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Ground state isomerism and dual emission of the β-carboline anhydrobase (N_2-methyl-9H-pyrido[3,4-b]indole) in aprotic solvents

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Abstract

The spectral and photophysical properties of the betacarboline anhydrobase, N_2-methyl-9H-pyrido[3,4-b]indole, BCA, have been studied in aprotic solvents. The influence of solvent polarity and hydrogen-bonding interactions on the absorption, steady-state and time-resolved fluorescence spectra provides founded proofs on the existence of two ground state BCA isomers whose equilibrium concentrations change with the medium polarity. We propose that the isomers possess quinonoid, Q, and dipolar zwitterionic, Z, structures, respectively. Upon excitation, each isomer gives rise to a double emission. To account for this phenomenon, photophysical diagrams based on the simultaneous emission from locally excited states, LE, and charge transfer excited states, CT, are proposed.

Keywords: Isomerism; Dual fluorescence; β-Carboline; Anhydrobase

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1. Introduction

Betacarboline (1), 9H-pyrido[3,4-b]indol, belongs to the interesting class of aromatic molecules capable of experiencing phototautomerism [1,2]. The reinforcement, upon light absorption, of the respective acid–base properties of the pyrrolic and pyridinic nitrogen atoms in this molecule provides the driving force for the phototautomerisation process [2].

More than twenty years ago, Sakurovs and Ghiggino attributed the long wavelength emission of betacarboline in aqueous basic solutions to a phototautomer of zwitterionic structure [3]. Since then, the phototautomerism of betacarboline has been thoroughly studied [4–13]. Interestingly, along the years, the controversy regarding the formation mechanism of the betacarboline phototautomer has not ceased, but its zwitterionic nature has never been questioned. This topic has been so universally accepted that it constitutes almost a "dogma" in the betacarboline photochemistry. However, in our recent study on the photophysics of N_1-methyldeltacarboline, (N_1-methyl-5H-pyrido[3,2-b]indole), we hypothesised that betacarboline phototautomers could not have, as previously assumed, a zwitterionic but a quinonoid structure [14]. Recently, Reyman and col. have also postulated quinonoid structures for other betacarboline derivatives [15].

Since this hypothesis could drastically modify the current mechanistic interpretations on the phototautomerism of betacarbolines, we were prompted to study the photophysics of N_2-methylbetacarboline (2) or betacarboline anhydrobase, BCA. The term anhydrobase or anhydronium base, used to name the neutral forms of *N*-pyrido methyl carbolines, indicates that it is derived from the quaternary hydroxides by the loss of a water molecule. As BCA can be considered the prototype of the betacarboline phototautomer, most of the authors prefer to formulate this compound with a zwitterionic structure (2Z) instead of a quinonoid one (2Q).

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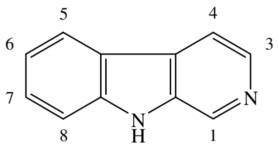

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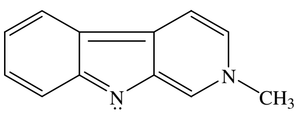

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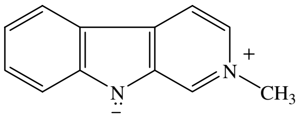

(2Z)

In this paper we report the results of a photophysical study of the betacarboline anhydrobase in aprotic solvents aimed to gain further insight on the nature of the betacarboline phototautomer. The results of the present study will show that BCA possesses an interesting and peculiar photophysics, much more complex than that of the parent BC. Thus, in non-hydrogen bonding solvents, two BCA ground-state isomers co-exist in equilibrium. Upon light excitation, each BCA isomer gives rise to a dual emission.

2. Experimental

Betacarboline anhydrobase was synthesised and purified as described elsewhere [16]. Spectral grade solvents stored on molecular sieves were used. Other reagents were of analytical grade and were used without further purification. Absorption and fluorescence spectra of the reagents and solvents did not show indication of impurities.

