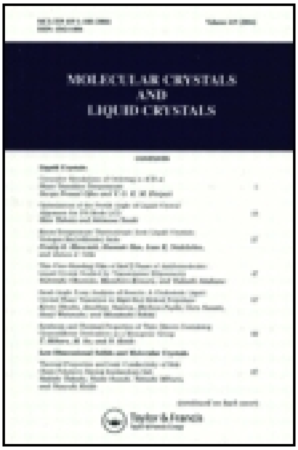

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Absorption, Fluorescence and Chemiluminescence Spectra of 2,4,5-Triphenylimidazole (Lophine) and 2-(p-Dimethyl-Aminophenyl)-4,5-Diphenylimidazole in Micellar Solutions

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ABSORPTION, FLUORESCENCE AND CHEMILUMINESCENCE SPECTRA OF 2,4,5-TRIPHENYLIMIDAZOLE (LOPHINE) AND 2-(p-DIMETHYLAMINOPHENYL)-4,5-DIPHENYLIMIDAZOLE IN MICELLAR SOLUTIONS

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Abstract Lophine and its derivatives, well known for their chemiluminescent properties, are exceptionally hydrophobic. The solubilization of lophine and 2-p-dimethylamino-substituted lophine in micellar solutions enabled us to conduct spectroscopic and chemiluminescence studies in these media. From absorption, fluorescence and chemiluminescence spectra, it became evident that lophine is solubilized in the Stern layer-core region of the cationic CTAB micelle and in the outer polar region of the anionic SDS micelle, while 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole is found in the polar region of CTAB micelle. This work is still in progress.

INTRODUCTION

Micellar solutions of Cetyltrimethylammonium Bromide (CTAB) and Sodium Dodecyl Sulfate (SDS) enhanced the solubilization of the exceptionally hydrophobic 2,4,5-triphenylimidazole (lophine) and 2-(p-dimethylaminophenyl)-4,5-triphenylimidazole. The standard problem of investigating the locus of solubilization of each substance inside the micelle had to be faced in comparing their absorption and fluorescence spectra to those obtained in ethanolic solution. Then according to the well-known Kosower empirical scale[1] it was possible to assign the appropriate micro-environment at the site of addend solubilization. The absorption and fluorescence spectra shown below proved satisfactory for this end.

It is well-known that lophine and its derivative

2-(p-dimethylaminophenyl)-4,5-diphenylimidazole exhibit chemiluminescence[2,3] on reaction with atmospheric oxygen as well as with singlet oxygen. It is also known that micellar media affect the rates and quantum yields of most photochemical reactions, as well as the emission wavelength of the chemiluminescent ones[4]. In the present work, chemiluminescence emission from both compounds was achieved in micellar media (SDS and CTAB) and the corresponding chemiluminescence spectra were obtained, although with some difficulty in the case of SDS, and were compared with those in ethanol.

ABSORPTION SPECTRA[6]

The absorption spectra of lophine in CTAB and SDS compared to those in solvents of increasing polarity (i.e. n-Hexane, n-Hexane-Ethanol mixture, Ethanol and Ethanol-water mixtures) are shown in Figure 1.

