

Photophysical Behavior of β -Carboline-3-Carboxylic Acid *N*-Methylamide

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The solvent and temperature effect of fluorescence and phosphorescence and its polarization characteristics for β -carboline-3-carboxylic acid *N*-methylamide were studied. From the results obtained it is concluded that the first excited singlet state changes from the $\pi\pi^*$ type in a polar solvent (EPA) to the $n\pi^*$ type in a nonpolar solvent (MC) and that the lowest singlet excited states ($\pi\pi^*$ type and $n\pi^*$ type) interact by vibronic coupling. In the nonpolar solvent (MC) the lowest singlet excited states are very close in energy and consequently the vibronic coupling is stronger. It has been found that the 0–0 band of the phosphorescence emission in EPA is polarized out of plane, using the excitations corresponding to absorptions into the first and second excited $\pi\pi^*$ singlet states. This fact and the order of lifetime measured indicate an emitting triplet that is $\pi\pi^*$. The origin of this polarization is very likely $^1(n\pi^*) \xrightarrow{SO} ^3(\pi\pi^*)$ mixing as a result of spin–orbit coupling. However, the vibrational structures and changing polarization outside the 0–0 band indicate that second-order effects involving spin–orbit coupling and vibronic interactions are important and the mixing scheme appears to be $^1(\pi\pi^*) \xrightarrow{VIB} ^1(n\pi^*) \xrightarrow{SO} ^3(\pi\pi^*)$ and $^1(\pi\pi^*) \xrightarrow{SO} ^3(n\pi^*) \xrightarrow{VIB} ^3(\pi\pi^*)$. The “proximity effect” can qualitatively explain the absence of phosphorescence and the stronger vibronic interaction between the $n\pi^*$ and the $\pi\pi^*$ states of β -carboline-3-carboxylic acid *N*-methylamide in a hydrocarbon solvent (MC).

KEY WORDS: β -carboline-3-carboxylic acid *N*-methylamide; Phosphorescence; polarization; vibronic coupling.

INTRODUCTION

The emission properties of nitrogen heterocyclic compounds have been studied extensively [1–3]. Interactions of electronic and nuclear motions leading to the appearance of electronic transitions which are forbidden in the fixed-nuclei approximation represent one of the most important topics in molecular emission spectroscopy. The theory of electronic transitions due to vibrational–electronic (vibronic) interactions was developed

by Herzberg and Teller [4] and it has been extended by Albrecht [5], Liehr [6], and Murrell and Pople [7].

Vibronic interactions between close-lying $n\pi^*$ and $\pi\pi^*$ states have important consequences in luminiscence and radiationless transitions of heteroaromatic compounds [8–10].

For many heterocyclic and aromatic compounds it is known that the lowest excited singlet state changes from the $\pi\pi^*$ type in polar solvents to the $n\pi^*$ type in nonpolar solvents [11–14].

Two important mechanisms through which the emitting $^3(\pi\pi^*)$ state acquires dipole-allowed character [15] are (a) first-order spin–orbit perturbation of the $^3(\pi\pi^*)$ state by an out-of-plane polarized $^1(n\pi^*)$ singlet–singlet transition and (b) second-order mechanisms con-

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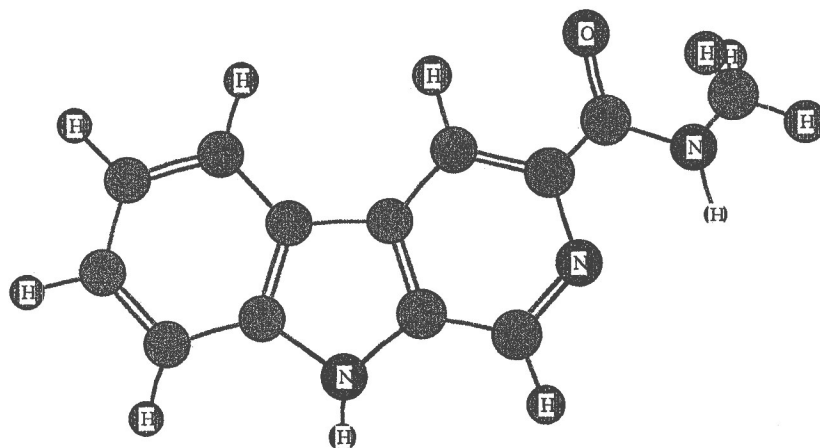


