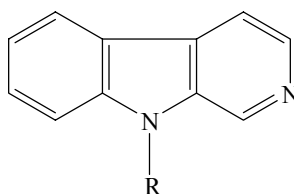


Betacarboline Tautomerism Induced by Temperature. Dual Emission of Betacarboline Self-Associated Hydrogen Bond Aggregates.

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A systematic study of the influence of the gradual decrease of temperature, from room temperature up to 118 K, on the UV-vis absorption and fluorescence emission spectra of betacarboline, 9H-pyrido[3,4-b]indole, BC, has been carried out in 2-methylbutane, 2MB. For the sake of comparison, the effect of the decreasing temperature on the behavior of other model systems, such as BC plus N₉-methyl-9H-pyrido[3,4-b]indole, MBC, and BC plus pyridine, PY, has also been analyzed.



R = H **BC**

R = CH₃ **MBC**

These studies have allowed concluding that the observed spectral changes are due to the formation of hydrogen bonded self-associated BC aggregates. Initially, up to ~ 208K, red shifts, around 20 nm, are observed in the absorption and emission spectra. The emission shift is accompanied by a strong fluorescence quenching of the structured emission at 342 nm and 358 nm. These changes have been ascribed to the formation of a hydrogen bond BC dimer with a proton transfer structure, PTC, the fluorescence quenching being due to an electron-driven proton-transfer in the PTC which leads to an ultra fast internal conversion.

At lower temperatures, the quenching is non-operative and the emission intensity increases up to 178 K. Further, from 178 K to 118 K, and only for BC in 2MB, dual emission is observed. The emission at low wavelength decreases and, concomitantly, the typical BC large Stokes shifted emission, around 500 nm, appears. Isoemissive points are observed in the spectra. These last changes are ascribed to the formation of ground state cyclic tetrameric BC hydrogen bond aggregates. In these complexes, the tautomeric form that emits dual fluorescence, from its locally excited state, LE, and its intramolecular charge transfer state, ICT, is generated by a quadruple proton transfer in the hydrogen bonded tetramer.