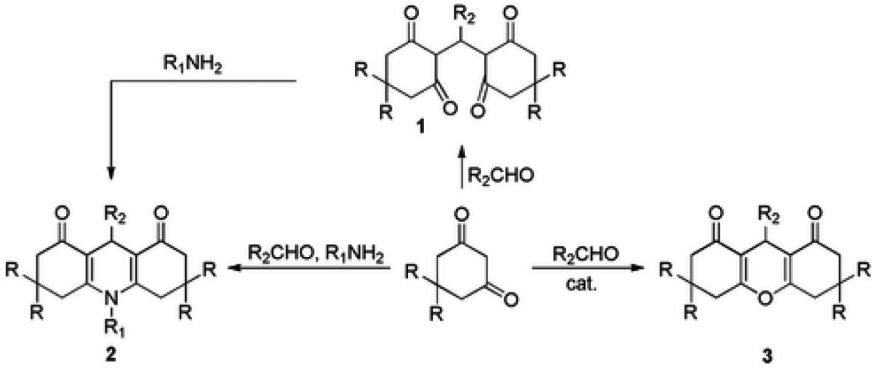
INTRODUCTION

During recent decades, a large number of studies have been focused on the development of new classes of laser dyes. Among the new fluorophores developed, acridinedione and xanthene dyes have emerged as new materials with advance optical properties.[1–3] Specifically, acridinedione and xanthenes derivatives, including rhodamines and fluoresceins, have lasing efficiency comparable to the well-know standard, coumarin-102. The most important photophysical properties of these dyes include high extinction coefficients in the ultraviolet–visible (UV-vis), excellent quantum yields, great photostability, and relatively long emission wavelengths. All these features make these systems highly favorable dyes to be used as light receptors or antennas in the synthesis of new multichromophore compounds.[4]

Acridones and acridinediones are well-known nitrogenated heterocycles in which one or two carbonyl groups are attached to the structure. Acridinedione dyes act as both electron donors and acceptors because of their bichromophoric structure, which include both the heterocyclic nitrogen and the carbonyl groups.[5–13] Additionally, depending on the chemical structure, these dyes can undergo interesting reactions in the excited states including excited-state intramolecular proton transfer,[14–19] energy transfer,[20] and intramolecular charge transfer.[21] The photophysical and photochemical properties of several acridinedione dyes in solution and in poly(methyl methacrylate) (PMMA) matrix have been extensively investigated.[13,17,21–23] Several reports show that these heterocycles present a broad range of biological activities[24–27] as well as applications in bioanalytical chemistry as fluorescent probes.[28] Within this class of compounds, the 9-aryl-decahydroacridine-1,8-dione derivatives have emerged as very interesting systems not only because of easy synthesis and biological activity as SITR1 inhibitors,[29] DNA intercalator,[30] calcium,[31] and potassium[32,33] channel modulators but also for their photophysical and photochemical properties. Additionally, the acridinedione derivatives have been widely used as chemosensors,[34,35] as laser dyes,[2,36,37] as initiators in photopolymerization,[38,39] in the preparation of blue light-emitting devises,[40] in dye-sensitized solar cells,[41] and as fluorescent probes for monitoring of polymerization processes.[42] These dyes are also important because of their structural similarity to the coenzyme nicotinamide adenine dinucleotide (NADH), which acts as a coenzyme in biological systems.[9,43–46]

The synthesis of these derivatives usually involves the reaction of dimedone or 1,3-ciclohexanedione with aromatic or aliphatic aldehydes and a source of nitrogen in a stepwise sequence reaction or in a one-pot multicomponent reaction. In the first methodology, two equivalents of the cyclic diketone is condensed with one equivalent of the aldehyde to form a tetraketone **1**, which reacts with an amine to yield the decahydroacridine-1,8-dione derivative **2**[2] (Scheme 1). Furthermore, in the multicomponent reaction approach, conventional heating using different solvents and catalyst such as HCl,[47] $CeCl_3 \cdot 7H_2O$,[48] ambelyst 15,[49] *p*-dodecylbenezenesulfonic acid,[50] and ceric ammonium nitrate (CAN)[51] have been reported. Alternative procedures involve the use of microwave irradiation,[52] ionic liquids,[53] and solvent-free reactions.[54]

