# Luminescence of 5-Phenyltetrazole and its Derivatives. Part II. Phosphorescence

I. Gryczyński and A. Kawski
Luminescence Research Group, Institute of Experimental Physics,
University of Gdańsk, Gdańsk, Poland

Z. Grzonka and A. Rażyńska
Institute of Chemistry, University of Gdańsk, Gdańsk, Poland

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The phosphorescence spectra, mean lifetimes of phosphorescence and ratios of phosphorescence/fluorescence quantum yields have been measured for 5-phenyltetrazole and its three methyl derivatives in a polyvinyl alcohol film over the temperature range of (77–250) K. Temperature responses of the non-radiative intersystem crossing constant, $K_{ST}$, and the non-radiative triplet state deactivation constant, $k_m$, have been investigated on the basis of these measurements. The energy of activation for the non-radiative transitions has been determined. With the methyl 5-phenyltetrazoles, the thermal deactivation of the triplet state, contrary to the intersystem crossing, has been found to be influenced by the position of the methyl substituent in the phenyl ring.

## 1. Introduction

In our previous paper [1], absorption and fluorescence spectra of 5-phenyltetrazole (5PhTH) and some of its derivatives have been discussed. Similarly to infrared absorption [2], chemical shifts [3] and acid-base equilibria [4, 5], the position and shape of the fluorescence band have been found to be influenced by the nature and position of the substituent on the phenyl ring. In addition, strong electron-accepting substituents, such as CN or COOH, have been found to generate dual fluorescence in liquid solutions, promoted by twisting of the phenyl and tetrazole rings.

In this paper, the phosphorescence spectra of 5PhTH and its three derivatives, viz. ortho-, meta- and para-$CH_3$-5PhTH, have been analysed. Temperature responses of the non-radiative transitions occurring *via* the triplet state have also been explored.

## 2. Experimental

5PhTH and its methyl derivatives were synthesized and purified as described elsewhere [5]. Polyvinyl alcohol (PVA) films were preparated by a technique resembling that employed by Tonizaki et al. [6]. The emission spectra were recorded on the instrument described in [7]. The ratios of the phosphorescence/fluorescence quantum yields as well as the decays of phosphorescence were measured by a method described in [8] using two synchronic choppers and two coupled diaphragms. A specially constructed cryostat adapted for ultraviolet spectroscopy enabled the measurement of emission spectra over the range (77–250) K. The measuring cell was thermostated to ± 1 K.

## 3. Results and Discussion

### 3.1. *Phosphorescence spectra*

The phosphorescence spectra of 5PhTH and its methyl derivatives in PVA films at 77 K are shown in Figure 1. With the methyl derivatives, there are small bathochromic shifts in their spectra as compared to that of 5PhTH, accompanied by vanishing oscillational structure, the effects being most pronounced for the ortho-isomer. The energies for the triplet states of 5PhTH, o-, m- and p-$CH_3$5PhTH, determined for the positions of the utmost short-wave oscillational bands of phosphorescence are 25600, 25000, 25200 and 25300 $cm^{-1}$, respectively. Similarly as in the case of the positions of the singlet states [1], those of the triplet states increase in the series

$$E_T^{\mathrm{ortho}} < E_T^{\mathrm{meta}} < E_T^{\mathrm{para}} .$$

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Reprint requests to Prof. Dr. Alfons Kawski, Instytut Fizyki Doświadczalnej, Uniwersytet Gdański, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

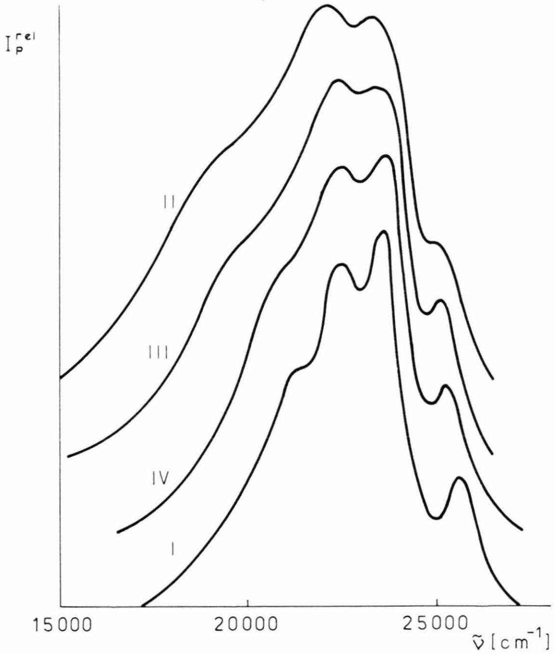
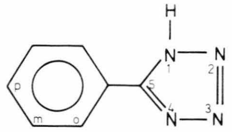


