Luminescence of 5-Phenyltetrazole and its Derivatives Part III. Quantum Yields and Mean Lifetimes of Fluorescence

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Quantum yields and mean lifetimes of fluorescence have been measured of 5-phenyltetrazole and its three methyl derivatives, para-, meta- and ortho-methyl-5-phenyltetrazole. The rate constants, k_F, of the radiative transition $S_1 \rightarrow S_0$ have been deduced from these measurements. The mean lifetimes, τ_F, the quantum yields of fluorescence and the rate constants have been found to be clearly dependent on the position of the methyl substituent in the ring and could be arranged as follows:

$$\tau_F^p > \tau_F^m > \tau_F^0 \quad \text{and} \quad k_F^0 > k_F^m > k_F^p .$$

1. Introduction

5-phenyltetrazole (PhTH) and its derivatives (Fig. 1) have recently been extensively studied by physical-chemical methods. Among others, the effect of the position of substituent in the ring on the infrared [1] and ultraviolet [2] spectral characteristics and on acid-base properties [3, 4] has been studied. With para- and meta-derivatives, a good correlation has usually been observed band positions and dissociation constants on one hand and substituent constants δ_P and δ_m on the other.

Much attention has been payed to the tautomerism ($1\,H \rightleftharpoons 2\,H$) of the phenyltetrazoles. With unsubstituted 5 PhTH, there was a heavy preponderance of the 1 H tautomer (86:14, from ^{13}C nmr spectroscopy in DMSO-water 4:1 *v/v* [5]). Equally strong preponderance of that tautomer was observed in polar media with a variety of substituted 5 PhTH [6, 7]. In non-polar media, 1 H-tautomers of methyl 5 PhTH were slightly less abundant (60:40) as demonstrated by dielectric experiments [8].

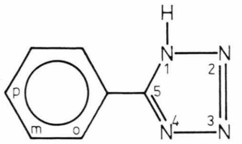

Fig. 1. Structural formula of 5 PhTH.

Inspection of the fluorescence spectra of the phenyltetrazoles in methanol [9] did not reveal both forms in solution, which might have appeared there owing to their appreciably different polarity.

A preceding study [10] on the spectra, quantum yields and mean lifetimes of phosphorescence of the phenyltetrazoles in poly(vinyl alcohol) films showed also that one of the tautomers preponderated.

The purpose of this work was to measure the quantum yields and mean lifetimes of fluorescence of 5 PhTH, ortho-, meta- and para 5 PhTH in methanol.

2. Experimental

5 PhTH and its methyl derivatives were synthesized and purified as describes elsewhere [4]. Spectroscopic grade methanol (Fluka AG) was transparent in the ultraviolet region.

Absorption spectra were recorded on a Beckman Model 25 spectrophotometer. Fluorescence spectra were taken with a previously reported [11] spectrofluorimeter. Mean lifetimes of fluorescence were measured by means of a pulse fluorimeter, deconvolution being accomplished by a method of Demas and Crosby [12]. Excitations were generated by means of a dye laser working on rhodamine 6G utilizing the second harmonic (SHG) generated in KDP crystal ($l = 2$ cm).

The quantum yields of fluorescence of methanolic solutions of the phenyltetrazoles were determined

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relative to an aqueous solution of L-tryptophan, which has commonly been employed as a standard for the quantum yield of fluorescence excited in the ultraviolet region ($\varphi_0 = 0.13$ [13]). The quantum yield was calculated from the equation

$$\varphi = \varphi_0 \frac{\int_0^\infty J(\tilde{\nu})\,\mathrm{d}\tilde{\nu}}{\int_0^\infty J_0(\tilde{\nu})\,\mathrm{d}\tilde{\nu}} \, \frac{1 - 10^{-A_0}}{1 - 10^{-A}} \, \frac{n^2}{n_0^2}, \qquad (1)$$

where the ratio of the integrals corresponds to the quotient of the areas of the fluorescence spectra of the solution investigated and that of the standard, A and A_0 are the absorbances (at the exciting wavelength, $\lambda_{\mathrm{exc}} = 282$ nm) of the solution and standard, respectively, and n and n_0 are the refractive indices of methanol and water, respectively.

3. Results and Discussion

3.1. *Quantum yields of fluorescence*

The absorption and fluorescence spectra of the phenyltetrazoles are shown in Figure 2. In each absorption spectrum there is a strong short-wave band. The $S_0 \rightarrow S_1$ bands, retaining a certain symmetry relative to the fluorescence spectra, appear in the background of the strong short-wave band and are relatively weak. The fluorescence spectra in the ultraviolet region exhibit vanishing oscillational patterns, which are strongest for 5 PhTH. Band locations in the fluorescence spectra depend on the position of the methyl substituent in the ring and, similarly to the bands in the absorption spectra [9], follow the sequence $\lambda^{\mathrm{p}}_{\max} < \lambda^{\mathrm{m}}_{\max} < \lambda^{0}_{\max}$.

On the basis of the normalized absorption and fluorescence spectra, the positions of energy levels S_1 (the electronic transition o–o) have been determined for the phenyltetrazoles in methanol. Similarly as in the case of the lower triplet levels T_1 [10], also for the singlet levels the energy increases in the sequence $E^{0}_{S_1} < E^{\mathrm{m}}_{S_1} < E^{\mathrm{p}}_{S_1}$ (Table 1). It is worth noting that the compounds are characterized by relatively large spans of energy levels, $\Delta E_{S-T} = E_{S_1} - E_{T_1}$, of about 9000 cm^{-1}.

