

Multiple Fluorescence of 7-Hydroxylepidone

Otto S. Wolfbeis* and E. Lippert

I. N. Stranski-Institut für Physikalische und Theoretische Chemie der Technischen Universität, Berlin

Z. Naturforsch. **33a**, 238–239 (1978);
received November 23, 1977

The fluorescence spectra of the title compound have been measured in ethanol and in aqueous solutions of different pH. In ethanol the neutral molecule's fluorescence (at 360 nm) is observed, whereas in aqueous solutions emission occurs from the anion (at 428 nm) and from a "tautomeric" species (at 460 nm), but not from the neutral molecule. An aqueous solution at pH 3, which contains about 30% of ethanol gives a broad fluorescence band ranging from the near uv to the orange region of the spectrum. Contrarily, 7-methoxylepidone has no fluorescence maximum in the visible part of the spectrum.

Tunable laser emission from 391 to 567 nm due to a variety of fluorescence bands in acidified ethanolic solutions of 4-methylumbelliferone (4-MU) has been reported [1]. This phenomenon has subsequently been studied intensely [2], and fluorescence of 4-MU has been shown to occur from anionic, neutral, "photoautomeric" and protonated species [3].

We wish to report the fluorescence behaviour of a similar compound, namely 7-hydroxy-1,2-dihydro-2-quinolone (7-hydroxylepidone, 7-HL).

Lepidones form a well known and commercially available class of heterocyclic laser dyes [4, 5]. 7-HL fluoresces stronger and its emission maxima are shifted towards the uv-region, as compared to 4-MU [6]. The pH-dependent absorption and emission spectra of 7-HL are depicted in Figure 1. The longwave absorption band at 351 nm in alkaline solution can be assigned to the anion A, whose fluorescence has a maximum at 428 nm [7]. When pumped with frequency tripled Nd³⁺ laser

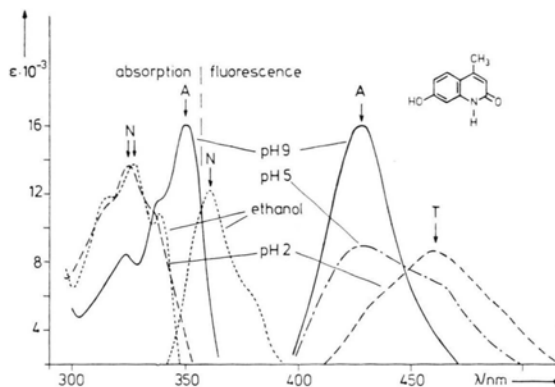


Fig. 1. Absorption and corrected fluorescence spectra of 7-HL in ethanol and in aqueous solution of different pH. Conc.: 1.2×10^{-5} Mol/lit. The height of the most intense fluorescence band was set equal to the height of the corresponding absorption band (pH 9).

light ($\lambda = 353$ nm) [8], alkaline solutions of 7-HL lase efficiently with a maximum at 438 nm [9].

With increasing acidity of the solution (pH 8) the neutral molecule 7-HL is formed in the ground state (absorption $\lambda_{\max} = 335$ and 320 nm). In the pH 8 to 5 region, however, still the fluorescence band of the anion is observed, even when the neutral molecule is excited. The fluorescent anion may be formed through photolysis of the 7-OH bond since it is well known that i.e. phenols are stronger acids in the excited state than in the ground state [10, 11, 12].

No such pH- and solvent effects are found with 7-methoxylepidone (7-ML): In ethanolic or aqueous solution it does not exhibit an emission maximum in the visible part of the spectrum (Table 1). Its fluorescence maximum at 357 nm in the pH 13 to 2 region is shifted towards 380 nm in more acidic solutions, presumably as a result of excited state O-protonation at the carbonyl oxygen, thus forming a photocation PC. Similar O-protonations have been found in a variety of related laser dyes [13].

In aqueous solutions of pH 4 to 0 the absorption spectrum of 7-HL remains unchanged, whereas a new emission peak at 460 nm arises. Due to its red

* Visiting scientist from the Institut of Organische Chemie der Universität, A-8010 Graz.