Fig. 1. Phosphorescence spectra in PVA films at 77 K: I: 5PhTH; II: o-$CH_3$-5PhTH; III: m-$CH_3$-5PhTH; IV: p-$CH_3$-5PhTH.

Also the intensites of particular oscillational peaks within the phosphorescence bands vary with varying position of the methyl group in the ring.



### *3.2. Decay of phosphorescence and the ratio of the phosphorescence/fluorescence quantum yields*

Both 5PhTH and its derivatives display monoexponential phosphorescence decay patterns characterised by relatively long lifetimes $\tau_P$. Below 100 K, the mean lifetimes of the phosphorescence do not vary appreciably, being virtually constant (see Figure 2). The fixed mean lifetimes of phosphorescence, $\tau_P^0$, of the methyl-5PhTH's depend distinctly upon the position of the methyl substituent and increase in the series:

$$\tau_P^0(\text{ortho}) < \tau_P^0(\text{meta}) < \tau_P^0(\text{para}) .$$

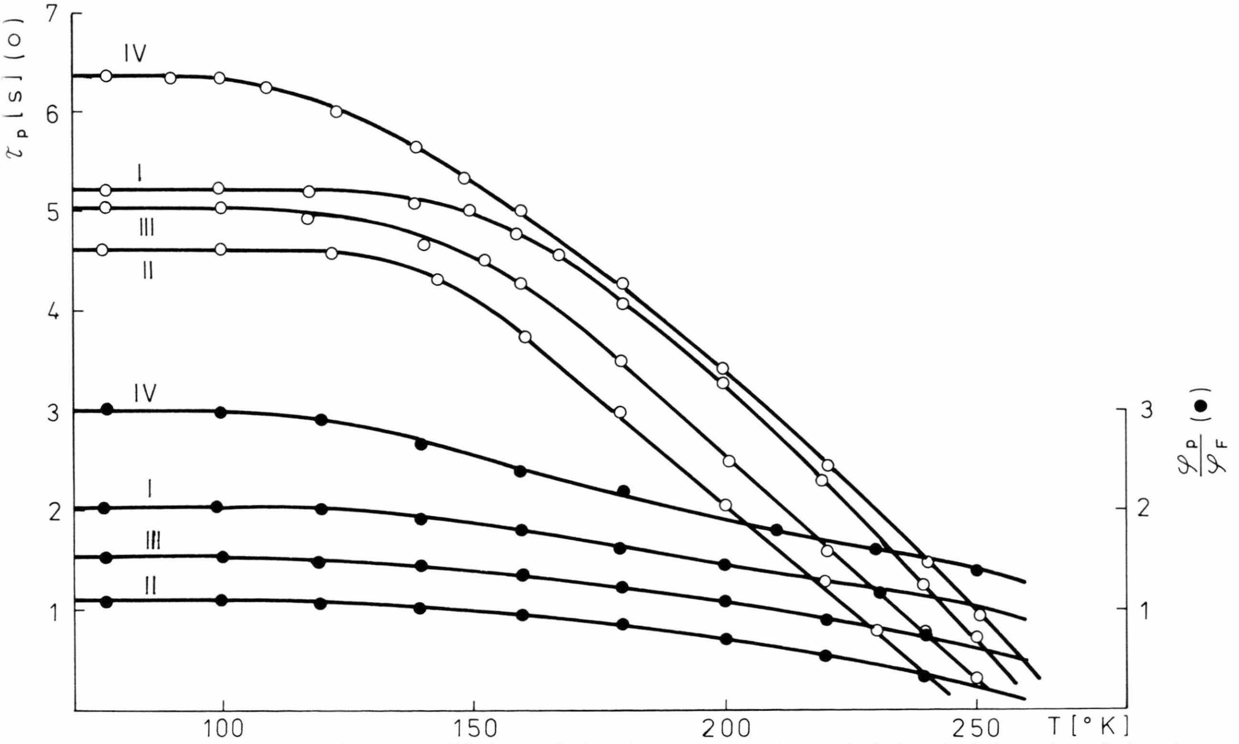


Fig. 2. Temperature response of the mean lifetimes of phosphorescence $\tau_P$ (open circles) and of the ratios of phosphorescence/fluorescence quantum yields $\varphi_P/\varphi_F$ (solid circles) in PVA films: I: 5PhTH; II: o-$CH_3$-5PhTH; III: m-$CH_3$-5PhTH; IV: p-$CH_3$-5PhTH.

