Luminescence of 5-phenyltetrazole and its Derivatives. Part I. Absorption and Fluorescence Spectra

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Absorption and fluorence spectra of a series of 5-phenyltetrazole derivatives have been measured. Compounds carrying electron-accepting CN or COOH groups in the phenyl ring exhibit dual fluorescence. Investigations carried out in acid and basic media and a comparison of the fluorescence of p-cyano-5-phenyltetrazole and 1-methyl-5-(4′-cyano) phenyltetrazole show the anions of respective 5-phenyl-tetrazole derivatives to be responsible for the long-wave fluorescence ($\lambda_{\max} \approx 400$ nm). The long-wave fluorescence of some 5-phenyltetrazole derivatives is associated with a considerable charge delocalization between the tetrazole and phenyl rings, this being accompanied by mutual twisting of the rings in the excited state. This finding has been confirmed by the absence of the long-wave fluorescence in rigid media.

1. Introduction

The physico-chemical properties of 5-phenyltetrazole (5 PhTh) and its derivatives have since long been the subject of numerous investigations. In particular, acid-base equilibria [1, 2], infrared absorption spectra [3], ultraviolet spectra [4, 5], chemical shifts [6] and mass spectra [7] have been studied to afford in general satisfactory correlations with Hammett's substituent constants. Luminescence of these compounds has not yet been studied, however. One can hope that studies on the luminescence of 5 PhTH derivatives will give information on the excited electronic states S_1 and T_1 of these compounds and the interaction of the phenyl group with the tetrazole ring. In the present paper, the absorption and fluorescence spectra of some 5 PhTH derivatives are dealt with.

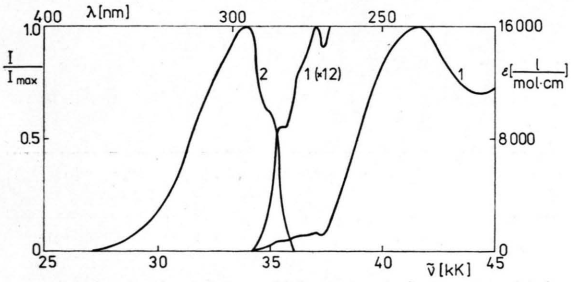
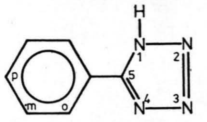


Fig. 1. Absorption (1) and fluorescence (2) spectra of 5-phenyl-tetrazole in methanol. $C = 5 \cdot 10^{-4}$ M, $\tilde{\nu}_{\text{exc}} = 37000$ cm^{-1}.



2. Experimental

The synthesis of ortho-, meta- and para-5 PhTH derivatives has been described elsewhere [2]. 1-methyl-5-(4′-cyano)phenyltetrazole was synthesized as follows: 5 mMol (0.855 g) of 5-(4′-cyano)phenyltetrazole was dissolved in a methanol-water (10 : 1) mixture. An ethereal diazomethane solution was added to the stirred solution at ambient temperature until a permanent yellow colour appeared. The solvent was removed under reduced pressure and the residue was washed with a 1% NaOH solution. The precipitate was crystallized three times from methanol to give 0.3 g (32%) of the chromatographically homogeneous 1-methyl-5-(4′-cyano)phenyltetrazole (the 2,5-disubstituted isomer was absent), m.p. 211 °C. $C_9H_7N_5$ (M 185.2) requires 58.3% C, 3.8% H, 37.8% N. Found: 57.9% C, 4.0% H, 38.1% N.

The absorption spectra were measured on a Beckman Model 25 spectrophotometer and the fluorescence spectra on instruments described in

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[8]. The concentrations ranged from $5 \cdot 10^{-5}$ to $3 \cdot 10^{-3}$ M. Spectrograde solvents (methanol and ethanol) were used.