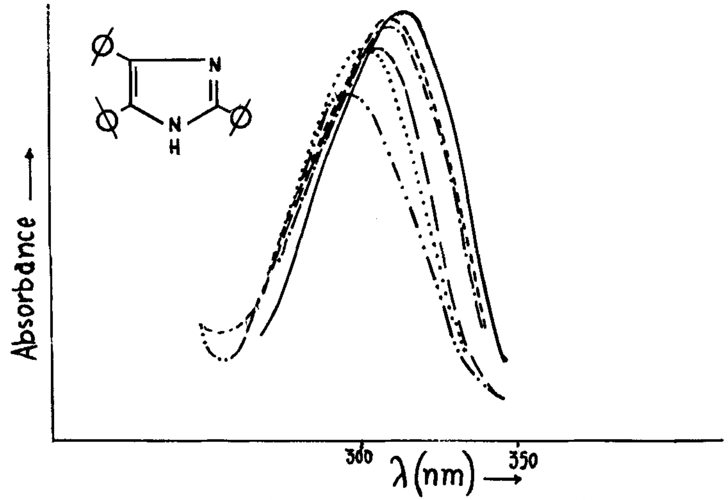

FIGURE 1. Absorption spectra of lophine in —— n-Hexane; -.- Hexane-Ethanol; — — —Ethanol; ... Ethanol-H_2O ---- CTAB; -..- SDS.

The maxima of the spectra above are listed in Table I. As we can clearly see the absorption maximum in CTAB micelles lies at 308 nm resembling that in the Ethanol-Hexane mixture. In SDS micelles the maximum lies at 298 nm. These observations allow us to conclude that lophine is solubilized in the Stern layer-core region of the CTAB micelles, while in the case of SDS it is found in the outer Stern layer near the anionic polar regions.

TABLE I

Solvent	Absorption maximum (nm)	ε (molar ext. coeff.)
n-Hexane	312	26817[a]
n-Hexane-Ethanol (5:1)	306	26644
Ethanol	302 (lit 305[2])	24660 (lit:27200[2])
Ethanol-H_2O (2:3)	300.5	
CTAB	306	25645
SDS	298	18800

[a] Found with extrapolation from several n-Hexane-Ethanol mixtures.

In alkaline solutions unreacted lophine anion[2] exhibited a red-shifted absorption with decreasing micellar concentrations (Figure 2). A similar shift was observed in various mixtures of Ethanol-water with increasing ethanol percentage. This fact suggests that the anion moves to more polar environments when micellar concentration increases, probably because of diminished repulsion caused by OH^- bound to every micellar aggregate. Similar spectra were recorded for 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole (Figure 3). The absorption maxima are summarized in Table II.

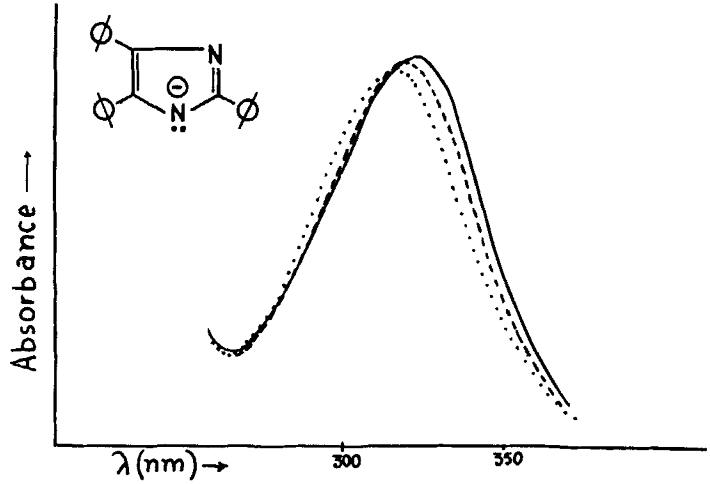

FIGURE 2. Absorption spectra of lophine anion
—— CTAB 1.0×10^{-2}M, --- CTAB 2.0×10^{-2}M,
... CTAB 4.0×10^{-2}M. In every case, total OH^- concentration remains constant (0.0027 M).

From the peak at 322 nm in CTAB micelles we conclude that the lophine derivative is located in the polar region.