Fig. 1. Molecular structure of β -carboline-3-carboxylic acid *N*-methylamide.

sisting of vibronic coupling of the $^3(\pi\pi^*)$ state with a higher-lying $^3(n\pi^*)$ state which is spin-orbit coupled to the in-plane polarized $^1(\pi\pi^*)$ state and/or spin-orbit coupling of the $^3(\pi\pi^*)$ state with the $^1(n\pi^*)$ state which is vibronically coupled to the in-plane polarized $^1(\pi\pi^*)$ state.

We have investigated the solvent and temperature effects on fluorescence and phosphorescence and its polarizations characteristics of β -carboline-3-carboxylic acid *N*-methylamide, with the aim of characterizing the singlet and the triplet states responsible for emission as well as elucidating qualitatively the importance of the first-order and second-order spin-coupling effects in relation to the mechanisms of the phosphorescence process.

EXPERIMENTAL

β -Carboline-3-carboxylic acid *N*-methylamide (Fig.1) was obtained from Sigma Chemical Co.

The solvents used in these studies were EPA (5:5:2, by volume, of ethyl ether, isopentane, and ethanol) and methylcyclohexane (MC). Ethyl ether, isopentane (Uvasol grade from Merck Co.), absolute ethanol (for spectroscopy from Scharlau), and methylcyclohexane (spectrophotometric grade from Aldrich) were used without further purification.

The concentration of the samples was 10^{-4} M before freezing.

The absorption spectra were recorded using a Cary 3E UV-visible spectrophotometer. Corrected fluorescence and phosphorescence were measured using an Aminco Bowman series 2 Luminescence spectrometer equipped with a low temperature and polarization ac-

cessories. The degrees of polarization of fluorescence and phosphorescence were obtained by the method of photoselection [16] at liquid nitrogen temperature (77 K).

The degree of polarization P is defined as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

where I_{\parallel} and I_{\perp} are the intensities of fluorescence or phosphorescence polarized parallel and perpendicular to the polarization of the exciting light.

The mean lifetime of the phosphorescence was determined from the emission decay curve by means of an Aminco Bowman Series 2 luminescence spectrometer.

RESULTS AND DISCUSSION

Figure 2 presents the absorption spectra of β -carboline-3-carboxylic acid *N*-methylamide in EPA and MC at 25°C. The wavelength of the maxima (λ_{\max}) in absorption spectra are summarized in Table I.

In EPA two bands appear in the wavelength range 250–360 nm. The first band (349, 334, and 320 nm) is similar to that of other β -carbolines and it is assigned to the $\pi\pi^*$ state [17].

However, in the absorption spectrum in nonpolar solvent MC a first band (364 nm) is observed that does not correspond to the blue-shift characteristic of a $\pi\pi^*$ transition with decreasing solvent polarity. The red shift is explained like a $n\pi^*$ transition, which signifies a change in the nature of the lowest singlet excited state in MC with respect to EPA: $n\pi^*$ in the nonpolar solvent and $\pi\pi^*$ in the polar solvent (see Fig. 3).

Figure 4 presents the fluorescence and phosphorescence spectra ($\lambda_{\text{ex}} = 290$ nm), their polarizations, and

