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1,3,5-Triarylpyrazoles as Phosphorescing Impurities in 1,3,5-Triaryl-2-prazolines

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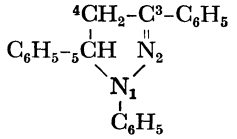
Synopsis. The origin of the phosphorescence observed for 1,3,5-triphenyl-2-pyrazoline and its substituted derivatives was investigated. Unlike the previously accepted conclusion, our conclusion is that the phosphorescence originates from the corresponding pyrazoles formed from the pyrazolines by the action of light.

Numerous studies have been made of the electronic absorption and emission spectra of 1,3,5-triphenyl-2-pyrazoline (TPP) and its derivatives. These compounds exhibit three absorption bands, *i.e.*, two intense bands in the wavelength regions at around 230—260 nm and 350—420 nm, and a less intense one appearing frequently in the form of an inflection at the 300—330 nm region.[1,2] On excitation in the longest wavelength absorption band, an intense fluorescence with a quantum yield of close to unity appears in nonpolar solvents, no phosphorescence being observed.[3,4] It has been reported, however, that a weak, long-lived green phosphorescence is observed with TPP and some of its derivatives on excitation in the shorter wavelength absorption band by the light of 313 nm, and the phosphorescence has been ascribed as due to the 5-aryl group that constitutes an independent set of singlet and triplet levels from the conjugated π-electron system Ar–N–N=C–Ar in the pyrazoline ring which is responsible for the characteristic spectral features of TPP and its derivatives.[2] This conclusion has been cited also in a recent publication by an independent researcher.[5]



TPP

As a part of our studies on the physical and chemical properties of TPP and its derivatives,[6] we have reinvestigated the origin of the phosphorescence emission observed for TPP and its derivatives. Three compounds, *i.e.*, TPP, 1,5-diphenyl-3-(*p*-methoxyphenyl)-2-pyrazoline (MTPP), and 1,5-diphenyl-3-(*p*-dimethylaminophenyl)-2-pyrazoline (DMATPP), were examined in the present study. The use of the amino-substituted TPP has made the assignment of the phosphorescence emission easy and successful. As shown in Fig. 1, TPP and MTPP purified by repeated recrystallizations exhibit a very weak phosphorescence in the wavelength region of 400 to 500 nm on excitation by the light of 300 to 320 nm, whereas only intense fluorescence appears in the wavelength region of 400 to 500 nm on excitation in the long-wavelength absorption band of these compounds. The phosphorescence was so weak that it was detected under conditions of the maximum sensitivity of the instrument with a wide slit width. On the other hand, DMATPP purified by repeated recrystallizations shows a much more intense phosphorescence in the wavelength region of 440 to 550 nm on excitation by the light of 300 to 340 nm (Fig. 2d), whereas on excitation in the long-wavelength absorption band, only intense fluorescence of DMATPP appears in the wavelength region of 400 to 500 nm (Fig. 2a). It was also found that, in the total emission spectrum (Fig. 2c), the appearance of the phosphorescence is accompanied by the appearance of a new fluorescence at around 350 to over 400 nm. The excitation spectra for the phosphorescence and the new fluorescence were found to be the same with each other, but different from that for the DMATPP fluorescence at the 400 to 500 nm region which corresponds to the absorption spectrum of DMATPP.

These results indicate that the phosphorescence and the new fluorescence (in the case of DMATPP) observed on excitation by the light of 300 to 340 nm do not result from the singlet and triplet levels of the 5-phenyl group in the pyrazoline ring as has been stated in the literature. Emitting impurities conceivable to be incorporated into the pyrazoline compounds during the synthetic process were examined, but their emission spectra did not agree with those shown in Figs. 1 and 2. It was found that the intensity of the phosphorescence and the new fluorescence observed for DMATPP increases when a sample solution was left to stand as it is for long days or after spectral measurements were repeated, and that these emissions are extremely weak with respect to a virgin sample prepared in the dark throughout the processes of purification, drying, and preparation of a solution (Fig. 2b). These

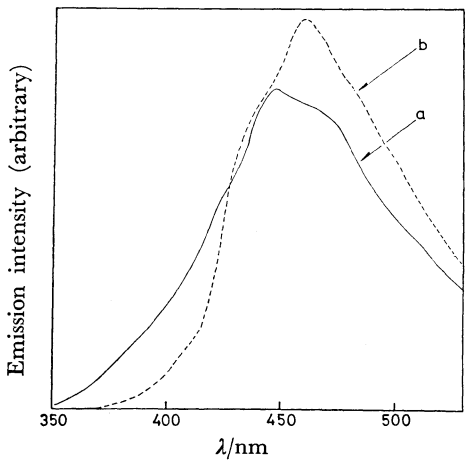


Fig. 1. Corrected phosphorescence spectra observed for TPP (a) and MTPP (b) on excitation by the light of 320 nm in MTHF at 77 K.