FLUORESCENCE SPECTRA[5,6]

The fluorescence spectra of lophine were obtained in n-Hexane, n-Hexane-Ethanol mixture, Ethanol and Ethanol-water mixture, as well as in CTAB and SDS (Figure 4). The results are **discussed** below. The existence of vibronic bands in fluorescence spectra depends upon solvent polarity. In the case of lophine these bands do not exist in n-Hexane, but they are present in Ethanol and its mixtures with water, more intensely in the latter which is more polar. Increased polarity also caused a slight broadening of the spectrum. The spectrum in CTAB shows no vibronic bands or broadening indicating a non-polar environment for

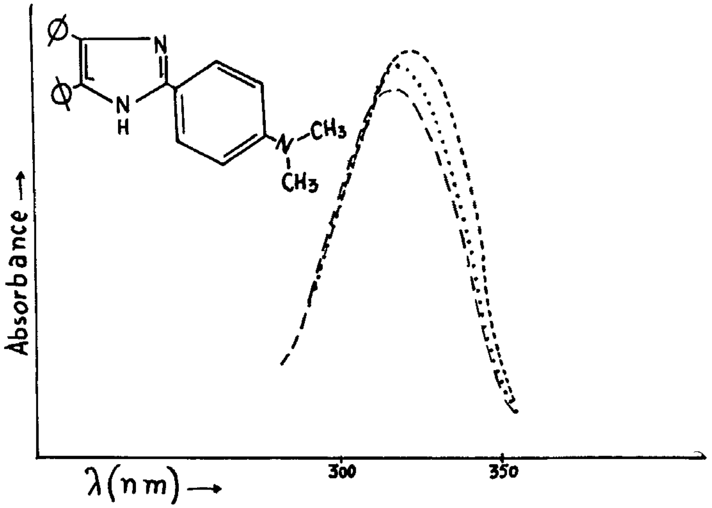

FIGURE 3. Absorption spectra of 2-(p-dimethylamino-phenyl)-4,5-diphenylimidazole in —— Hexane, — — — Ethanol, ... Ethanol-H_2O, --- CTAB.

TABLE II

Solvent	Absorption maximum (nm)	ε (molar ext. coeff.)
n-Hexane	317	
Ethanol	318.5 (lit. 319 nm)[2]	35.140 (lit. 36.800)[2]
Ethanol-H_2O (1:2)	320	
CTAB	322	37.700

lophine in this type of micelle. On the other hand, the broadening of the fluorescence spectrum in SDS, indicates a resemblance to that in ethanol-water, suggesting a more polar environment for the solubilized lophine. These facts are in complete agreement with those derived from absorption spectra. The fluorescence maxima of the lophine anion were also red-shifted on decreasing the CTAB concentrations

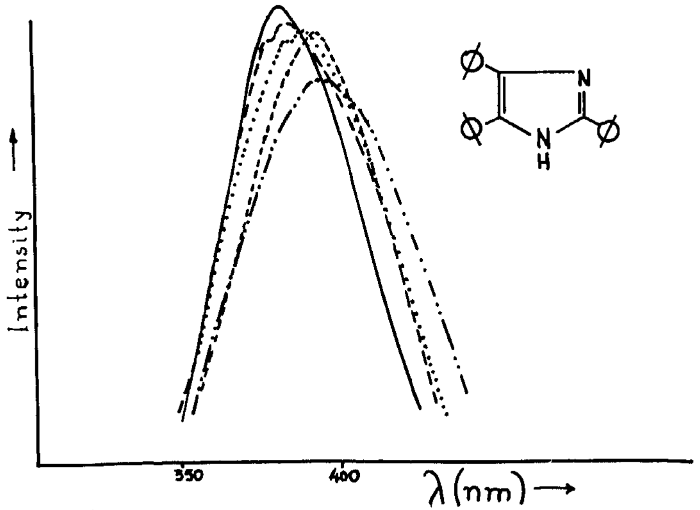

FIGURE 4. Fluorescence spectra of lophine: —— Hexane; —.— Hexane-Ethanol; — — — Ethanol; ... Ethanol-H_2O; --- CTAB; —..— SDS