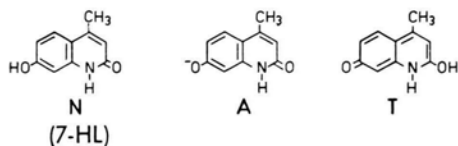
Reprint requests to Prof. Dr. E. Lippert, I. N. Stranski-Institut für Physikalische und Theoretische Chemie der Technischen Universität, Straße des 17. Juni 112, D-1000 Berlin 12.

	pH 5	pH 2	1 N HCl	2 N H ₂ SO ₄	ethanol
$\lambda_{\max}(\text{abs})$	321, 333	319, 333	322 ^a , 330	324 ^a , 333	323, 337
$\lambda_{\max}(\text{flu})$	357	357, 371	380, 405 ^b	379, 390 ^b , 405 ^b	360, 375 ^a
$\lambda_{\max}(\text{exc})$	321	319	330	333	323

Table 1. pH-effects on absorption and fluorescence spectra of 7-methoxylepidone (7-ML).

^a shoulder; ^b inflexion.

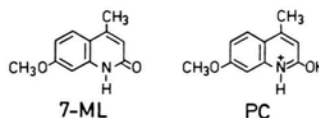
shift it cannot be assigned to the neutral molecule (fluorescence $\lambda_{\max} = 360$ nm in ethanol), but rather to an excited state complex, which may be formulated as a tautomer T, having a certain zwitterionic character and presumably being able to form a rather strong exciplex [1–3, 14].



This excited state tautomerism appears to be the first example in the quinoline series [15]. The

fluorescence behaviour of 7-HL parallels that of 4-MU, but shows some advantages: Its photo-tautomerism takes place at lower solution acidities, and its fluorescence bands cover more of the near uv-region.

We are now investigating, whether lactam-lactim-tautomerisms are being involved in these multiple fluorescence processes.



- [1] C. V. Shank, A. Dienes, A. M. Trozzolo, and J. A. Myer, *Appl. Phys. Lett.* **16**, 405 (1970).
- [2] a) E. Lippert, In: *The Hydrogen Bond*, Vol. I, P. Schuster, G. Zundel, and C. Sandorfy, eds., North Holland Publish. Comp., Amsterdam 1976.
b) A. Bergman and J. Jortner, *J. Luminescence* **6**, 390 (1973).
- [3] For a recent discussion, see: G. S. Beddard, S. Carlin, and R. S. Davidson, *J. Chem. Soc. Perkin II*, **1977**, 262.
- [4] K. H. Drexhage, *Structure and Properties of Laser Dyes*, In: *Dye Lasers* (F. P. Schäfer, edit.), Springer-Verlag, Berlin 1973.
- [5] E. J. Schimitschek, J. A. Trias, P. R. Hammond, R. A. Henry, and L. Atkins, *Optics Comm.* **16**, 313 (1976).
- [6] C. W. Wheelock, *J. Amer. Chem. Soc.* **81**, 1348 (1959).
- [7] 7-Aminolepidone (Eastman Carbostyryl 124) is iso-electronic to the 7-HL anion and fluoresces at 419 nm (in water).
- [8] The experimental setup is described in: O. S. Wolfbeis, W. Rapp, and E. Lippert, *Monatsh. Chem.*, submitted.
- [9] Acidic solutions of 7-HL do not absorb sufficiently at 353 nm and are laser inactive under these conditions for this reason.
- [10] A. Weller, *Progr. React. Kinet.* **1**, 188 (1961).
- [11] E. Van der Donckt, *Progr. React. Kinet.* **5**, 273 (1970).
- [12] E. Lippert, In: *Org. Molecular Photophysics*, Vol. 2 (J. B. Birks, ed.), Wiley, 1975, p. 1.
- [13] O. S. Wolfbeis, *Monatsh. Chem.*, submitted.
- [14] P. E. Zinsli, *J. Photochem.* **3**, 55 (1974, 1975).
- [15] a) S. G. Schulman, A. C. Cappomacchia, and B. Tussey, *Photochem. and Photobiol.* **14**, 733 (1971).
b) S. G. Schulman, *Fluorescence and Phosphorescence Spectroscopy; Physicochemical Principles and Practice*, Pergamon Press, Oxford 1977, p. 95.