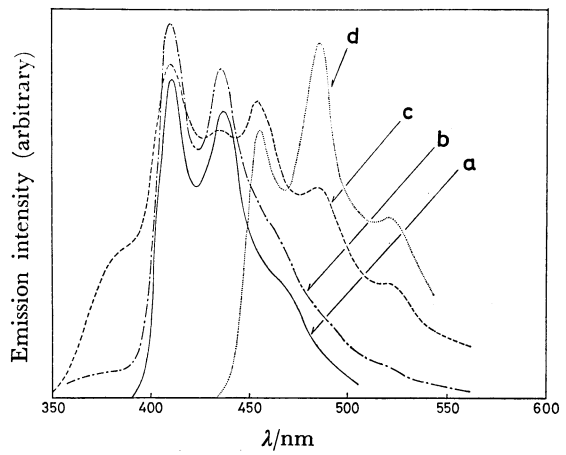


Fig. 2. Corrected emission spectra observed for DMATPP in MTHF at 77 K.
a, b, and c: Total emission spectra; d: delayed emission spectrum.
a: Fluorescence spectrum inherent to DMATPP observed on excitation by the light of 370 nm. b: Emission spectrum observed for a virgin smaple prepared in the dark on excitation by the light of 320 nm. c: Emission spectrum observed on excitation by the light of 320 nm. d: Phosphorescence spectrum observed on excitation by the light of 320 nm.

results indicate that the impurity which is responsible for these emissions is derived from the pyrazoline compound probably by the action of light such as sunlight, light from fluorescent room lamps, and the light employed for spectral measurements. Confirmation for this conjecture was obtained from the result that the intensity of the new emissions for DMA-TPP increases gradually on illuminating a sample solution by the light of 366 nm using a 500 W high pressure mercury lamp, while the intensity of the DMATPP fluorescence decreases with an isoemissive point at 396 nm.[7]

The phosphorescence and the new fluorescence observed for DMATPP on excitation in the ostensible shorter wavelength absorption band were identified as the ones originating from the excitation of 1,5-diphenyl-3-(*p*-dimethylaminophenyl)pyrazole (DMATPPzole) based on the identity of the shape and position of the emission bands, the excitation spectra, and the lifetimes of the emissions with those of the authentic DMATPPzole (τ_f=7.2 ns at room temp, τ_p=0.97 s at 77 K, in a degassed solution of 2-methyltetrahydrofuran). Likewise, the phosphorescences observed for TPP and MTPP were found to be identical with those of the corresponding pyrazoles, although the resolution of the vibrational structure of the phosphorescence bands shown in Fig. 1 is lower as compared with the phosphorescence bands of the authentic 1,3,5-triphenylpyrazole (TPPzole) and 1,5-diphenyl-3-(*p*-methoxyphenyl)pyrazole (MTPPzole). The major reason why the emission due to the impurity pyrazole is much more intense for DMATPP as compared with TPP and MTPP is that DMATPPzole absorbs the light of 300 to 340 nm much more strongly than TPPzole and MTPPzole (λ_{max}(log ε) in MTHF at room temp: 257 nm(4.46) for TPPzole; 261 nm (4.51) for MTPPzole: 290 nm(4.54) for DMATPPzole).

Although the photochemical conversion of TPP and its derivatives into the corresponding pyrazoles has been known,[8] the present sudy of the measurement of the emission spectra has revealed that these compounds are very sensitive to light. The phenomena observed in the emission spectra seem to be general with many other derivatives of TPP which undergo photodehydrogenation. TPP and its derivatives have found applications for practical use, *e.g.*, as fluorescent whitening agents,[9] and as material for electrophotography.[10] The chemical properties described above should be taken into account in evaluating the function of these materials.

Experimental

Materials. TPP (mp 141—2 °C), MTPP (mp 140.5—141.5 °C) were prepared according to the known procedure,[11] purified by repeated recrystallizations from EtOH and dried *in vacuo*. DMATPP (mp 199.5—201 °C) was synthesized in a similar manner by the reaction of phenylhydrazine with 1-(*p*-dimethylaminophenyl)-3-phenyl-2-propenone which was obtained by the reaction of *p*-dimethylaminoacetophenone with benzaldehyde, purified by repeated recrystallizations from EtOH and dried *in vacuo*. TPPzole (mp 138—138.5 °C), MTPPzole (mp 141—142 °C), and DMATPPzole (149—149.5 °C) were prepared from the corresponding pyrazolines by the dehydrogenation reaction with chloranil in refluxing xylene, followed by column chromatography over neutral alumina, recrystallized several times from EtOH, and dried *in vacuo*.

Spectral Measurement. The electronic absorption spectra were recorded with a Hitachi 124 spectrophotometer. The emission and excitation spectra were recorded with a Hitachi MPF-3 spectrofluorometer fitted with a R446 photomultiplier. The concentration of the solution was *ca.* 2×10^{-5} mol/l. The fluorescence lifetime was measured by means of a pulsed N_2 laser with a pulse width of *ca.* 2 ns and repetition of *ca.* 3 Hz.

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