Figure 2 shows temperature response of the mean lifetimes of phosphorescence for the compounds and the ratios of the phosphorescence/fluorescence quantum yields, $\varphi_P/\varphi_F$. The shape of function $\varphi_P/\varphi_F(T)$ for the methyl derivatives resembles that of the relation between $\tau_P$ and temperature, being likewise influenced by the position of the methyl substituent.

### 3.3. *Temperature response of the non-radiative intersystem crossing and thermal deactivation of the lowest triplet states*

According to denotations in the Jabłoński diagram (Fig. 3), the following relationship holds:

$$\frac{\varphi_P}{\varphi_F}\frac{1}{\tau_P}=\frac{k_P}{k_F}K_{ST}. \tag{1}$$

Further considerations will be based on two assumptions:

(i) the rate constants of the radiative transitions, $k_P$ and $k_F$, are only slightly temperature-dependent as compared to those of the non-radiative transitions, $k_n$, $K_{ST}$ and $k_m$;

(ii) the temperature response of the rate constants for non-radiative transitions is given by

$$k_x=k_x^0+A_x\exp\left(-\frac{E_x^A}{kT}\right), \tag{2}$$

where $x$ stands for n, m or ST.

It is felt that with 5PhTH and its derivatives, the frequently employed relationship

$$\varphi_T=1-\varphi_F,$$

where $\varphi_T=\dfrac{K_{ST}}{k_F+k_n+K_{ST}}$ is the quantum yield of filling the triplet state, cannot be employed owing to the fact that even at low temperatures the quantum yields of fluorescence and phosphorescence for 5PhTH and its derivatives attain values of several to ten or so percent. In consequence, the contribution of the non-radiative transition, $k_n$, in the deactivation of the singlet state $S_1$, cannot be ignored. Owing to assumption (i), the temperature response of (1) should reflect the nature of the temperature response of $K_{ST}$ responsible for the filling of the triplet state. This relationship is presented in Figure 4. It is seen that beyond 180 K the filling of

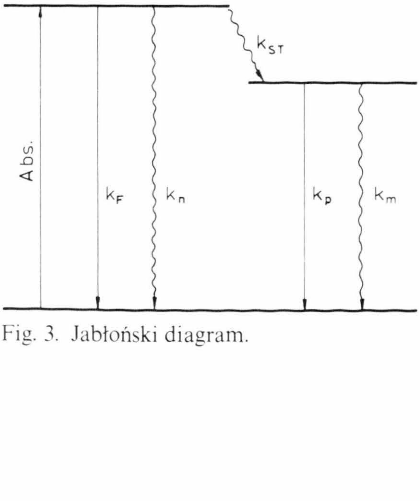


Fig. 3. Jabłoński diagram.

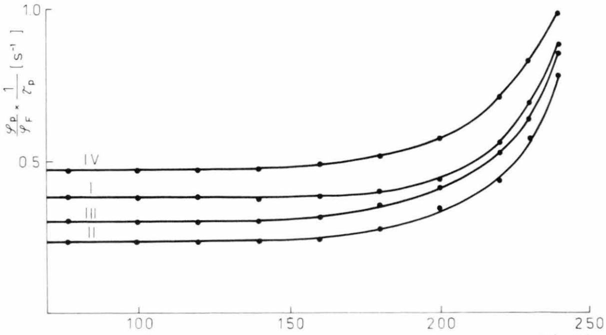


Fig. 4. Temperature response of (1).

