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Preliminary photostability studies of benzo[*a*]phenoxazinium chlorides

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Abstract - Photostability studies of a series of functionalised benzo[*a*]phenoxazinium chlorides were carried out in ethanol and water at physiological pH, under irradiation at 419 and 350 nm. These compounds showed good to excellent photostability in ethanol and moderate photostability in water in the wavelengths tested.

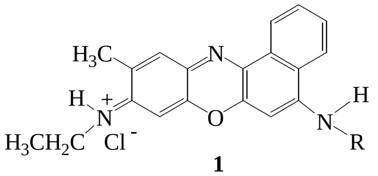
1. Introduction

One of the major limitations in the complete use of long-wavelength dyes for several applications is the short number of fluorophores with high fluorescence efficiency and good stability.[1-2] For their use as probes in biological studies in an aqueous medium, another problem which arises is poor water solubility, a fundamental prerequisite to avoid the disadvantages of dye aggregation and binding with inadequate components. As a result, the interest in the development of water soluble long-wavelength dyes with considerable photostability for bioassays is of extreme importance.

Bearing this in mind, and in connection with our previous work,[3] we decided to study the photofading of several water-soluble benzo[*a*]phenoxazine dyes and we thus report the preliminary results obtained in this investigation here.

2. Results and Discussion

Benzo[*a*]phenoxazinium chlorides **1a-f** were prepared according to the procedure previously reported.[4] Solutions of these dyes in ethanol and water at physiological pH (pH 7.4) with a concentration of 1×10^{-5} M were irradiated in a Rayonet RPR-100 reactor at 419 and 350 nm.



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a R = $CH_2CH_2CH_2CO_2CH_2CH_3$
b R = $CH_2CH_2CH_2CO_2H$
c R = $CH_2CH_2CH_2OH$
d R = $CH_2CH_2CH_2Cl$
e R = $CH_2CH_2CH_2NH_2$
f R = H

After two hours of irradiation at 419 nm, photostability of compounds **1a-f** in ethanol, was higher for compounds **1d**, **1f**, **1a** and **1c** than for compounds **1b** and **1e**. The remaining absorption was equal or superior to 93% for the first group (96% **1d**, 93% **1c**) and ~ 84%, in the latter. After a long period of irradiation (7 hours), the photostabilities were in the order of **1d** > **1f** > **1c** > **1a** > **1b** > **1e** and the remaining absorption varied from ~ 96% (**1d**) to ~ 62% (**1e**).

Although the photostability of these fluorophores decreased in water at physiological pH (pH 7.4), after 2 hours of irradiation their values were located between 79% (**1a**) and 44 % (**1b**), whereas after 7 hours of irradiation, compounds **1a** (~ 48% of remaining absorption) and **1f** (~ 23% of remaining absorption) were the most and least stable, respectively.

Studies of the behaviour of compounds **1a**-**f** under UV irradiation of 350 nm wavelength were also carried out in ethanol and water (pH 7.4). In ethanol, the results revealed that, after 2 or 7 hours of light exposition, compounds **1c**, **1f** and **1d** were the most stable as occurred at 419 nm, with the exception of compound **1c** whose absorption was not affected by the light. Photofading values were lower when compared to 419 nm (for example, **1f** 89% at 350 nm and 96% at 419 nm). Compound **1b** was not stable under UV irradiation (~ 1% of remaining absorption, after 7 hours).

After 7 hours of irradiation, photostability in water at 350 nm was in the order of **1b** > **1e** >**1c** > **1d** > **1f** > **1a** and the remaining absorption varied from 99% (**1b**) to 40% (**1a**). With the exception of compound **1b**, photofading was superior in water when compared to ethanol, at 350 nm (for example, **1d** 82 % in ethanol, 62% in water) as occurred under irradiation at 419 nm.

These results suggest that the photostability of the benzo[*a*]phenoxazines studied are related to the solvent used (ethanol or water at physiological pH), as well as to the wavelength of irradiation. There was also a relationship between the functional group of the side-chain and the photostability of these cationic dyes. Further studies will be carried out for a better comprehension of this correlation.

3. Experimental

*Photofading of compounds **1a**-**f***: Compounds **1a**-**f** were dissolved in ethanol or water (pH 7.4) with concentrations of 1×10^{-5} M. The samples were irradiated at 419 nm or 350 nm, in a Rayonet RPR-100 chamber reactor with 10 lamps. The photostabilities were expressed in terms of remaining absorption (%) calculated from the change of absorption intensities at the absorption maximum before and after irradiation.

Acknowledgments

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