On the other hand, xanthenes are a very interesting class of oxygen-containing heterocycles. In particular, the 1,8-dioxo-octahydroxanthenes have shown potential



Scheme 1. Synthetic procedures commonly used for the synthesis of decahydroacridine-1,8-diones and 1,8-dioxo-octahydroxanthenes.

in different applications both in the field of medicinal chemistry[55] and materials science.[56] As in the synthesis of decahydroacridine-1,8-dione derivatives, the synthesis of 1,8-dioxo-octahydroxanthenes **3** is commonly performed by the condensation of the appropriate aldehyde and dimedone or 1,3-ciclohexanedione (Scheme 1). Several synthetic procedures with solvent-free conditions using different catalysts,[57–63] ionic liquids,[53,64–66] homogeneous[67,68] and heterogeneous[69–73] catalysts, and microwave-[74] and ultrasound- assisted[75–77] synthesis have been reported.

During recent years, our research group has been interested in developing efficient synthetic routes that allow us to obtain different laser dyes based on the acridinedione and/or xanthenes dyes and use them to photosensitize macromolecular systems. The indirect electronic excitation of a molecular system through auxiliary chromophores is of great importance for light-harvesting applications. For example, recently, we have reported a photoinduced energy transfer study in bichromophoric pyrene– phenylenevinylene (PV) systems (antenna–bridge–acceptor systems with variable length) and showed that the energy-transfer process is especially efficient in systems where the linker is formed by eight atoms.[78] In this preliminary work we explore the possibility of using heterocyclic compounds to perform a study in which the heterocycle can be used as antenna in a multichromophoric system. Taking into account that the acridinedione dyes operate in the blue-green region of the UV-vis spectrum and their efficient lasing yield, we believe that these systems can be used as light receptors in the synthesis of new multichromophore oligomers derived from PV. In this study, we report both the unexpected results obtained with the one-pot method for the synthesis and the steady-state spectroscopy for 9-aryl-decahydroacridine-1,8-diones.

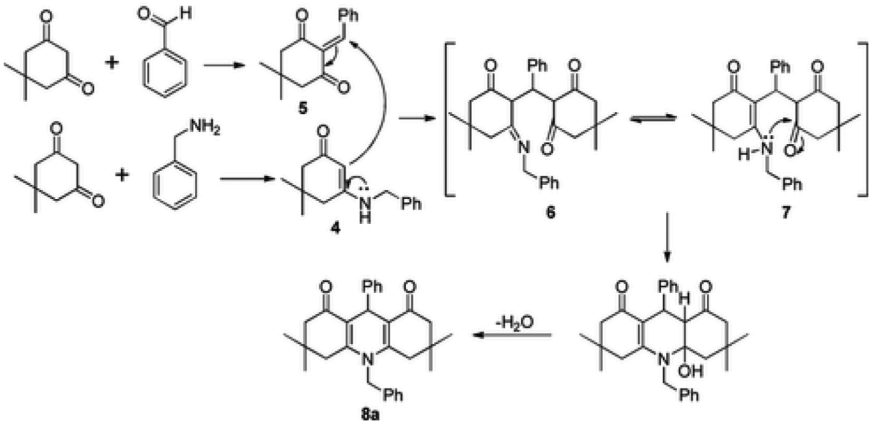
RESULTS AND DISCUSSION

To obtain a set of 9-aryl-decahydroacridine-1,8-dione derivatives, we performed the synthesis of the desired molecules using dimedone as cyclic diketone. Our synthetic methodology was based on the reaction of aromatic aldehydes, dimedone, and benzylamine via one-pot, three-component reaction synthesis under conventional heating using acetic acid as solvent. Initially, benzaldehyde (1 eq.), dimedone (2 eq.), and benzylamine (1 eq.) were mixed in 10 mL of acetic acid. The progress of the reaction was monitored by thin-layer chromatography (TLC) and the mixture was refluxed until the starting materials were consumed. After completion of reaction, the product was purified by chromatography on silica gel using ethyl acetate–*n*-hexane 2:3 as eluent to give two compounds.