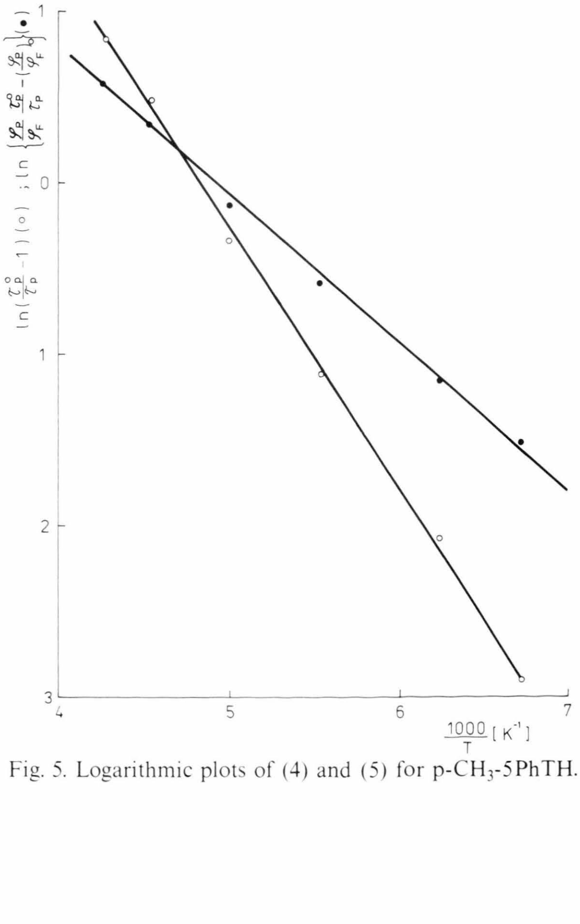


Fig. 5. Logarithmic plots of (4) and (5) for p-$CH_3$-5PhTH.

Table 1. Phosphorescence parameters of the lowest triplet states.

| No. | Compound | $\varepsilon_T$ [cm$^{-1}$] | $\tau_P^0$ [s] | $\left(\frac{\varphi_P}{\varphi_F}\right)_0$ | $E^A_{ST}$ [cm$^{-1}$] | $A_m$ [s$^{-1}$] | $E^A_m$ [cm$^{-1}$] |
|---|---|---|---|---|---|---|---|
| I | 5PhTH | 25600 | 5.2 | 2.01 | 1760 | 0.97 | 728 |
| II | o-$CH_3$-5PhTH | 25000 | 4.6 | 1.10 | 1022 | 1.36 | 832 |
| III | m-$CH_3$-5PhTH | 25200 | 5.0 | 1.56 | 1055 | 1.20 | 805 |
| IV | p-$CH_3$-5PhTH | 25300 | 6.4 | 3.02 | 1043 | 0.66 | 570 |

triplet becomes strongly dependent on temperature. Below that temperature, $K_{ST}$ is virtually constant. In accord with (2) we have

$$\frac{\varphi_P}{\varphi_F}\cdot\frac{1}{\tau_P}-\left(\frac{\varphi_P}{\varphi_F}\cdot\frac{1}{\tau_P}\right)_0=\frac{k_P}{k_F}A_{ST}\exp\left(-\frac{E^A_{ST}}{kT}\right). \qquad (4)$$

This equation enables the determination of the energy of activation for the intersystem crossing, $E^A_{ST}$.

Deactivation of the triplet state $T_1$ in 5PhTH and its derivatives might occur either in the radiative fashion (rate constant $k_P$) or in the non-radiative fashion (rate constant $k_m$), as neither retarded fluorescence nor photoreaction has been noted. Thermal deactivation of the triplet state can be described by the following relationship:

$$k_m-k_m^0=\frac{1}{\tau_P}-\frac{1}{\tau_P^0}=A_m\exp\left(-\frac{E^A_m}{kT}\right). \qquad (5)$$

An illustrative example (in a logarithmic scale) the relationships (4) and (5) for p-$CH_3$-5PhTH is provided by Figure 5. Numerical values of $E^A_{ST}$, $E^A_m$ and $A_m$ are listed in Table 1. A comparison of the energies of activation for the non-radiative processes leads to the conclusion that with the methyl derivatives of 5PhTH the energy of activation for intersystem crossing is independent of the position of the methyl group. In the case of the energy of activation for non-radiative deactivation of triplet states, $E^A_m$, the decidedly lowest value has been recorded for para-$CH_3$-5PhTH. This may by attributed to an enhanced (compared to the remaining derivatives) freedom of performing limited motions by the phenyl ring in the polymer matrix.

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