Influence of the Irradiation Time on the Absorption and Emission Spectra of *p*-Cyano-N,N-Dialkylanilines in Polar Solvents

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Dedicated to Professor Czesław Bojarski on the occasion of his 80th birthday.

The effect of the time of irradiation with the excitation wavelength $\lambda_{\rm exc}$ on the absorption and emission spectra of p-cyano-N,N-dimethylaniline (CDMA), p-cyano-N,N-diethylaniline (CDEA) and N,N- dimethylaniline (DMA) in acetonitrile and in n-hexane, as well as the effect of high temperature is studied. It is found that after sufficiently long irradiation of CDMA and CDEA in acetonitrile the short wavelength SE band intensity strongly increases compared to that of the long wavelength LE band. This phenomenon is caused by the photolysis of CDMA and CDEA in polar solvents. In each case both the irradiation time and the delivery of suitable thermal energy leads to irreversible processes.

Investigations of the λ_{exc} effect on the location and intensity distribution of emission bands have shown their independence of λ_{exc} ranging from 260 nm to 330 nm in the LE band. However, a pronounced effect of λ_{exc} on the intensity appears in the SE band. In this spectral region DMA molecules formed due to the photolysis of CDMA absorb strongly.

Excitation at $\lambda_{exc} = 340 - 360$ nm in the dimeric absorption band leads to a new emission band overlapping the LE band, which indicates the presence of luminescing dimers.

Key words: p-Cyano-N,N-Dialkylanilines; Dual Fluorescence; Irradiation Time;

Absorption and Emission Spectra; Photolysis.