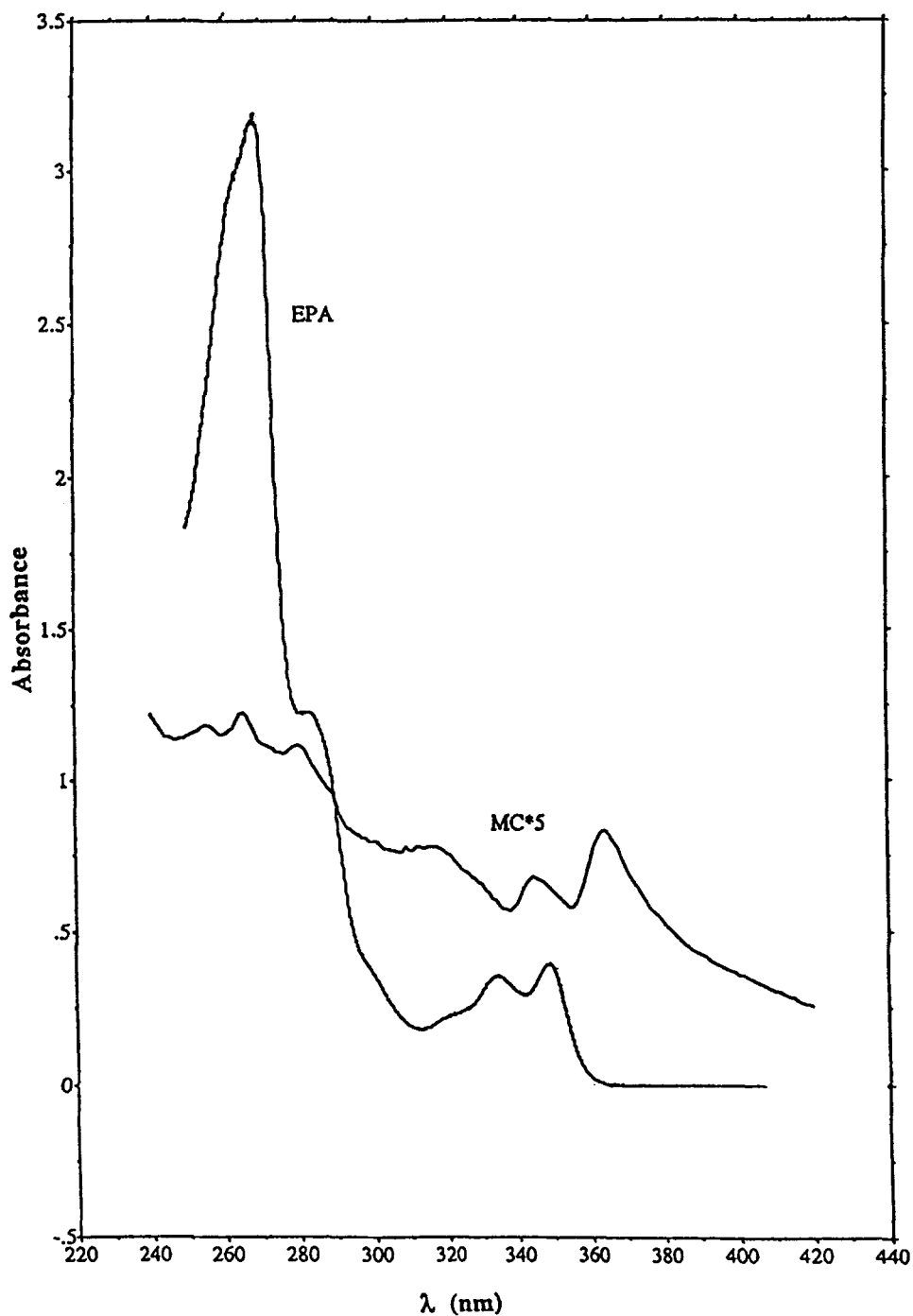


Fig. 2. Absorption spectra of β -carboline-3-carboxylic acid *N*-methylamide in polar (EPA) and nonpolar (methyl cyclohexane; MC) solvents.

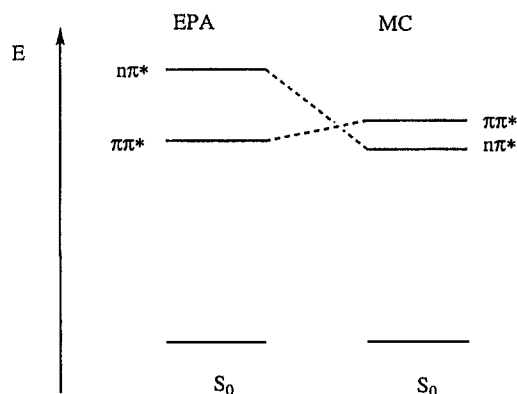
the temperature effect in EPA. It is found that the fluorescence intensity increases with decreasing temperature and the emission wavelength maxima are independent of temperature (see Table II). This is the

normal behavior for organic molecules because at high temperatures the quenching processes are increased.