3. Results and Discussion

The absorption and fluorescence spectra of 5 PhTH in methanol are shown in Figure 1. As can be seen from the figure, the absorption $S_0 \rightarrow S_1$ ($\lambda_{max} = 270$ nm) leading to the fluorescent state appears in the background of the much more intense short-wave $S_0 \rightarrow S_2$ band ($\lambda_{max} = 241$ nm). A similar situation was observed with 5 PhTH derivatives, whereby the intensity of the $S_0 \rightarrow S_1$ band depends on the substituent position, being the highest for the ortho-isomers. Also the position of the $S_0 \rightarrow S_1$ band depends on the substituent position:

$$\lambda_{max}^{ortho} > \lambda_{max}^{meta} > \lambda_{max}^{para} .$$

These findings have been confirmed by quantum-chemical calculations [5]. Table 1 gives the measured and calculated parameters of the absorption ($S_0 \rightarrow S_1$) and fluorescence bands of 5 PhTH derivatives. Such a clear-cut dependence of the luminescence spectrum on the substituent position suggests that the inductive effect influences predominantly the physico-chemical properties of the compounds examined, this fact having also been noted earlier [2, 5].

The fluorescence intensity distribution of 5 PhTH derivatives, which is more or less symmetric to the long-wave $S_0 \rightarrow S_1$ absorption band, is also affected by the position of the substituent, similarly as for the absorption bands

$$(\lambda_{max}^{ortho} > \lambda_{max}^{meta} > \lambda_{max}^{para}, \text{ Table 1}).$$

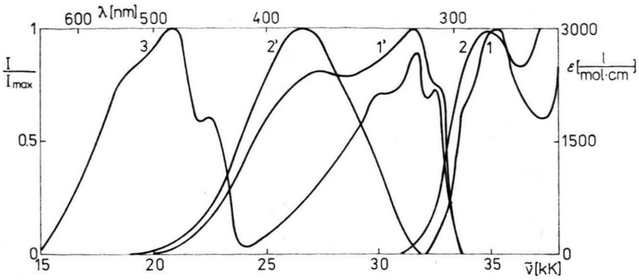

Fig. 2. Absorption and emission spectra of o-cyano-5-phenyl-tetrazole in ethanol: 1 and 1′ — absorption and fluorescence, respectively, at $C = 5 \cdot 10^{-4}$ M; 2 and 2′ — absorption and fluorescence, respectively, at $C = 5 \cdot 10^{-5}$ M; 3 — emission spectrum (fluorescence and phosphorescence) at $C = 5 \cdot 10^{-5}$ M, $T = 77$ K and $\tilde{\nu}_{exc} = 35000$ cm^{-1}.

Fluorescence spectra of 5 PhTH derivatives with strongly electron-accepting CN and COOH groups differ substantially from those of 5 PhTH itself or its methyl derivatives. The whole fluorescence spectrum consists of two bands: the shortwave (equivalent to the 5 PhTH fluorescence) and the longwave band devoid of vibrational structure with $\lambda_{max} = 400$ nm. The dual fluorescence of the CN- and COOH-substituted 5 PhTH resembles the fluorescence of N,N-dimethyl-p-cyanoaniline, this having been studied by many authors [9, 10]. It differs, however, from that latter in a strong concentrational response (Figure 2). The relative band intensities in the fluorescence spectra of the CN- and COOH-substituted 5 PhTH are independent of temperature in the range 20 ÷ 70 °C, thus permitting to rule out, in principle, the formation of intermolecular complexes in solution.

Table 1. Measured and calculated parameters of absorption $S_0 \rightarrow S_1$ and fluorescence bands of 5-phenyltetrazole derivatives.