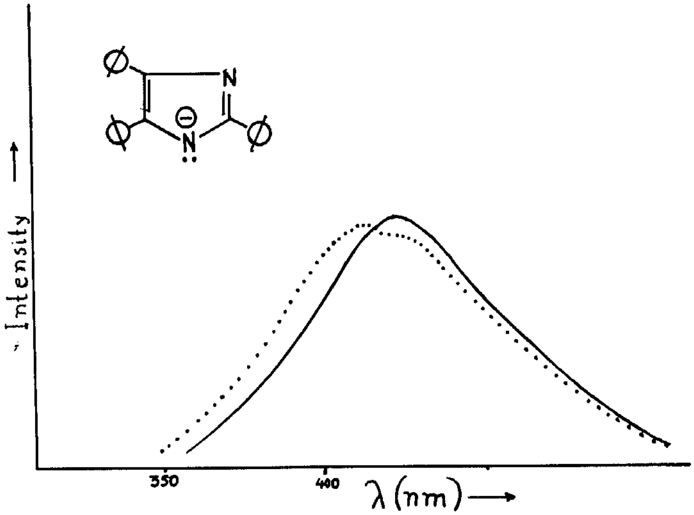

FIGURE 5. Fluorescence spectra of lophine anion in: — CTAB 1.0×10^{-2}M; ... CTAB 4.0 10^{-2}M. In each case the total OH^- concentration was kept constant (0.0027 N).

(Figure 5). The fluorescence spectra of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole exhibit their maxima at a broader range than those of lophine (Figure 6) in solvents of increasing polarity.

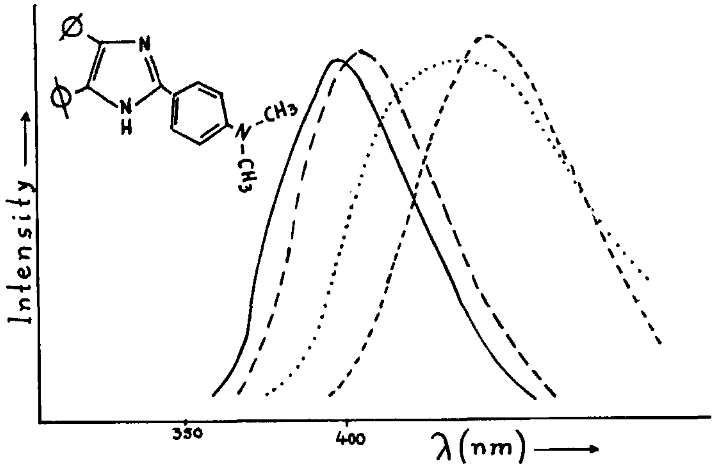

FIGURE 6. Fluorescence spectra of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole in: —— n-Hexane; – – – Ethanol; ... Ethanol-H_2O; --- CTAB.

The basic fact here is that no vibronic bands are observed in the more polar environments(except a slight shoulder in ethanol), while broadening of the spectrum is noted in the case of ethanol-water mixtures. A small broadening also exists in the case of CTAB micelle indicating a polar environment.

CHEMILUMINESCENCE SPECTRA

Air oxidation of alkaline lophine solutions in ethanol result in light emission. The spectrum of this emission (0.0027 M KOH) gives a weak peak at 520 nm (lit. 530[2]). Light emission is more intense with singlet oxygen oxidation (sodium hypochlorite and hydrogen peroxide). Chemiluminescence emission was also exhibited with singlet oxygen in neutral solution with a maximum at 510 nm. This fact, confirmed here for ethanolic solution, has not been previously reported.

Air oxidation of alkaline lophine solution in CTAB (Figure 7b) gives a peak at 510 nm; this is more intense with singlet oxygen. In SDS, there was no light emission with atmospheric oxygen. Singlet oxygen oxidation, however, gave a weak chemiluminescent peak at 521 nm.