It has been found that the 0-0 band of the phosphorescence emission is polarized out of plane (negative)

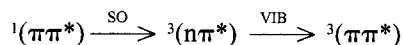
Table I. Wavelength of the Maxima λ (max) in Absorption Spectra at 25°C

Absorbance λ (nm)		
EPA	349, 334, 320 (${}^1n\pi^* S_0 \rightarrow S_1$)	Between 349 and 320 (${}^1n\pi^* S_0 \rightarrow S_2$)
MC	364 (${}^1n\pi^* S_0 \rightarrow S_1$)	341, 326, 317 (${}^1\pi\pi^* S_0 \rightarrow S_2$)

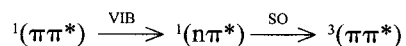
**Fig. 3.** Schematic illustration of the solvent effect on the energy of ${}^1n\pi^*$ and ${}^1\pi\pi^*$ excited states in β -carboline-3-carboxylic acid *N*-methylamide.

using the excitation corresponding to absorptions into the first (330 nm) and second (290 nm) excited $\pi\pi^*$ singlet states. This fact and the order of the lifetime measured (3.3 s) indicate an emitting triplet that is ${}^3\pi\pi^*$ in this solvent. The origin of this polarization is very likely due to the first order spin-orbit coupling ${}^1(n\pi^*) \xrightarrow{SO} {}^3(\pi\pi^*)$.

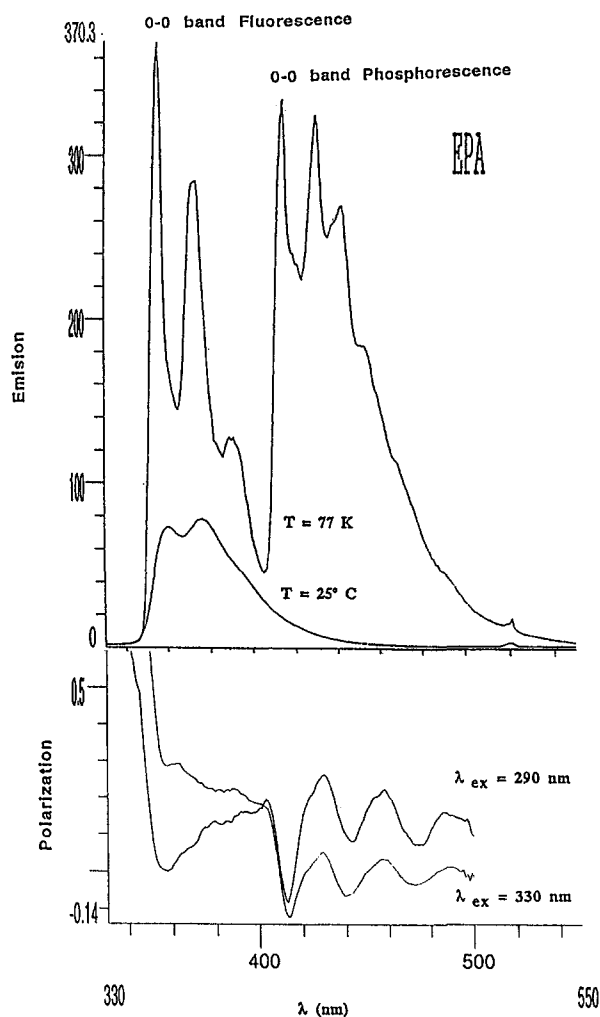
However, the vibrational structure and changing polarization outside the 0-0 band indicate that the second-order effects involving spin-orbit coupling and vibronic interaction are important. The following mechanism accounts for the observed phosphorescence polarization:



The fluorescence polarization is seen to be wavelength dependent. This fact is very likely due to vibronic coupling ${}^1(n\pi^*) \xrightarrow{VIB} {}^1(\pi\pi^*)$ corresponding to the second-order mechanism in the phosphorescence:



The solvent effect causes a small energy gap between the lowest singlet ${}^1\pi\pi^*$ and the ${}^1n\pi^*$ states and a change in the nature of the lowest singlet excited state in MC

**Fig. 4.** Fluorescence, phosphorescence and polarization spectra of β -carboline-3-carboxylic acid *N*-methylamide in EPA.**Table II.** Wavelength of the Maxima λ (max) in Fluorescence and Phosphorescence Spectra

	<i>T</i> (K)	Fluorescence		Phosphorescence		
		λ (nm)		λ (nm)		
EPA	298	357	374	393		
	77	356	372	393	415	430 442
MC	298	346	362	380		
	77	—	365	373	—	—

with respect to EPA: ${}^1n\pi^*$ in the nonpolar solvent and ${}^1\pi\pi^*$ in the polar solvent (see Fig. 3).