Nr.	Substituent	Absorption		Fluorescence		Quantum-chemical calculations (from [5])	
		λ_{max} (nm)	ε (l/mol · cm)	λ (nm)	λ′ (nm)	ΔE ($S_0 \rightarrow S_1$) (nm)	Oscillator Strength
I a	H	270	1200	296	—	266.4	0.005
I b	o-CH_3	279	1100	312	—	—	—
I c	m-CH_3	278	850	308	—	—	—
I d	p-CH_3	274	700	300	—	—	—
I e	o-COOH	288	700	320	410	276.5	0.015
I f	m-COOH	286	400	318	406	276.4	0.012
I g	p-COOH	285	300	316	388	275.0	0.009
I h	o-CN	290	3000	318	384	—	—
I i	m-CN	285	1400	317	372	—	—
I j	p-CN	284	1100	315	360	—	—

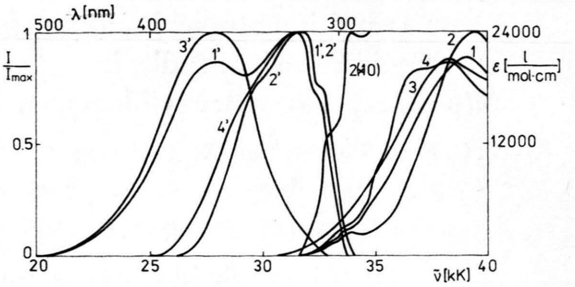

Fig. 3. Absorption and fluorescence spectra: 1 and 1′ of p-cyano-5-phenyltetrazole in methanol $C = 5 \cdot 10^{-5}$ M; 2 and 2′ of p-cyano-5-phenyltetrazole in methanol and H_2SO_4 (0.01%); 3 and 3′ of p-cyano-5-phenyltetrazole in methanol and NaOH; 4 and 4′ of 1-methyl-5-(4′-cyano)-phenyltetrazole in methanol ($C = 5 \cdot 10^{-5}$ M).

Tetrazole and ist derivatives, including 5-PhTH, are acids with pK_a values ranging from 4 to 5 [2]. At low solute concentrations the molecules dissociate and thus both the molecules and the anions are present in the solution. By raising the concentration the dissociation of the acids is suppressed, and the equilibrium is shifted toward the molecules. The concentration-dependent changes observed in the absorption spectra reveal that the dissociation occurs already in the ground state. Since the pK_a value decreases in the excited state, the equilibrium is shifted toward the dissociated species. The presence of an electron-accepting group displaces the charge from the tetrazole ring to the phenyl ring, this being accompanied by a twisting of the rings, similar to that of the $N(CH_3)_2$ group in the molecule N,N-dimethyl-p-cyanoaniline. Such intramolecular rearrangement of both the structure and the charge results in the fluorescence occurring from another, markedly lowered energy level. The lack of the long-wave fluorescence in frozen solutions (Fig. 2) indicates that the twisted (as compared to the ground state) conformation of the anion of a respective 5 PhTH derivative is responsible for such fluorescence. The fact that the anion of the solute molecule is responsible for the long-wave band of the dual fluorescence of 5 PhTH derivatives is further confirmed by the fluorescence of 1-methyl-5-(4′-cyano)-phenyltetrazole in which the acidic hydrogen atom is replaced by the methyl group. The fluorescence of this compound exhibits no dual character, it is not influenced by the solute concentration and resembles the short-wave fluorescence band of p-cyano-5-phenyltetrazole (Figure 3). Change in the pH of the medium also affects substantially the nature of the fluorescence of those 5 PhTH derivatives which contain electron-accepting groups. Figure 3 shows an example of the fluorescence of p-cyano-5-phenyltetrazole in alkaline and acid media. It is seen that the fluorescence spectrum of this compound is a superposition of spectra of the molecule and its anion.

All the above-mentioned findings lead to the following conclusions:

(i) 5 PhTH derivatives containing electron-accepting groups (e. g. CN or COOH) in the phenyl ring exhibit dual fluorescence;

(ii) the dual fluorescence of some 5 PhTH derivatives is due to the anions of the solute molecules. In the excited state, a twisting of the phenyl ring with respect to the tetrazole ring occurs which is accompanied by charge delocalization from the tetrazole ring to the phenyl ring;

(iii) the concentrational response of the dual fluorescence of 5 PhTH derivatives can be explained in terms of the acidic nature of tetrazoles.

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