The structure of the first compound isolated, labeled as **8a**, was elucidated by Fourier transform–infrared (FT-IR), ^{1}H NMR, ^{13}C NMR, and gas chromatography–mass spectrometry (GCMS). FT-IR spectra showed characteristic absorptions between 2957 and 3000 cm^{-1}, which were assigned for the aromatic rings, while absorptions between 2928 and 2868 cm^{-1} were attributed to asymmetric and symmetric aliphatic stretches. The carbonyl group was remarked at a strong stretch absorption in 1632 cm^{-1}. In the ^{1}H NMR spectra the signals corresponding to the aromatic protons from the phenyl and benzyl ring are located at 7.15–7.20 and 7.28–7.41 ppm, respectively. Two singlets at 5.34 and 4.90 ppm were assigned to protons at C9 and the CH_2 in the benzyl group, respectively. Signals at 2.30–2.49 and 2.19 ppm were assigned to protons at C4, C5 and C2, C7. The signals observed at 0.99 and 0.88 ppm correspond to the methyl protons. ^{13}C NMR spectra showed characteristic peaks at 195.6 ppm for the carbonyl group and 125.4–145.8 ppm for the aromatic substituent. Signals at 150.5 and 115.4 ppm were attributed to C=C in the pyridyl core, while peaks at 50.0 and 48.8 ppm were assigned to the carbon atoms at C2, C7, and the CH_2 of the benzyl group respectively. The remaining signals correspond to C4, C5 at 40.2 ppm, quaternary carbons C3, C6 at 32.7 ppm, methine carbon C9 at 32.1 ppm, and methyl carbons of dimedone at 28.4 and 28.2 ppm. The mass spectra showed the corresponding molecular ion peak at 439 (40%). All this information supports the desired acridinedione **8a**.

For the second compound labeled as **10a**, the ^{1}H NMR spectra showed three aromatic signals between 7.21 and 7.03 ppm corresponding to five aromatic protons, two singlets at 4.08 ppm and 2.39 ppm corresponding to one and four protons respectively, a double doublet at 2.13 ppm for four protons, and two singlets at 1.03 and 0.92 ppm for six protons each. The ^{13}C NMR spectra showed seven peaks between 196.5 and 115.8 ppm and six peaks between 50.9 and 27.5 ppm for each one of the nonequivalent carbons present in **10a**. FT-IR spectra for this compound showed absorptions between 3032 and 3061 cm^{-1}, which were assigned for the aromatic rings.

Absorptions between 2956 and 2854 cm^{-1} were attributed to asymmetric and symmetric aliphatic stretches. A strong stretch absorption band at 1662 cm^{-1} was assigned to a cyclic carbonyl group. The mass spectra exhibited a molecular ion peak at 350 (71%). All this information indicates that the structure of the compound corresponds to the octahydroxanthene **10a**. These results show that under the reaction conditions two competitive processes occur simultaneously: the formation of the decahydroacridine-1,8-dione **8a** and the formation the of 1,8-dioxo-octahydroxanthene derivative **10a**. The obtention of the first heterocycle can be explained by the mechanism proposed by Shi et al.[79] and Rostamizadeh et al.[54] According to the proposed mechanism, one equivalent of dimedone reacts with benzylamine to yield the enamine **4**. The second equivalent of dimedone reacts with benzaldehyde to



Scheme 2. Mechanism proposed to obtain **8a**.

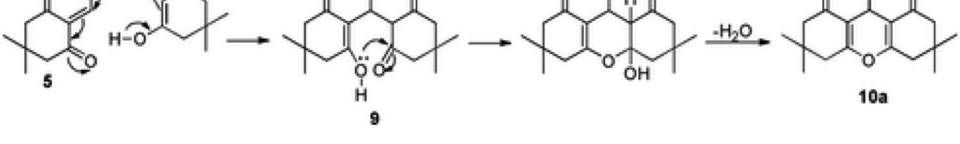
yield the condensation intermediate **5**, which undergoes a Michael addition with **4**, affording the intermediate **6**. Then isomerization of intermediate **6** occurred to give **7**, which after an intramolecular cyclization and dehydration yields the product **8a** (Scheme 2).

Similarly, obtaining the octahydroxantene can be explained by the mechanism proposed by Kantevari et al.[59] and Verma et al.[62] in which the enol form of the dimedone reacts with benzaldehyde to give the Knoevenagel adduct **5**. Then **5** may further undergo Michael addition with another molecule of dimedone to form the intermediate **9**, which after a dehydration reaction yields the compound **10a** (Scheme 3).