This small energy gap between the lowest singlet states $n\pi^*$ and $\pi\pi^*$ in the MC solvent involves a stronger vibronic coupling with respect to EPA. This

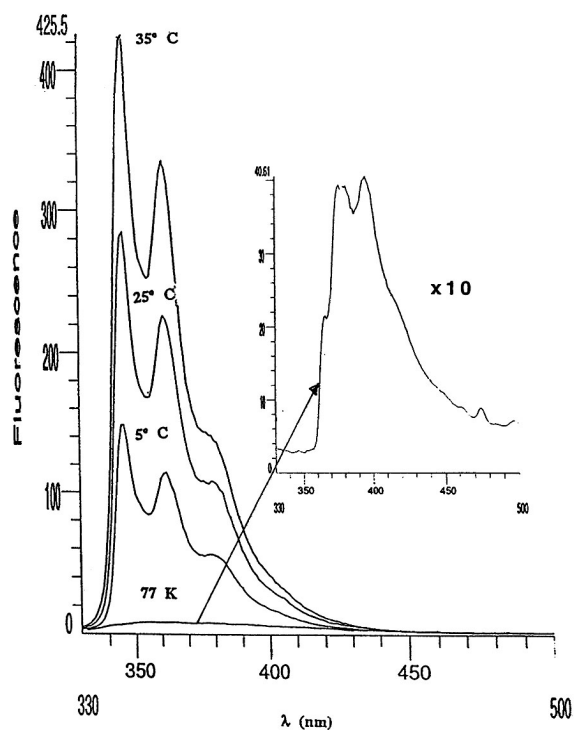


Fig. 5. Fluorescence spectra of β -carboline-3-carboxylic acid *N*-methylamide in methyl cyclohexane at different temperatures.

“proximity effect” implies that S_1 is not a “pure” $n\pi^*$ state. In reality, the wave function of S_1 has a finite amount of $\pi\pi^*$ character mixed into it. We must describe the wave function for S_1 as

$$\Psi(S_1) = \Psi(^1n\pi^*) + \lambda\Psi(^1\pi\pi^*)$$

where λ is the mixing coefficient or the amount of $\pi\pi^*$ character mixed into S_1 .

For the same reason the wave function of S_2 can be described as

$$\Psi(S_2) = \Psi(^1\pi\pi^*) + \lambda'\Psi(^1n\pi^*)$$

The mixing coefficient λ is given by

$$\lambda = \frac{\langle \Psi_a | H | \Psi_b \rangle}{E_a - E_b}$$

The wave functions for the S_1 and S_2 states in EPA solvent can be described in the same way as for the MC solvent but the difference between them is the λ value. In EPA the mixing coefficient λ is lower than in MC because the separation energy is larger and therefore the vibronic coupling is weaker in the polar solvent.

The temperature dependence of fluorescence of β -carboline-3-carboxylic acid *N*-methylamide in MC is shown in Fig. 5. It is found that the fluorescence intensity decreases with decreasing temperature and the emission wavelength maxima are independent of temperature. An enlargement of the 77 K spectrum is shown in Fig. 5. It is found that the more energetic peak (346 nm) disappears from the spectrum.

The temperature dependence of fluorescence spectra can be consistent with dual fluorescence from the $^1n\pi^*$ and $^1\pi\pi^*$ states at high temperatures due to thermal equilibration, while at low temperatures (77 K), the emission is only from the lowest $^1n\pi^*$ state. This agrees with the red shift observed in this solvent at low temperatures (77 K).

The absence of phosphorescence in aprotic solvent can be attributed to a very efficient radiationless transition $T_1 \rightarrow S_0$ resulting from the closeness of the lowest-energy $^3n\pi^*$ and $^3\pi\pi^*$ states (proximity effect).

The phosphorescence of several polycyclic diazines also shows a similar solvent dependence, and it is known, for example, that the emission from cinnoline [18], phthalazine [19], and 9,10-diazaphenanthrene [20] is observable only in protic solvents.

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