The UV/Vis absorption spectra were measured in a Perkin–Elmer Lambda-5 spectrophotometer equipped with thermostatted cell holders. Steady state fluorescence measurements were made in a Hitachi F2500 spectrofluorometer. Time resolved fluorescence studies were performed by using the time-correlated single-photon counting (SPC) technique in a FL-900CD Edinburgh Analytical Instrument. The excitation source, a nanosecond, nF900, flashlamp filled with 1.5 bar N_2, operated at 40 kHz with 6 kV applied across 0.25 mm electrode gap was used. Fluorescence decays from the samples were acquired to $(5–10) \times 10^3$ counts in the peak and were fitted by deconvolution analysis to a sum of exponential functions with amplitudes, α_i, and lifetimes, τ_i.

$$I(t) = \sum \alpha_i \exp(-t/\tau_i). \tag{1}$$

The goodness of the individual fits was judged by the magnitude of the reduced χ_r^2 and the shape of the autocorrelation function of the weighted residuals.

3. Results

3.1. Absorption spectra

BCA solvatochromism is readily observable. Thus, as the solvent polarity increases, the pale-yellow colour of the BCA solutions in low polar solvents abruptly changes and becomes orange-yellow. The room temperature UV–Vis absorption spectra of BCA in different aprotic solvents are shown in Fig. 1. Because BCA is sparingly soluble, its solutions, in most of the solvents, were prepared almost at saturation limit. Therefore, since the concentrations of these BCA solutions remain unknown, the spectra in Fig. 1 serve only for qualitative comparison purpose.

As Fig. 1 shows, in the region at shorter wavelengths, the absorption spectra of BCA in different solvents show two bands: a first medium intensity band centred at 290 nm, A_3, and a second structured weak band with peaks at 330–350 nm, A_2. As the solvent polarity increases, a third very weak and wide absorption band at 450 nm, A_1, becomes increasingly evident. The position, shape and extremely weak intensity of this band suggest a forbidden charge transfer transition.

A perusal of these spectra reveals that solvent polarity induces profound and very intriguing changes on the absorption spectra. Thus, the increase of solvent polarity changes noticeably both the shape and position of the absorption bands. To analyse more thoroughly the puzzling spectral changes induced by solvent polarity, we have recorded the BCA absorption spectra in *n*-hexane–toluene mixtures containing different toluene proportions and fixed BCA concentration. These spectra, reported in Fig. 2, help to clarify the influence of solvent polarity on the absorption spectra of BCA. As can be seen in Fig. 2, upon increasing the toluene proportion, i.e. the medium polarity, the profiles of the absorption bands change completely and, as the inset of this figure shows, a blue shift is observed.

An additional and very convincing proof of the existence of two different BCA ground state isomers is provided by the changes that hydrogen bonding interactions produce on the cyclohexane and toluene BCA absorption spectra. Thus, as Figs. 3 and 4 show, the addition of increasing amounts of the strong proton donor hexafluoroisopropanol, HFIP, shifts the absorption spectrum of BCA

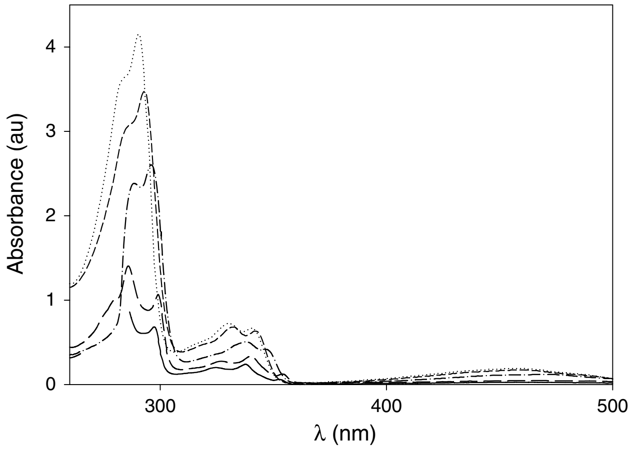

Fig. 1. Room temperature UV–Vis absorption spectra of BCA in different solvents; (—) *n*-hexane, (- - -) cyclohexane, (-·-) toluene, (–) chloroform and (···) dichloromethane.