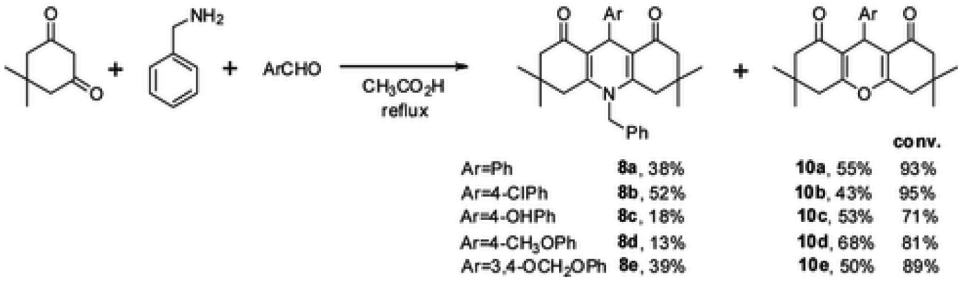
Based on these results we concluded that this methodology may allow us to obtain two heterocyclic compounds in one single procedure. Then, following the same procedure described before for obtaining compounds **8a** and **10a**, we performed the synthesis of a set of structural analogs, obtaining always both the target acridine-1,8-dione and the octahydroxantene. The results are summarized in Scheme 4.

Steady-State Spectroscopy

Because of the extended electronic conjugation both products are expected to exhibit optical properties according to the literature reports of analogous systems,[62] and therefore, it was important to perform a study of the photophysical characterization of the acridinediones and the xanthenes. The steady-state absorption and emission spectra of compounds **8a–e** in methanol solutions are shown in Figs. 1 and 2. The absorption spectra of the different acridinedione derivates show an



Scheme 3. Mechanism proposed to obtain **10a**.



			conv.
Ar=Ph	**8a**, 38%	**10a**, 55%	93%
Ar=4-ClPh	**8b**, 52%	**10b**, 43%	95%
Ar=4-OHPh	**8c**, 18%	**10c**, 53%	71%
Ar=4-CH$_3$OPh	**8d**, 13%	**10d**, 68%	81%
Ar=3,4-OCH$_2$OPh	**8e**, 39%	**10e**, 50%	89%

Scheme 4. Simultaneous one-pot synthesis of decahydroacridine-1,8-diones **8a–e** and 1,8-dioxo-octahydroxanthenes **10a–e**.

intense broad band at 350–425 nm. This band has been assigned to the intramolecular charge-transfer (ICT) due to the transfer of charge from the ring nitrogen to the carbonyl oxygen in the acridinedione fluorophore.[80] The rigid structure of the acridinediones favors the charge-transfer transition, which is sensitive to the solvent environment as reported by Srividya et al.[80] The absorption spectra of the acridinediones **8b–e** do not display any significant change in the shape and position relative to the absorption spectrum of **8a**, maintaining the characteristic broad band despite the different substituents on the phenyl ring.

The emission spectra of the acridinediones **8a–e** in methanol solutions were recorded using an excitation wavelength tuned at the ICT band. The fluorescence spectra of the acridinediones (Fig. 2) exhibit a single structureless broad band with a maximum approximately at 430 nm that has been assigned to the emission of the local excited state.[81] In contrast to the absorption spectrum, the position of the emission band is shifted depending on the nature of the substituent over the phenyl moiety. Also, it is well known that the position of the emission band is red shifted with increasing the solvent polarity.[10] This result indicates that the charge-transfer excited state is stabilized in polar media. The absorption, emission, and Stokes shift values for all the compounds in methanol are given in Table 1.

Figure 3 shows the absorption spectra of the xanthene derivates **10a–e** in methanol solutions. In general, the UV–vis absorption spectra of the substituted

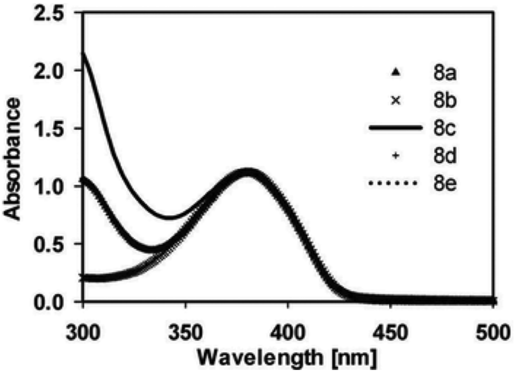


Figure 1. Absorption spectra for the acridinedione derivates **8a–e**.