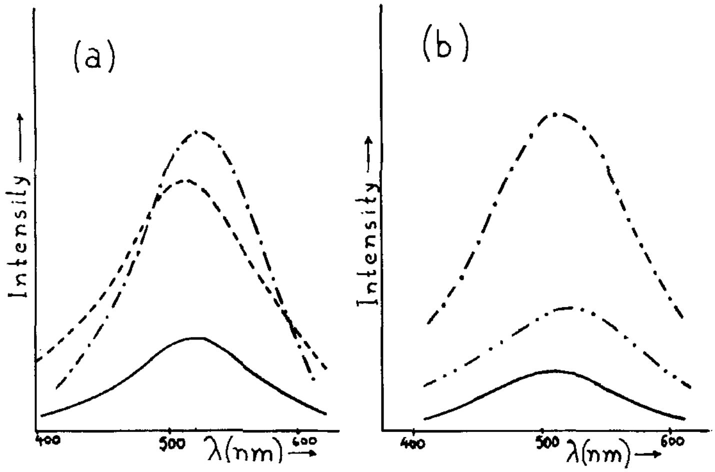

FIGURE 7. Chemiluminescence spectra of lophine.
(a) Ethanolic solutions: —— reaction with atmospheric oxygen; —.— reaction with $^1O_2$; --- reaction with $^1O_2$ in neutral solution; (b) Micellar solutions: —— reaction with atmospheric oxygen in CTAB; —.— reaction with singlet oxygen in CTAB; -..- reaction with singlet oxygen in SDS. In all alkaline solutions OH^- concentration was 0.0027 M.

Reaction of alkaline solutions (0.0027 M) of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, was more efficiently chemiluminescent (Figure 8a). Air oxidation gave a peak at 493-495 nm (lit. 492 nm)[2] and the same peak was obtained with singlet oxygen. In a 0.23 M KOH solution a new shoulder appeared at 430 nm. Air oxidation of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole in CTAB solution (Figure 8b) gave a maximum with two shoulders at 490 and 504 nm. Singlet oxygen oxidation resulted in a stronger emission at 498 nm, which in the course of the reaction was split into two new shoulders at 498 and 508 nm (curve 2).

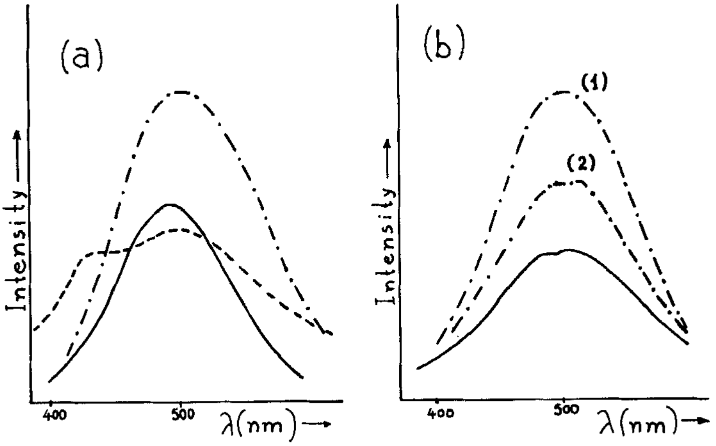

FIGURE 8. Chemiluminescence spectra of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole.
(a) Ethanolic solutions: — reaction with atmospheric oxygen; —.— reaction with $^1O_2$; --- reaction with atmospheric oxygen (OH^- concentration 0.23 M); (b) micellar solutions: — reaction with atmospheric oxygen in CTAB; —.— reaction with $^1O_2$. In all cases OH^- concentration was 0.0027 M except where noted.

CONCLUSION

The spectroscopic studies of lophine and 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole were carried out to determine the locus of solubilization of these two substances in micellar media. The appropriate information having now been gained, it should be more easy to study the behavior of the two chemiluminescent compounds inside anionic or cationic micellar media. As this work is still in progress, there are further observations to be reported, not fully confirmed at the moment, as, for example, the spectra of 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole in SDS micelles.

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