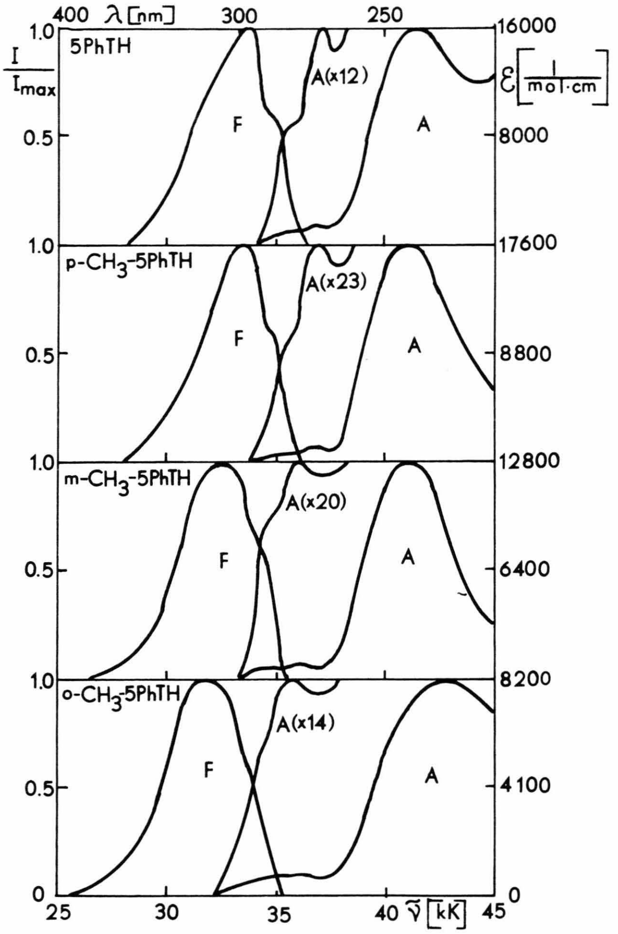

Fig. 2. Absorption and fluorescence spectra of 5 PhTH, p-CH_3-5 PhTH, m-CH_3-5 PhTH and o-CH_3-5 PhTH in methanol at 25 °C.

The results of the measurements of the quantum yields of fluorescence are shown in Table 1. The highest quantum yield is observed for m-CH_3-5 PhTH (0.243) and the lowest for 5 PhTH (0.147).

Table 1. Fluorescence parameters of 5-phenyltetrazole and its derivatives.

Compound	φ_F	τ_F [ns]	$k_F \times 10^9$ [s^{-1}]
5 PhTH	0.147	8.33	0.0176
p-CH_3-5 PhTH	0.185	9.35	0.0198
m-CH_3-5 PhTH	0.243	8.03	0.0303
o-CH_3-5 PhTH	0.223	5.92	0.0377

3.2. *Mean lifetimes of fluorescence*

An illustrative example of the exciting pulse and the fluorescence decay for p-CH_3- 5 PhTH is shown in Figure 3.

The results of the measurements of the mean lifetimes of fluorescence are summarized in Table 1.

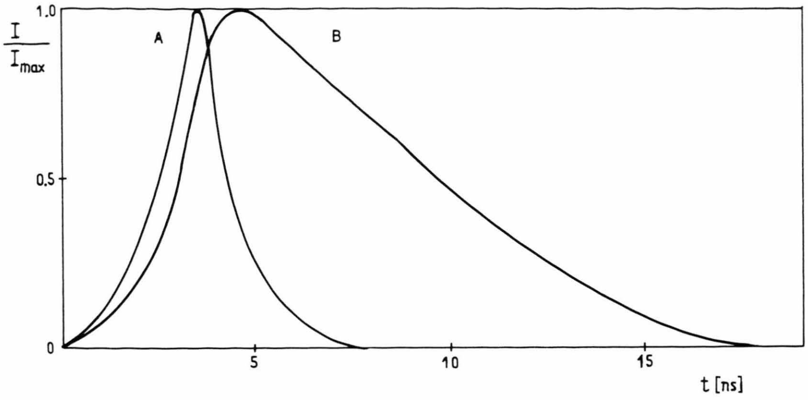

Fig. 3. Time dependence of the flash (A) and fluorescence decay (B) of p-CH_3-5PhTH.

They reach from 5.9 ns (o-CH_3-5PhTH) to 9.3 ns (p-CH_3-5PhTH). The correlation coefficients obtained during the determination of the mean decay times, on the assumption of a monoexponential pattern of the fluorescence decay, are extremely high, amounting to 0.9993, 0.9992, 0.9987 and 0.9986 for 5PhTH, p-CH_3-5PhTH, m-CH_3-5PhTH and o-CH_3-5PhTH, respectively. On the basis of the measured mean lifetimes of fluorescence and quantum yields of fluorescence, the rate constants for radiative transitions

$$k_{\mathrm{F}} = \frac{1}{\tau_{\mathrm{F}}} \cdot \varphi_{\mathrm{F}} \qquad (2)$$

were determined.

The k_{F} values for 5PhTH and its methyl derivatives are shown in the last column of Table 1. The constants follow the sequence

$$k_{\mathrm{F}}^{\underline{p}} < k_{\mathrm{F}}^{\underline{m}} < k_{\mathrm{F}}^{\underline{o}}.$$

Such an increase was not found with the quantum yields of fluorescence.

The monoexponential decay of fluorescence observed with the phenyltetrazoles suggests that only one tautomer exists in the excited state. The recent theoretical study [14] on both the free and solvated molecules has virtually revealed that in the lowest excited singlet state the tautomeric equilibrium is displaced well in favour of the 2H-tautomer.

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