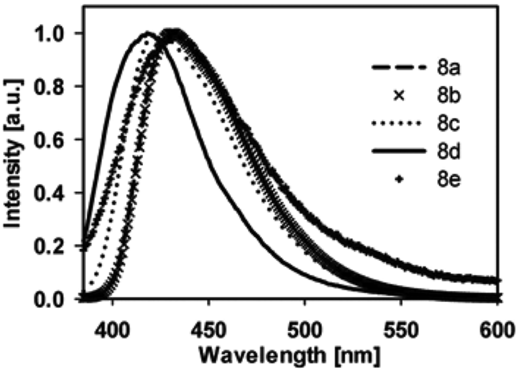


Figure 2. Emission spectra for the acridinedione derivates **8a–e**.

1,8-dioxo-octahydroxanthenes show an intense band around 260–314 nm, very short-wavelength spectral range compared with the absorption spectra of standard xanthene derivatives such as rhodamine and fluorescein derivatives. These differences can be explained based on the different degree of conjugation between the octahydroxanthenes and xanthenes. Additionally, as can be observed in Fig. 3, the absorption spectrum of compound **10e** extends to longer wavelengths and shows a shoulder at 360 nm.

On the other hand, reliable emission spectra from the 1,8-dioxo-octahydroxanthenes **10a–e** in methanol solution could not be obtained. This contradicts the early report of Verma et al.,[62] who detected fluorescence emission for compounds **10a–d** in several solvents, including methanol, tetrahydrofuran, cyclohexane, and acetonitrile. After performing careful unsuccessful attempts to detect fluorescence in all these solvents, and based on the previously reported spectroscopic data[59,64,73] and our NMR spectra, mass spectrometry, and FTIR data that clearly proved chemical structure of the 1,8-dioxo-octahydroxanthenes **10a–e**, we can assume that the emission spectra in that report could be due to the presence of some impurities.

Quantum Yield of Fluorescence

The fluorescence quantum yields (Qy) in methanol for all the acridinediones are given in Table 1. As can be observed, the quantum yield values of the acridinediones **8a–e** are between 0.04 and 0.18. According to literature reports, acridinediones with N-H or N-CH_3 functional groups present quantum yields of about

Table 1. Optical properties of the acridinediones **8a–e** in methanol solution

Compound	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Quantum yield (Φ)	Stokes shift (cm^{-1})
8a	373	443	0.10	4236
8b	380	440	0.06	3588
8c	378	424	0.18	2870
8d	375	438	0.05	3836
8e	381	422	0.04	2550

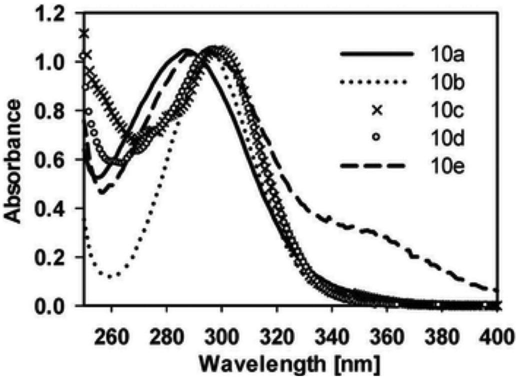


Figure 3. Absorption spectra of xanthene derivates **10a–e**.

0.9, whereas, modification either on the nitrogen or in the carbon at the 9-position with aromatic groups results in a considerable decrease of the Qy. These results have been explained by Srividya et al.[10] based on the well-known behavior of the substitution with benzene-like groups, which favor the intersystem crossing relaxation mechanism, and therefore, result in systems with greater triplet yields. Also, it is important to note that all the acridinediones synthesized in this work have a benzyl substituent in the nitrogen atom, which can increase the efficiency of the singlet-triplet transition. Finally, the lower fluorescence quantum yield of acridinediones **8b, 8d**, and **8e** compared to **8a** and **8c** is also attributed to the presence of electron-donating (ED) methoxy and chloride groups in the *para*-position of the phenyl ring.[16] The presence of these ED groups results in the photoinduced electron transfer process through space between $-OCH_3$ or –Cl group and the acridinedione moiety, as has been shown by Rajendran et al.[18] The low Qy values presented in Table 1 agree very well with the aforementioned optoelectronic mechanisms. Photophysical properties of the acridinedione compounds are summarized in Table 1.

EXPERIMENTAL

A solution of dimedone (3.56 mmol), benzylamine (1.78 mmol), and the selected aldehyde (1.78 mmol) in acetic acid (4 mL) was heated under reflux for the appropriate time. After completion of the reaction (TLC) and distillation of acetic acid, the crude was washed with a solution of potassium carbonate (10%) and extracted with chloroform (3 × 10 mL). The organic layers were recovered and dried over anhydrous sodium sulfate, and the solvent was evaporated. Finally, the crude product was purified by silica-gel column chromatography (ethyl acetate–*n*-hexane 2:3).

10-Benzyl-9-phenyl-3,3,6,6-tetramethyldecahydroacrydin-1,8-dione (8a)

Yellow solid. Yield 38% (300.2 mg, 0.68 mmol), mp 182–184 °C.[82] FT-IR (KBr pellet, cm^{-1}): 3000, 2957, 2928, 2868, 1632, 1565, 1380. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28–7.41 (m, 5H), 7.15–7.20 (m, 5H), 5.34 (s, 1H), 4.90 (s, 2H), 2.49 (d, 2H, $J = 16.6$ Hz), 2.30 (d, 2H $J = 16.6$ Hz), 2.19 (m, 4H), 0.99 (s, 6H), 0.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.6, 150.5, 145.8, 137.1, 129.2, 128.7, 127.9, 125.9, 125.4, 115.4, 50.0, 48.8, 40.2, 32.7, 32.1, 28.8, 28.2. GCEM (EI) (*m*/*z*): 439 $[M]^+$. Anal. calcd. for $C_{30}H_{33}NO_2$: C, 81.97; H, 7.57; N, 3.19; O, 7.28. Found: C, 81.87; H, 3.10; N, 7.38; O, 7.45.

3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione (10a)

White solid. Yield 55% (344.1 mg, 0.98 mmol), mp 201–203 °C.[59,64] FT-IR (KBr pellet, cm^{-1}): 2956, 2854, 1662, 1491.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (dd, 2H, $J_1 = 7.0$ Hz, $J_2 = 1.5$ Hz), 7.14 (t, 2H, $J = 5.6$ Hz), 7.03 (t, 1H, $J = 7.3$ Hz), 4.08 (s, 1H), 2.39 (s, 4H), 2.13 (m, 4H), 1.03 (s, 6H), 0.92 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.5, 162.4, 144.2, 128.5, 128.2, 126.5, 115.8, 50.9, 41.0, 32.3, 32.0, 29.4, 27.5. GCEM (EI) (*m*/*z*): 350 $[M]^+$. Anal. calcd. for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48; O, 13.70. Found: C, 78.67; H, 7.39; O, 13.75.

CONCLUSIONS

We describe a simple, practical, and economically viable one-pot method for easy simultaneous access to functionalized decahydroacridine-1,8-diones and 1,8-dioxo-octahydroxanthenes by the condensation of aldehydes, benzylamine, and 5,5-dimethyl-1,3-cyclohexanedione. By means of steady-state spectroscopy, we have studied the photophysics of the acridinediones in methanol solution. The results showed that both the substitution on the nitrogen atom by a benzyl group and the carbon-9 with *p*-aromatic groups results in a highly fluorescence quenching because these substituents favor the intersystem crossing relaxation mechanism. On the other hand, the shape and position of the absorption band of the local excited state remain constant upon the aforementioned chemical modifications. Additionally, despite the poor quantum yields of the model acridinedione systems, we believe these systems could be good candidates, acting as antennas in bichromophoric system, for energy-transfer applications because of the expected long-lived triplet excited states.

SUPPORTING INFORMATION

General experimental information, spectroscopic and characterization data for compounds **8b–e 10b–e**, ^{1}H and ^{13}C NMR, GCMS spectra for selected compounds, and quantum yield calculations can be found via the Supplementary Content section of this article's Web page.

ACKNOWLEDGMENT

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